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# Evaluation of gas-particle partition of dioxins in flue gas II: Estimation of gas-particle partition of dioxins in dust-rich flue gas by parallel sampling with different conditions

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## Abstract

For an accurate determination of the gas-particle partition of polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs) and dioxin-like biphenyls (DLPCBs) in dust-rich flue gas, a parallel monitoring procedure with an isokinetic and a non-isokinetic train was used. For four flue gas samples, the two trains gave a significantly different weight of the collected fly ash particles despite the equal gas volume sampled. On the basis of the quantitative values of PCDD/F and DLPCB homologues and the weight of the collected particles, ratios of each homologue in the real flue gas samples in gaseous form were predicted using simultaneous equations. For the four flue gas samples examined, the predicted gaseous ratios were considerably higher that those calculated using a previously reported equation, suggesting that there are some properties which affect partitions of PCDD/Fs in flue gas besides their saturation vapor pressures and fly ash concentration. The partitions for higher temperature flue gases obtained by fractional determinations of each collection device were additionally different from those predicted by the parallel collection, indicating that conventional determination by fractional measurements is subjected to large errors in dust-rich flue gas due to severe adsorption of gaseous PCDD/Fs and DLPCBs onto particles collected on a low-temperature collection device.
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## 1. Introduction

Toxic dioxins, namely polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in the environment mainly originate in emissions from thermal processes such as waste incineration or metallurgical process [1–3]. Adequate control of PCDD/Fs from thermal processes is hence extremely important to reduce their contamination levels in the environment. Information on the gas-particle partition of PCDD/Fs in flue gas helps to develop an efficient cleaning system of emission gas, that is,

an effective removal system addressing both the gaseous form and the particle-bound form.

The gasification behavior of fly ash PCDD/Fs was reported in a separate paper [4], stating that fly ash PCDD/Fs gasified in the range of 350–400 °C, suggesting that this is the threshold of their gas-particle partition in flue gas within the temperature region. It is, however, difficult to determine the partitions of PCDD/Fs on the basis of gas temperature only, since their physical states depend on other properties as well.

In the sampling train used as a part of the conventional sampling and analytical procedures for PCDD/Fs in flue gas [5–7], dioxins-carrying particles (fly ash) are collected on a thimble filter installed at the front of the train, while gaseous analytes passing through the filter to be trapped at downstream

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devices by absorption or adsorption. Some researchers estimated the gas-particle partition of PCDD/Fs on the basis of their partition in each collection device, and varying results are reported [1,8–13]. Variations seem to be attributed to the obvious difference in temperature between flue gas and collection devices. Conventional methods fix the temperature of a particle collection device to below 120 °C during gas sampling in order to prevent secondary formation of PCDD/Fs on collected particles, which can result in adsorption of collected gaseous analytes onto the particles (i.e., cold-trap effect). Chi et al. [14,15] recommended that the acceptable amount of particles loaded onto a thimble filter should be lower than $1.4\,mg\,cm^{-2}$ in order to prevent the adsorption of vapor-phase PCDD/Fs. Although such control method is easily applied to a cleaned flue gas (e.g., bag filter outlet), it is quite difficult for collection of dust-rich flue gas. Adsorption should hence not be ignored despite sufficient control but due to a considerable difference in temperature of the collection device and the actual flue gas. Desorption of particle-bound analytes from collected particles (i.e., blow-off effect) may moreover occur. It seems difficult to determine gas-particle partitions of PCDD/Fs on the basis of the results of fractional determination of each collection device.

Conventional methods establish isokinetic sampling to ensure a representative collection of fly ash particles. When parallel sampling is performed using a combination of an isokinetic and a non-isokinetic trains, due to inertia acting on fly ash the amount of collected particles should be different for the same volume of sample gas collected [16]. In this case, assuming that every in-flight ash particle carries entirely the same amount of PCDD/Fs irrespective of its size or density, the collected amounts of particle-bound PCDD/Fs should be proportional to the amount of collected particles, whereas the collected amounts of gaseous analytes should be identical. It is thus expected that the actual gas-particle partitions of flue gas PCDD/Fs would be more accurately determined by comparing their relative quantitative values and the amounts of collected particles obtained from both sampling trains.

This study examined the parallel sampling using both isokinetic and non-isokinetic sampling trains for four dust-rich flue gases to determine the gas-particle partitions of each PCDD/F homologue. In addition, the obtained partitions are compared with those obtained on the basis of the fractional determination of collection devices and those calculated using a previously reported formula. Dioxin-like polychlorinated biphenyls (DLPCBs) of similar toxicity to PCDD/Fs [17,18] were simultaneously investigated.

## 2. Experimental

### 2.1. Apparatus

Suction of flue gas was performed using an NG-17S gas pump (Nigorikawa Rikakogyo Corp., Tokyo). The sucked gas volume was measured using a wet gas meter W-NK-1A also from Nigorikawa. An automated gas analyzer PG-230 (Horiba, Tokyo) was used for measurement of $O_2$, $CO_2$, and CO con-

tents in flue gas during sampling. Pressurized liquid extraction (PLE) was performed using ASE-200 and ASE-300 (Dionex Corp., Sunnyvale, CA) instruments. PCDD/Fs and DLPCBs were analyzed by high-resolution gas chromatography/mass spectrometry (HRGC-HRMS) with an HP-6890 Plus (Agilent, Palo Alto, CA) gas chromatograph coupled to a JMS-700D mass spectrometer (JEOL, Tokyo). The analytes were determined with BPX-DXN (SGE, Austin, TX) and HT-8PCB (Kanto Chemicals, Tokyo) capillary columns.

### 2.2. Materials and reagents

A quartz thimble filter for flue gas sampling (25 mm i.d., 90 mm length) was purchased from Whatman International Ltd. (Maidstone, England). A DiOANA® filter was supplied by Miura Kogyo Corp. (Ehime, Japan). All dioxin-analytical-grade solvents and adsorbents were purchased from either Wako Pure Chemical Industries (Osaka, Japan) or Kanto Chemicals. PCB-analytical-grade hydrochloric acid was obtained from Kanto.

PCDD/F and DLPCB standards, including $^{13}$C-labeled homologues, were purchased from Wellington Laboratories (Ontario, Canada) or Cambridge Isotope Laboratories Inc. (Andover, MD). The abbreviations for the number of chlorine atoms are as follows: tetra, Te; penta, Pe; hexa, Hx; hepta, Hp; and octa, O. All DLPCBs are referred to by their International Union of Pure and Applied Chemistry (IUPAC) numbers.

A surrogate solution (SuS) was prepared in toluene. This solution contained 17 $^{13}$C-labeled 2,3,7,8-chlorinated PCDD/F congeners (2,3,7,8-TeCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD, 2,3,7,8-TeCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF, and OCDF) and 12 $^{13}$C-labeled DLPCBs (4 non-*ortho* congeners whose IUPAC Nos. are 77, 81, 126, and 169, and 8 mono-*ortho* congeners whose IUPAC Nos. are 105, 114, 118, 123, 156, 157, 167, and 189), each at a concentration of $10\,\mu g\,L^{-1}$, with the exception of $^{13}$C-OCDD/F at $20\,\mu g\,L^{-1}$.

A recovery standards solution (RS) in nonane was prepared containing $^{13}$C-labeled 1,2,7,8-TeCDF, 1,2,3,4,7-PeCDD, 1,2,3,4,6,9-HxCDF, 1,2,3,4,6,8,9-HpCDF, 2,3′,4′,5-TeCB (#70), 2,2′,3,4,4′-PeCB (#85), 2,2′,3,4,4′,5′-HxCB (#138) and 2,2′,3,3′,5,5′,6-HpCB (#178), each at a concentration of $10\,\mu g\,L^{-1}$.

A sampling standard solution (SaS) in toluene was prepared containing $^{13}$C-labeled 1,2,3,4-TeCDD at a concentration of $20\,\mu g\,L^{-1}$.

### 2.3. Flue gas sampling and analysis of PCDD/Fs and DLPCBs

We examined the four flue gas samples collected at four municipal waste incinerators in Saitama, Japan. Properties of the gases are shown in Table 1. All samples were collected upstream of a bag filter. Prior to collection, temperature and velocity of the gas were measured according to JIS Z8808 [16],

Table 1
Properties of the investigated flue gas of four incinerators

|  | Sample 1 | Sample 2 | Sample 3 | Sample 4 |
|---|---|---|---|---|
| Furnace type | Stoker | Fluidized bed | Stoker | Fluidized bed |
| Capacity (t h$^{-1}$) | 2.9 | 3.1 | 6.2 | 3.0 |
| Temperature (°C) | 190–210 | 190–210 | 240–250 | 330–380 |
| $CO_2$ (%) | 8.6 | 9.1 | 11 | 8.4 |
| $O_2$ (%) | 11.4 | 10.9 | 9.0 | 12.0 |
| Water (%) | 39.6 | 33.2 | 34.4 | 32.5 |
| Particulate matter concentration (g Nm$^{-3}$)[a] | 0.68 | 6.4 | 0.96 | 3.2 |

[a] Derived from the weight of the particulate matter collected by an isokinetic sampling of each flue gas.

Table 2
Sampling conditions of the investigated flue gas

|  | Sample 1 | | Sample 2 | | Sample 3 | | Sample 4 | |
|---|---|---|---|---|---|---|---|---|
|  | Iso[a] | Non[b] | Iso | Non | Iso | Non | Iso | Non |
| Flue gas flow rate (m s$^{-1}$) | 26.4 | | 8.7 | | 9.1 | | 9.7 | |
| Nozzle diameter (mm) | 6 | 10 | 8 | 20 | 8 | 12 | 8 | 12 |
| Performed sampling rate (L min$^{-1}$) | 18.0 | | 10.6 | | 10.6 | | 15.0 | |
| Sampling volume (Nm$^3$) | 1.38 | | 1.18 | | 0.810 | | 1.10 | |
| Collected particulate matter (g) | 0.927 | 1.82 | 7.60 | 28.0 | 0.788 | 1.58 | 7.80 | 16.6 |

[a] Isokinetic sampling.
[b] Non-isokinetic sampling.

and an isokinetic ratio was determined on the basis of these data.

The type-II sampling train set by JIS K0311 [7] was employed, in which dust particles and gaseous analytes are trapped on a thimble filter and a Dioana® filter, respectively. The DiOANA® filter was spiked with 25 μL SaS for all collections to confirm correct sampling. The temperature of the thimble filter and the DiOANA® filter was maintained at 100–120 °C during collection.

Conditions of the performed parallel samplings are shown in Table 2. Sampling with one train was performed isokinetically, and the other non-isokinetic train was equipped with a nozzle whose inner diameter was larger than that of the isokinetic train. Both samplings were performed at a same suction rate. As shown in Table 2, the amounts of dust collected by the non-isokinetic train were higher than those by the isokinetic train at the same collected gas volume.

After sampling, fly ash particles adsorbed on the inside wall of the nozzle were recovered with small amount of quartz wool and put together with those collected onto the thimble filter. Thereafter the fly ash was dried in a desiccator with silica gel granules until constant weight, which was recorded.

The analytical procedures of PCDD/Fs and DLPCBs in each collection device are shown in Fig. 1, which generally followed JIS K0311. Collected fly ash was pretreated with 2 M-HCl, air-dried and Soxhlet extracted with toluene (24 h). The DiOANA® filter was extracted by PLE with toluene under the conditions described in Table 3. In addition, fly ash particle residues after Soxhlet extraction were submitted to PLE with toluene in order to confirm the extraction efficiency of the analytes by Soxhlet, whose extraction conditions are also presented in Table 3. SuS were added to the fly ash extracts before cleanup, and to the Dioana® filter before PLE. The distributions of PCDD/Fs and

DLPCBs in each device were analyzed separately. The obtained extracts were cleaned, as shown in Fig. 1, and were submitted to HRGC-HRMS analysis whose conditions were described elsewhere [19].
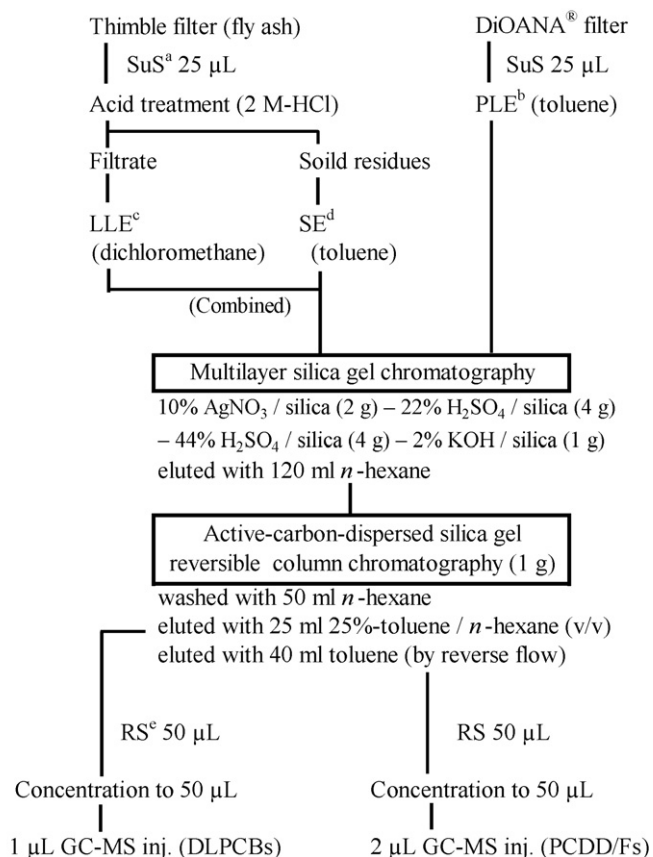


Fig. 1. Analytical procedure of PCDD/Fs and DLPCBs in flue gas.

Table 3
PLE conditions

|  | DiOANA® filter | Additional extraction from a thimble filter |
|---|---|---|
| PLE instrument | ASE-200 | ASE-300 |
| Cell volume (mL) | 33 | 99 |
| Cell temperature (°C) | 150 | 200 |
| Cell pressure (psi) | 1500 | 1500 |
| Preheat time (min) | 0 | 0 |
| Static time (min) | 7 | 7 |
| Flush volume (% of cell volume) | 70 | 100 |
| Purge time (s) | 60 | 60 |
| Static cycle | 2 | 2 |
| Method repetition | 2 | 2 |

### 2.4. Accuracy control

An instrumental blank, reproducibility of the quantitative values of HRGC-HRMS analysis, and a procedure blank were evaluated as described elsewhere [19]. This study requires high accuracy of flue gas sampling and analysis. Highly accurate determination of PCDD/Fs and DLPCBs in flue gas requires: (a) a high reproducibility of gas sampling, (b) their adequate extraction from collection devices (in particular extraction from fly ash particles), and (c) quality control on cleanup process of the extract. First, the assay accuracy was defined by determining the fly ash sample, within the intercalibration exercise organized by the Japanese Ministry of the Environment in 2001, and the results were described elsewhere [19]: for all 2,3,7,8-chlorinated PCDD/F congeners, PCDD/F homologues, and DLPCB congeners, the absolute values of the $z$-score were below 2, and the relative standard deviations of values of all PCDD/F homologues in triplicate determinations were in the range of 1.4–6.1%, proving the high accuracy and reproducibility of the determinations. Also, for all determinations in this study, recovery of SuS was over 70%, proving the validity of the sample treatment.

Next, prior to this study, dual measurements by using identical isokinetic trains were conducted. As shown in Table 4, in three pairs of determinations, the differences of all PCDD/F homologues and DLPCBs (non-*ortho* groups and mono-*ortho* groups) were in the range of 0.9–13%, proving the high reproducibility of the determination including gas sampling. In addition, for all determinations in this study, recovery of the sampling spike was in the range of 84–94%, proving the high efficiency of gas sampling in this study.

Finally, fly ash residues after Soxhlet extraction were additionally extracted by PLE with toluene, and analyte residues in the extracts were determined: amounts of the analytes detected in the PLE extracts were negligible (below 3% of the amounts in the Soxhlet extracts), proving that the analytes were sufficiently extracted by Soxhlet.

## 3. Results and discussion

The results of determinations of PCDD/Fs and DLPCBs in the four flue gas samples are shown in Table 5. The dust concentration in the sample was calculated on the basis of the weight

Table 4
Results of dual measurements of PCDD/Fs and DLPCBs in flue gas

|  | Concentration (ng Nm⁻³) | | Difference (%)[a] |
|---|---|---|---|
|  | Value1 | Value2 | |
| **Trial-1 (furnace type: fluidized bed, gas temperature: 325–360 °C)** | | | |
| TeCDDs | 4.27 | 4.50 | 5.4 |
| PeCDDs | 3.63 | 3.72 | 2.5 |
| HxCDDs | 1.93 | 2.17 | 12 |
| HpCDDs | 0.539 | 0.587 | 8.9 |
| OCDD | 0.325 | 0.328 | 0.88 |
| TeCDFs | 5.78 | 5.62 | −2.8 |
| PeCDFs | 2.95 | 3.20 | 8.8 |
| HxCDFs | 1.56 | 1.65 | 6.0 |
| HpCDFs | 0.687 | 0.757 | 10 |
| OCDF | 0.506 | 0.556 | 9.9 |
| non-*ortho* DLPCBs | 0.683 | 0.673 | −1.6 |
| mono-*ortho* DLPCBs | 1.68 | 1.66 | −1.2 |
| **Trial-2 (furnace type: batch, gas temperature: 165–175 °C)** | | | |
| TeCDDs | 1.94 | 1.80 | −7.2 |
| PeCDDs | 1.64 | 1.52 | −7.3 |
| HxCDDs | 0.794 | 0.814 | 2.5 |
| HpCDDs | 0.0877 | 0.0936 | 6.7 |
| OCDD | ND[b] | ND | – |
| TeCDFs | 2.56 | 2.64 | 3.1 |
| PeCDFs | 0.965 | 1.04 | 7.8 |
| HxCDFs | 0.257 | 0.264 | 2.7 |
| HpCDFs | 0.0154 | 0.0147 | −4.5 |
| OCDF | ND | ND | – |
| non-*ortho* DLPCBs | 0.128 | 0.131 | 2.3 |
| mono-*ortho* DLPCBs | 0.154 | 0.149 | −3.2 |
| **Trial-3 (furnace type: batch, gas temperature: 75–80 °C)** | | | |
| TeCDDs | 0.814 | 0.915 | 12 |
| PeCDDs | 0.874 | 0.954 | 9.2 |
| HxCDDs | 1.14 | 1.23 | 7.9 |
| HpCDDs | 0.551 | 0.587 | 6.5 |
| OCDD | 0.358 | 0.362 | 1.1 |
| TeCDFs | 1.23 | 1.21 | −1.6 |
| PeCDFs | 0.824 | 0.858 | 4.1 |
| HxCDFs | 0.593 | 0.642 | 8.3 |
| HpCDFs | 0.244 | 0.239 | −2.0 |
| OCDF | ND | ND | – |
| non-*ortho* DLPCBs | 0.288 | 0.326 | 13 |
| mono-*ortho* DLPCBs | 0.595 | 0.639 | 7.4 |

[a] Difference (%) = (Value2 − Value1)/Value1.
[b] Not detected.

of collected fly ash and the collected gas volume by the isokinetic train. Ratios of the gaseous forms ($R_G1$) were calculated by means of the following simultaneous equations on the basis of the quantitative results of the parallel sampling:

$$(C_{PB} \times W_{iso}) + (C_{gas} \times V_{iso}) = A_{iso}$$

$$(C_{PB} \times W_{non}) + (C_{gas} \times V_{non}) = A_{non}$$

$$R_G1 = \frac{(C_{gas} \times V_{iso})}{A_{iso}} \times 100$$

where $C_{PB}$: concentration of the particle-bound analytes in the fly ash of the real flue gas (ng g⁻¹), $C_{gas}$: concentration of the gaseous analytes in the real flue gas (ng Nm⁻³), $W_{iso}$: weight of the collected particles by the isokinetic sampling (g), $W_{non}$:

Table 5
Results of parallel measurements of four flue gas samples

| | Quantitative value (ng) | | | | | | Calcd. $C_{PB}$[c] (ng g$^{-1}$) | Calcd. $C_{gas}$[d] (ng Nm$^{-3}$) | $R_G 1$ (%)[e] |
|---|---|---|---|---|---|---|---|---|---|
| | Isokinetic sampling | | | Non-isokinetic sampling | | | | | |
| | TF[a] | DF[b] | Sum ($A_{iso}$) | TF | DF | Sum ($A_{non}$) | | | |
| **(Sample 1)** | | | | | | | | | |
| TeCDDs | 0.970 | 1.67 | 2.64 | 1.80 | 1.55 | 3.36 | 0.786 | 1.39 | 72 |
| PeCDDs | 1.95 | 1.92 | 3.86 | 3.91 | 1.55 | 5.46 | 1.77 | 1.62 | 57 |
| HxCDDs | 3.24 | 1.78 | 5.02 | 6.51 | 1.28 | 7.80 | 3.10 | 1.56 | 43 |
| HpCDDs | 3.31 | 0.936 | 4.25 | 6.83 | 0.731 | 7.56 | 3.71 | 0.587 | 19 |
| OCDD | 3.23 | 0.521 | 3.75 | 6.46 | 0.393 | 6.85 | 3.48 | 0.382 | 14 |
| TeCDFs | 3.87 | 7.82 | 11.7 | 5.54 | 7.23 | 12.8 | 1.13 | 7.74 | 91 |
| PeCDFs | 4.35 | 6.35 | 10.7 | 7.11 | 5.71 | 12.8 | 2.31 | 6.23 | 80 |
| HxCDFs | 5.15 | 4.65 | 9.80 | 8.19 | 3.39 | 11.59 | 1.94 | 5.82 | 82 |
| HpCDFs | 3.78 | 1.52 | 5.30 | 6.08 | 1.14 | 7.22 | 2.12 | 2.43 | 63 |
| OCDF | 1.58 | 0.288 | 1.87 | 2.44 | 0.193 | 2.64 | 0.850 | 0.789 | 58 |
| non-*ortho* DLPCBs | 0.231 | 0.516 | 0.747 | 0.342 | 0.524 | 0.866 | 0.171 | 0.429 | 79 |
| mono-*ortho* DLPCBs | 0.306 | 0.808 | 1.11 | 0.415 | 0.808 | 1.22 | 0.167 | 0.698 | 86 |
| **(Sample 2)** | | | | | | | | | |
| TeCDDs | 4.57 | 1.29 | 5.85 | 8.90 | 0.758 | 9.66 | 0.187 | 3.74 | 76 |
| PeCDDs | 6.83 | 1.29 | 8.12 | 13.7 | 0.730 | 14.4 | 0.309 | 4.87 | 71 |
| HxCDDs | 8.97 | 0.740 | 9.71 | 20.8 | 0.587 | 21.3 | 0.570 | 4.54 | 55 |
| HpCDDs | 4.26 | 0.096 | 4.35 | 10.5 | 0.178 | 10.7 | 0.309 | 1.69 | 46 |
| OCDD | 2.37 | 0.007 | 2.38 | 6.32 | 0.040 | 6.36 | 0.195 | 0.755 | 38 |
| TeCDFs | 2.66 | 1.67 | 4.33 | 4.81 | 1.85 | 6.66 | 0.115 | 2.92 | 80 |
| PeCDFs | 1.83 | 0.878 | 2.70 | 3.73 | 1.17 | 4.90 | 0.108 | 1.59 | 70 |
| HxCDFs | 1.40 | 0.404 | 1.81 | 3.07 | 0.688 | 3.76 | 0.096 | 0.910 | 60 |
| HpCDFs | 0.787 | 0.088 | 0.875 | 1.69 | 0.188 | 1.88 | 0.049 | 0.422 | 57 |
| OCDF | 0.406 | 0.003 | 0.409 | 0.881 | 0.023 | 0.904 | 0.024 | 0.190 | 55 |
| non-*ortho* DLPCBs | 0.497 | 0.382 | 0.879 | 0.864 | 0.390 | 1.254 | 0.018 | 0.624 | 84 |
| mono-*ortho* DLPCBs | 0.570 | 0.476 | 1.05 | 1.03 | 0.629 | 1.656 | 0.030 | 0.691 | 78 |
| **(Sample 3)** | | | | | | | | | |
| TeCDDs | 0.120 | 0.082 | 0.202 | 0.148 | 0.070 | 0.217 | 0.024 | 0.224 | 91 |
| PeCDDs | 0.186 | 0.066 | 0.252 | 0.209 | 0.069 | 0.278 | 0.037 | 0.272 | 88 |
| HxCDDs | 0.239 | 0.060 | 0.299 | 0.292 | 0.053 | 0.345 | 0.065 | 0.302 | 83 |
| HpCDDs | 0.167 | 0.022 | 0.189 | 0.212 | 0.018 | 0.230 | 0.056 | 0.177 | 77 |
| OCDD | 0.110 | ND[f] | 0.110 | 0.134 | ND | 0.134 | 0.032 | 0.103 | 77 |
| TeCDFs | 0.332 | 0.432 | 0.764 | 0.461 | 0.347 | 0.808 | 0.073 | 0.862 | 92 |
| PeCDFs | 0.272 | 0.214 | 0.486 | 0.339 | 0.201 | 0.540 | 0.078 | 0.518 | 87 |
| HxCDFs | 0.264 | 0.133 | 0.397 | 0.339 | 0.130 | 0.469 | 0.099 | 0.389 | 80 |
| HpCDFs | 0.179 | 0.051 | 0.229 | 0.234 | 0.051 | 0.285 | 0.075 | 0.208 | 74 |
| OCDF | 0.122 | 0.013 | 0.135 | 0.155 | 0.014 | 0.169 | 0.046 | 0.120 | 73 |
| non-*ortho* DLPCBs | 0.025 | 0.034 | 0.059 | 0.034 | 0.034 | 0.068 | 0.013 | 0.060 | 83 |
| mono-*ortho* DLPCBs | 0.037 | 0.063 | 0.101 | 0.053 | 0.056 | 0.109 | 0.012 | 0.111 | 90 |
| **(Sample 4)** | | | | | | | | | |
| TeCDDs | 0.777 | 1.75 | 2.52 | 1.08 | 1.50 | 2.58 | −0.018 | 2.61 | 104 |
| PeCDDs | 1.22 | 1.43 | 2.65 | 1.46 | 1.04 | 2.50 | −0.040 | 2.91 | 111 |
| HxCDDs | 1.31 | 0.990 | 2.30 | 1.58 | 0.552 | 2.13 | −0.039 | 2.56 | 112 |
| HpCDDs | 0.586 | 0.179 | 0.77 | 0.606 | 0.073 | 0.680 | −0.016 | 0.873 | 115 |
| OCDD | 0.302 | 0.040 | 0.34 | 0.293 | 0.018 | 0.311 | −0.006 | 0.384 | 113 |
| TeCDFs | 1.13 | 4.17 | 5.31 | 1.76 | 3.20 | 4.96 | −0.085 | 5.86 | 111 |
| PeCDFs | 0.730 | 1.90 | 2.63 | 1.12 | 1.12 | 2.25 | −0.064 | 3.08 | 118 |
| HxCDFs | 0.502 | 0.706 | 1.21 | 0.630 | 0.337 | 0.967 | −0.036 | 1.46 | 122 |
| HpCDFs | 0.241 | 0.179 | 0.42 | 0.319 | 0.089 | 0.407 | −0.005 | 0.452 | 109 |
| OCDF | 0.132 | 0.052 | 0.18 | 0.178 | 0.012 | 0.190 | 0.001 | 0.175 | 96 |
| non-*ortho* DLPCBs | 0.239 | 0.499 | 0.74 | 0.425 | 0.328 | 0.753 | −0.005 | 0.765 | 105 |
| mono-*ortho* DLPCBs | 0.298 | 0.765 | 1.06 | 0.70 | 0.539 | 1.239 | 0.008 | 0.977 | 93 |

[a] Thimble filter.
[b] DiOANA® filter.
[c] Concentration of the particle-bound form calculated on the basis of the quantitative values obtained by the parallel sampling.
[d] Concentration of the gaseous form calculated on the basis of the quantitative values obtained by the parallel sampling.
[e] Ratio of the gaseous form calculated on the basis of the quantitative values obtained by the parallel sampling.
[f] Not detected.

weight of the collected particles by the non-isokinetic sampling (g), $V_{iso}$: sample gas volume collected by the isokinetic sampling ($Nm^3$), $V_{non}$: sample gas volume collected by the non-isokinetic sampling ($Nm^3$), $A_{iso}$: amount of the analytes collected by the isokinetic sampling (ng), $A_{non}$: amount of the analytes collected by the non-isokinetic sampling (ng) and $R_G1$: ratio of the gaseous analytes in the real flue gas (%).

DLPCBs were grouped under a non-*ortho* group and a mono-*ortho* group (i.e., expressed as results of a total amount of all congeners in the groups), because all congeners exhibited similar results.

For samples 1 and 2, whose gas temperatures were relatively low (190–210 °C), obvious differences between $R_G1$ values of each PCDD/F homologue were observed: $R_G1$ decreased with increasing number of substituted chlorine atoms. In addition, $R_G1$ of a P$n$CDD homologue was lower than that of the P$n$CDF homolog ($n = 4$–8). These differences are most probably due to the differences in their vapor pressures. Similar differences were also observed for sample 3, whose temperature was relatively high (240–250 °C), although the difference was lower than for samples 1 and 2. As for sample 4, whose temperature was the highest (330–380 °C), the quantitative values of PCDD/F homologues obtained by the two trains were approximately consistent with each other despite obvious differences in the amounts of collected particles, indicating that almost analytes were in the gaseous form in the real flue gas.

Next $R_G1$ values were compared with the expected gaseous ratios obtained by fractional determination of the thimble filter and the DiOANA filter ($R_G2$), and those on the basis of the following previously reported formula [14] ($R_G3$).

$$\log\left(\frac{C_{gas}}{C_{PB}}\right) = m \log P_L^O + \log\left(\frac{c}{PM}\right)$$

where $C_{gas}$: concentration of the gaseous PCDD/Fs in the real flue gas (ng $Nm^{-3}$), $C_{PB}$: concentration of the particle-bound PCDD/Fs in the real flue gas (ng $Nm^{-3}$), $P_L^O$: saturation vapor pressure of PCDD/F at temperature in the flue gas (Pa), PM: particulate matter concentration (mg $Nm^{-3}$), $m$: a parameter dependent on the type of gas cleaning devices upstream of the flue gas and $c$: a parameter dependent on the characteristic of particulate matter in flue gas.

Here $m$ and $c$ were assumed to be 1.11 and 0.042, respectively, according to the previous paper [14], and the saturation vapor pressures of each PCDD/F homologue were estimated by extrapolation using the values in the range of 25–125 °C reported by Rordolf [20].

The results are compared in Fig. 2. Sample 1, whose temperature and particulate matter concentration were both relatively low, exhibited similar $R_G1$ and $R_G2$ values of PCDDs but different ones of PCDFs. On the other hand, sample 2 to sample 4 exhibited obvious differences between the two values for all homologues. The temperature and/or particulate matter concentration of these samples were higher than those of sample 1. It is suggested that the difference between the two values for the latter samples should be attributed to adsorption of gaseous PCDD/Fs, which were predominant in the real flue gas, to the particulate matter collected on the thimble filter during sam-
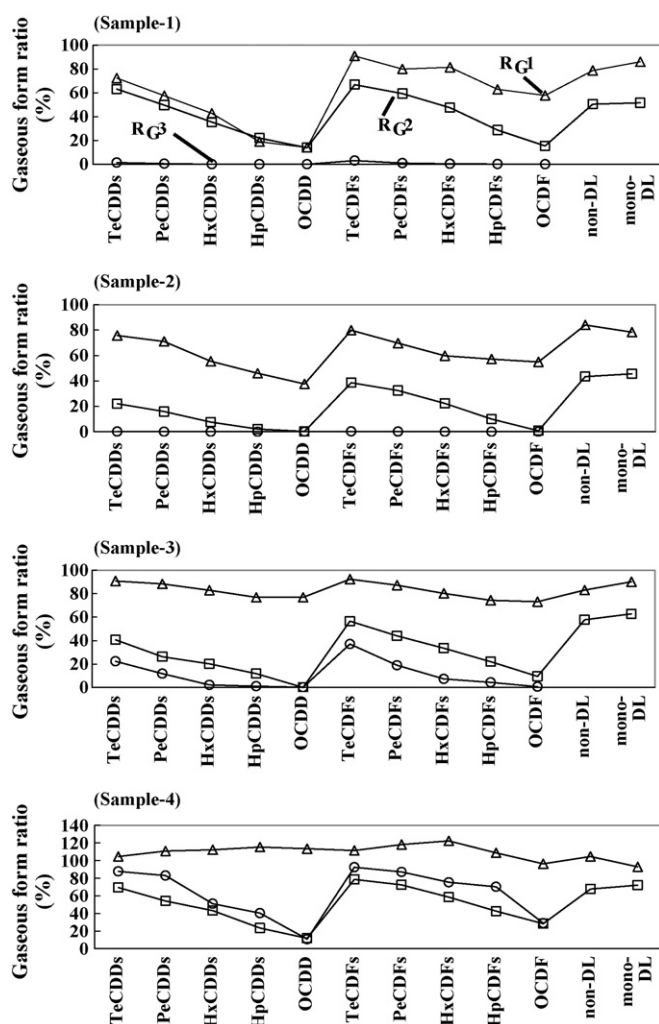


Fig. 2. Comparisons of gaseous form ratios of PCDD/Fs and DLPCBs in four flue gases. Non-DL: non-*ortho* DLPCBs. mono-DL: mono-*ortho* DLPCBs.

pling, and that a higher amount of the collected particulate matter would result in a higher amount of adsorbed gaseous analytes. All samples, however, exhibited obvious differences between $R_G1$ and $R_G3$ for all PCDD/F homologues. In the equation proposed by Chi et al., gas-particle partitions of PCDD/Fs in flue gas depend on their saturation vapor pressures and particulate matter concentration. Thus, with respect to samples 1 and 2, whose temperature is low enough and particle concentration is high enough, the equation gives a prediction of obvious predominance of all PCDD/F homologues in the particle-bound form. However, $R_G1$ values obtained by parallel sampling were as high as 14–91%. In addition, for samples 3 and 4, $R_G1$ values were as high as 73–122% for all homologues, whereas $R_G2$ and $R_G3$ of higher-chlorinated homologues were similarly low (0.2–43%). The proposed equation by Chi et al. was generalized on the basis of the partitions obtained by fractional determinations of each collection device. Therefore, with respect to particle-rich flue gas, adsorption of gaseous PCDD/Fs onto collected particles during sampling would be source of error in predicting gas-particle partitions using the equation: such obvious difference in $R_G1$ and $R_G3$ suggests that gas-particle partitions of

PCDD/Fs in flue gas do not depend only on saturation vapor pressure of each analyte and particle concentration of the gas. In a separate paper [4] we observed that fly ash PCDD/Fs started to gasify in the range of 350–400 °C. However, our results suggest that a high proportion of PCDD/Fs would be in the gaseous form in sample 1 to 3 whose temperature was apparently lower than the gasification range. The high gaseous form ratio even in low-temperature flue gas may be associated with the behavior of gaseous PCDD/Fs in flue gas: although fly ash PCDD/Fs would promptly gasify under a high-temperature condition (over 350 °C), the gaseous PCDD/Fs may not be easily adsorbed onto fly ash particles even under a low-temperature condition due to too low particle concentration and low adsorption capacity of fly ash [12,21]. Such behavior as gasification or adsorption of PCDD/Fs would depend on various properties of the gas and in-flight ash. For detailed elucidation of their behavior in flue gas, information on some properties of the fly ash (e.g., elements composition or particle size) would be necessary. In addition, it is required to accurately estimate gas-particle partitions of PCDD/Fs in flue gases which have various properties (e.g., temperature, gas composition, water content) and to estimate the relationship between the properties and the partitions.

The results demonstrate that the procedures used lead to a large error of prediction for dust-rich flue gas because of cold-trap separation of gaseous analytes onto a low-temperature collection device. The procedure to define gas-particle partitions by parallel sampling proposed in this study is applicable to dust-rich flue gas, because variations of partitions in a sampling train by cold-trap and/or blow-off effects can be ignored. It seems reasonable to employ the proposed procedure and the procedure employed by Chi et al. [14,15] for evaluation of a raw gas and a cleaned gas, respectively.

On the basis of the results of dual measurements (Table 4), the quantitative values of PCDD/F homologues and DLPCBs are considered to have an accuracy of 10–20%. The odd $R_G 1$ values (over 100%) would be attributed to an analysis error. The accurate definition of gas-particle partitions requires to measure the difference in the weights of collected fly ash particles by isokinetic and non-isokinetic samplings, and e.g., the use of a large-bore nozzle for a non-isokinetic train (a 20-mm nozzle for collection of sample 3) are encouraged. Also, the procedure is premised on the same burden of dioxins on every in-flight ash particle. It should be noted that variation of burden of dioxins with particle size would be responsible for erroneous estimation of their partition due to the difference of the size distribution of collected ash by isokinetic sampling from that by non-isokinetic sampling. In the future, it will be necessary to analyze the particle size distribution of collected ash by both trains and to estimate the relationship between the size distribution of collected particles and the amount of particle-bound dioxins.

## 4. Conclusion

The paper describes a parallel sampling procedure with an isokinetic and a non-isokinetic train in order to accurately determine gas-particle partitions of dioxins in real dust-rich flue gas. The predicted partitions of PCDD/Fs and DLPCBs derived from their quantitative values and the weights of the collected fly ash by both the trains were different, particularly for high-temperature flue gas, with those derived from the fractional determinations of each collection device: a conventional determination by fractional analyses is not so precise due to adsorption of gaseous dioxins onto low-temperature collected particles. In addition, the partitions derived from the procedure were significantly different from those calculated using the previously reported equation for all flue gases examined. It is concluded that the results derived by the proposed procedure cannot be influenced by adsorption of gaseous analytes onto collected particles and desorption of particle-bound analytes during collection.

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