Measurement of Lower Chlorinated Hydrocarbons in Flue Gas from Municipal Solid Waste Incinerators and the Relationships to PCDD/Fs

Watanabe,I.[A], Matsuzawa,Y.[A], Kawakami,I[B],Tanaka,M.[A]

[A]National Institute of Public Health, 4-6-1 Shirokanedai Minato-ku Tokyo 108 Japan
[B]Sumitomo Heavy Industries, Lts., 2-1 Kanda Nishikicho Chiyoda-ku Tokyo 101 Japan

1. Introduction

Lower chlorinated hydrocarbons (HC-Cln) such as chloroform ($CHCl_3$), tetrachloromethane (CCl_4), trichloroethylene(C_2HCl_3) and tetrachloroethylene(C_2Cl_4) are toxic compounds and the level in the air is of concern and subject to the environmental quality standard or emission standards in several countries. The data on their emission from MSW(municipal solid waste) incinerators, however, are not sufficient to evaluate the significance.

In addition, their level in flue gas of MSW incinerators is of interest in connection with the emission of PCDD/Fs. Some recent studies[1)-3)] indicate the potential importance of their role in the formation of chlorinated aromatics, key precursors of PCDD/Fs, in combustion systems. Froese and Hutzinger[3)] found that chlorinated aromatics might be formed from non-aromatic compounds in the higher temperature post-combustion zone allowing further reactions in the 300°C zone to produce PCDD/Fs. Thus, we developed the sampling and analytical methods for HC-Cln in flue gas and the relationships to PCDD/Fs were investigated at two incineration plants of mechanized batch combustion type.

2. Field studies and the facilities.

Field surveys were carried out three times under different conditions at two incineration plants of mechanized batch combustion type. They are the first survey under original designed condition at A plant (10ton/8h/line, electronic pres.) on 1991/2/13-15, the second survey under improved condition at A plant on 91/12/3-5 and the third survey at B plant (12.5ton/8h/line, bag house) constructed with "Japanese Guidelines" for emission reduction of PCDD/Fs on 92/10/14-16. The sampling train at waste combustion facilities consists of; a glass probe with glass fiber filter, water trap cooled with ice, a sample bottle (volume: ca. 1 L) with Teflon stop valves at each end, and a suction pump. Sample gas was sucked for 10 to 20 min at 1 L/min, so sampling trains and a bottle was displaced completely with sample gas.

3. Analytical methods for HC-Cln

Lower chlorinated hydrocarbons(HC-Cln) and related compounds in flue gas were analyzed by gas chromatography (GC). The stainless steel tube (2m-long, 1.5mm-I.D.) packed with 10% Na_2SO_4 on Porasil A was used for an analytical column of HC-Cln with N_2 carrier gas (29 ml/min) under the oven temperature as initial (100°C)--2°C/min--final(138°C, 20min). The detector was ECD(^{63}Ni,10mmCi) at 320°C. Other compounds in the sample gases were also analyzed by GC with the conditions listed in Table 1.

4.2 Emission factors

The amount of waste incinerated in furnaces varies continuously and the emission values of HC−Cln in sample bottles result from the instantaneous burning of waste. Therefore, the weight of waste feeding into the hopper of a furnace for certain period is not appropriate for the calculation of emission factor (EF). Thus, for batch type operation, we calculated EF from the total emission of HC−Cln, which was estimated the concentration and the flow rate, and the total waste burned during the test day

EFs calculated from the measurement for two days of the second survey are; $CHCl_3$; 0.3g/ton, C_2HCl_3; 0.7, C_2Cl_4; 0.9. The magnitude of HC−Cln emission from MSW incinerators estimated from this results is considered not to be high, compared to the total estimated HC−Cln emission rate in Japan. The accumulation as to various sources of HC−Cln, however, is essential to elucidate consistently the contribution of each sources and to formulate a strategy of HC−Cln reductions.

4.3 Relationships between HC−Cln and PCDD/Fs

PCDD/Fs in flue gas was measured with using the recommended method of Japan Waste Research Foundation by another groups in this project. The relationships between HC−Cln and PCDD/Fs were obtained from the data by the second survey at plant A and the third at B, and were shown in Fig.2. Relatively good correlations between C_2Cl_4 (or C_2HCl_3) and total PCDDs (or total PCDFs), compared to $CHCl_3$, are observed. Any practical differences can not be found in the relation of HC−Cln to PCDDs and PCDFs.

We also measured the concentration of carbon monoxide (CO) and lower hydrocarbons (HC) in flue gas. The relationship between CO and PCDD/Fs was not good, compared to HC−Cln, and those of HC to PCDD/Fs is similar to HC−Cln.

These results suggest that the lower chlorinated hydrocarbons or aliphatic compounds may play the important role in chlorinated aromatics formation and their concentration in flue gas may be index of PCDD/Fs emission in some case and is better than CO for the preliminary estimation. Chlorobenzenes or chlorophenols may be better than HC−Cln as index, however, the sampling and analysis for them are complicated and need more experience and instrumental capabilities.

4.4 Further improvement of measurement methods for HC−Cln

The samples taken by the method mentioned in section 2 represent the flue gas for only a few minutes, therefore, many samples had to be taken to follow the accurate change in unstable emission such as "start up" or "shut down" of a incinerator, and it is virtually impossible to monitor HC−Cln in flue gas for long periods by this method.

Thus, we developed the new instrument and system for the continuous monitoring as shown in Fig.3. It is principally consisted of a main gas suction unit (3−5 L/min), a averaged sampling unit using a 100ml Magnum syringe driven at a certain constant rate, a sample introduction unit, GC equipped with wide bore column (Ultra Alloy−CW) and non−radiation type ECD for HC−Cln, portable GC for N_2, O_2, CO_2, CO and CH_4, and the unit of system controller and data processor. The sampling interval can be set 10 to 60 min for the purpose. The sampling duration time is 70−80 % of the sampling interval.

The monitoring of HC−Cln with the developed system was done in the plant B on Nov.29−Dec.1 in 1993. The sampling interval and time were set 10 min and 7 min for day−time or 30 min and 25 min for night, respectively. A part of the analytical results is shown in Fig.4, where high level emission was observed until early morning after shut−down with "burn out". These data in midnight or in early morning can be easily obtained with this system. In addition,

5. Conclusions

Simple sampling and analytical methods for lower chlorinated hydrocarbons were developed, and field studies on their emission were carried out in incinerators of municipal solid waste. The emission factors were estimated and their emission in Japan is considered not to be significant. The relationship between HC–Cln and PCDD/Fs in the flue gas was observed to be good and the concentration of HC–Cln in flue gas may be index of PCDD/Fs emission in some cases. Thus, the improved instrument and system for the continuous monitoring was developed and the usefulness of it was confirmed in a field study.

6. Acknowledgement

The authors wish to thank Mr. Shinji Uehara, Mr. Kazuto Tezuka and Mr. Makoto Simadzu for their assistance in sampling and analysis for this study.

7. Reference

1) Yasuhara, A. and Morita, M. (1990): Formation of Chlorinated Compounds in Pyrolysis of Trichloroethylene: Chemosphere, 21, 479–486.
2) Stromberg,B. (1991): Low Temperature formation and Minimization of Chlorinated Hydrocarbons: Chemosphere, 23, 1515–1525.
3) Froese,K.L. and Hutzinger, O. (1993): The Formation of Chlorinated Benzenes in Flyash Catalysed Reactions of Trichloroethlene: Dioxin'93 (Short Papers) Vol. 12, 367–370.