Online Measurement of Organic Halogenated Compounds (OHC) for Monitoring of Dioxins at Waste Incinerator

Hiroyuki Nakui[1], Gou Watanabe[1], Tsuyoshi Matsuda[1], Akio Yamagami[2], Shirou Nemoto[2], Kazumasa Koshiba[2]

[1]Electric Power Development Co., Ltd.
[2]North Fujisawa Incinerator

Introduction

The analysis of Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) needs much time and cost because of many steps e.g. sampling, extraction, clean-up and HRGC-HRMS operating, which make daily gas monitoring difficult to perform.

The group parameter of organic halogenated compounds (OHC) is considered to be a good indicator or surrogate for PCDD/Fs [1,2)]. Watanabe and co-researchers had reported that a fairly good correlation between low-volatile organic chlorine and PCDD/Fs was found [3)].

We continuously measured the OHC with an online monitor at a stoker type incinerator in order to evaluate a trend with respect to dioxins. Here, we report the results.

Materials and Methods

OHC monitor

Fig. 1 presents the process flow of OHC continuous measurement utilizing a J-Power OHC monitor 201. Fig. 2 shows an outline of the monitor.

In the monitor, a pretreatment process removed dust, moisture and inorganic halogens from the flue gas. OHC in the gas was adsorbed and concentrated on carbon black, and then desorbed by heating at 450 deg. Celsius with argon as the carrier gas. The desorbed OHC was combusted at 900 deg. Celsius under oxygen gas, and decomposed into inorganic halogens. The halogens were determined by coulometric titration with a silver electrode, and then computed for chlorine concentration (g-Cl/m^3N).

The OHC adsorbent was packed in two quartz columns. OHC was alternately adsorbed or desorbed at the columns and continuously measured.

Flue gas → Pre-treatment → Adsoption & Concentration
→ Heating Desorption → Combusting Decomposition
→ Coulometric Titration → Computing

Fig. 1 Process flow of OHC continuous measurement

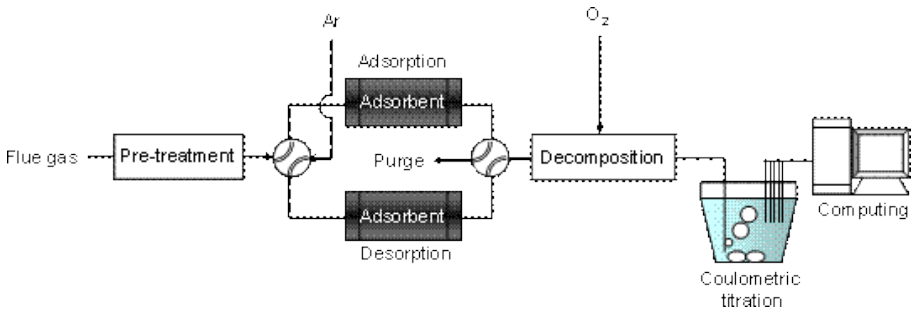


Fig. 2 Outline of OHC monitor

Measurement

The OHC monitor was placed at North Fujisawa Incinerator (NFI) No. 2 (Fig. 3) and connected to the flue before the stack. The plant incinerates 150 tons of municipal waste per 24 h and has a bag filter to remove dust from the flue gas. That was periodically stopped for 2 days every 2 weeks in order to clean the incinerator.

The flue gas was sampled at 2 L/min for 2 h, and the OHC in that sample was quantitated every 2 h. The OHC was continuously measured for 3 months.

Fig. 3 North Fujisawa Incinerator

Results and Discussion

Continuous measurement of OHC

Fig. 4 shows the results of OHC measurement under usual operation (without scheduled stop) of the incinerator. The OHC concentration was in the range of 0.2 to 6μg-Cl/m^3N, and the average was 1.7 μg-Cl/m^3N. A notable observation from these results is that the concentrations of OHC have been extremely high at every restart of the incinerator following a scheduled stop.

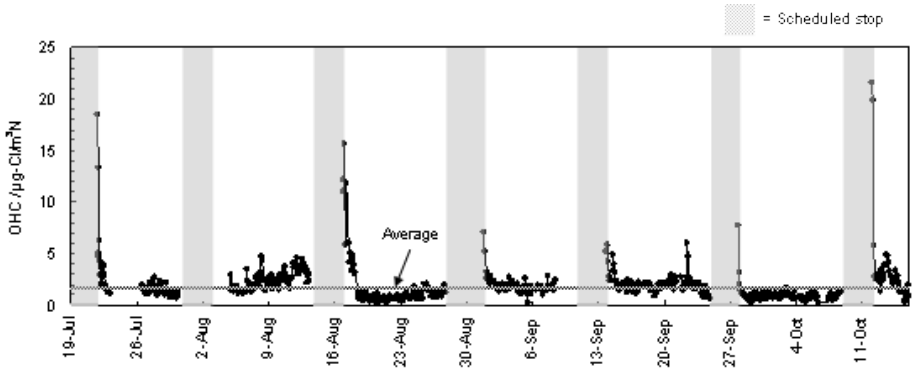
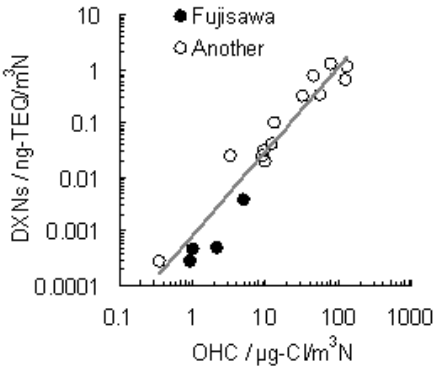


Fig. 4 Results of OHC measurement at usual operation of incinerator

Correlation of OHC with Dioxins (DXNs)

DXNs were measured 4 times with HRGC/HRMS by Japanese Industrial Standards (JIS) K 0311. Fig. 6 shows the correlation of OHC with the DXNs. Positive correlations were observed with a linear regression having a correlation coefficient, r = 0.97. We converted a concentration of OHC to DXNs by the regression equation.

The correlations were similar to another 5 plants (Fig. 5).



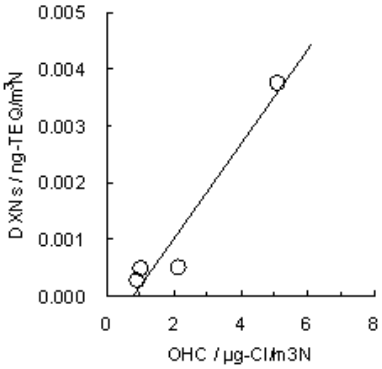


Fig. 5 Correlation of OHC with DXNs at various plants Fig. 6 Correlation of OHC with DXNs at NFI

Conversion to concentration of DXNs

Fig. 7 shows the DXNs concentration predicted from OHC using the regression equation. The values were high (>0.005 ng-TEQ/m^3N) upon startup of the incinerator, but fell under 0.002 ng-TEQ/m^3N during stable operation.

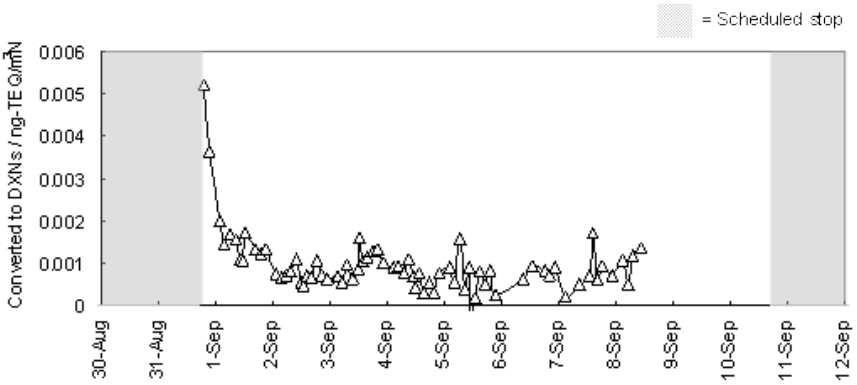


Fig. 7 Results of converted concentration to DXNs

OHC at stop and restart of incinerator

Fig. 8 shows the trend of OHC at scheduled stop for cleaning of the incinerator. The OHC increased when the gas temperature fell or rose. The peaks of OHC were observed when the gas temperature was in the range of 300 to 500 deg. Celsius. DXNs have been assumed to increase by *de novo* synthesis within that temperature range.

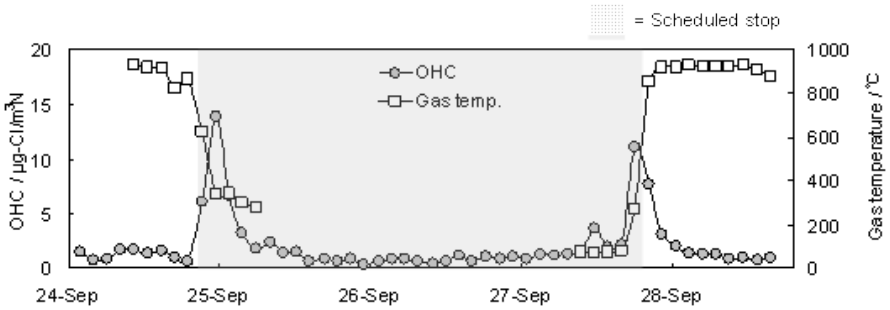


Fig. 8 Trend of OHC at scheduled stop for cleaning

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