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Surrogate study for dioxins from municipal waste incinerator in startup condition: applicability as a dioxin control indicator and an organohalogen emission warning

Abstract Dioxins and their surrogates were continuously monitored during the startup of two municipal waste incinerators (MWIs). The surrogates studied included low-volatility organohalogen compounds (LVOH) sampled by online systems, as well as chlorobenzenes (CBs) and chlorophenols (CPs). The changes in levels of LVOH, CBs, and CPs corresponded well with the trend of the toxicity equivalent quantity (TEQ). The correlation of LVOH with TEQ was fairly good, whereas that of CBs and CPs with TEQ was not consistent. The correlation of LVOH with TEQ involved a memory effect related to the delayed emission of less volatile compounds. The isomer analysis of the dioxins present under startup conditions showed evidence of the memory effect, i.e., highly chlorinated isomers were emitted slowly, whereas low-chlorinated isomers and LVOH decreased rapidly as the temperature rose. LVOH cannot act as a perfect dioxin surrogate, but it can give a versatile, quick, and comprehensive warning of the presence of organohalogen compounds because it is free from the memory effect and covers many kinds of organohalogen compounds, including dioxins.

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Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzo furans (PCDFs), and coplanar polychlorinated biphenyl compounds (PCBs) from municipal waste incinerators (MWIs) are a matter of serious concern. Currently, the laws in Japan require the measurement of dioxins once a year. However, dioxin formation in MWIs fluctuates, especially during startup and shutdown processes;[1,2] therefore, it is difficult to estimate the real emissions throughout the year. Accordingly, two monitoring approaches have been suggested: long-term sampling over a period of some weeks and surrogate monitoring, which is expected to be able to predict dioxins.[3–6] If surrogate monitoring can be done less costly and quicker than dioxin measurements, it can be useful as an effective control indicator. This article presents the development, limitations, and possible future utilization of the surrogate approach.

So far, chlorinated benzenes (CBs),[7,8] chlorinated phenols (CPs),[9] and low-volatility organohalogen compounds (LVOH)[10,11] have been used as representative surrogates. CBs and CPs are analyzed in an identical way using gas chromatography and/or mass spectrometry, whereas LVOH is the sum of organohalogen compounds grouped according to volatility.[10–12] Previous work on these surrogates in MWIs has demonstrated a good correlation between the surrogates and dioxins under certain limited conditions; however, the prediction ability of the surrogates should be critically evaluated for the following three reasons.[13] First, since the removal efficiencies of the surrogate and the dioxins in flue gas treatment devices are not the same, the correlation depends on the sampling site. Second, dioxins are less volatile than surrogates;

therefore, dioxins will adsorptively remain in facilities longer than surrogates; this phenomenon is sometimes called the memory effect. Third, the ratio of surrogate to toxicity equivalent quantity (TEQ) becomes poor in the low concentration range, as is true with the ratio of total dioxins to TEQ.

Nevertheless, the surrogate approach is still considered to be interesting for its comprehensiveness, because a surrogate can detect potentially toxic compounds including dioxins. Dioxins make up only a part of the many kinds of organohalogen compounds. Analysis of dioxins involves digestion and cleaning processes, during which dioxins can survive, whereas fragile or reactive compounds are lost. A comprehensive surrogate could preserve those compounds, because surrogate analysis does not involve as many analytical procedures.

In this article, the surrogate CBs, CPs, and LVOH were comparatively examined in five runs at two MWIs under startup conditions. The applicability of using the surrogates to predict dioxin levels was critically examined considering the three difficulties mentioned above. Consequently, LVOH was found to be able to serve as a comprehensive warning for the presence of organohalogen compounds resulting both from their formation and incomplete destruction in the MWI.

Experimental

Sites and conditions

Two stoker-type MWIs were selected. A-MWI was equipped with two lines and had a capacity of 150×2 metric tons day^{-1}.

All the experiments in A-MWI were conducted using line 1. The flue gas treatment train consisted of a boiler, gas cooler, dry injection (lime, activated carbon, and urea), bag filter, and stack, as shown in Fig. 1a. Three experimental runs in A-MWI were performed, as listed in Table 1. In runs A1 and A3, flue gas was sampled at the outlet of the bag filter, whereas in run A2, gas sampling was conducted before the dry injection.

B-MWI's capacity was 450×2 metric tons day^{-1}. Runs B1 and B2 were conducted using lines 1 and 2, respectively. The gas treatment train consisted of a bag filter, wet scrubber and catalyst for the destruction of dioxins and nitrogen oxides, followed by a stack (Fig. 1b). The bag filter in B-MWI was operated with neither lime nor activated carbon injection. In runs B1 and B2, the flue gas was sampled between the bag filter and the wet scrubber followed by the catalyst.

During the startup of the MWIs, natural fuel gas was provided to heat the furnace, followed by municipal solid waste (MSW) input. The sampling of dioxins, CBs, and CPs began immediately after the furnace temperature reached a steady state, i.e., approximately 900°C. The sampling was repeated five times, four of which were at intervals of 2 h, followed by the final 4 h of sampling 20 h later. An LVOH monitor was continuously operated before and after the startup procedure.

Flue gas monitoring

The flue gas sampling and monitoring procedures are described in Fig. 2. Dioxins, CBs, and CPs were manually

(a) A - Municipal Waste Incinerator

(b) B - Municipal Waste Incinerator
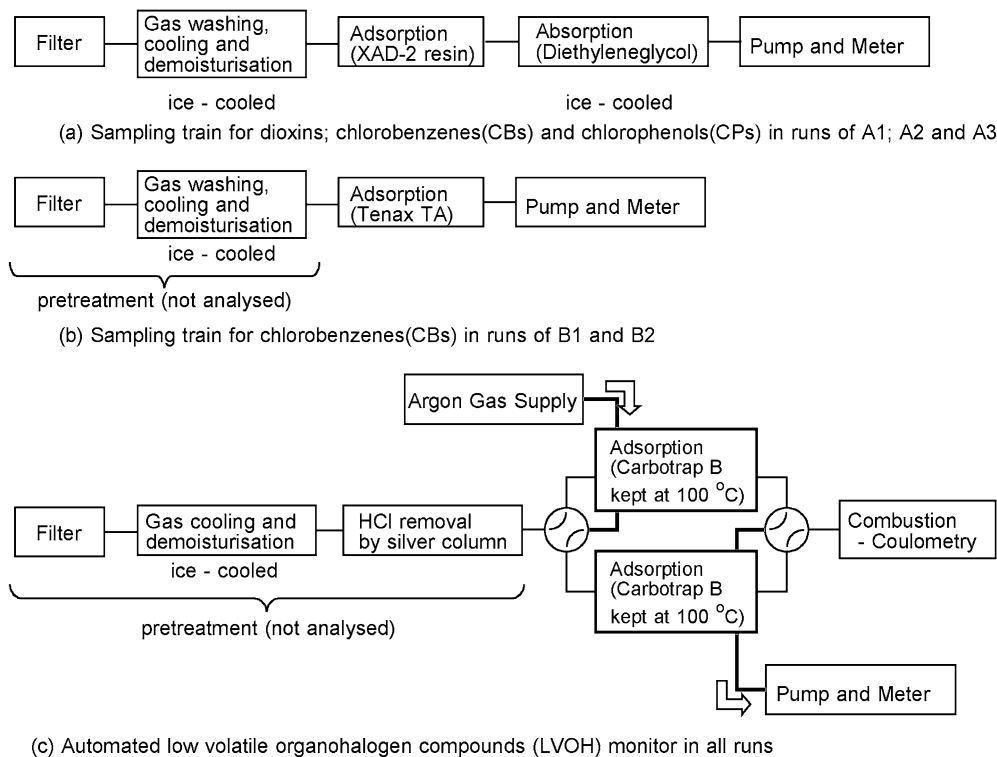
◉ : Sampling point
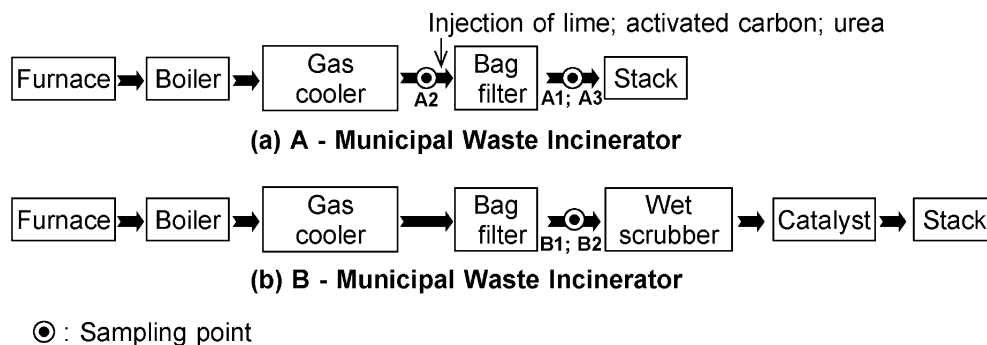
Fig. 1. The air pollution control devices in the two municipal waste incinerators studied (A-MWI and B-MWI) are shown. Both facilities were continuously operated stoker-type incinerators. In A-MWI, lime, activated carbon, and urea were injected and a bag filter was employed. The sampling sites were the outlet of the bag filter (runs A1 and A3) and before the injection (run A2). The gas treatment in B-MWI comprised a bag filter, a wet scrubber, and a catalyst for NOx and dioxin removal. The gas was sampled between the bag filter and the wet scrubber (runs B1 and B2)

Table 1. Flue gas sampling was conducted in two MWIs: A-MWI with three runs and B-MWI with two runs

Run	Sample collection site	On-line monitoring	Manual Sampling		
		LVOH	Dioxins	CBs	CPs
A1 and A3	After bagfilter	Semi-Continuously monitored every 2 hours	5 times sampled	From dioxins sampling train	From dioxins sampling train
A2	Before injection	Semi-Continuously monitored every hour	5 times sampled	From dioxins sampling train	From dioxins sampling train
B1 and B2	Between bagfilter and wet scrubber	Semi-Continuously monitored every 2 hours	5 times sampled	Tenax TA (Demoisturised by 0°C cooling before adsorption tube	From dioxins sampling train

Fig. 2. Processes associated with the three types of flue gas sampling devices used

(a) Sampling train for dioxins; chlorobenzenes(CBs) and chlorophenols(CPs) in runs of A1; A2 and A3

(b) Sampling train for chlorobenzenes(CBs) in runs of B1 and B2

(c) Automated low volatile organohalogen compounds (LVOH) monitor in all runs

collected and analyzed in a laboratory. On-line LVOH monitoring provided results every 1 or 2 h.

Dioxins

All sampling and analysis procedures were based on JIS K 0311.[14] 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 meter (Fig. 2a). The probe rinse and filter were treated with 2 mol l^{-1} HCl and filtered. The filtrate was combined with the drain water from the gas washing bottles and diethylene glycol, which was followed by extraction with dichloromethane. The filter residue and XAD-2 resin were Soxhlet extracted with toluene. The obtained dichloromethane and toluene extracts were combined and condensed to 10 ml to form a crude extract. Some aliquots from this crude extract were used for the CBs and CPs analyses. For dioxin analysis, further clean up and condensation was performed for high-resolution gas chromatography/ mass spectrometry (GC-MS, JEOL JMS-700D). The analytical results were reported in terms of isomers of PCDDs, PCDFs, and PCBs, from which the TEQ was calculated.

Chlorobenzenes

In runs A1, A2, and A3, CBs were analyzed from the crude extracts obtained in the dioxin analyses. Before the solvent conversion to toluene/dichloromethane, an internal standard of CBs solution was spiked. However, monochlorobenzene could not be sufficiently recovered because of its considerable volatility.

In runs B1 and B2, CBs were sampled using a Tenax TA adsorption tube, which was followed by thermal desorption (ATD400, Perkin Elmer) and GC-MS analysis (HP6890-HP5973, Agilent Technologies). Adsorptive sampling without a drain trap was also attempted in A1, A2, and A3. However, the large amount of moisture in the sampling train interfered with the sampling and analysis, resulting in failure. As shown in Fig. 2b, an ice-cooled bottle for gas washing, cooling, and demoisturization was placed in the front of a Tenax TA adsorption tube, and this led to the procedure being successfully carried out.

Based on the above analytical procedure, the following species were quantified: 1,2-dichlorobenzene; 1,3-dichlorobenzene; 1,4-dichlorobenzene; 1,2,3-trichlorobenzene; 1,2,4-trichlorobenzene; 1,3,5-trichlorobenzene; 1,2,3,4-tetrachlorobenzene; 1,2,3,5- and 1,2,4,5-tetrachlorobenzenes; pentachlorobenzene; and hexachlorobenzene, which are collectively called CBs in this paper. Monochlorobenzene was only quantified in runs B1 and B2; therefore, this compound was excluded in the following discussion regarding CBs.

Chlorophenols

In all runs, CPs were analyzed from the crude extracts obtained in the dioxin analyses. The analytical instrumentation used was the same as that for the dioxin analysis. The quantified species were the isomers of chlorophenol, dichlorophenols, trichlorophenols, tetrachlorophenols, and pentachlorophenol, which were collectively called CPs in this article.

Low-volatility organohalogen compounds (LVOH)

An automated LVOH monitor (J-power, Japan) was installed at the site. The procedural steps are presented in Fig. 2c. Filtered flue gas was sampled at a rate of several liters per minute and fed to the inlet of the LVOH monitor. The gas sample (2 l min^{-1}) was first demoisturized by a Peltier cooling device (3°–4°C); afterwards, HCl was removed using a column filled with 20 g of granular silver (425–850 μm). Because of the cooling device and the silver column, some of the semi-volatile organic compounds could not be recovered. Compounds with a boiling point (b.p.) of 180°C were recovered at a rate higher than 90%, whereas those with a b.p. of 250°C were recovered at a rate of about 60%.[15] Those semi-volatile compounds with a b.p. higher than 300°C could not be recovered. An adsorption tube filled with 0.1 g of Carbotrap B 20/40 mesh (nominal surface area: 100 m^2 g^{-1}, Supelco, Sigma Aldrich), maintained at 100°C, was used to collect LVOH. After being supplied with Ar gas, the adsorption tube was heated at 450°C for 10 min and its off-gas was introduced to a combustion-coulometry halogen determination system (Mitsubishi Chemistry, Japan). Since it was possible to quantify values as low as 0.1 μg Cl at the detector, the LVOH quantification limit was 0.4 μgCl m^{-3} with a 2-h sampling period. For the sake of continuous monitoring, separate lines for adsorption and desorption were installed and connected to the sampling and detector line with two four-way switching valves.

The adsorption tube of Carbotrap B was kept at 100°C, which was selected for the following reasons. At the beginning of the study, Carbotrap C (nominal surface area: 10 m^2 g^{-1}, Supelco, Sigma Aldrich) at room temperature was used. The expected b.p. range of the collected compounds was higher than 170°C.[16] However, the ambient temperature cannot be rigorously regulated in on-site instrumentation. Moreover, unignorable moisture in the sampled gas might cause deterioration of the adsorption tube and detector. Hence, the idea arose of using Carbotrap B at 100°C. Most of the moisture and high/medium volatility compounds would pass through the adsorption tube. Carbotrap B at room temperature trapped 1,1,1-trichloroethane (b.p. 74°C) completely, while the recovery rate decreased to 60% at 50°C, and 0% at 100°C.[17] On the other hand, 1,1,2,2-tetrachloroethylene (b.p. 147°C) was completely trapped at the 25°–100°C range. In other words, Carbotrap B maintained at 100°C could be used to cut off volatile compounds such as 1,1,1-trichloroethane while sufficiently recovering compounds with a b.p. higher than 147°C.

Results and discussion

Time course of LVOH, TEQ, CBs, and CPs

The furnace temperature and the levels of LVOH, TEQ, CBs, and CPs in runs A1, A2, and A3 are presented in Fig. 3. In accordance with the increase in furnace temperature, LVOH increased followed by a rapid decrease. The changes in LVOH, CBs, and CPs levels agreed with changes in TEQ. The concentrations of LVOH, TEQ, CBs, and CPs in runs A1 and A3 were the same, while A2 showed higher levels of TEQ. Sampling for run A2 was conducted before the bag filter; therefore, the TEQ in A2 involved particulate dioxins, while TEQ in A1 and A3 did not.

In the last half of run A2, a peak in LVOH, TEQ, CBs, and CPs levels was observed. A combustion fluctuation presumably took place. This event suggested that surrogates LVOH, CBs, and CPs could be useful to detect temporary increases in TEQ.

The B-MWI results, runs B1 and B2, are presented in Fig. 4. In the same manner as for runs in A-MWI, consistent decreases in LVOH, TEQ, CBs, and CPs were observed. The concentrations in B1 and B2 were higher than those in A1 and A3 because the gas of A1 and A3 was treated by activated carbon injection, whereas that of B1 and B2 was not. In addition, slow emission of accumulated organohalogen compounds that were formed between the last shutdown and the present startup in B-MWI was suspected. This is discussed in the section on dioxin isomer analysis.

Correlation of LVOH, CBs, and CPs with TEQ

All the surrogates (LVOH, CBs, and CPs) might be expected to be good indicators from the time course data shown in Figs. 3 and 4. However, the correlation of surrogates versus dioxins throughout different runs must be examined; therefore, all data sets for LVOH–TEQ, CBs–TEQ and CPs–TEQ were plotted in Figs. 5, 6, and 7, respectively. The data are grouped into three categories: the outlet of the bag filter in A-MWI (runs A1 and A3), the inlet of the bag filter in A-MWI (run A2), and the outlet of the bag filter in B-MWI (runs B1 and B2). It should be noted that the data from run A2 involved particulate dioxins, whereas LVOH took the form of a gaseous fraction only.

The LVOH–TEQ plots in Fig. 5 fit two lines. The data from run A2 were correlated with a separate line (correlation coefficient: r = 0.89). On the other hand, the data from runs A1, A3, B1, and B2 could be correlated with a unified line (r = 0.98). It is reasonable that the data were divided into two groups because the TEQ data from run A2 included particulate dioxins, whereas the data from other runs did not.

On the other hand, the correlation of CBs to TEQ was site specific. In other words, the data from A1 and A3 were located far from those of B1 and B2, although those data were based on gaseous TEQ (Fig. 6). Presumably, CBs could not predict TEQ with a unified line. The same was also true for CPs, as presented in Fig. 7.

However, the results should be critically evaluated since the current correlation line is different from a previously reported line of low-volatility organochlorine (LVOCl) versus TEQ (depicted with a thick gray line in Fig. 5).[12] The line of the present study was apparently located in a high TEQ zone compared to the previously reported line. The difference could partly be attributed the differences in sampling site. In the present study, the gas was sampled at the outlet of an activated carbon-injected bag filter (A-MWI),

Fig. 3. Levels of low-volatility organohalogen compounds (*LVOH*), toxicity equivalent quantity (*TEQ*), chlorobenzenes (*CBs*), and chlorophenols (*CPs*) in A-MWI for **a** run A1 (outlet of bag filter), **b** run A2 (inlet of bag filter), and **c** run A3 (outlet of bag filter). *Dashed line*, temperature (°C); *solid line*, LVOH (μgCl Nm^{-3}); *horizontal bars*, TEQ (ngTEQ Nm^{-3}); *squares*, CBs (μgCl Nm^{-3}); *triangles*, CPs (μgCl Nm^{-3})
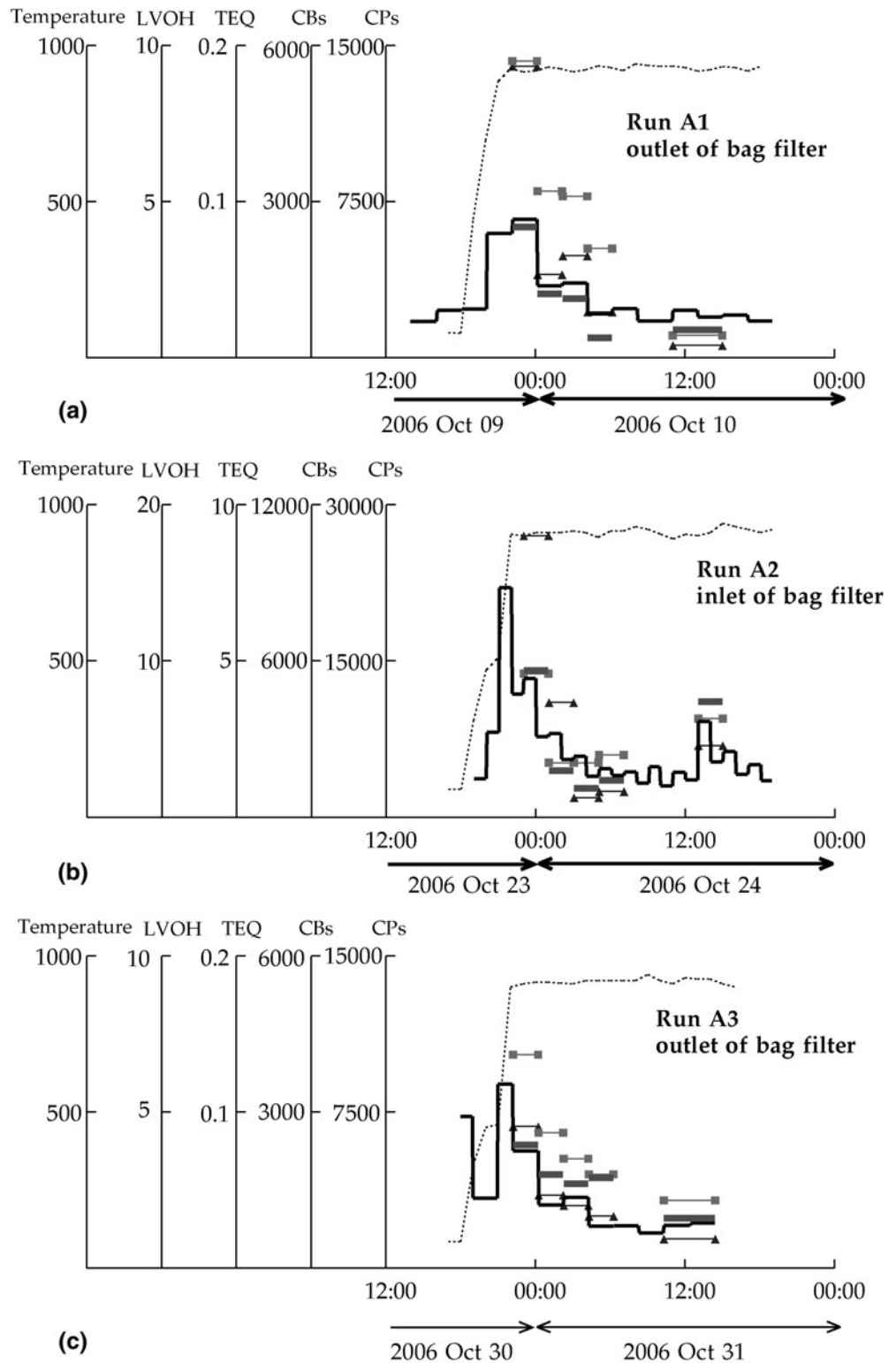
and a bag filter with no activated carbon injection (B-MWI) connected to a wet scrubber and catalyst. In contrast, most of the previous studied sites were sampled after the wet scrubber and activated carbon-circulating bag filter. Thus, less-volatile compounds would have been more effectively captured by the latter devices. LVOH–TEQ correlation is thus affected by such air pollution control devices.

Dioxin isomer analysis

One of the other mechanisms which could affect LVOH–TEQ correlation is the memory effect in the startup condition. In the steady state, the rate of dioxin formation and emission must be the same, whereas the two rates could differ in startup and shutdown conditions. In other words,

Fig. 4. Levels of LVOH, TEQ, CBs, and CPs in B-MWI for **a** run B1 and **b** run B2


(a)

(b)
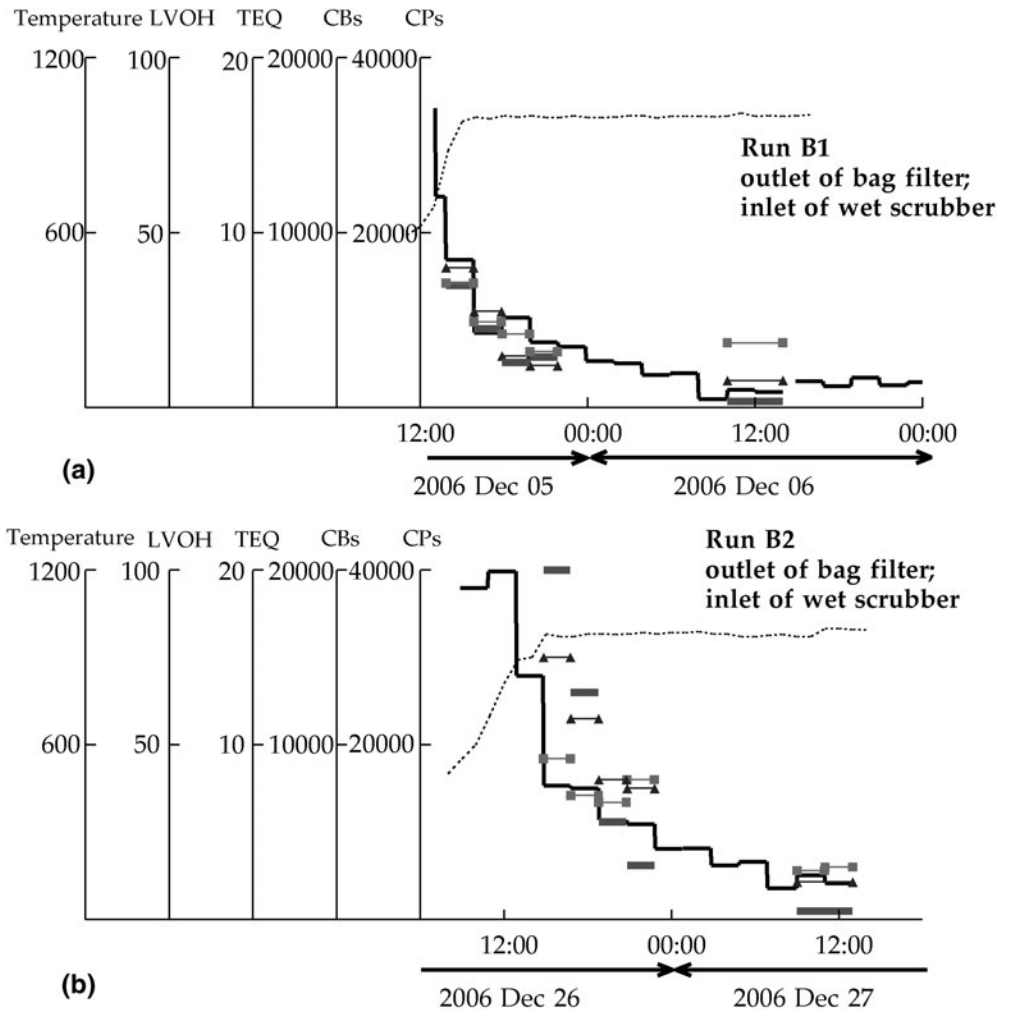
Fig. 5. Correlation plots of LVOH versus TEQ. The data from runs A1, A3, B1, and B2 could be correlated by one unified line, whereas the data from run A2, which involved particulate dioxins, were located separately. Comparing the current data with the correlation line of low-volatility organic chlorine versus TEQ from a previous article, the present data are shifted to a high TEQ zone. *BF*, bag filter
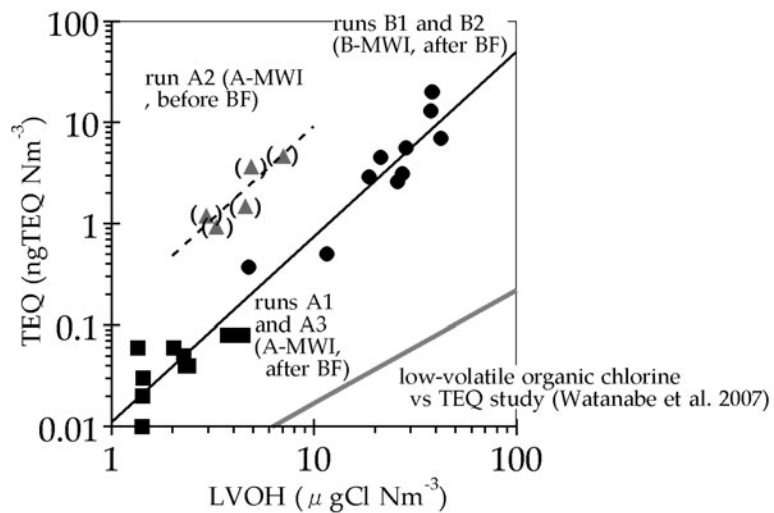
run A2 (before bagfilter): $\log_{10}(TEQ) = -0.867 + 1.83 \log_{10}(LVOH)$ $r = 0.89$

runs A1;A3;B1 and B2 (after bagfilter) : $\log_{10}(TEQ) = -1.939 + 1.82 \log_{10}(LVOH)$ $r = 0.98$

Fig. 6. Correlation plots of CBs versus TEQ. The data from A-MWI and B-MWI resulted in notably different lines
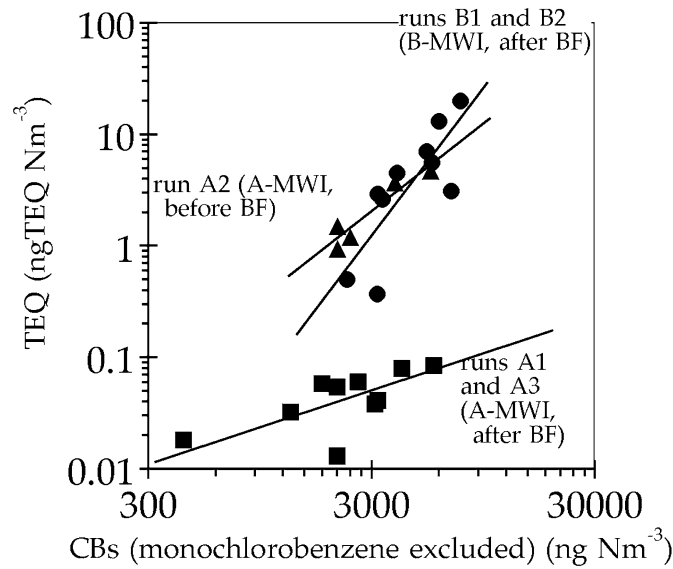
run A2 (before bagfilter): $\log_{10}(TEQ) = -5.19 + 1.58 \log_{10}(CBs)$ $r = 0.95$

runs A1 and A3 (after bagfilter) : $\log_{10}(TEQ) = -3.62 + 0.66 \log_{10}(CBs)$ $r = 0.52$

runs B1 abd B2 (after bagfilter) : $\log_{10}(TEQ) = -9.10 + 2.64 \log_{10}(CBs)$ $r = 0.81$

Fig. 7. Correlation plots of CPs versus TEQ. As was also the case for CBs versus TEQ (Fig. 6), the correlation lines could not be unified
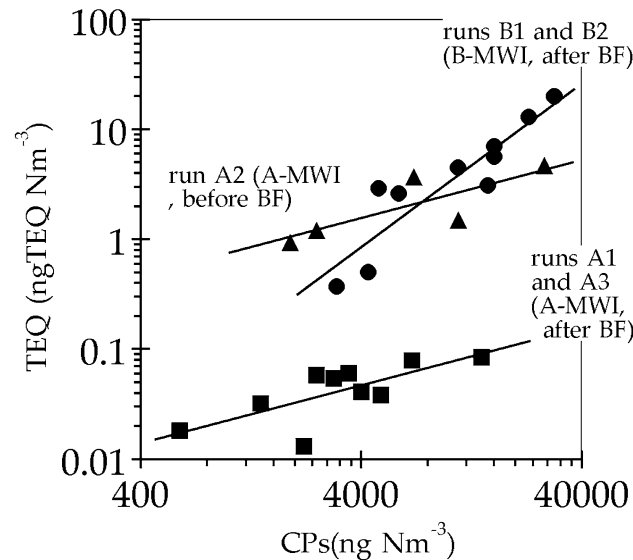

run A2 (before bagfilter): $\log_{10}(TEQ) = -1.73 + 0.53 \log_{10}(CPs)$ $r = 0.81$

runs A1 and A3 (after bagfilter) : $\log_{10}(TEQ) = -3.25 + 0.53 \log_{10}(CPs)$ $r = 0.63$

runs B1 and B2 (after bagfilter) : $\log_{10}(TEQ) = -5.46 + 1.50 \log_{10}(CPs)$ $r = 0.91$

some of the generated compounds are not emitted at the same rate but will adsorptively remain in the facilities, followed by gradual desorption according to the temperature. The less volatile the compound is, the more persistently it will remain. In order to determine the behavior dependency on volatility, the trend of each dioxin isomer was examined using normalization by the initial data:

$$(\text{Normalized concentration}) = (\text{Measured concentration})/(\text{Initial concentration}) \times 100\%$$

(1)

The initial concentration was set as the first measured relevant isomer concentration; LVOH was normalized in the same way. The results from A-MWI and B-MWI are presented in

Fig. 8. Levels of normalized LVOH and each isomer of polychlorinated dibenzo-*p*-dioxins/dibenzo furans (PCDD/DFs) in A-MWI. Measured real concentrations were normalized by dividing by the initial values, which were collected at the first dioxin measurement as shown in Eq. 1. No notable differences between LVOH and PCDD/DFs isomer levels were found. **a** DDs in A1, **b** DFs in A1, **c** DDs in A2, **d** DFs in A2, **e** DDs in A3, **f** DFs in A3
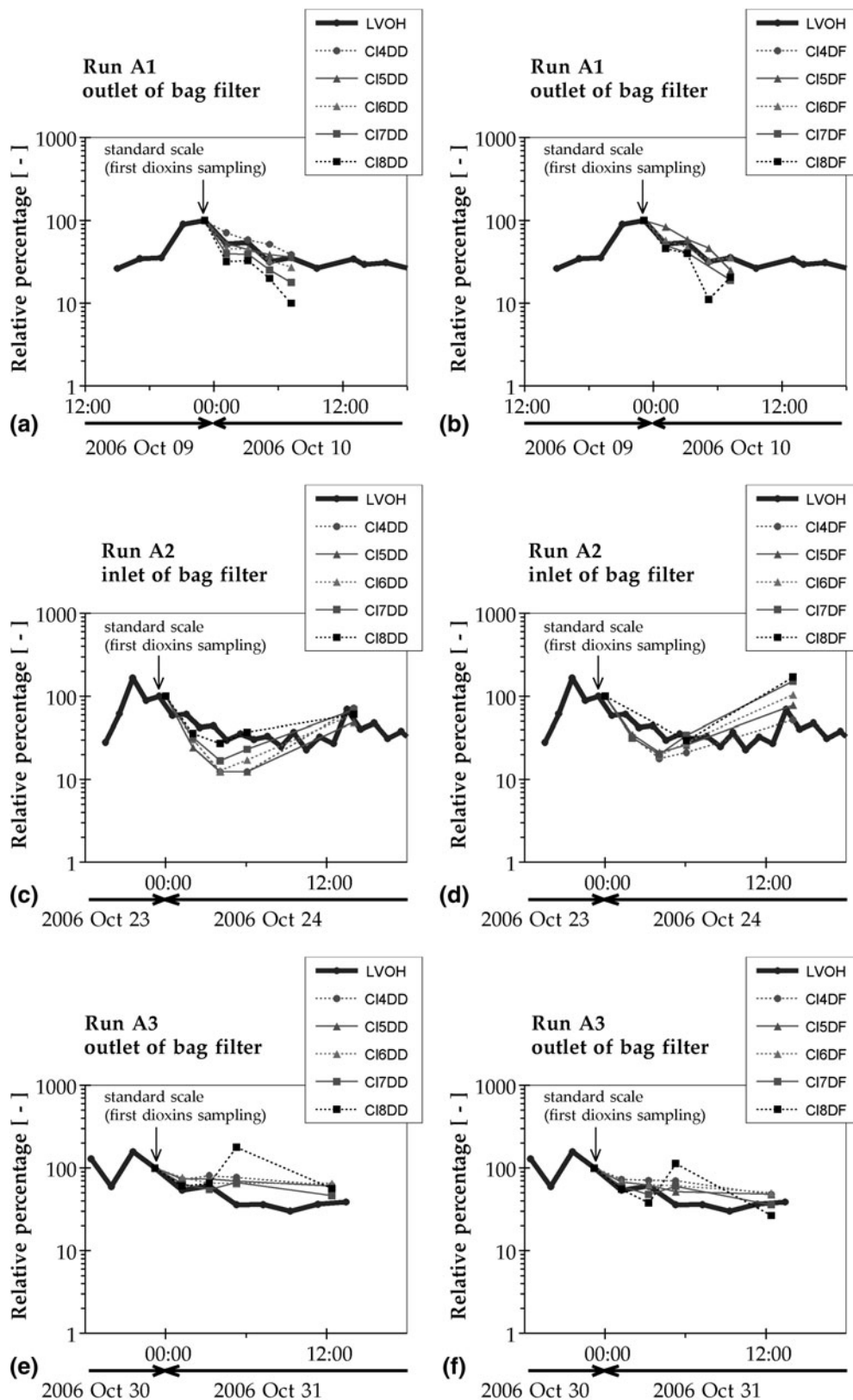

Figs. 8 and 9, respectively. The isomers of PCDDs and PCDFs are plotted separately. The results from A-MWI showed little change in isomer pattern; however, results from B-MWI showed a notable change. Moderately chlorinated congeners, such as Cl_4-DD/DFs, decreased to less than 10% of the initial value, whereas less volatile congeners, such as Cl_7- and Cl_8-DD/DFs, did not greatly decrease. Moreover, Cl_8-DD/DFs concentration increased in the early samples.

Fig. 9. Levels of normalized LVOH and each congener of PCDD/DFs in B-MWI. Moderately chlorinated dioxins, such as Cl_4- and Cl_5-substituted, decreased more quickly than the others, whereas highly chlorinated dioxins decreased more slowly. The LVOH levels were located between these two groups. The levels of highly chlorinated isomers (Cl_7- and Cl_8-substituted) often increased in the early samples
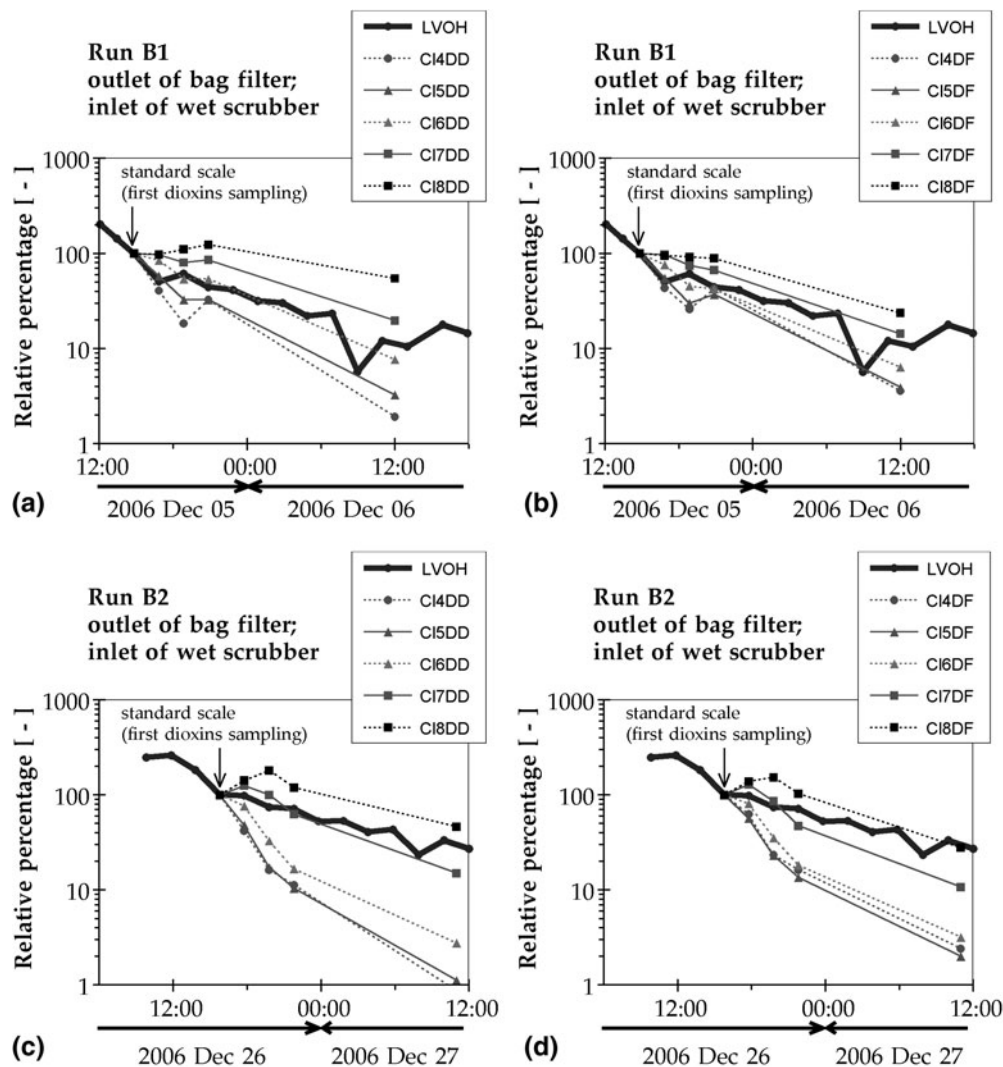
It could be suggested that a significant amount of dioxins were formed in B-MWI during the furnace downtime, i.e., between the last incineration shutdown and the present startup. The condition of the furnaces during shutdown was different in A- MWI and B-MWI. In A-MWI, air exchange was maintained in the furnace at ambient temperature, whereas in B-MWI the furnace was completely closed, hence the temperature was kept higher than ambient conditions. The condition of B-MWI might have caused formation and accumulation of organohalogen compounds. This hypothesis agrees with the explanation that the accumulated compounds were swept out with the temperature increase on startup.

LVOH as an organohalogen emission warning surrogate

Previous studies[18–22] on dioxin formation mechanisms have suggested multiple pathways and factors, e.g., the in-fire and on-ash formation mechanisms of Hunsinger et al.,[21] and the incomplete combustion and chlorinating activity of Öberg and Öhrström.[22] Hence, it is difficult for any pathway-specific compounds to act as suitable surrogates. On the other hand, LVOH without identifying compounds can cover various products from various pathways. In addition, not only the organohalogen compounds formed but also those present due to incomplete destruction of burned materials will be included in LVOH. As seen in the present work (i.e., Fig. 9), the response of LVOH is quicker than that of dioxins. LVOH can be considered to be superior to dioxins themselves in warning of dioxin formation.

Conclusions

Low-volatility organohalogen compounds (LVOH), chlorobenzenes (CBs), and chlorophenols (CPs) were comparatively evaluated as dioxin surrogates through startup flue gas monitoring in five runs at two MWIs. The level changes of all surrogates corresponded to changes in TEQ. The correlation of LVOH versus TEQ was consistent in different runs; however, those of CBs versus TEQ and CPs versus TEQ depended on the site. A number of competing formation pathways, whose contribution ratios are changeable,

was thought to affect the ratio of CBs, CPs, and dioxin formation. In contrast, the correlation of LVOH versus TEQ was seen to be stable, because LVOH covers a number of organohalogen compounds through various pathways.

However, it should be noted that flue gas treatment devices affect the correlation of LVOH versus TEQ. The other significant factor affecting the correlation of LVOH versus TEQ was considered to be the memory effect, i.e., delayed emission of less volatile compounds. An attempt was made to obtain evidence of the memory effect by dioxin isomer analysis under startup conditions; consequently, a quick decrease of relatively volatile compounds and the delayed emission of less volatile compounds were found in one MWI, but not in the other. From this observation, it might be suspected that a significant amount of organohalogen compounds was formed in the furnace during the furnace downtime, i.e., between the last incineration shutdown and the next startup; as a result, the accumulated organohalogen compounds were gradually emitted.

In general, dioxin formation can be monitored by surrogates; LVOH, being independent of formation pathway, is a good candidate. CBs and CPs are less effective as surrogates because the ratios of CBs to TEQ and CPs to TEQ are not as stable as those of LVOH due to variations in the formation pathways. Dioxin emissions can be predicted by LVOH at a determined site if the conditions are free from the memory effect, which results in the delayed emission of less volatile organic compounds.

However, LVOH can act as a useful dioxin formation indicator because its response is quicker than those of the dioxins themselves. Moreover, since LVOH includes various organohalogen compounds from incomplete destruction of burned materials, LVOH is considered to be a versatile surrogate for organohalogen compounds, including dioxins.

References

1. Nordsieck HO, Neuer-Etscheidt K, Orasche J, Zimmermann R (2004) Changes in PCDD/PCDF formation process during instationary phases of combustor operation. Organohal Comp 66:1153–1159
2. Tejima H, Nishigaki M, Fujita Y, Matsumoto A, Takeda N, Takaoka M (2007) Characteristics of dioxin emissions at startup and shutdown of MSW incinerators. Chemosphere 66:1123–1130
3. Lee CW, Tabor DG, Cowen KA (2008) Environmental technology verification (ETV) test of dioxin emission monitors. J Mater Cycles Waste Manag 10:38–45
4. Oeberg T, Neuer-Etscheidt K, Nordsieck H, Zimmermann R (2002) Dioxin surrogates – a comparison of approaches. Organohal Comp 59; 37–44. (Revised version with a corrected reference list is available at http://www.tomasoberg.com/pdf/surrogates.pdf)
5. Lemieux PM (2004) The use of surrogate compounds as indicators of PCDD/F concentrations in combustor stack gases. EPA-600/R-04-024
6. US Environmental Protection Agency (2007) Environmental technology verification program, dioxin emission monitoring system. Available at: http://www.epa.gov/etv/pubs/600s07002.pdf
7. Blumenstock M, Kettrup A, Zimmermann R, Schramm K-W (2001) Identification of surrogate compounds for the emission of PCDD/F (I-TEQ value) and evaluation of their on-line real-time detectability in flue gases of waste incineration plants by REMPI-TOFMS mass spectrometry. Chemosphere 42:507–518
8. Yamada M, Waki I, Sakairi M, Sakamoto M, Imai T (2002) Real-time monitoring of dioxin precursors by APCI-ITMS: control of catalyst injection. Organohal Comp 59:65–68
9. Watanabe I, Kudo M, Kurata Y, Yamasaki K, Terashima C, Ikeguchi T (2002) Analysis of chlorophenols in flue gas of waste incinerators by HPLC/ECD installed sequential automated monitoring instrument as well as by HPLC/MS and GC/MS. Organohal Comp 59:89–92
10. Kato M, Urano K, Tasaki T (2000) Development of semi- and nonvolatile organic halogen as a new hazardous index of flue gas. Environ Sci Technol 34:4071–4075
11. Kawamoto K, Imaizumi T, Fujiyoshi H, Tanaka M (2002) Application of concentration of organohalogen compounds in flue gas for the management of dioxins. Organohal Comp 59:53–56
12. Watanabe N, Takakura A, Minami Y, Mizutani S, Takatsuki H (2007) Correlation of low-volatile organic chlorine (LVOCl) and PCDD/Fs in various municipal waste incinerators (MWIs). Chemosphere 67:S198–S204
13. Weber R (2005) On-line PCDD/PCDF and PCDD/PCDF surrogate monitoring. Basic difficulties due to formation characteristics, memory effects and removal efficiency of air pollution control devices. Organohal Comp 67:321–325
14. Japanese Industrial Standards Committee (2005) Method for determination of tetra- through octachlorodibenzo-p-dioxins, tetra- through octachlorodibenzofurans and dioxin-like polychlorinated biphenyls in stationary source emissions. JIS K0311
15. Watanabe N, Takakura A, Nakui H, Watanabe G, Sun I (2007) A study on the pretreatment of gas sampling for adsorption/thermal desorption analysis (in Japanese). J Environ Chem 17:461–469
16. Watanabe N, Minami Y, Mizutani S, Takatsuki H (2004) Collection efficiency and determination equivalency on the measurement of semi and low volatile organic chlorine (SLVOCl) in flue gas (in Japanese). J Environ Chem 14:597–604
17. Takakura A, Nakui H, Koyama H, Watanabe G, Watanabe N (2007) Study on sampling of organic halogenated compounds in flue gas (in Japanese). In: Proceedings of the 18th Annual Conference of The Japan Society of Waste Management Experts. Tsukuba, Japan, pp 588–590, Nov 19–21, 2007
18. Addink R, Olie K (1995) Mechanism of formation and destruction of polychlorinated dibenzo-p-dioxins and dibenzofurans in heterogeneous systems. Environ Sci Technol 29:1425–1435
19. Huang H, Bueckens A (1995) On the mechanism of dioxin formation in combustion processes. Chemosphere 31:4099–4117
20. Tuppurainen K, Halonen I, Ruokojärvi P, Tarhanen J, Ruuskanen J (1998) Formation of PCDDs and PCDFs in municipal waste incineration and its inhibition mechanisms: a review. Chemosphere 36:1493–1511
21. Hunsinger H, Jay K, Vehlow J (2002) Formation and destruction of PCDD/F inside a grate furnace. Chemosphere 46:1263–1272
22. Öberg T, Öhrström T (2003) Chlorinated aromatics from combustion: influence of chlorine, combustion conditions, and catalytic activity. Environ Sci Technol 37:3995–4000