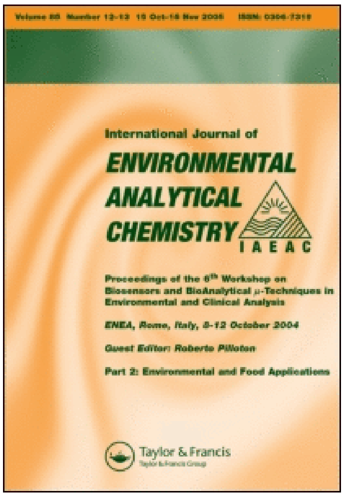

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Validation of methods for measuring polychlorinated dibenzo-<i>p</i>-dioxins and furans, and dioxin-like polychlorinated biphenyls in flue gas

Naoki Yokohama[a][b]; Hiroaki Otaka[c]; Munetaka Nakata[b]
[a] Saitama-Ken Environmental Analysis and Research Association, Saitama 330-0855, Japan [b] Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Tokyo 184-8588, Japan [c] National Environmental Research and Training Institute, Ministry of the Environment, Saitama 359-0042, Japan

To cite this Article Yokohama, Naoki , Otaka, Hiroaki and Nakata, Munetaka(2007) 'Validation of methods for measuring polychlorinated dibenzo-<i>p</i>-dioxins and furans, and dioxin-like polychlorinated biphenyls in flue gas', International Journal of Environmental Analytical Chemistry, 87: 3, 177 — 194

To link to this Article: DOI: 10.1080/03067310600929258

URL: http://dx.doi.org/10.1080/03067310600929258

Intern. J. Environ. Anal. Chem.
Vol. 87, No. 3, 15 March 2007, 177–194

Taylor & Francis
Taylor & Francis Group

Validation of methods for measuring polychlorinated dibenzo-*p*-dioxins and furans, and dioxin-like polychlorinated biphenyls in flue gas

NAOKI YOKOHAMA*†‡, HIROAKI OTAKA§ and
MUNETAKA NAKATA‡

†Saitama-Ken Environmental Analysis and Research Association,
1450-11 Kamikomachi, Omiya-ku, Saitama-shi, Saitama 330-0855, Japan
‡Graduate School of Bio-Applications and Systems Engineering, Tokyo University of
Agriculture and Technology, 2-24-16 Naka-cho, Koganei-shi, Tokyo 184-8588, Japan
§National Environmental Research and Training Institute, Ministry of the
Environment, 3-3 Namiki, Tokorozawa-shi, Saitama 359-0042, Japan

(*Received 28 March 2006; in final form 12 July 2006*)

Method validation was performed on the collection and extraction procedures for an analysis of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like polychlorinated biphenyls (DLPCBs) in flue gas. The adoption of the rapid pressurized liquid extraction (PLE) technique was evaluated for extraction from polyurethane foam plugs (PUFPs) and fly ash. With respect to extraction from PUFPs, dichloromethane PLE showed an extraction efficiency equivalent to that of conventional acetone Soxhlet, while toluene PLE was found to have a lower extraction efficiency from fly ash than toluene Soxhlet. The collection ability of three sampling methods, employed in the Japanese standard analytical method JIS K0311 (revised in 2005) was evaluated by evaluating the distribution of gaseous PCDD/Fs and DLPCBs in each collection compartment in sampling trains. A DiOANA® fibrous alumina filter and a PUFP, newly employed trapping devices in the revised JIS method, were found to trap gaseous analytes effectively. The validation of the two newly employed sampling methods (DiOANA and PUFP) was tested by parallel measurements of the methods with a conventional five-impinger method, and good agreements on the PCDD/Fs and DLPCBs quantities were demonstrated.

Keywords: Polychlorinated dibenzo-*p*-dioxins; Polychlorinated dibenzofurans; Dioxin-like polychlorinated biphenyls; Flue gas; Validation; Sampling; Extraction

1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are mainly released into the environment by waste-incineration facilities [1]. Therefore, adequate management of PCDD/F emission from incinerations is required to decrease their burden on the environment. The Japanese Ministry of the Environment

---

*Corresponding author. Fax: +81-48-649-5543. Email: n.yokohama@saitama-kankyo.or.jp

International Journal of Environmental and Analytical Chemistry
ISSN 0306-7319 print/ISSN 1029-0397 online
DOI: 10.1080/03067310600929258

announced that PCDD/F emission has decreased over the years—by 95% from 1997 to 2003—mainly as a result of adequate management of incinerators [2]. Moreover, by 2010, the ministry aims to decrease emission levels from 2003 levels by 15% [3]. Thus, there will be continuous requirements on the adequate management of emission sources and the accurate estimation of PCDD/F emission from incinerations.

Polychlorinated biphenyls are widespread and constant industrial pollutants. The emission of 'dioxin-like' polychlorinated biphenyls (DLPCBs) should also be monitored, since their toxicity is similar to that of PCDD/Fs. The Japanese standard analytical method of PCDD/Fs and DLPCBs in flue gas (JIS K0311) [4] defines 4 non-*ortho* PCBs (IUPAC Nos 77, 81, 126, and 169) and eight mono-*ortho* PCBs (IUPAC Nos 105, 114, 118, 123, 156, 157, 167, and 189) as DLPCBs. Thus, these 12 congeners must be quantified in Japan together with toxic 2,3,7,8-chlorinated PCDD/Fs.

The usual methods of sample collection for the determination of PCDD/Fs and DLPCBs in flue gas conform to the requirements defined by various government agencies. JIS K0311 was revised in June 2005 such that three sampling systems received recognition (figure 1). The traditional sampling train, which is a modified system of the USEPA method 23a [5], consists of five impingers and one column packed with XAD-2 resin (5-IMP train). One of the newly recognized systems involves a DiOANA® filter, a fibrous alumina filter trap, instead of the impingers and XAD-2 columns of the 5-IMP method (DiOANA train), while the other has two impingers together with polyurethane foam plugs (PUFPs) trap (PUFP train). An efficient method of flue gas sampling for PCDD/Fs and DLPCBs must collect them both in the particle-bound phase and in the vapour phase. In a sampling train, dioxins-carrying particles (fly ash) are collectable on a thimble filter installed at the front of the train, while gaseous analytes passing through the filter can be trapped at the backward devices by absorption or adsorption. The traditional 5-IMP train poses difficulties in handling, for example, difficulty in carriage, a higher risk of breakage of the impingers during transport, and complications in analysis. Both newer trains have simpler back devices than the 5-IMP train and are thus expected to resolve the above-mentioned problems of the 5-IMP method.

Hamada *et al.* validated the trapping ability of PCDD/Fs and DLPCBs with the DiOANA® filter by sampling various waste-incineration facilities and metal-recovery facilities [6]. EN 1948-1, the European standard for analysis of PCDD/Fs in flue gas [7], recognizes a PUFP collection system that has been validated only for PCDD/Fs by some researchers [8, 9]. After all, the number of validated data for both methods is still small.

Further, the revised JIS method approves other analytical procedures (extraction and cleanup procedures) after confirmation of the validity of the procedures. Though Soxhlet extraction is a conventional extraction procedure for PCDD/F and DLPCB analysis, it involves such problems as long-term extraction, high amounts of solvent use, and risk of fire. Therefore, in recent years, various alternative techniques for extraction have been evaluated. Pressurized liquid extraction (PLE) [10] has drawn much attention, and the efficiencies have been evaluated for such organic pollutants as PCDD/Fs [11], PCBs [12], and polycyclic aromatic hydrocarbons [12, 13] from various environmental solid samples. The use of PLE seems to be preferable even for PCDD/Fs and DLPCBs analysis in flue gas, in view of its extraction efficiency, time saving, and reduction of solvents for use.

The present study evaluates the sampling and extraction procedures for PCDD/F and DLPCB analysis in flue gas. First, we evaluated the efficiency of PLE for the extraction

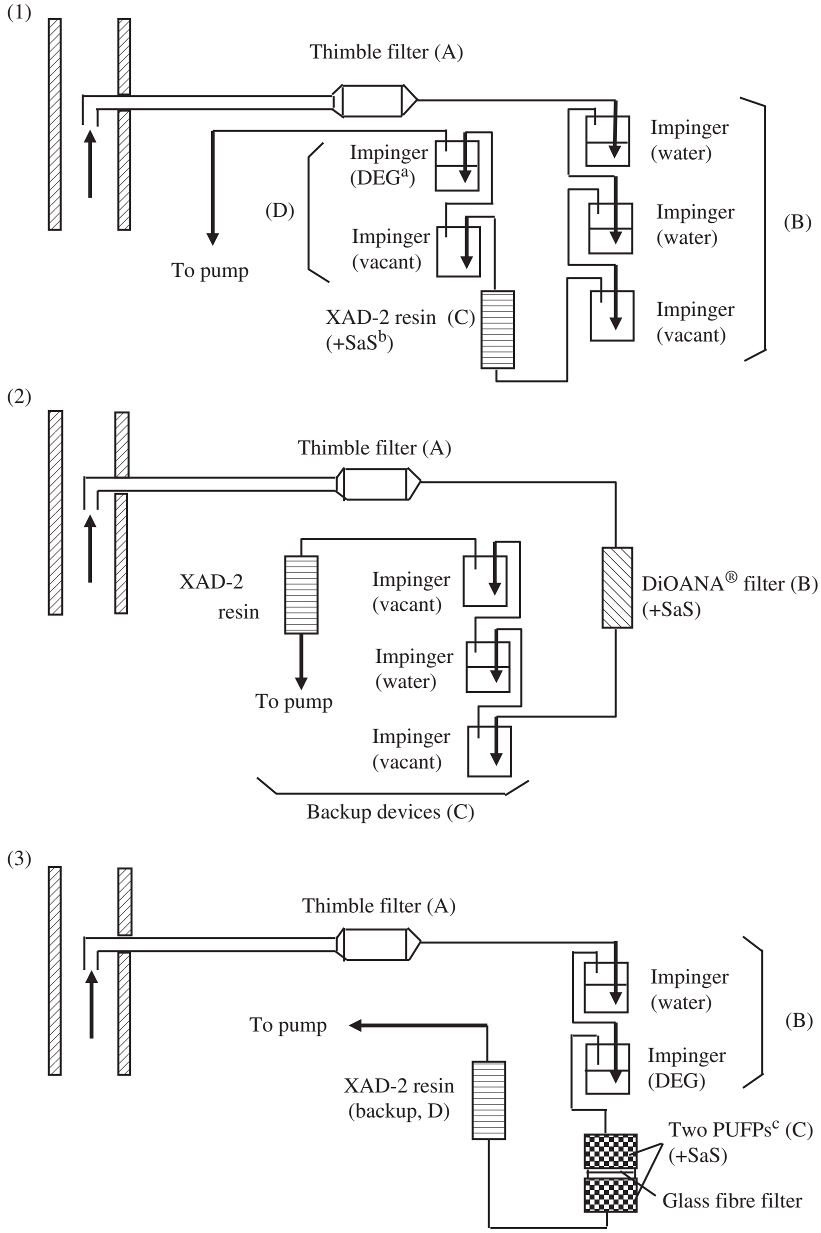

Figure 1. Schematic drawing of the three sampling trains included in the comparative study for the collection of PCDD/Fs and DLPCBs in flue gas: (1) 5-IMP method, (2) DiOANA method, and (3) PUFP method. Upper-case letters in each train indicate segmentation of the sub-samples. [a]Diethylene glycol. [b]Sampling standard. [c]Polyurethane foam plugs.

of PCDD/Fs and DLPCBs from PUFP and fly ash. Next, we tested validation of three sampling procedures employed in the revised JIS method (5-IMP, DiOANA, and PUFP) by measuring dust-rich flue gas. Each collection compartment in the sampling trains was analysed separately to evaluate the trapping ability of gaseous analytes by each compartment. In addition, comparative evaluation was performed by parallel measurements of the three sampling methods.

2. Experimental

2.1 *Apparatus*

A high-volume air sampler (HV-700F, Shibata Science Technology, Tokyo) and a high-volume water sampler (DS690, GL Sciences, Tokyo) were used for sampling the ambient atmosphere and tap water, respectively. PLE was performed with ASE-200 and ASE-300 (Dionex Corp., Sunnyvale, CA) instruments. FS-405, a drying oven (Advantec Tokyo, Tokyo), was used for drying the PUFPs before extraction.

PCDD/Fs and DLPCBs were analysed 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 sample was injected into GC using a Combi-PAL autosampler (CTC Analytics, Zwingen, Switzerland). The analytes were determined using BPX-DXN (SGE, Austin, TX) and HT-8PCB (Kanto Chemicals, Tokyo) capillary columns.

2.2 *Materials*

A quartz thimble filter for flue gas sampling (25 mm i.d., 90 mm length) was purchased from Whatman (Maidstone, UK). PUFPs used for the collection of gaseous PCDD/Fs and DLPCBs in flue gas or ambient air (90 mm i.d., 50 mm thickness) and the collection of dissolved analytes in tap water (100 mm i.d., 50 mm thickness) were obtained from Shibata and GL Sciences, respectively. An XAD-2 resin (Supelpak-2) was obtained from Supelco Inc. (Bellefonte, PA). 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.

Two fly ash samples were used in this study—one was used for the intercalibration exercise organized by the Japanese Ministry of the Environment in FY 2001, while the other was a municipal waste incinerator (MWI) fly ash sample collected at a MWI (fluidized bed furnace, $3\,\mathrm{t\,h^{-1}}$ combustion) located in Saitama, Japan. A suburban topsoil sample was collected in Tokorozawa, Saitama, Japan. The fly ash and soil were air-dried, crushed, and passed through a 1-mm-mesh sieve.

PCDD/F and DLPCB standards, including ^{13}C-labelled 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 surrogates solution (SuS) was prepared in toluene. This solution contained 17 ^{13}C-labelled 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,

Table 1. Properties of the flue gas analysed in this study.

Temperature (°C)	330–380
Flow ($m\,s^{-1}$)	13.7–15.7
Water (v/v%)	31–34
O_2 (v/v%)	11.5–12.6
CO_2 (v/v%)	8.0–8.5
CO (v/v ppm)	5.0–10

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-labelled DLPCBs (four non-*ortho* congeners and eight mono-*ortho* congeners, whose details are provided in section 1), 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-labelled 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-labelled 1,2,3,4-TeCDD at a concentration of $20\,\mu g\,L^{-1}$.

2.3 *Flue gas and sampling methods*

In this study, dust-rich flue gas was collected at the MWI at which the above-mentioned fly ash sample was collected (details are described in section 2.2). The samples were obtained at the front of a bug filter (before blowing active carbon powder). The properties of the samples are listed in table 1.

The flue gas was taken using three sampling methods in parallel: 5-IMP, DiOANA, and PUFP, as shown in figure 1. The flue gas was obtained using three sampling methods (5-IMP method, DiOANA method, and PUFP method). The schematic drawings of the three sampling systems are shown in figure 1.

For all collections, the adsorption devices in all trains were spiked with 25 μL of SaS to confirm correct sampling. During collection, the temperature of the thimble filter and the DiOANA® filter was maintained at 100–120°C, while all other devices were cooled with dry ice/water (<4°C). All collections were carried out isokinetically for representative sampling of the particulate form. The sampling volumes were in the range of $1–2\,m_N^3$.

2.4 *Validation of PLE from PUFP and fly ash*

In this study, we estimated the extraction efficiency of PCDD/Fs and DLPCBs from PUFPs using PUFP-adsorbing native analytes. Following our experiences, we prepared PUFP carrying native analytes by sampling ambient air and tap water with PUFP trains.

Ambient air ($1000\,m^3$) and tap water (2000 L) were sampled in parallel with two sampling apparatuses. Ambient air was drawn through a quartz-fibre filter and two PUFPs, and tap water was drawn through a glass-fibre filter and four PUFPs.

Table 2. PLE conditions.

	Fly ash and soil	DiOANA® filter	PUFP
PLE instrument	Dionex ASE-200	Dionex ASE-200	Dionex ASE-300
Cell volume (mL)	33	33	66
Cell temperature (°C)	150	150	50
Cell pressure (psi)	1500	2000	1500
Preheat time (min)	0	0	0
Static time (min)	7	2	7
Flush volume (% of cell volume)	60%	70%	100%
Purge time (s)	60	60	120
Static cycle	2	5	2
Extracting solvent	Toluene	Toluene	Dichloromethane

After sampling, the PUFPs were dried in an oven at 40°C and then extracted using acetone Soxhlet or PLE with dichloromethane.

The fly ash samples (intercalibration exercise sample: 0.5 g, MWI fly ash: 3 g) were pretreated with 2 M HCl according to JIS K0311, air-dried, and extracted by either Soxhlet Dean–Stark extraction (SDSE) or PLE with toluene. Soxhlet extraction was conducted for 20 h. The PLE conditions for extraction from PUFPs, fly ash, and soil are listed in table 2. The extracts were spiked with 20 µL of SuS, redissolved in *n*-hexane, and cleaned by column chromatography on a multilayer silica gel column and an active-carbon dispersed silica gel column according to the procedure outlined in figure 2. Each eluate was concentrated to about 2 mL on a rotary evaporator at 40°C (for *n*-hexane or dichloromethane) or 60°C (for toluene) under reduced pressure. The concentrate was transferred to a 10 mL centrifuge tube with dichloromethane and spiked with 20 µL of RS. Thereafter, the solvent was removed by purging under a nitrogen stream, and the sample was finally dissolved in 20 µL of *n*-nonane.

2.5 *Extraction and clean-up procedures for flue-gas collection devices*

The extraction of PCDD/Fs and DLPCBs from each collection device in the sampling trains generally followed JIS K0311 (figure 2). The thimble filters carrying fly ash were pretreated with 2 M HCl and extracted by SDSE with toluene (20 h). Water or diethylene glycol (DEG) in the impingers was extracted with dichloromethane. The XAD-2 resin was Soxhlet-extracted with toluene for 20 h. The DiOANA® filter was extracted by PLE with toluene under the conditions published by Miura Kogyo [14] (table 2). PUFPs were extracted with dichloromethane under the conditions listed in table 2.

All the compartments were spiked with SuS before extraction. For evaluation of the distributions of PCDD/Fs and DLPCBs in each collection compartment, all the compartments were analysed separately. Segmentation of the sub-samples is demonstrated in figure 1(A)–(D). The obtained extracts were cleaned, as shown in figure 2.

2.6 *Quantification of dioxin concentrations by HRGC-HRMS*

Aliquots (1 or 2 µL) of the solutions obtained after clean-up and concentration were injected into a GC equipped with a BPX-DXN column for analysis of

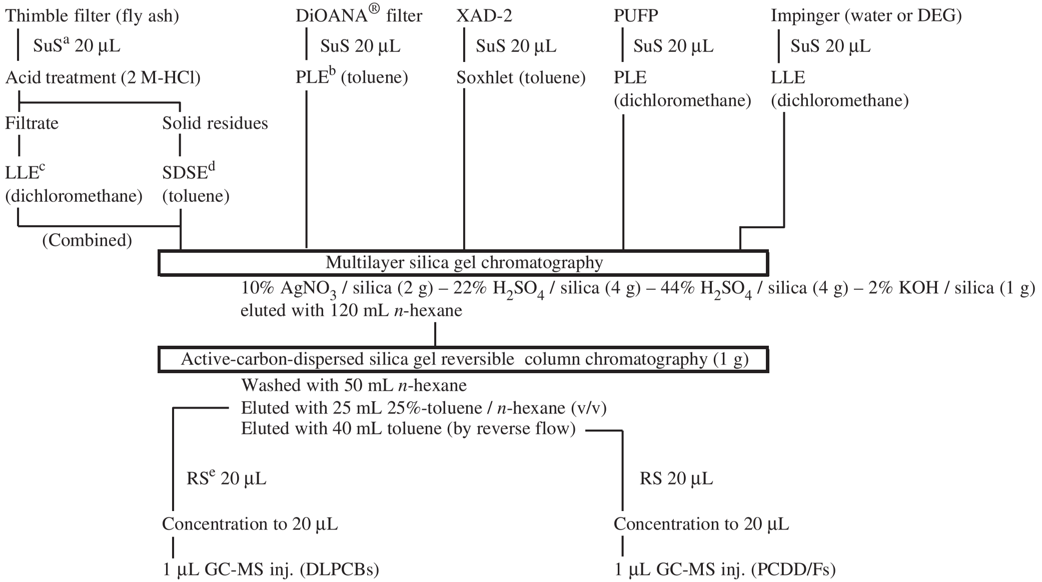

Figure 2. Analytical protocol for the determination of PCDD/Fs and DLPCBs in each collection compartment of the flue gas sampling trains. [a]Surrogates solution. [b]Pressurized liquid extraction. [c]Liquid–liquid extraction. [d]Soxhlet Dean–Stark extraction. [e]Recovery standards solution.

Table 3. GC–MS analytical conditions.

Column	BPX-DXN	HT-8PCB
Carrier-gas (helium) flow ($mL\,min^{-1}$)	1.5 (constant flow)	
Split-off time (min)	1.5	
Split gas (helium) flow ($mL\,min^{-1}$)	40	
GC oven-temperature programme		
Injection temperature (°C)	290	290
Initial temperature (°C)	130	130
Initial time (min)	1.5	1.5
Rate 1 ($^\circ C\,min^{-1}$)	20	20
Final temperature 1 (°C)	210	210
Rate 2 ($^\circ C\,min^{-1}$)	3	3
Final temperature 2 (°C)	315	300
Final time (min)	1	1
Interface temperature (°C)	315	300
MS		
Resolution	*c*. 10,000	
Ion current (μA)	550	
Electron voltage (eV)	38	
Ion-source temperature (°C)	290	

PCDD/Fs (60 m × 0.25 mm i.d.) and an HT-8PCB column for analysis of DLPCBs (60 m × 0.25 mm i.d.), in the splitless mode. The GC/MS conditions are listed in table 3, and we set the mass numbers for selected ion monitoring (SIM) mode following reference [15].

Toxicity equivalency (TEQ) values for all 2,3,7,8-chlorinated congeners were calculated using 2,3,7,8-TeCDD toxicity equivalency factors (TEF) reported by the World Health Organization [16].

2.7 *Accuracy control*

Glassware was rinsed with acetone and *n*-hexane prior to use. Glass- and quartz-fibre filters were heated at 450 and 600°C, respectively, for 4 h to remove analyte residues. PUFPs and XAD-2 were also prewashed by refluxing them using a Soxhlet apparatus with dichloromethane and toluene, respectively (for 24 h).

Variations in the HRGC-HRMS analysis were estimated by multiple determinations of an identical resulting solution of a fly-ash sample. The relative standard deviations of every PCDD/F homologue and DLPCB congener were confirmed to be less than 5%.

An instrumental blank was measured prior to the GC–MS analysis by injecting clean *n*-nonane, and it was confirmed that no analyte was detectable. Analysis of a method blank was carried out for each sample batch to confirm that the background was sufficiently low. Through this study, the quantities of all the method blanks were constantly as low as $\sim 0.001\,ng\,m^{-3}$ for lower-chlorinated PCDD/F homologues (i.e. TeCDD/Fs to HxCDD/Fs) and all DLPCB congeners. The method blank values were subtracted from all quantitative values of each sub-sample.

Table 4. Quantitative results of PCDD/Fs and DLPCBs in the intercalibration exercise sample (fly ash).[a]

	Intercalibration exercise results ($n = 136-153$)[b]		Results in this study ($n = 3$)			
	Average	SD[c]	Average	SD	CV%[d]	*z*-score
2,3,7,8-TeCDD	3.94	0.466	4.20	0.19	4.5	0.56
1,2,3,7,8-PeCDD	27.6	3.33	26.0	2.2	8.4	−0.48
1,2,3,4,7,8-HxCDD	38.3	5.03	40.0	1.2	3.0	0.34
1,2,3,6,7,8-HxCDD	37.7	5.31	35.8	1.3	3.6	−0.36
1,2,3,7,8,9-HxCDD	47.3	7.38	51.0	2.3	4.5	0.50
1,2,3,4,6,7,8-HpCDD	240	45.2	217	4.6	2.1	−0.50
OCDD	267	59.7	290	8	2.8	0.38
2,3,7,8-TeCDF	6.66	0.91	6.96	0.27	3.9	0.33
1,2,3,7,8-PeCDF	21.8	3.42	24.2	1.0	4.1	0.70
2,3,4,7,8-PeCDF	22.7	3.42	23.8	0.64	2.7	0.33
1,2,3,4,7,8-HxCDF	43.4	6.25	43.6	0.93	2.1	0.03
1,2,3,6,7,8-HxCDF	43.8	5.76	45.7	1.5	3.2	0.32
1,2,3,7,8,9-HxCDF	3.18	0.958	3.46	0.49	14	0.29
2,3,4,6,7,8-HxCDF	37.3	5.88	39.1	0.6	1.5	0.30
1,2,3,4,6,7,8-HpCDF	157	30	142	8.3	5.8	−0.49
1,2,3,4,7,8,9-HpCDF	17.5	3.96	17.3	1.2	7.2	−0.04
OCDF	59.6	13.6	68.8	4.2	6.1	0.67
TeCDDs	53.9	7.51	58.4	1.9	3.3	0.59
PeCDDs	175	20	157	8.2	5.2	−0.90
HxCDDs	384	53.1	389	10.6	2.7	0.10
HpCDDs	398	74.3	357	6.8	1.9	−0.56
TeCDFs	208	28.7	206	8.1	3.9	−0.08
PeCDFs	319	42.9	325	8.3	2.5	0.14
HxCDFs	399	51.4	414	5.6	1.4	0.30
HpCDFs	253	50.6	237	6.1	2.6	−0.32
#77-TeCB	3.29	0.416	3.28	0.11	3.2	−0.03
#81-TeCB	0.433	0.053	0.456	0.019	4.2	0.43
#126-PeCB	4.15	0.522	3.96	0.12	3.1	−0.36
#169-HxCB	2.01	0.376	1.91	0.08	4.4	−0.27
#105-PeCB	2.35	0.365	2.44	0.35	14	0.25
#114-PeCB	0.161	0.0347	0.160	0.023	14	−0.03
#118-PeCB	1.66	0.216	1.41	0.14	9.6	−1.2
#123-PeCB	0.443	0.0679	0.403	0.062	15	−0.59
#156-HxCB	1.88	0.264	1.66	0.07	4.5	−0.82
#157-HxCB	1.37	0.182	1.28	0.05	4.2	−0.49
#167-HxCB	1.13	0.155	1.07	0.04	3.6	−0.41
#189-HpCB	1.92	0.265	1.90	0.15	7.7	−0.06

[a] Units are $ng\,g^{-1}$.

[b] Calculated after rejection of outliers by the Grubbs test.

[c] Standard deviation.

[d] Coefficient of variation.

All the sub-samples were spiked with SuS (including the blank tests), and the recoveries of the standards were confirmed before data processing. The recoveries from all the samples fell within the range of 70–110%, which proved the validity of the analytical method. The recoveries of SaS were also in the range of 85–105% for all collections of flue gas, proving the correctness of the collection.

The assay accuracy was estimated by determining the fly-ash intercalibration sample, as shown in table 4. 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, thus proving the high accuracy of the determinations.

3. Results and discussion

3.1 *Extraction of PCDD/Fs and DLPCBs from PUFP and fly ash*

We first validated the extraction efficiency of PCDD/Fs and DLPCBs from solid traps by PLE for optimization of the analytical procedure. The extraction conditions for DiOANA® filter followed the optimized conditions [14], and the validity of extraction efficiency from PUFP and fly ash was evaluated.

Recovery experiments (i.e. spiking experiments) are generally employed for the estimation of the extraction efficiency, for various analyses. However, the physical states of the analytes added onto PUFPs may be different from those of the native analytes adsorbed onto PUFPs during sampling. Therefore, we considered it more reasonable to perform extraction experiments using native-analytes-carrying PUFPs than using spiked PUFPs. For preparation of the PUFP adsorbing 'free' (gaseous or dissolved) native analytes, ambient air and tap water were sampled with PUFP sampling trains. Moreover, although JIS K0311 prescribes the use of acetone for extraction from PUFPs, we used dichloromethane for the following reasons:

1. The Japanese standard for analysis of PCDD/Fs and DLPCBs in raw and treated water [17] prescribes dichloromethane Soxhlet for extraction from PUFPs after sampling; therefore, it is reasonable to consider that dichloromethane extraction is adequately validated.
2. Dichloromethane is inflammable and is safer than acetone (e.g. at low risk for fire accident during Soxhlet extraction).
3. Since dichloromethane is used for a foaming aid of urethane for production of commercial PUFP [18], it may have a higher permeability to PUFPs and accessibility to compounds adsorbed to the PUFP material than other solvents.
4. Dichloromethane is easier to solvent-exchange to hexane prior to multilayer silica-gel column treatment.

Figure 3 shows the comparison of the extracted amounts of PCDD/Fs and DLPCBs (only homologues with significant quantities) from PUFPs after collection of ambient air and tap water by acetone Soxhlet and dichloromethane PLE. Both procedures showed good agreement in the extracted amounts, proving that the extraction efficiency of dichloromethane PLE is equivalent to that of the conventional acetone Soxhlet extraction. A sufficient extraction efficiency of dichloromethane PLE is also proved by good recoveries of the SaS from the PUFPs, as described in section 2.7. As shown in figure 4, however, SDSE and PLE showed an apparent difference in the extraction efficiency between PCDD/Fs and DLPCBs from fly ash. In the comparative experiments using the fly-ash intercalibration exercise sample, the extracted amounts of higher-chlorinated PCDD/Fs (i.e. HpCDD/Fs and OCDD/F) by toluene PLE were lower than those by toluene SDSE (73–86% of SDSE). With regard to the MWI fly ash, the extracted amounts of all the dioxin homologues including DLPCBs by toluene PLE were 50–78% of those by toluene SDSE. As a reference, when the suburban soil was subject to extraction, as shown in figure 5, toluene PLE showed an apparently higher extraction efficiency than SDSE (112–132% of SDSE), even under the same PLE conditions as those for fly-ash extraction. It has been reported that PCDD/Fs in soil strongly interact with humic substances, which dominate their extractability [19].

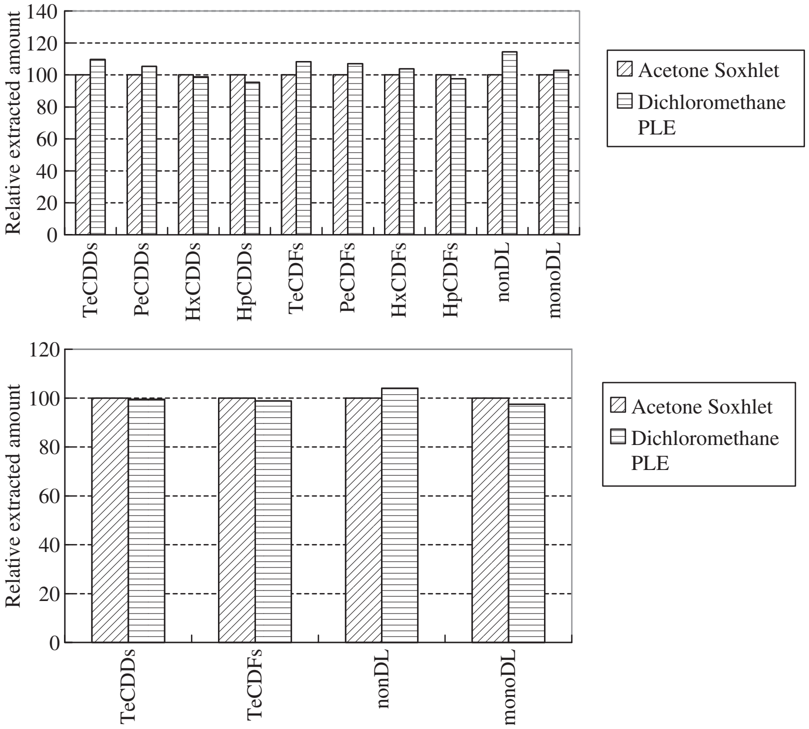

Figure 3. Comparison of extracted amounts of PCDD/Fs and DLPCBs from PUFP by acetone soxhlet extraction and dichloromethane PLE, with the Soxhlet value set at 100%. Upper: ambient air. Lower: tap water. Only homologues with significant quantitative values were exhibited. nonDL: non-ortho DLPCBs. monoDL: mono-ortho DLPCBs.

On the other hand, PCDD/Fs in fly ash do not interact with such organic substances, but interact with some inorganic components. The difference in extractability of PCDD/Fs from fly ash and soil can be attributed to the above-mentioned difference in the physical states of PCDD/Fs in each sample. At all events, the results suggest that rapid PLE is unfavourable for sufficient extraction of PCDD/Fs from fly ash. Although a higher extraction temperature (near 200°C) can increase the efficiency [20], the increase may also result in decomposition of more highly chlorinated PCDFs [20, 21]. Therefore, in the present study, we employed toluene SDSE for the extraction of PCDD/Fs and DLPCBs from fly ash.

3.2 *Validation of three sampling methods employed in JIS K0311*

In order to evaluate the trapping ability of the collection devices as a trap of gaseous PCDD/Fs and DLPCBs, each of the sub-samples (impingers, XAD-2 resin, DiOANA$^{®}$ filter, PUFP) in the sampling trains was analysed separately. Here, only less-chlorinated PCDD/Fs and DLPCBs were evaluated, since gaseous, more highly chlorinated PCDD/Fs were hardly detected (even though a proportion of gaseous more highly chlorinated PCDD/Fs exists in high-temperature flue gas, it should be adsorbed onto the cooled fly ash trapped onto the filter).

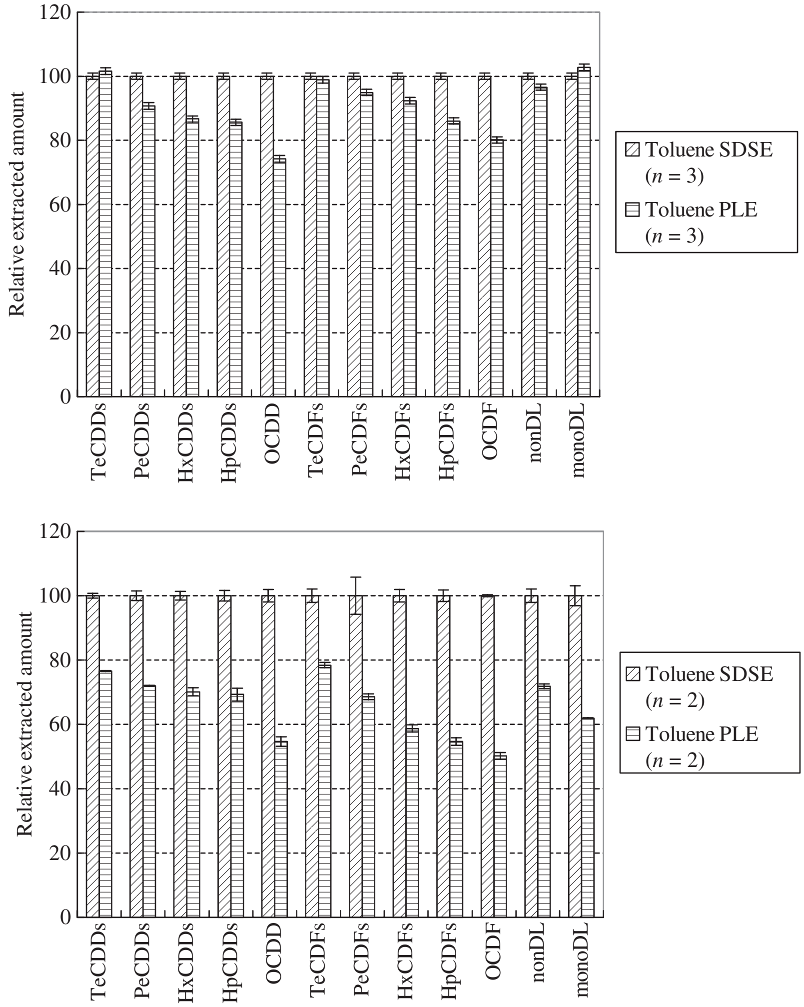

Figure 4. Comparison of extracted amounts of PCDD/Fs and DLPCBs from fly ash by toluene SDSE and toluene PLE, with the SDSE value set at 100%. Upper: fly-ash intercalibration exercise sample. Lower: MWI fly ash. The confidence interval at the top of each bar indicates the coefficient of variation.

Table 5 shows the quantities in each collection compartment in the conventional 5-IMP train. In Run 1 and Run 2, 63–91% of the total gaseous less-chlorinated PCDD/Fs and 39–67% of the total gaseous DLPCBs were distributed in the front impingers (water, water and vacant in figure 1b), and almost all the rest were distributed in the XAD-2 resin (figure 1c). The XAD-2 resin exhibited a high trapping ability for gaseous analytes, because only a small amount of the analytes (<1%) was detected from the backward impingers (vacant and DEG, figure 1d).

On the basis of these results, we evaluated the trapping ability of the devices in the DiOANA train and the PUFP train by installing XAD-2 as a backup device downstream from each train. As for the quantities obtained by the DiOANA method, as shown in table 6, almost all the gaseous analytes were distributed in all runs in the

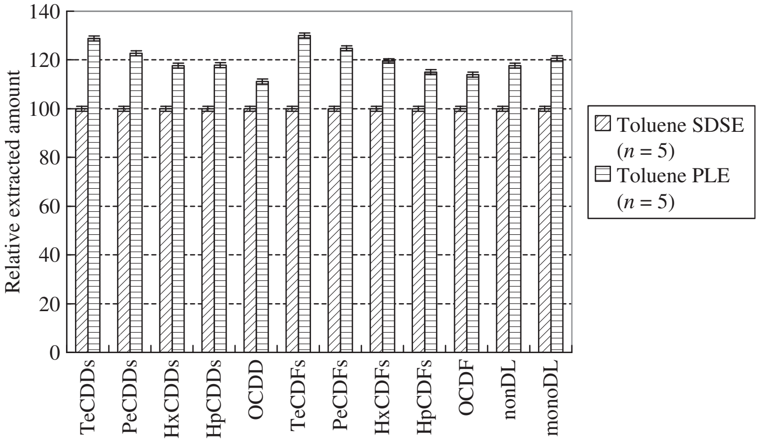

Figure 5. Comparison of extracted amounts of PCDD/Fs and DLPCBs from suburban soil by toluene SDSE and toluene PLE, with the SDSE value set at 100%. The confidence interval at the top of each bar indicates the coefficient of variation.

DiOANA® filter, and only small amounts were detected from the backup. In Run 1 and Run 3, relative quantities of DLPCBs and HxCDDs in the backup compartments were somewhat higher (10% of HxCDDs in Run 1 and 6–9% of DLPCBs in Run 3), most probably by the influence of the background. As for the PUFP method, as shown in table 7, 84–90% of the total gaseous analytes was distributed in the front impingers (water and DEG (B)) (Run 2). A higher distribution in the front impingers compared with that of the 5-IMP method indicates a higher trapping ability of DEG than water. Urano *et al.* reported that the complete collection of gaseous PCDD/Fs is achieved by only two impingers of cooled water and DEG [22]. In our experiment, however, about 10% of gaseous lower-chlorinated PCDD/Fs and DLPCBs passed through the impingers and were trapped onto the back PUFPs, despite severe cooling of the impingers with dry ice/water. The trapping ability of the impingers would be dominated by such conditions as gas flow rate and temperature of other devices. Our results suggest that some backup devices are required downstream from the two impingers. In Run 2, a slight amount of analytes was detected from the backup XAD-2 resin (<3% of the total), proving the high trapping ability of PUFPs.

In order to evaluate the further trapping ability of PUFPs, we collected flue gas with a modified PUFP method in which a DEG impinger was replaced with a water impinger (i.e. two front impingers of water) (Run 4 in table 7). We assumed that this modification would introduce a sample gas that has a higher amount of water vapour and gaseous analytes than the standard PUFP method. As expected, the distribution of analytes detected from the water–water impingers (32–58% of the total) was apparently lower than that in the water–DEG impingers (Run 2). In addition, we visually confirmed water droplets on the inside wall of the interface between the impinger and the PUFP housing, indicating that moisture-rich gas was introduced into the PUFP housing. Even under these conditions, a small amount of the analytes was detected from the backup XAD-2 resin (<1%). This finding proves that PUFPs can effectively trap gaseous analytes even in moisture-rich gas.

Table 5. Distribution of gaseous dioxins in the 5-IMP train of JIS K0311.

	Frontward impinger (B)		XAD resin (C)		Backward impinger (D)	
	Concentration (ng m^{-3})	Relative concentration[a]	Concentration (ng m^{-3})	Relative concentration	Concentration (ng m^{-3})	Relative concentration
Run 1						
TeCDDs	0.14	80	0.036	20	< 0.001	< 1
PeCDDs	0.069	87	0.010	13	< 0.001	< 1
HxCDDs	0.067	90	0.0071	10	< 0.001	< 1
TeCDFs	0.80	70	0.34	30	< 0.001	< 1
PeCDFs	0.39	87	0.058	13	< 0.001	< 1
HxCDFs	0.19	91	0.019	9	< 0.001	< 1
Non-ortho DLPCBs	0.14	63	0.084	38	< 0.001	< 1
Mono-ortho DLPCBs	0.28	67	0.14	33	< 0.001	< 1
Run 2						
TeCDDs	3.5	80	0.80	18	0.049	1.1
PeCDDs	1.1	80	0.26	19	0.0065	< 1
HxCDDs	0.38	81	0.085	18	0.0013	< 1
TeCDFs	7.0	69	3.1	31	0.037	< 1
PeCDFs	2.4	74	0.85	26	0.010	< 1
HxCDFs	0.85	81	0.20	19	0.0058	< 1
Non-ortho DLPCBs	0.30	41	0.43	59	0.0024	< 1
Mono-ortho DLPCBs	0.38	39	0.59	61	0.0041	< 1

[a] Relative concentration to the summed quantitative values (B + C + D).

Table 6. Distribution of gaseous dioxins in the DiOANA train of JIS K0311.

	DiOANA® filter (B)		Backup (C)	
	Concentration (ng m^{-3})	Relative concentration[a]	Concentration (ng m^{-3})	Relative concentration
Run 1				
TeCDDs	0.17	97	0.0049	3
PeCDDs	0.070	97	0.0018	3
HxCDDs	0.036	90	0.0042	10
TeCDFs	1.2	99	0.0092	1
PeCDFs	0.46	99	0.0018	1
HxCDFs	0.18	98	0.0029	2
Non-ortho DLPCBs	0.23	99	0.0031	1
Mono-ortho DLPCBs	0.40	99	0.0033	1
Run 2				
TeCDDs	5.5	~100	<0.001	<1
PeCDDs	3.4	~100	<0.001	<1
HxCDDs	1.4	~100	0.0043	<1
TeCDFs	17	~100	0.0035	<1
PeCDFs	8.1	~100	0.003	<1
HxCDFs	2.7	~100	0.0029	<1
Non-ortho DLPCBs	0.81	~100	<0.001	<1
Mono-ortho DLPCBs	0.96	~100	0.0046	<1
Run 3				
TeCDDs	0.25	~100	<0.001	<1
PeCDDs	0.092	97	0.0027	3
HxCDDs	0.048	~100	<0.001	<1
TeCDFs	1.2	97	0.034	3
PeCDFs	0.50	97	0.013	3
HxCDFs	0.24	~100	<0.001	<1
Non-ortho DLPCBs	0.2	94	0.012	6
Mono-ortho DLPCBs	0.46	91	0.043	9

[a] Relative concentration to the summed quantitative values (B + C).

Table 8 shows the comparisons of dioxin quantities obtained by the parallel measurements of the DiOANA method and/or the PUFP method with the 5-IMP method. In all runs, the total emission levels of PCDDs, PCDFs, DLPCBs, and TEQ from the two or three sampling methods are within ±30% of the average values (a criterion in JIS K0311), proving that the collection ability of the DiOANA and PUFP methods is comparable with that of the conventional 5-IMP method.

On the basis of the results in this study, we present the following conclusions:

(1) In the conventional 5-IMP method, almost all amounts of gaseous PCDD/Fs and DLPCBs can be trapped by the front impingers and subsequent XAD-2 resin.

(2) In the PUFP method, DEG installed upstream PUFPs have a higher trapping ability for gaseous PCDD/Fs and DLPCBs than the water trap. In addition, DEG is expected to increase the trapping ability of PUFP by removing the water vapour in the sample gas.

(3) Both DiOANA® filter in the DiOANA train and PUFPs in the PUFP train have a high trapping ability for gaseous PCDD/Fs and DLPCBs. Therefore, the measurement accuracy of the two newly employed methods in the revised JIS K0311 is equivalent to that of the traditional 5-IMP method.

Table 7. Distribution of gaseous dioxins in the PUFP train of JIS K0311.

	Frontward impingers (B)[a]		PUFP (C)		Backup XAD (D)	
	Concentration ($ng\,m^{-3}$)	Relative concentration[b]	Concentration ($ng\,m^{-3}$)	Relative concentration	Concentration ($ng\,m^{-3}$)	Relative concentration
Run 2						
TeCDDs	4.9	88	0.64	12	0.013	<1
PeCDDs	2.7	87	0.37	12	0.021	<1
HxCDDs	1.0	89	0.11	10	0.015	1.4
TeCDDs	11	87	1.6	13	0.061	<1
PeCDFs	5.5	88	0.70	11	0.048	<1
HxCDFs	1.8	90	0.17	9	0.026	1.3
Non-ortho DLPCBs	0.73	86	0.11	13	0.0089	1.0
Mono-ortho DLPCBs	1.0	84	0.16	14	0.018	1.6
Run 4						
TeCDDs	0.15	40	0.23	60	<0.001	<1
PeCDDs	0.12	47	0.13	53	<0.001	<1
HxCDDs	0.081	58	0.058	42	<0.001	<1
TeCDDs	1.1	36	1.9	64	<0.001	<1
PeCDFs	0.60	41	0.86	59	0.0024	<1
HxCDFs	0.29	52	0.27	48	0.0011	<1
Non-ortho DLPCBs	0.16	32	0.34	68	<0.001	<1
Mono-ortho DLPCBs	0.27	35	0.51	65	0.0012	<1

[a] Two impingers of water and DEG (in Run 2) or water (in Run 4).
[b] Relative concentration to the summed quantitative values (B + C + D).

Table 8. Comparison of quantitative values of dioxins in the flue gas by three sampling techniques.

	5-IMP	DiOANA	PUFP
Run 1			
Total PCDDs (ng m^{-3})	3.4	3.9	–[a]
Total PCDFs (ng m^{-3})	9.9	10	–
Total DLPCBs (ng m^{-3})	2.0	2.1	–
Total TEQ (ngTEQ m^{-3})	0.35	0.41	–
Run 2			
Total PCDDs (ng m^{-3})	21	19	23
Total PCDFs (ng m^{-3})	30	39	40
Total DLPCBs (ng m^{-3})	2.7	2.5	2.9
Total TEQ (ngTEQ m^{-3})	0.94	1.2	1.4
Run 3			
Total PCDDs (ng m^{-3})	11	11	–
Total PCDFs (ng m^{-3})	12	11	–
Total DLPCBs (ng m^{-3})	2.3	2.4	–
Total TEQ (ngTEQ m^{-3})	0.39	0.35	–
Run 4			
Total PCDDs (ng m^{-3})	7.5	–	5.9
Total PCDFs (ng m^{-3})	8.0	–	8.9
Total DLPCBs (ng m^{-3})	1.8	–	2.0
Total TEQ (ngTEQ m^{-3})	0.27	–	0.26
Run 5			
Total PCDDs (ng m^{-3})	16	16	–
Total PCDFs (ng m^{-3})	35	35	–
Total DLPCBs (ng m^{-3})	3.5	3.6	–
Total TEQ (ngTEQ m^{-3})	0.95	0.97	–

[a] Not tested.

The trapping ability of gaseous PCDD/Fs and DLPCBs at each trapping device is greatly affected by the gas temperature. Therefore, the temperature of each device during sampling of flue gas should be precisely controlled. As regards future research, we expect to evaluate the relation between the trapping ability of PUFPs and the gas temperature as well as the moisture content of gas.

With regard to all the sampling trains examined in this study, a thimble filter was installed downstream a nozzle for the collection of fly ash. However, the PUFP method in the revised JIS K0311 does not employ such a filter [4]. Fängmark *et al.* found that minute particles in flue gas (<2 µm) can penetrate impingers and PUFPs in a PUFP train [8]. A glass-fibre filter installed between two PUFPs in the PUFP method can trap minute particles. However, it should be noted that PCDD/Fs on fly ash cannot be sufficiently extracted by acetone Soxhlet extraction [20, 23], which is employed as the extraction procedure from PUFP in the JIS method. If minute particles are confirmed on a filter between PUFPs, it should be extracted by toluene Soxhlet separately from the PUFPs. In addition, the installation of a thimble filter at the forefront of the train is strongly recommended in sampling of dust-rich flue gas with the PUFP train.

Acknowledgements

The authors thank Professor Kozo Kuchitsu (BASE, Tokyo University of Agriculture and Technology), for his helpful suggestions for English presentations.

References

[1] A. Wehrmeier, D. Lenoir, K.W. Schramm, R. Zimmermann, K. Hahn, B. Henkelmann, A. Kettrup. *Chemosphere*, **36**, 2775 (1998).

[2] Press release from Ministry of the Environment, Japan. *Dioxins Emission Inventory*, 27 September (2004).

[3] Press release from Ministry of the Environment, Japan. *Government Plan to Reduce Dioxin Levels Resulting from Business Activities in Japan*, 20 June (2005).

[4] Japanese Industrial Standards Committee. *Method for Determination of Tetra- Through Octachlorodibenzo-p-dioxins*, *Tetra- Through Octachlorodibenzofurans and Dioxin-like Polychlorinated Biphenyls in Stationary Source Emissions*, *JIS K0311* (2005).

[5] US EPA. *Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Stationary Sources*, *Method 23a* (1994).

[6] N. Hamada, H. Nakamura, K. Honda. *'Kankyou Kagaku' (in Japanese)*, **14**, 613 (2004).

[7] CEN. *Stationary Source Emissions*, *Determination of the Mass Concentration of PCDDS/PCDFS*, *Part I: Sampling*, *EN1948-1* (1996).

[8] I. Fängmark, L.E. Wikström, S. Marklund, C. Rappe. *Chemosphere*, **20**, 1333 (1990).

[9] S. Marklund, G. Söderström, K. Ljung, C. Rappe, M. Kraft, H. Hagenmaier. *Waste Manage. Res.*, **10**, 21 (1992).

[10] US EPA. *Test Methods for Evaluating Solid Waste*, *Method 3545 Update III* (1997).

[11] B.E. Richter, J.L. Ezzell, D.E. Knowles, F. Hoefler. *Chemosphere*, **34**, 975 (1997).

[12] B.E. Richter, B.A. Jones, J.L. Ezzell, N.L. Porter. *Anal. Chem.*, **68**, 1033 (1996).

[13] J. Hollender, B. Koch, C. Lutermann, W. Dott. *Int. J. Environ. Anal. Chem.*, **83**, 21 (2003).

[14] H. Nakamura, M. Yamashita, M. Ouchi, K. Honda, O. Kajikawa, T. Fujii. In *9th Symposium on Environmental Chemistry of the Japanese Society of Environmental Chemistry*, Hokkaido, Japan, 20 June, Abstracts, pp. 28–29 (2000).

[15] J.F. Focant, G. Eppe, C. Pirard, E.D. Pauw. *J. Chromatogr. A*, **925**, 207 (2001).

[16] M. Van der Berg, L. Birnbaum, A.T.C. Bosveld, B. Brunström, P. Cook, M. Feeley, J.P. Giesy, A. Hanberg, R. Hasegawa, S.W. Kennedy, T. Kubiak, J.C. Larsen, F.X.R. van Leeuwen, A.K.D. Liem, C. Nolt, R.E. Peterson, L. Poellinger, S. Safe, D. Schrenk, D. Tillitt, M. Tysklind, M. Younes, F. Waern, T. Zacharewski. *Environ. Health Perspect.*, **106**, 775 (1998).

[17] Ministry of Health, Labour and Welfare. *Examination Manual of Dioxins in Raw and Treated Water* (1999).

[18] Japanese Industrial Standards Committee. *Flexible Polyurethane Foam for Cushion*, *JIS K6401* (1997).

[19] H. Otaka, M. Shinomiya, T. Amagai. *Int. J. Environ. Anal. Chem.*, **85**, 515 (2005).

[20] H. Murayama, T. Suzuki, H. Taneoka, T. Takai, K. Yanaka, N. Shibuya, S. Hashimoto, H. Ito. In *12th Symposium on Environmental Chemistry of the Japanese Society of Environmental Chemistry*, Niigata, Japan, 26 June, Abstracts, pp. 604–605 (2003).

[21] F. Iimura, Y. Sasaki, H. Sasaki, T. Yoshizawa, K. Hanno, S. Hashimoto, H. Ito. In *13th Symposium on Environmental Chemistry of the Japanese Society of Environmental Chemistry*, Shizuoka, Japan, 7 July, Abstracts, pp. 304–305 (2004).

[22] K. Urano, M. Kato, Y. Nagayanagi, Y. Saito, A. Aono, J. Nagata, H. Syudo. *Chemosphere*, **43**, 425 (2001).

[23] H. Otaka, Y. Ishiwata, N. Nishioka, X. Wang, N. Umetsu. In *11th Symposium on Environmental Chemistry of the Japanese Society of Environmental Chemistry*, Kanagawa, Japan, 4 June, Abstracts, pp. 388–389 (2002).