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Short Communication

Online measurements of low-volatile organic chlorine for dioxin monitoring at municipal waste incinerators

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ABSTRACT

In this study, an automatic sampling device and an analysis device have been developed for the measurement of low-volatile organic chlorine (LVOCl) in flue gas. The concentrations of dioxins (polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, and dioxin-like polychlorinated biphenyls) have been estimated by online measurements of LVOCl at a municipal solid waste incinerator (MSWI) using these devices. The LVOCl concentration at the outlet of the selective catalyst reactor (SCR) of the MSWI increased momentarily up to 95 µg Cl m^{-3} during the startup period of the MSWI; subsequently, it gradually decreased to less than 1.0 µg Cl m^{-3} after 50 h from the start of waste feeding. The concentration of toxic equivalent quantity (TEQ)-Dioxins at the SCR outlet had a linear positive relationship with the LVOCl concentrations. Moreover, the level of TEQ-Dioxins concentration can be estimated by using this relationship with LVOCl. From our results, since the LVOCl concentrations in a flue gas can thus be automatically analyzed every hour by online measurements, the operators of an MSWI would be able to monitor approximate TEQ-Dioxin emissions on a daily basis.

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1. Introduction

The emission of dioxins has attracted considerable attention because of their adverse environmental impacts. It is extremely important to reduce dioxin pollution from industries and effluents. An important source of dioxins is municipal solid waste incinerators (MSWIs). In order to operate MSWIs with low dioxin emissions, it is necessary to first setup a dioxin monitoring system. However, current analysis techniques of dioxin concentrations are time consuming and expensive because of the number of steps involved, such as sampling, extraction, clean-up, and the use of a high-resolution gas chromatograph/mass spectrometer (HRGC/MS); this makes it difficult to perform regular or daily gas monitoring.

Therefore, other more easily measurable parameters must be used as indicators of dioxin concentrations in flue gases at MSWIs. These parameters are typically compounds called surrogates (Lemieux, 2004). Various organic halogenated compounds have already been proposed as surrogates for measuring dioxin concentrations in flue gases from waste incinerators, and many correlations with dioxins have been examined (Öberg et al., 2002). Kato et al. (2000) measured semi-volatile and non-volatile organic halogen (SNVOX) concentrations in flue gases at MSWIs by using a total or-

ganic halogen analyzer and found a correlation between the international toxic equivalent quantity (I-TEQ) values and SNVOX concentrations. Recently, Watanabe and coworkers (2007) developed a new measuring method of middle- and low-volatile organic chlorine (M/LVOCl) concentrations by atomic emission spectrometry (AES) using radiofrequency helium plasma (RHP), and they measured the M/LVOCl concentrations in flue gases at various MSWIs. In their paper, they reported that LVOCl concentrations correlated well with those of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs).

Since it is mechanically simple to use AES with RHP, the measurement technique can be automated for fast measurements of flue gas. In this study, we have developed an automatic sampling device and an analysis device adopting the AES. Further, we have attempted to continuously monitor the emission of PCDD/Fs and dioxin-like polychlorinated biphenyls (PCBs) from an MSWI plant by conducting online measurements of LVOCl (the surrogate) concentrations using these devices.

2. Experimental

2.1. Investigated facility

LVOCl concentrations were measured and compared with the concentrations of PCDD/Fs and dioxin-like PCBs in flue gases at

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an MSWI plant located in Japan. This plant has been operational since 2001 and incinerates 450 tons of MSWs per day using a stoker type furnace. The combustion gas has a temperature roughly between 850 °C and 950 °C. A boiler is used to absorb the gas heat and decrease the gas temperature to approximately 200 °C. The combustion gas is cooled even further to approximately 150 °C in a gas cooler. Any fly ash in the cooled gas is then removed by bag filters (BFs). Subsequently, hydrogen chloride (HCl) and sulfur oxide (SOx) are removed using a wet gas scrubber. The remnant gas is then heated to approximately 230 °C by using a gas reheater; subsequently, it is treated in a selective catalyst reactor (SCR) in order to remove nitrogen oxide (NOx). No absorbents such as activated carbon are added to the upstream of the BF. The clean gas is transferred to a stack by an induced draft fan (IDF) and released into the atmosphere. The flue gas for measurements was sampled at the outlet of the SCR. It is noteworthy that the backup burners of the plant are operated with town gas such as liquefied natural gas (LNG).

2.2. Measurement of LVOCl

LVOCl in a flue gas was automatically measured using an online system, as shown in Fig. 1. The system continuously collected only the gas phase sample through a cylindrical filter at a flow rate ranging from 0.5 to 1.5 L min^{-1}. A Teflon® tube and a glass tube were used at the sampling line, and the temperature of the sampling gas was maintained using a heat insulator. Moisture was condensed and eliminated from the sampling gas using electronic coolers controlled at 3 °C. HCl in flue gases, which causes measurement errors, was removed from the sampling gas through a column containing silver granules. The column comprised two glass tubes, and 10 g of silver granules with specific surface area of 5.11 m^2 g^{-1} and diameter between 0.42 and 0.85 mm were filled in each tube. The HCl was adsorbed on the silver granules as silver chloride. It was observed that the HCl concentrations decreased

from more than 60 ppm to less than 1 ppm at the outlet of the silver granule column. It is noteworthy that HCl is normally eliminated using water or alkaline solution in a washing bottle (JIS, 2002). However, wet processes such as the washing bottle method eliminate not only HCl but also other water-soluble compounds such as chlorophenols from sampling gases. Chlorophenols are known to be one of the surrogates for PCDD/Fs (Lemieux, 2004), and they should not be lost during the sampling process. Hence, the dry process using the silver granule column has been adopted in this study.

LVOCl in the sampling gas was adsorbed and concentrated on the adsorbent at 100 °C for 60 min and then desorbed by heating at 380 °C or more with helium as the carrier gas. Graphite carbon, with a specific surface area of 100 m^2 g^{-1} and diameter from 0.4 to 0.6 mm, was used as the adsorbent, and 0.3 g of this graphite carbon was packaged in two quartz glass columns. The dominant organic halogens adsorbed by this sampling method were identified as pentachlorobenzene, hexachlorobenzene, 1,2,3,4-tetrachlorobenzene and 2,4,6-trichlorophenol by the New Energy and Industrial Technology Development Organization (NEDO, 2007), Japan. While one adsorbent column adsorbed LVOCl, the other column desorbed it. Further, the two columns alternately repeated adsorption and desorption. LVOCl concentrations were normalized to standard temperature and pressure (0 °C and 101.3 kPa).

Takakura and coworkers (2007) have previously investigated the recovery ratios of various standard substances by using this sampling method. In their study, the total recovery ratios of the substances with high boiling points were higher than those with relatively low boiling points; in particular, the recovery ratios of substances with boiling points ranging from 150 to 220 °C were more than 80%. Hence, this sampling method can be used to selectively collect high-boiling point LVOCl by heating the adsorbent column at 100 °C.

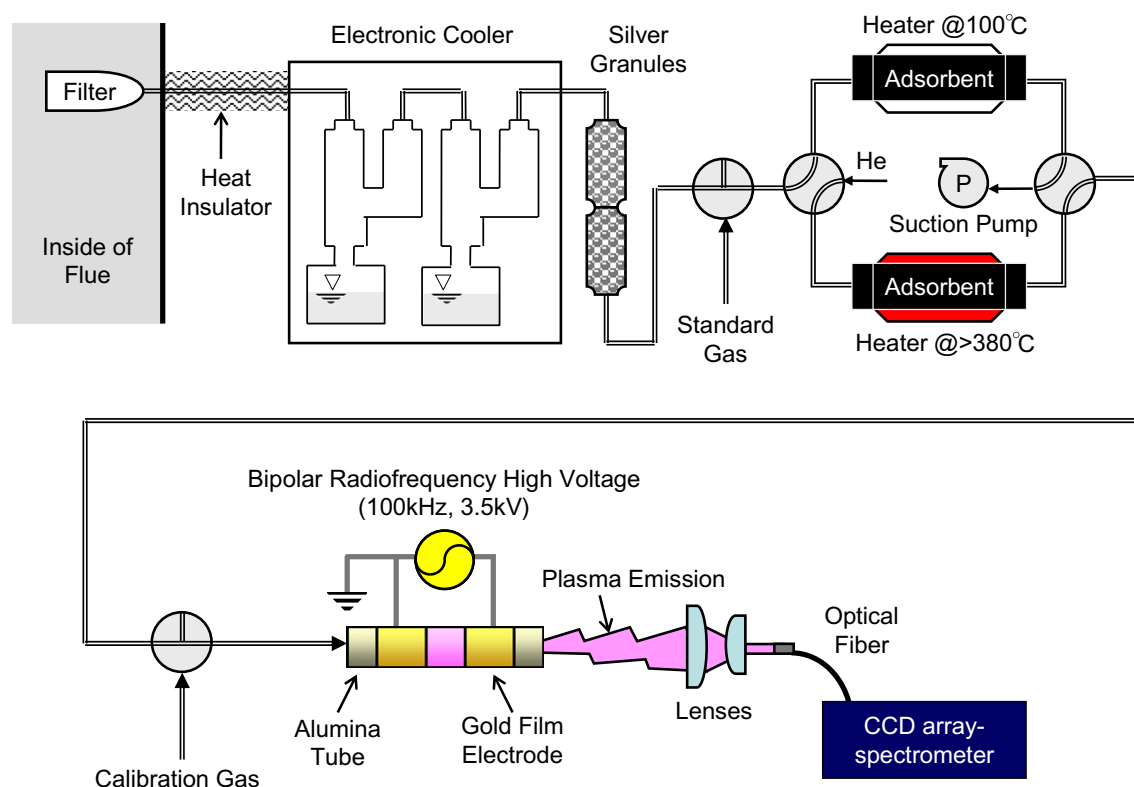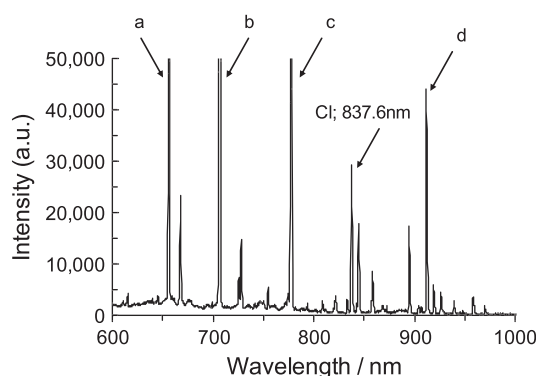The desorbed LVOCl from the adsorbent was automatically detected by AES using radiofrequency helium plasma (Watanabe

Fig. 1. Schematic view of low-volatile organic chlorine (LVOCl) online measurement system.

Fig. 2. Emission spectrum of 1,1,2-trichloroethane. Wavelength of 837.6 nm was used as Cl signal in this study. Emissions of a, b, c, and d were signals of H, He, O, and Cl, respectively.

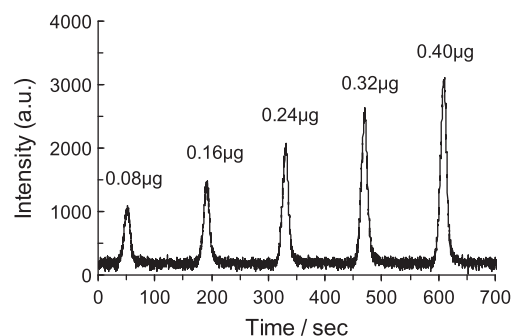**Fig. 3.** Analytical chart of various amounts of 1,1,2-trichloroethane.

et al., 2002). A discharge tube with two gold film electrodes was prepared using an alumina tube. One electrode was earthed, while the other was supplied a radiofrequency bipolar high voltage (100 kHz, 3.5 kV) from a radiofrequency power supplier. By supplying helium gas at a flow rate of 200 mL min^{-1}, atmospheric helium plasma was stably created in the discharge tube between the electrodes. Optical emission from the discharge tube was condensed with a compound lens and transferred to a spectrometer with a charge-coupled device (CCD, Ocean Optics, USB4000) through an optical fiber. Using this procedure, it took approximately 15 min to analyze one sampling gas.

The spectrum of the emission lines of 1,1,2-trichloroethane is shown in Fig. 2. An emission line at a wavelength of 837.6 nm was recorded as the signal of chlorine, while that at the wavelength of 835.2 nm was used as the background. The AES detector was calibrated to introduce a standard reference gas (Sumitomo Seika Chemicals Co., Ltd., 1.0 ppm 1,1,1-trichloroehtane in helium). The amount of chlorine was quantified by a peak area using the calibration and expressed as "μg Cl".

From the results of five repeated analyses of the standard substance (1,1,2-trichloethane), the coefficient of variation (CV) was determined to be 2.8%. An analytical chart of the various amounts of the standard substance is presented in Fig. 3. The relationship between the amount of the standard substance and peak area was linear for an amount ranging from 0.08 to 8.8 μg Cl, and the correlation coefficient (r) was 0.9983. This linear relationship could be expressed as $y = 420941x$, where y = peak area and x = amount of standard substance (μg Cl). This relationship can be used as a calibration curve for a linear range. The amount range with linearity broadly corresponds to the concentrations of flue gases under normal operating conditions at the MSWI being used for the investigations (0.9–98 μg Cl m^{-3}). The detection limit was estimated to be 0.06 μg Cl or less by an amount equivalent to 3 times the standard deviation of blank signals; subsequently, the detection limit of flue gas measurement was calculated as 0.667 μg Cl m^{-3}.

2.3. Measurement of dioxins

All sampling and analysis procedures were based on the JIS method (JIS, 2005), as specified in the US EPA method (US EPA, 1994). The sampling train consisted of a probe, filter, gas washing bottles for cooling and demoisturization, an adsorption tube (XAD-2 resin) and absorption bottle of diethylene glycol, followed by a pump and a meter. The filtrated dust and XAD-2 resin were soxhlet extracted with toluene. The diethylene glycol and toluene extracts were combined and condensed for analysis.

Each homologue and toxic isomer of PCDD/Fs and dioxin-like PCBs (non-ortho and mono-ortho PCBs) were analyzed with a GC/MS (JEOL, JMS-700) after chromatographic purification using a multilayer silica column and activated carbon column. The actual detection limits of tetrachlorodibenzo-p-dioxins by this analysis method were 0.0003–0.0004 ng m^{-3}. In this paper, the total PCDD/Fs and dioxin-like PCBs are henceforth described together as "total-Dioxins." The toxic equivalency quantity (TEQ) value was determined using the toxic equivalent factor (TEF) prescribed by the WHO/IPCS in 1998 and 2006. The TEQ values of PCDD/Fs and dioxin-like PCBs are described together as "TEQ-Dioxins" in this paper.

3. Results and discussion

3.1. Changes in LVOCl concentration during startup

Watanabe and coworkers (2010) reported that organohalogens in flue gas increased during startup of MSWIs; further, they showed a high correlation between organohalogens and TEQ-Dioxins. Their report motivated us to measure LVOCl in flue gas of MSWI with our online measurement device in order to investigate the changes in the concentration during startup after annual plant revision. Fig. 4 demonstrates the changes in the concentration of the LVOCl and furnace temperature over time. The temperature increased linearly after burner ignition, and it reached 640 °C after 14 h. When the waste feeding started, the temperature decreased temporarily to 580 °C, and subsequently, it again increased linearly. After the temperature reached 900 °C at 20 h, the incinerator was continuously operated at this or higher temperatures.

During the heat-up period, the LVOCl concentration changed considerably. As the furnace temperature increased, two peaks of the LVOCl concentration appeared. The first and larger peak, reaching a maximum value of 95 μg Cl m^{-3}, appeared at the temperature range from 300 to 500 °C. The second and smaller peak of the LVOCl concentration, at 40 μg Cl m^{-3}, occurred with a temporary decrease in the temperature just before the waste feeding began. For insufficiently high incinerator temperatures (below 800 °C), the unstable combustion conditions at these times may have led to incomplete combustion. The poor combustion conditions during the heat-up were sufficient for the formation of halogenated products during incomplete combustion (Etscheidt et al., 2006).

3.2. Changes in dioxin concentrations after start of waste feeding

A few studies have previously reported on the emissions of PCDD/Fs during the startup process of MSWIs. Tejima and coworkers (2007) have indicated that a large part of the total annual dioxin emission from MSWIs could be attributed to startup periods. Wang and coworkers (2007) have reported that one startup proce-
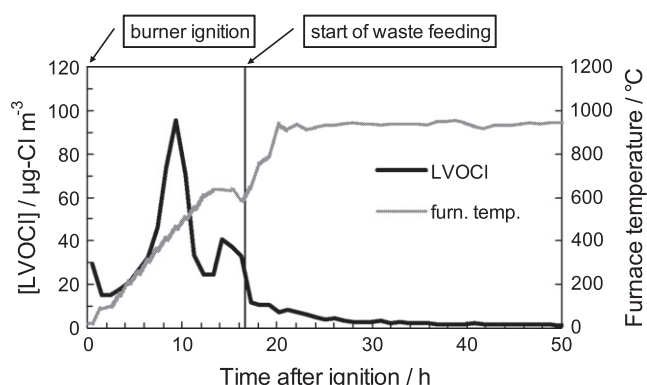
Fig. 4. Changes in LVOCl concentrations in flue gas at selective catalyst reactor (SCR) outlet and furnace temperature at start-up of municipal solid waste incinerator (MSWI).

dure of MSWIs could generate a maximum of 60% of PCDD/Fs emissions for one entire year of normal operations.

These studies stimulated us to sequentially measure TEQ-Dioxins in flue gas in order to investigate the changes in their concentrations after the start of waste feeding during startup of MSWI. The changes in the concentrations of the TEQ-Dioxins and LVOCl are expressed in logarithmic scales in Fig. 5. The concentration of TEQ-Dioxins was 0.032 ng TEQ m^{-3} just after the start of waste feeding; subsequently, it decreased to less than 0.001 ng TEQ m^{-3} within 80 h. Similarly, the LVOCl concentration was more than 10 μg Cl m^{-3} just after the start of waste feeding; subsequently, it decreased to less than 1.0 μg Cl m^{-3} after 50 h. The ratios of PCDF to PCDD were 2–4. These observations supported the dominant role of the *de novo* synthesis, as shown by Everaert and Baeyens (2002). The *de novo* synthesis occurs mostly between 200 and 400 °C. In the heat-up period, the LVOCl increased significantly within the temperature range of the *de novo* synthesis, as illustrated in Fig. 4; further, dioxins might have formed simultaneously. Although the concentration of TEQ-Dioxins just after the start of waste feeding was still rather high, it was evidently lower than the Japanese emission regulation of 1.0 or 0.1 ng TEQ m^{-3}.

3.3. Relationship between concentrations of LVOCl and dioxins

In order to investigate the relationship between LVOCl and dioxins, the concentrations of dioxins during the startup and normal plant operations were measured during the automatic measurement of LVOCl in the same flue gas. The measured concentrations are given in Table 1. The results of LVOCl measure-
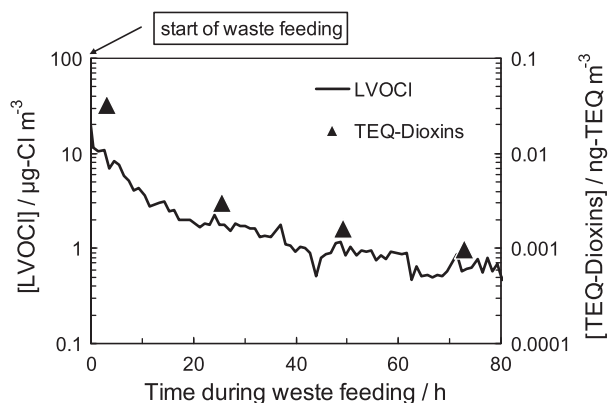

Fig. 5. Changes in concentrations of LVOCl and toxic equivalent quantity (TEQ)-Dioxins in flue gas at SCR outlet after start of waste feed. The concentrations are plotted on logarithmic scales.

Table 1
Concentrations of dioxins and LVOCl in flue gases at SCR outlet of MSWI.

No.	Total-Dioxins (ng m^{-3})	TEQ-Dioxins (ng TEQ m^{-3})	LVOCl (μg Cl m^{-3})	Plant operation
1	3.6	0.032	9.20	Startup
2	0.54	0.0030	1.83	Startup
3	0.32	0.0016	1.05	Startup
4	0.25	0.00099	0.670	Startup
5	0.37	0.0011	0.606[*]	Normal
6	0.66	0.0013	0.420[*]	Normal

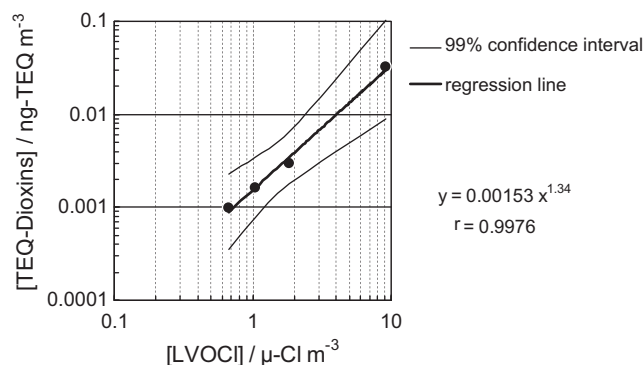[*] Less than detection limit (0.667 μg Cl m^{-3}).

Fig. 6. Relationship of logarithmic concentrations of TEQ-Dioxins and LVOCl concentration in flue gas at SCR outlet of MS.

ments during normal plant operation were less than the detection limit of 0.667 μg Cl m^{-3}. The relationship between the logarithmic concentrations of LVOCl (except for the results below the detection limit) and TEQ-Dioxins is shown in Fig. 6. The regression line of TEQ-Dioxins on LVOCl and its 99% confidence interval are illustrated along with the relationship. The TEQ-Dioxins concentration had a linear positive relationship with the LVOCl concentration in the range of 0.00099–0.032 ng TEQ m^{-3}. The result of regression analysis showed the r value to be 0.9976 ($n = 4$), and the equation of the regression line could be expressed as $y = 0.00153x^{1.34}$, where $y =$ TEQ-Dioxins (ng TEQ m^{-3}) and $x =$ LVOCl (μg Cl m^{-3}).

The high r value implies that it is possible to obtain accurate estimates of the TEQ-Dioxins emission by measuring LVOCl in flue gases. However, when estimating the concentrations of TEQ-Dioxins by using the relationship with LVOCl, it must be noted that the concentration includes a maximum of 10 times the errors in the 99% confidence interval. Therefore, an order of magnitude of the TEQ-Dioxins concentration could be simply estimated in the range of the confidence interval. If the LVOCl concentration is 10 μg Cl m^{-3}, it is estimated that the concentration of TEQ-Dioxins has a range of 0.01–0.1 ng TEQ m^{-3} with 99% probability. Therefore, it can be concluded that TEQ-Dioxin emissions do not exceed a concentration of 0.1 ng TEQ m^{-3} for plants operating under emission levels of 10 μg Cl m^{-3} of LVOCl.

4. Conclusions

By using an automatic sampling device and an analysis device, LVOCl in flue gas was automatically measured at the SCR outlet under various operating conditions of the MSWI. During the heat-up period at startup of the MSWI, the LVOCl concentration increased momentarily to a maximum value of 95 μg Cl m^{-3}; this was approximately 100 times higher than the concentration during normal plant operation. The high LVOCl emission was considered to result from *de novo* synthesis; in addition, PCDD/Fs might have formed simultaneously. The relationship between the concentra-

tions of TEQ-Dioxins and LVOCl show a linear positive correlation and a high *r* value more than 0.99. However, a maximum of 10 times the error must be considered for the estimation of TEQ–Dioxin concentrations by using the above correlation.

Therefore, since the LVOCl concentrations in flue gas can be automatically analyzed per hour by online measurements, the operators of a MSWI would be able to perform daily monitoring of the approximate concentrations of TEQ-Dioxin emission. In our future studies, we will seek to improve the accuracy of TEQ-Dioxin estimation by the accumulation of measurement data.

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