Journal of Chromatography, 643 (1993) 25–33
Elsevier Science Publishers B.V., Amsterdam

CHROMSYMP. 2640

Practical method for monitoring polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans in the atmosphere

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ABSTRACT

A practical method is described for monitoring tetra- to octachlorodibenzo-*p*-dioxins (T_4–O_8CDDs) and tetra- to octachlorodibenzofurans (T_4–O_8CDFs) in atmospheric samples at ground level. The substances in air were sampled on quartz fibre and polyurethane foam plugs by using a high-volume air sampler. The sample congeners were extracted with acetone, washed with sulphuric acid after transfer into a hexane layer, fractionated by silica gel and alumina column chromatography and subsequently analysed by gas chromatography–mass spectrometry. Thirty three peaks found for 47 congeners out of 49 T_4–O_8CDDs and 58 peaks found for 82 congeners out of 89 T_4–O_8CDFs could be monitored.

INTRODUCTION

Many reports have been published on sources, toxicity, mechanisms of formation and analytical methods for polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). As PCDDs and PCDFs are amongst the most hazardous chemicals found in the environment [1–6], monitoring has recently been conducted even for airborne PCDDs and PCDFs in order to investigate their toxcity to human health and carcinogenic risks [7–14]. However, various congeners present in ambient air are at ultra-trace levels corresponding to 1/100–1/1000th of the concentrations in emission gas from an incinerator, and ambient air could include a great number of organics that interfere in the analysis. More recently, since the toxicity of the individual congeners has been evaluated by using the toxicity equivalence quantity (TEQ) of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-T_4CDD), all the congeners of tetra- to octachlorodibenzo-*p*-dioxins (T_4–O_8CDDs) and dibenzofurans (T_4–O_8CDFs) could be simultaneously determined in ambient air. In field investigations, a number of samples should be sampled at a time at various sites and accurately analysed in a limited period. In addition, a practical method must be consistent with low analysis costs, a simple procedure and easy maintenance of analytical instruments. Conventional techniques for analyses for PCDDs and PCDFs are time-consuming, laborious and not completely satisfactory.

In this paper, a convenient method is proposed for monitoring trace levels of T_4–O_8CDDs and T_4–O_8CDFs in the atmospheric environment at ground level. Air is sampled by using a high-volume air sampler on a quartz fibre filter (QFF) and polyurethane foam plugs (PUFPs). The trapped sample is extracted, washed with sulphuric acid, purified by silica gel and alumina column chromatography and then analysed by gas chromatography–mass spectrometry (GC–MS). The method has been successfully used for monitoring PCDD and PCDF con-

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geners in the atmospheric environment at ground levels for several years.

EXPERIMENTAL

Standard reagents and materials

^{13}C-labelled and unlabelled PCDDs and PCDFs as 10 μg/ml solutions (see Table I) were purchased from Cambridge Isotope Laboratories (Cambridge, MA, USA). Another standard mixture was prepared in toluene by extracting fly ash from a incinerator [15] for adjusting and/or confirming the analytical conditions and identifying PCDD and PCDF congeners. *n*-Hexane, acetone and dichloromethane were of pesticide residue analysis grade from Wako (Osaka, Japan) and other solvents or reagents were of either chromatographic or special grade from Wako.

Silica gel for silica gel column chromatography (Si-CC) was Wakogel (Wako) activated by heating at 130°C for 4 h. A 3-g amount of the silica gel was slurry packed into a 30-cm × 10-mm I.D. glass column. The top of the gel was covered with a 10-mm layer of anhydrous sodium sulphate. Alumina for alumina column chromatography (A1-CC) was of basic type with activity 1 from Merck (Darmstadt, Germany), activated by heating at 130°C for 4 h. A 5-g amount of the alumina was slurry packed into a 30-cm × 10-mm I.D. glass column. The top of the column was covered with a 10-mm layer of anhydrous sodium sulphate. The PUFP was cut as a 50-mm × 90-mm diameter piece from a polyurethane foam sheet (0.020 g/cm^3 density and 50 mm thick; Ether-type) available from Bridge Stone (Tokyo, Japan) and washed with acetone for 24 h. The QFF was QR-100 from Advantic Toyo (Tokyo, Japan).

TABLE I

UNLABELLED AND ^{13}C-LABELLED PCDD AND PCDF CONGENERS USED AS STANDARDS

The analytical responses to the native congeners in the SIM mode were corrected by using relative response of the listed ^{12}C-labelled congeners to the equivalent ^{13}C isotopes.

[^{12}C]- and [^{13}C]PCDDs	[^{12}C]- and [^{13}C]PCDFs
2,3,7,8-T_4CDD	2,3,7,8-T_4CDF
1,2,3,7,8-P_5CDD	1,2,3,7,8-P_5CDF
1,2,3,6,7,8-H_6CDD	1,2,3,4,7,8-H_5CDF
1,2,3,4,6,7,8-H_7CDD	1,2,3,4,6,7,8-H_7CDF
1,2,3,4,6,7,8,9-O_8CDD	1,2,3,4,6,7,8,9-O_8CDD

Apparatus

The apparatus for sampling PCDDs and PCDFs is shown in Fig. 1 [16]. The sampling apparatus was attached to a Kimoto Electric (Osaka, Japan) HV-120 high-volume air sampler equipped with a Kansai Gas Meter (Osaka, Japan) N2-K838 integrating gas flow meter. An Ogasawara (Tokyo, Japan) A-1250 automatic recording thermometer with a platinum thermo-sensor was set next to the sampling apparatus.

The specification and operating conditions of the gas chromatograph–mass spectrometer used are given in Table II. For GC–MS analysis the selected ion monitoring (SIM) mode was used. The resolution of the mass spectra was 3000–5000. The number of mass ion monitoring channels was four for both PCDD and PCDF congeners in one analytical run.

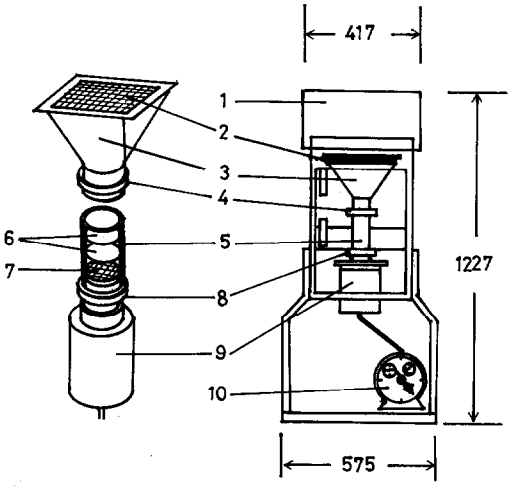

Fig. 1 Sampling apparatus for sampling PCDD and PCDF congeners in air. 1 = Shelter; 2 = filter and stainless-steel wire net (5 mm mesh); 3 = filter holder; 4 = screw clasp with PTFE packing; 5 = PUFP holder (200 mm × 84 mm I.D. aluminium tube); 6 = two PUFPs (50 mm × 90 mm diameter in series); 7 = stainless-steel wire mesh (50 mm mesh); 8 = screw clasp with PTFE packing; 9 = high-volume air-suction pump (Kimoto Electronic HV-120); 10 = integrating gas flow meter (Kansai Gas Meter N2-K838). The dimensions of the apparatus are indicated in millimeters.

TABLE II

ANALYTICAL CONDITIONS FOR GC–MS

Apparatus: Hewlett-Packard (Avondale, PA, USA) model 5790A gas chromatograph and Japan Electronic (Tokyo, Japan) DX303/DA5000 mass spectrometer.

Parameter	T_4-, P_5- and H_6C congeners			H_7- and O_8C congeners		
Column	Supelco (Bellefonte, PA, USA), 30 m × 0.25 mm I.D., 0.20 μm film thickness, SP-2331 chemically bonded fused-silica capillary column (63% cyanopropyl polysiloxane)			Hewlett-Packard, 25 m × 0.31 mm I.D., 0.52 μm film thickness, Ultra-1 chemically bonded fused-silica capillary column (non-polar, cross-linked methylsilicone)		
Injection	Splitless (90 s)			Splitless (90 s)		
Injection temperature	260°C			260°C		
Column head pressure	1.0 kg/cm²			1.0 kg/cm²		
Column conditions	160°C for 2 min, programmed at 8°C/min to 200°C and 3°C/min to 265°C and held at 265°C for 30 min			160°C for 2 min, programmed at 20°C/min to 200°C and 5°C/min to 310°C and held at 310°C for 30 min		
		^{12}C	^{13}C		^{12}C	^{13}C
Mass number of selected ion monitor (SIM)	T_4CDDs	320, 322	332, 334	H_7CDDs	424, 426	436, 438
	T_4CDFs	304, 306	316, 318	H_7CDFs	408, 410	420, 422
	P_5CDDs	356, 358	368, 370	O_8CDDs	460, 462	470, 472
	P_5CDFs	340, 342	350, 352	O_8CDFs	442, 444	452, 454
	H_6CDDs	390, 392	402, 404			
	H_6CDFs	374, 376	386, 388			
Voltage of ion multiplier		2.0 kV			2.0 kV	
Electron ionization voltage		70 eV			70 eV	

Sampling

Ambient air was sampled at 0.6–0.7 m^3/min for 24 h from 10 a.m. to 10 a.m. the next day. The average temperature was calculated from the temperature recorded continuously throughout the day.

Clean-up of sample

The QFF and the PUFPs were each extracted with 500 ml of acetone in a Soxhlet extractor. The extracts were combined, concentrated to 5 ml in a Kuderna–Danish (KD) concentrator and evaporated to 1 ml by slowly flushing nitrogen over the sample from a needle.

The concentrated extract was mixed in a separating funnel with 150 ml of *n*-hexane and then with the internal standard solutions individually containing 7.5 ng of 10 ^{13}C-labelled PCDDs and PCDFs (see Table I). The mixed sample was repeatedly washed with 5 ml of sulphuric acid until the sample became colourless (normally three or four washings were required). The hexane layer was then washed three times with 50 ml of distilled water, dehydrated with 2 g of anhydrous sodium sulphate, evaporated to 5 ml in a KD concentrator and reduced to 3 ml by flushing nitrogen over it.

The sample was poured onto the silica gel columns and eluted with 250 ml of *n*-hexane. The eluate was evaporated to 5 ml and then reduced to 3 ml by slowly passing nitrogen over the sample.

The sample was poured onto the alumina column, washed with 20 ml of *n*-hexane and eluted with 50 ml of *n*-hexane–dichloromethane (1:1). The eluate was reduced to 3 ml in a similar way as above. The alumina column chromatographic purification was conducted twice for samples from heavily air-polluted sites. The sample was concentrated to 100 μl by flushing nitrogen over it, mixed with 200 μl of toluene and then concentrated to 50 μl by flushing nitrogen over it. The sample was then ready for analysis by GC–MS.

GC–MS analysis

A 3-μl volume of the sample was introduced into the GC–MS instrument with a microsyringe. In the GC–MS analysis (see Table II for the analytical

conditions), two mass ion channels were selected for an isomer gorup. The GC–MS analyses were performed five times for each sample. The first run was for T_4C and H_6C congeners (after T_4C congeners had been eluted, the channels were switched to those in the analysis of H_6C congeners), the second for P_5C congeners, the third for the fly-ash extract for identification of the T_4–H_6C congeners, the fourth for H_7C and O_8C congeners and the last for the fly-ash extract for identification of the H_7C and O_8C congeners. PCDD or PCDF congeners were identified by matching the retention times of the congeners with those of the corresponding congeners in the fly-ash extract, and positively quantified by peak areas in the cases that (1) the ratio of the relative peak areas of the two major characteristic ions monitored for a particular congener corresponded within ±30% to that resulting for the corresponding standard and (2) the signal-to-noise ratio was greater than 3 [12]. The analytical responses to the native congeners in the SIM mode were corrected by using the relative responses of the ^{12}C congeners to the equivalent ^{13}C isotopes listed in Table I.

Calculation of concentration of PCDDs and PCDFs

PCDDs and PCDFs were individually monitored as concentrations in pg/m^3 at 20°C under 1 atm for the atmospheric samples. The concentration of PCDD and PCDF congeners are presented as total concentrations of the individual PCDD and PCDF congeners, respectively. The TEQ calculation was made by the method of the North Atlantic Treaty Organization [12].

RESULTS AND DISCUSSION

Sampling

Since the PCDDs and the PCDFs are present at ultra-trace levels in the atmosphere, as much air sample as possible should be sampled to ensure detection of the congeners. The sampling apparatus, capable of sampling a large volume of air (*ca.* 1000 m^3/day), was similar to that for sampling polyclic aromatic hydrocarbons or PCDDs and PCDFs in ambient air [7,9,16]. The sampling rate (0.6–0.7 m^3/min) and the total sample volume were strictly checked and confirmed by an integrating gas flow meter calibrated before the sampling. The T_4–O_8C congeners were usually trapped at above 99% with the QFF and the first PUFP attached to the high-volumne air sampler [7,9]. In this instance two PUFPs were used, considering the high sampling temperature and the heavy air pollution near a busy road. However, very small amounts of T_4–O_8C congeners, leaving the QFF during the sampling process, were detected on the second PUFP.

Selection of internal standards

The use of as many ^{13}C-labelled standards as possible is desirable for minimizing analytical errors, but none of the congeners are commercially available, In addition, commercially available ^{13}C-labelled standards are much too expensive for routine work. Under the assumption that PCDD and PCDF isomers behaved in the clean-up procedure in the same way as the corresponding ^{13}C-labelled internal standards [12,17–20], five ^{13}C-labelled PCDDs and five ^{13}C-labelled PCDFs (see Table I) were used as internal standards.

Clean-up of air sample

The extracts from the QFF and the PUFPs were heavily contaminated with organic and inorganic substance and showed high viscosity. The viscous matter seemed to come mainly from the PUFPs but were effectivley reduced by the washing with sulphuric acid to remove fatty, basic and other organics. The extracts from ordinary samples should be washed at least three times until the the extracts become colourless. For samples from the heavily air-polluted areas, the extracted samples often included cotton-like suspended matter that must be removed by filtration after addition of the internal standards. Up to six washings with sulphuric acid were necessary until the extracts became colourless.

In conventional analysis [9–11,13–15,18,20,21], Al-CC and reversed-phase liquid chromatography (RPLC) using a silica-ODS column have been used for the purification of dioxin samples. However, the PCDD and PCDF congeners in air samples could not be determined, except for the O_8C congeners, because of interfering organics if all the congeners were collected in one fraction by RPLC. In addition, the RPLC procedure is laborious and time consuming and the samples often acquire contaminants from the injection port. It was found that Si-CC [19,21–24], which efficiently removes polar and

TABLE III

ELUTION ORDER OF PCDD CONGENERS ON THE SP-2331 AND THE ULTRA-1 COLUMNS

No.[a]	T_4CDDs[b]	No.[a]	P_5CDDs[b]	No.[a]	H_6CDDs[b]
1	1,3,6,8	1	1,2,4,6,8	1	1,2,3.4,6,8
2	1,3,7,9		1,2,4,7,9		1,2,4,6,7,9
3	1,3,7,8	2	1,2,3,6,8		1,2,4,6,8,9
4	1,2,4,7/1,2,4,8	3	1,2,4,7,8	2	1,2,3,6,7,9
	1,3,6,9	4	1,2,3,7,9		1,2,3,6,8,9
5	1,2,6,8	5	1,2,3,4,7	3[d]	1,2,3,4,7,8
6	1,4,7,8		1,2,4,6,9	4[d]	1,2,3,6,7,8
7[d]	2,3,7,8	6[d]	1,2,3,7,8	5	1,2,3,4,6,9
8	1,2,3,4/1,2,3,7	7	1,2,3,6,9	6[d]	1,2,3,7,8,9
	1,2,3,8/1,2,4,6	8	1,2,4,6,7	7	1,2,3,4,6,7
	1,2,4,7		1,2,4,8,9		
9	1,2,3,6/1,2,7,9	9	1,2,3,4,6	No.[a]	H_7CDDs[c]
10	1,2,7,8/1,4,6,9	10	1,2,3,6,7		
11	1,2,3,9	11	1,2,3,8,9	1	1,2,3,4,6,7,9
12	1,2,6,9			2[d]	1,2,3,4,6,7,8
13	1,2,6,7				
14	1,2,8,9			No.[a]	O_8CDDs[c]
				1[d]	1,2,3,4,6,7,8,9

[a] Elution order (or peak order).
[b] Separation on the SP-2331 capillary column.
[c] Separation on the Ultra-1 capillary column.
[d] 2,3,7,8-Substituted congeners used for calculating the toxicity equivalence quantity (TEQ) of 2,3,7,8-T_4CDD by the method of the North Atlantic Treaty Orgnization [12].

coloured substances, was effective in cleaning up the air samples. Hence the combined Si-CC and Al-CC system was useful for cleaning up the samples without multiple fractionation for the T_4–O_8CDD and T_4–O_8CDF congeners.

The recoveries of the standard PCDD and PCDF congeners using the clean-up procedure were ususally 70–90% though they differed depending on the level of contamination of the samples, the number of washing times with sulphuric acid and the number of Al-CC steps applied. Increased washings with sulphuric acid and Al-CC steps may have adverse effects on the recovery of the compounds. Heavily polluted samples required six washings and two Al-CC steps for clean-up and, as a result, the recoveries often decreased to *ca.* 50%. A larger Al-CC column might be used if elution data are confirmed for the PCDD and PCDF congeners.

GC–MS analysis

Recently, several analytical columns, such as DB-Dioxin, Quadrex DXN and Quadrex 23, have become commercially available with excellent resolution for PCDD and PCDF congeners, but it was difficult to use them owing to insufficient retention data for all of the congeners. The SP-2331 column was most useful for the analysis of the T_4–H_6C congeners as the resolution was excellent and the retention data had been clarified for these congeners [8,12,17,20,25–27]. However, the SP-2332 column showed heavy bleeding and low analytical accuracy at the elution temperature of the O_8C congeners. A non-polar Ultra-1 column (cross-linked methylsilicone) was therefore used to determine the H_7C and O_8C congeners.

The analytical mass numbers for SIM, listed in Table II, were selected so as to minimize the effects of interfering substances in the air samples especially in the analysis for P_5CDF, H_6CDF, O_8CDD and O_8CDF congeners.

Identification and determination of the PCDD and PCDF congeners were basically effected using EPA Method 8290 [12]. A standard sample for identification was prepared by extracting a fly-ash

sample from a city incinerator [12,15]. Tables III and IV and Fig. 2 show retention data for the PCDDs and the PCDFs from the fly-ash sample used for identification of the PCDD and PCDF congeners in air samples. The fly-ash sample contained much higher concentration levels of all the congeners than found in air, but with similar chromatographic patterns. The fly-ash sample was also useful for the adjustment and confirmation of the column and gas chromatographic conditions.

The detection limit for each PCDD and PCDF congener was 2 pg in GC–MS analysis and the minimum detectable concentration of each congener was 0.5 pg/m^3 for a 1000-m^3 air sample.

Analysis of atmospheric samples

The method was applied to monitoring of the PCDD and PCDF congeners in the atmospheric environment at industrial, commercial, residential and background sites in the Osaka prefecture in August and December 1988–92. The total number of samples analysed was 108. The PCDDs and the PCDFs were detected in all samples, even those from the countryside. However, 2,3,7,8-T_4CDD and 2,3,7,8-T_4CDF were difficult to determine even in heavily contaminated samples, although they were detected as trace peaks. The total concentrations of the PCDD and PCDF congeners were 2–100 and 2–200 pg/m^3, respectively. The TEQs were

TABLE IV

ELUTION ORDER OF PCDF CONGENERS ON THE SP-2331 AND THE ULTRA-1 CAPILLARY COLUMNS

No.[a]	T_4CDFs[b]	No.[a]	P_5CDFs[b]	No.[a]	H_6CDFs[b]
1	1,3,6,8	1	1,3,4,6,8	1	1,2,3,4,6,8
2	1,3,7,8/1,3,7,9	2	1,2,4,6,8	2	1,3,4,6,7,8
3	1,3,4,7	3	1,3,6,7,8		1,3,4,6,7,9
4	1,4,6,8	4	1,3,4,7,8	3	1,2,4,6,7,8
5	1,2,4,7/1,3,6,7	5	1,3,4,7,9/1,2,3,6,8	4	1,2,4,6,7,9
6	1,3,4,8	6	1,2,4,7,8	5[d]	1,2,3,4,7,8
7	1,2,4,8/1,3,4,6	7	1,2,4,7,9/1,3,4,6,7		1,2,3,4,7,9
8	1,2,4,6/1,2,6,8	8	1,2,4,6,7	6[d]	1,2,3,6,7,8
	1,2,3,7/1,4,7,8	9	1,2,3,4,7/1,4,6,7,8	7	1,2,4,6,8,9
	1,3,6,9	10	1,3,4,6,9	8	1,2,3,4,6,7
9	1,2,3,4/2,3,4,9	11[d]	1,2,3,4,8/1,2,3,7,8	9	1,2,3,6,7,9
10	1,2,3,6/1,2,3,8	12	1,2,3,4,6	10	1,2,3,4,6,9
	1,4,6,7/2,4,6,8	13	1,2,3,7,9		1,2,3,6,8,9
11	1,3,4,9	14	1,2,3,6,7	11[d]	1,2,3,7,8,9
12	1,2,7,8	15	1,2,4,6,9/2,3,4,8,9	12	1,2,3,4,8,9
13	1,2,6,7/1,2,7,9	16	1,3,4,8,9	13[d]	2,3,4,6,7,8
14	2,3,6,8/1,4,6,9	17	1,2,4,8,9		
	1,2,4,9	18	1,2,3,6,9	No.[a]	H_7CDFs[c]
15	2,4,6,7	19	2,3,4,6,8		
16	1,2,3,9/2,3,4,7	20	1,2,3,4,9	1[d]	1,2,3,4,6,7,8
17	1,2,6,9	21[d]	2,3,4,7,8	2	1,2,3,4,6,7,9
18[d]	2,3,7,8/2,3,4,8	22	1,2,3,8,9	3	1,2,3,4,6,8,9
19	2,3,4,6	23	2,3,4,6,7	4[d]	1,2,3,4,7,8,9
20	2,3,6,7/3,4,6,7				
21	1,2,8,9			No.[a]	O_8CDFs[c]
				1[d]	1,2,3,4,6,7,8,9

[a] Elution order (or peak order).
[b] Separation on the SP-2331 capillary column.
[c] Separation on the Ultra-1 capillary column.
[d] 2,3,7,8-Substituted congeners used for calculating the TEQ.

0–0.6 pg/m^3 for the PCDD congeners and 0–1.2 pg/m^3 for the PCDF congeners, although a few unresolved congeners overlapped with 2,3,7,8-T_4CDF and 1,2,3,7,8-P_5CDF (see Table IV).

Table V presents typical results of monitoring PCDD and PCDF congeners in the atmosphere in Osaka prefecture and Fig. 3 shows chromatograms for a sample from a central urban site close to busy roads. A number of peaks, appearing close to the isomers of T_4CDDs and T_4CDFs, might adversely affect the measurment of the T_4C congeners at ultra-trace levels as seen in Fig. 3. Thirty three peaks for 47 congeners out of 49 PCDDs and 58 peaks for 82 congeners out of 87 PCDFs, most of which were close to the detection limit (0.5 pg/m^3), could be quantitatively monitored in the atmospheric samples and the concentrations of PCDDs and PCDFs were represented as total concentrations of the individual PCDD and PCDF congeners, respectively. Thus, the analytical results could become significantly different unless the analytical conditions are precisely confirmed around the detection limits. More effective clean-up procedures and/or higher MS resolution may be necessary to determine the T_4-O_8CDD and T_4-O_8CDF congeners at levels lower than 0.5 pg/m^3 without effects of interfering substances.

TABLE V

TYPICAL MONITORING DATA OF PCDD AND PCDF CONGENERS IN THE ATMOPSHERIC ENVIRONMENT IN OSAKA

Sample	Congeners	Concentration of PCDDs and PCDFs (number of peaks, number of isomers)[a]					Total (TEQ)
		T_4C-	P_5C-	H_6C-	H_7C-	O_8C-	
Sample 1[b,g]	DDs	2.5(3, 4)	3.7(3, 5)	5.4(3, 6)	8.3(2, 2)	6.2(1, 1)	26.1(−)
	DFs	14.4(12, 22)	14.1(15, 20)	13.3(8, 11)	8.4(4, 4)	3.1(1, 1)	53.3(−)
Sample 2[b,h]	DDs	9.4(7, 8)	15.9(9, 12)	13.9(5, 8)	23.1(2, 2)	20.5(1, 1)	82.8(0.5)
	DFs	28.8(17, 31)	45.0(19, 24)	35.2(10, 13)	31.9(4, 4)	15.0(1, 1)	155.9(1.2)
Sample 3[c,g]	DDs	1.9(2, 2)	5.4(6, 9)	2.2(2, 5)	5.0(2, 2)	3.9(1, 1)	18.4(−)
	DFs	11.6(11, 25)	8.7(12, 17)	6.5(7, 10)	3.8(2, 2)	2.1(1, 1)	32.7(−)
Sample 4[c,h]	DDs	4.7(2, 2)	5.5(4, 5)	5.8(3, 6)	16.3(2, 2)	8.8(1, 1)	41.1(−)
	DFs	24.6(15, 30)	27.0(16, 21)	22.2(8, 11)	26.6(4, 4)	21.3(1, 1)	121.7(0.4)
Sample 5[d,g]	DDs	15.7(4, 10)	42.8(9, 12)	5.8(3, 6)	6.0(2, 2)	3.3(1, 1)	73.6(−)
	DFs	23.4(14, 29)	23.7(16, 21)	12.4(8, 11)	11.2(3, 3)	4.9(1, 1)	75.6(0.3)
Sample 6[d,h]	DDs	9.6(8, 12)	8.3(5, 8)	9.2(4, 7)	18.1(2, 2)	15.4(1, 1)	60.6(−)
	DFs	20.9(15, 32)	29.0(17, 22)	27.6(10, 13)	40.3(4, 4)	21.6(1, 1)	139.4(0.5)
Sample 7[e,g]	DDs	2.3(2, 2)	9.1(5, 7)	4.2(3, 6)	11.4(2, 2)	9.6(1, 1)	36.6(−)
	DFs	8.0(8, 20)	18.8(14, 19)	11.4(8, 11)	4.8(3, 3)	5.5(1, 1)	48.5(0.1)
Sample 8[e,h]	DDs	4.2(2, 2)	10.6(5, 7)	7.9(6, 9)	11.5(2, 2)	18.4(1, 1)	52.6(−)
	DFs	22.1(17, 32)	42.0(18, 23)	19.4(10, 13)	17.2(4, 4)	8.5(1, 1)	109.2(0.4)
Sample 9[f,g]	DDs	0.9(1, 1)	1.3(2, 3)	ND[i](−, −)	1.8(1, 1)	1.8(1, 1)	5.8(−)
	DFs	ND(−, −)	0.5(1, 1)	4.2(3, 4)	8.7(3, 3)	1.0(1, 1)	14.4(−)
Sample 10[f,h]	DDs	0.9(1, 1)	1.2(2, 3)	ND(−, −)	0.6(1, 1)	0.9(1, 1)	3.6(−)
	DFs	2.5(3, 5)	ND(−, −)	3.5(2, 3)	ND(−, −)	ND(−, −)	6.0(−)

[a] Daily average concentration in pg/m^3 at 20°C and 1 atm; the number of peaks and the number of isomers quantified in the SIM analysis are given in parentheses.
[b] Sampling site: adjacent to traffic roads in the urban central area.
[c] Sampling site: near to a traffic road in the urban residential area not far from the coast.
[d] Sampling site: north-inland residential area.
[e] Sampling site: coastal industrial area.
[f] Sampling site: south mountainous area.
[g] Sampling time: August 1990.
[h] Sampling time: December 1990.
[i] ND = not detected (the concentration of each congener less than 0.5 pg/m^3).

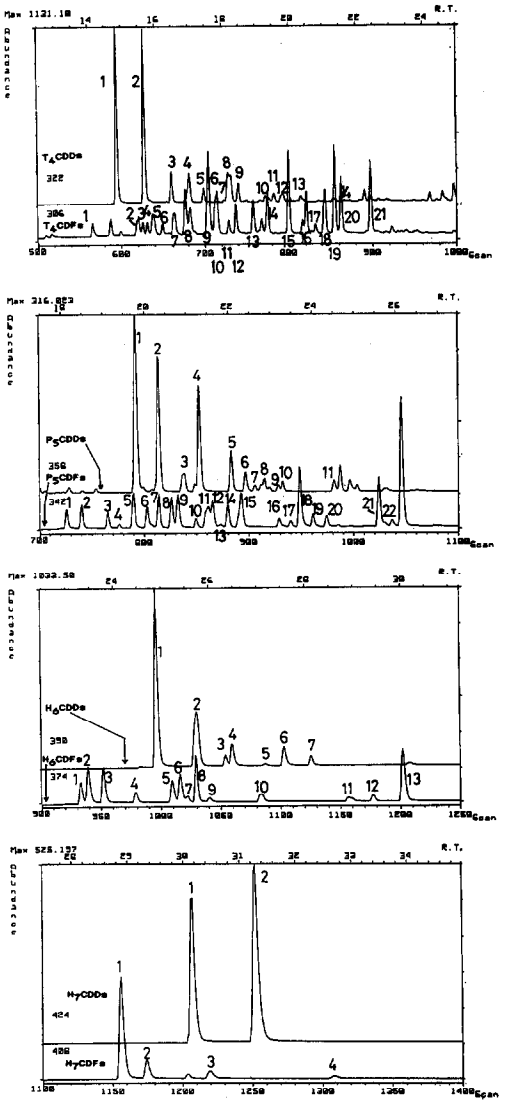

Fig. 2. SIM chromatograms showing elution orders of the PCDD and PCDF congeners in the fly ash extract. See Tables III and IV for peak numbers. R.T. = Retention time in min.

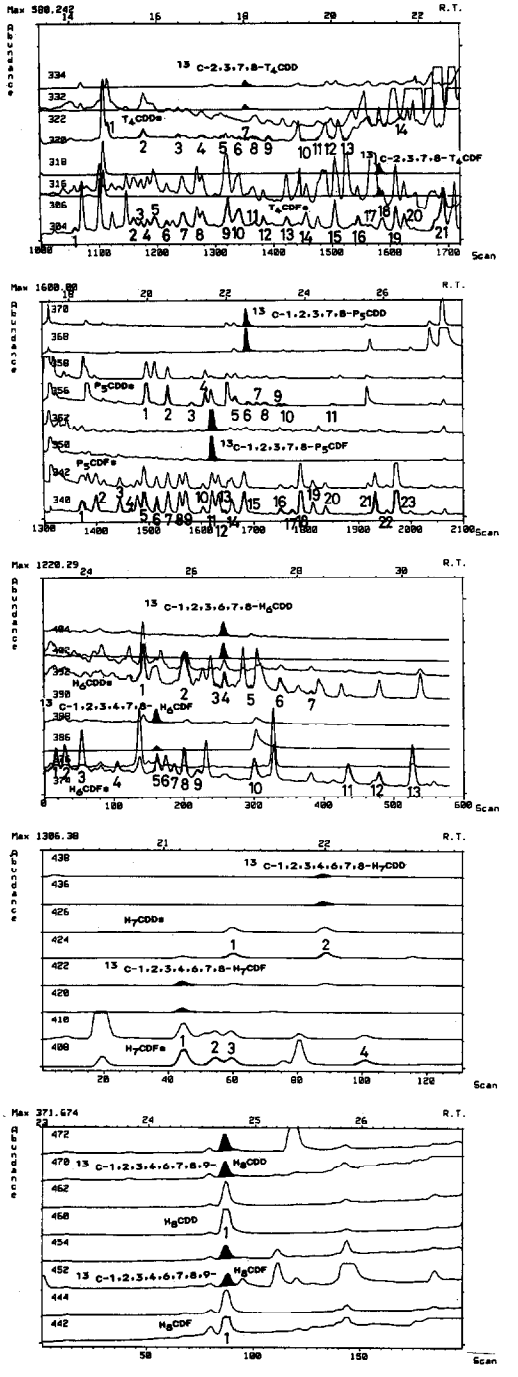

Fig. 3. Typical SIM chromatograms for the PCDD and PCDF congeners in urban air. See Tables III and IV for peak numbers. R.T. = Retention time in min.

CONCLUSIONS

The proposed method may be convenient for sampling high-volume air samples and determining the T_4–O_8CDD and T_4–O_8CDF congeners. The combined Si-CC and Al-CC system, after washing the samples with sulphuric acid, was effective in cleaning up the samples without multiple fraction-

ations for all the congeners. A fly-ash sample was useful for identification of the congeners and for adjustment of the column and GC–MS conditions. GC–MS analysis may be reasonable with a 3000–5000 resolution by selecting suitable internal standards and analytical mass numbers for SIM that are less affected by interfering substances. The method may be useful for analysing large numbers of airborne sample within a reasonable time.

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