Manual

on

Determination of Dioxins in Ambient Air

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&
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Determination of Dioxins in Ambient Air

Chapter 1 Outline of Determination Method

1. Introduction

Dioxins are highly toxic compounds that need to be controlled in order to prevent adverse effects on human health; there is serious public concern about them among environmental contaminants[1)].

It is necessary to identify current concentrations of dioxins in the environment and conditions of emission sources to promote the environmental protection measures against dioxin contamination, for which a reliable manual for the determination of dioxins is indispensable.

In the determination of dioxins, sampling procedures vary by characteristics of samples. Generally, concentrations of dioxins are very low. Dioxins are a group of various chlorinated congeners; each congener should be clearly separated and precisely quantified. In addition, to assure reliability of measured data it is necessary to have the manual providing quality control method.

This manual shows the analytical method to determine dioxins in the samples taken from ambient air. The innovation of analytical technology is remarkably rapid; it is important to adopt such new technology on time. Therefore, the manual does not strictly define certain analytical methods so that analysts in charge can adopt the method most suitable to given conditions. Accordingly, the manual presents the standard condition and criteria to control the quality of measured data.

2. Target Substances for Determination

This manual describes the determination of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and coplanar polychlorinated biphenyls (coplanar PCBs) in ambient air.

3. Definition of Terms

Dioxins: Dioxins, in a narrow sense, mean polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), but the term shall include coplanar PCBs in this manual.

Congener: Any particular member of the same chemical family. Congeners vary by the number of chlorine substitution and its position. There are 75, 135 and 209 congeners of chlorinated dibenzo-*p*-dioxins (CDDs), chlorinated dibenzofurans (CDFs) and chlorinated benzenes (CBs) respectively.

Homologue: A group of congeners that have the same degree of chlorination. There are eight homologues of CDDs and CDFs and ten homologues of CBs.

Isomer: Congeners that belong to the same homologous class but have different chlorine position. For example, there are 22 isomers that constitute the homologue of TeCDDs.

PCDDs: Polychlorinated dibenzo-*p*-dioxins

PCDFs: Polychlorinated dibenzofurans

TeCDDs: Tetrachloro dibenzo-*p*-dioxins

PeCDDs: Pentachloro dibenzo-*p*-dioxins

HxCDDs: Hexachloro dibenzo-*p*-dioxins

HpCDDs: Heptachloro dibenzo-*p*-dioxins

OCDD: Octachloro dibenzo-*p*-dioxin

TeCDFs: Tetrachlorodibenzofurans

PeCDFs: Pentachlorodibenzofurans

HxCDFs: Hexachlorodibenzofurans

HpCDFs: Heptachlorodibenzofurans

OCDF: Octachlorodibenzofuran

TeCBs: Tetrachlorobiphenyls

PeCBs: Pentachlorobiphenyls

HxCBs: Hexachlorobiphenyls

HpCBs: Heptachlorobiphenyls

Co-PCBs: Coplanar PCBs include 14 congeners of chlorinated biphenyls with coplanar structures with no, 1 or 2 chlorine atom(s) bonded in ortho position.

Non-*ortho* PCBs: Four congeners of PCBs with no chlorine atom substituting in ortho position.

Mono-*ortho* PCBs: Eight congeners of PCBs with 1 chlorine atom substituting in ortho position.

Di-*ortho* PCBs: Two congeners of PCBs with 2 chlorine atoms substituting in ortho position.

TEF: 2,3,7,8-TeCDD Toxicity Equivalency Factor

TEQ: 2,3,7,8-TeCDD Toxicity Equivalency Quantity. Index of toxicity of PCDDs/PCDFs and Co-PCBs as an equivalency quantity of 2,3,7,8-TeCDD which has the strongest toxicity among the dioxins.

PFK: Perfluorokerosene

HRGC: High Resolution Gas Chromatography or High Resolution Gas Chromatograph

HRMS: High Resolution Mass Spectrometry or High Resolution Mass Spectrometer

HRGC-HRMS: High Resolution Gas Chromatograph-Mass Spectrometry or High Resolution Gas Chromatograph-Mass Spectrometer

SIM: Selected Ion Monitoring

RRF: Relative Response Factor

QA/QC: Quality Assurance/Quality Control

% v/v: Volume per unit volume

% w/w: Weight per unit weight

ppm: Parts per million (10^{-6})

ppb: Parts per billion (10^{-9})

ppt: Parts per trillion (10^{-12})

ppq: Parts per quadrillion (10^{-15})

ìg: microgram; 10^{-6} g

ng: nanogram; 10^{-9} g

pg: picogram; 10^{-12} g

sps: Sampling spike

cs: Cleanup spike

ss: Syringe spike

DL: Detection Limit (Minimum value that can be distinguished from blank values; threefold of the standard deviation of determined values or the value whose SN ratio is 3.)

QL: Quantification Limit (Minimum value of reliable quantification; tenfold of the standard deviation of determined values or the value whose SN ratio is 10.)

This manual adopts “Target Quantification Limit (TQL)” to evaluate allowance level of Detection Limit (DL), Quantification Limit and the operation blank value. The TQL should be set considering the purpose of the determination. The TQL in this manual is set so as to quantify 1/10 of the legal standard value of dioxin concentrations in ambient air expressed in TEQ as shown in Table 1. However, DL shown in Table 2 is compatible to the TQL for convenience, as the value expressed only in TEQ might not be helpful in actual determination. It should be noticed that total TEQ value should be less than 1/30 of the standard value even if all the determined values are near the DL when the TEQ value is calculated based on the DL of each analysis.

If target concentrations of chlorinated compounds are set as DLs shown in Table 2 and are converted into the QL with the corresponding TEQs, the QL is about 0.04 pg-TEQ/m^3, which satisfies the TQL[2)].

It is not necessary to make DL of each congener less than the value listed in Table 2 if QL satisfies the TQL indicated in Table 1. Also, it is not necessary to keep the values of DL shown in Table 2, if dioxin concentrations in the samples are high enough to be determined.

Dioxin concentrations calculated with DLs may be 60 % of the TQL shown in Table 1 when DLs in Table 2 are adopted, but it is desirable for all institutions to make the DL as low as possible so as to determine low concentrations of dioxins, in order to identify dioxin concentrations in ambient air more accurately.

Table 1 Target Quantification Limit of Dioxins in Ambient Air

Target Quantification Limit	Ambient Air Quality Standard for Dioxins
0.06 (pg-TEQ/m^3)	0.6 (pg-TEQ/m^3)

Table 2 Detection Limit and Examples of Calculation of Dioxins in Samples of Ambient Air

Homologue	Toxicity Equivalency Factor (TEF) *	Detection Limit	
		Concentration (pg/m^3)	Toxicity Equivalency Quantity (pg-TEQ/m^3)
TeCDD	1	0.003	0.003
PeCDDs	1	0.003	0.003
HxCDDs	0.1 (3)	0.007	0.002
HpCDDs	0.01	0.007	0.00007
OCDD	0.0001	0.01	0.000001
TeCDF	0.1	0.003	0.0003
PeCDFs	0.05, 0.5	0.003	0.0017
HxCDFs	0.1 (4)	0.007	0.00028
HpCDFs	0.01 (2)	0.007	0.00014
OCDF	0.0001	0.01	0.000001
Co-PCBs	0.1 0.01 0.0001 (6) 0.0005 (3) 0.00001	0.007	0.00079
Total Toxic Equivalency Quantity	Detection Limit	-	0.011
	Quantification Limit	-	0.036

Note: Numbers in the brackets indicate the number of congeners.

* WHO-TEF (1998)

Commercial names referred in the manual are not for recommendation but for the readers' convenience. They were used in the experiments to verify the procedures described in the manual and are generally available.

4. Classification of Sampling and Analysis Methods

4.1 Sampling

Sample should be taken by a high volume air sampler with which a sampling tube with 2

pieces of polyurethane foam is attached below filter paper. For obtaining a 24-hour average concentration, sample should be collected at a high flow rate of 700 L/min for 24 hours. For obtaining a weekly average concentration, samples should be collected 7 times at a high flow rate of 700 L/min for 24 hours or collected continuously at a medium flow rate of 100 L/min for consecutive 7 days. Glass fiber filter shall be used as the filter paper for a high-volume air sampler.

4.2 Preparation

4.2.1 Solvent Extraction

Sample is extracted from glass fiber filter by Soxhlet extractor with toluene for 16 to 24 hours. This procedure is hereinafter referred to as toluene Soxhlet extraction.

For the polyurethane foam, sample is extracted by a Soxhlet extractor with acetone for 16 to 24 hours. This procedure is hereinafter referred to as acetone Soxhlet extraction.

4.2.2 Cleanup

The extract is divided into two fractions after removal of interfering substances in the extract by sulfuric acid-impregnated silica gel column chromatography or multilayered silica gel chromatography. One of the fractions is used for PCDDs/PCDFs determination and the other for coplanar PCBs. PCDDs/PCDFs and coplanar PCBs are separated from the fractions by alumina column chromatography[3)].

Activated carbon column on High Performance Liquid Chromatography (HPLC) or activated carbon impregnated silica gel column chromatography is employed if the interference in GC/MS analysis is found and if a finer cleanup procedure is needed. The HPLC is effective especially when it is necessary to separate PCDDs/PCDFs from non-*ortho* PCBs.

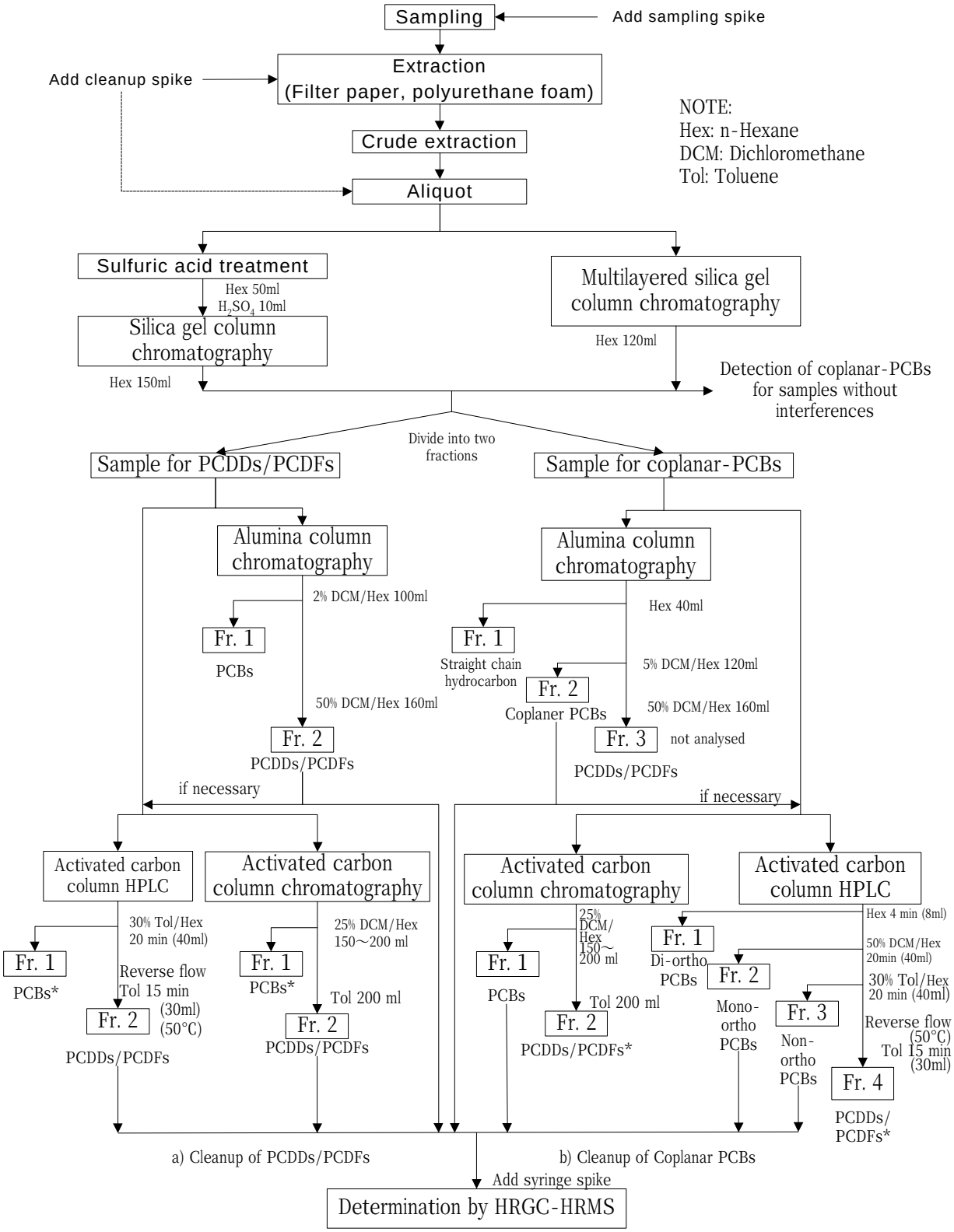
Figure 1 shows an example of a procedure flow of cleanup.

(1) Sulfuric Acid Treatment

The extract is concentrated and then transferred into hexane. Organic substances in hexane layer are removed with sulfuric acid. The solution obtained is cleaned up by silica gel column chromatography.

(2) Silica Gel Column Chromatography

Silica gel column chromatography is an effective way for removing strong-polar substances and pigments. It is used in the first stage of a column cleanup of the sample solution treated with sulfuric acid, and used as the sample preparation prior to a cleanup by alumina column chromatography.



* In the case that the alumina column chromatography is not used.

Figure 1 Procedure Flow of Cleanup of Dioxins

(3) Multilayered Silica Gel Column Chromatography

The column with a multi-layer of silica gel impregnated with potassium hydroxide, sulfuric acid and silver nitrate is used for further cleanup of the sample solution instead of sulfuric acid-impregnated silica gel column.

Silver nitrate-impregnated silica gel is effective in cleaning up the samples containing a lot of sulfur. This is the sample preparation for alumina column chromatography.

(4) Alumina Column Chromatography

PCDDs/PCDFs and PCBs in the two fractions are separated by activated alumina column. Each fraction containing PCDDs/PCDFs and coplanar PCBs is concentrated and replaced to nonane. This nonane solution is analyzed by GC/MS (Gas Chromatography-Mass Spectrometry).

(5) Fractional Activated Carbon Column High Performance Liquid Chromatography (HPLC)

Fractional activated carbon column combined with high performance liquid chromatography is used after the separation of PCDDs/PCDFs and PCBS by or in substitution for alumina column chromatography. It is an effective tool in removing the interfering matrices disturbing sensitivity of GC/MS and separating congeners which keep the same retention time in the capillary column of the GC/MS.

(6) Activated Carbon -Impregnated Silica Gel Chromatography

Activated carbon -impregnated silica gel chromatography is used to clean up the sample when interferences are found during the GC/MS measurement after cleanup by alumina column chromatography. It may also be used as the substitution for alumina column chromatography.

4.3 Analysis Procedure

Dioxins are identified and quantified by high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS) employing HRGC with a capillary column and double-focusing type HRMS.

Resolution should keep greater than 10,000 in general and may require greater than 12,000 depending on internal standards.

Selected ion monitoring (SIM) with lock mass techniques or other techniques which have the same or finer resolution should be employed to detect each congener.

Sensitivity is required to detect 0.1 pg for tetra- or penta- CDDs/DFs, 0.2 pg for hexa- or hepta- CDDs/DFs, 0.5 pg for octa-CDD/DF and 0.2 pg for coplanar PCB congeners[4)].

5. Representation

(1) Representation of the concentration

The concentration of PCDD/PCDF homologues should be presented as the concentration of each homologue from tetra-chlorinated to octa-chlorinated and that of total homologues. The concentration of PCDD/PCDF congeners should be represented as the concentration of each 2,3,7,8-chlorine substituted congener (17 congeners). The concentration of 1,3,6,8-TeCDD, 1,3,7,9-TeCDD, or 1,2,7,8-TeCDF should be determined and represented in order to trace the origin of the contaminants, if necessary.

The dioxin concentration in the sample should be expressed in pg/m^3 as the concentration of gaseous substances. The congeners to be represented are shown in Table 3.

Table 3 Example of Representation of the Dioxin concentrations

a) PCDDs and PCDFs

Chlorinated Level	PCDDs		PCDFs	
	Homologue	Congener	Homologue	Congener
Tetra-chlorinated	TeCDDs	2,3,7,8- 1,3,6,8- 1,3,7,9-	TeCDFs	2,3,7,8- 1,2,7,8-
Penta-chlorinated	PeCDDs	1,2,3,7,8-	PeCDFs	1,2,3,7,8- 2,3,4,7,8-
Hexa-chlorinated	HxCDDs	1,2,3,4,7,8- 1,2,3,6,7,8- 1,2,3,7,8,9-	HxCDFs	1,2,3,4,7,8- 1,2,3,6,7,8- 1,2,3,7,8,9- 2,3,4,6,7,8-
Hepta-chlorinated	HpCDDs	1,2,3,4,6,7,8-	HpCDFs	1,2,3,4,6,7,8- 1,2,3,4,7,8,9-
Octa-chlorinated	OCDD	1,2,3,4,6,7,8,9-	OCDF	1,2,3,4,6,7,8,9-
Σ (tetra to octa)	Total PCDDs		Total PCDFs	

b) Coplanar PCBs

Homologue	Non-*ortho* PCB congener	Mono-*ortho* PCB congener
TeCB	3,3',4,4'- (#77) 3,4,4',5- (#81)	
PeCB	3,3',4,4',5- (#126)	2',3,4,4',5- (#123) 2,3',4,4',5- (#118) 2,3,3',4,4'- (#105) 2,3,4,4',5- (#114)
HxCB	3,3',4,4',5,5'- (#169)	2,3',4,4',5,5'- (#167) 2,3,3',4,4',5- (#156) 2,3,3',4,4',5'- (#157)
HpCB		2,3,3',4,4',5,5'- (#189)
	Total non-*ortho* PCBs	Total mono-*ortho* PCBs
Total coplanar PCBs		

Note: Number with # in brackets indicates IUPAC No.

For coplanar PCBs, the concentrations of the following congeners should be represented.

- Each congener (4 non-*ortho* congeners and 8 mono-*ortho* congeners)
- Total of non-*ortho* congeners
- Total of mono-*ortho* congeners
- Total of all the coplanar PCB congeners

The concentration of each congener should be represented as:

- Determined value, when the concentration is equal to or greater than the quantification limit (QL).
- Determined value with a note indicating less reliability (e.g. putting the determined value in brackets), when the concentration is equal to or greater than the detection limit (DL) and lower than the quantification limit (QL).
- "< DL (value)," when the concentration is lower than the detection limit (DL).

Total of the determined values should be calculated by summing the determined values when the concentration is equal to or greater than the DL, or one-half the DL value when the concentration is lower than the DL.

(2) 2,3,7,8-TeCDD Toxicity Equivalency Quantity

The concentration of each congener should be expressed as Toxicity Equivalency Quantity (pg-TEQ/m^3) by being multiplied by 2,3,7,8-TeCDD Toxicity Equivalency Factor (TEF). TEFs of the dioxin congeners are listed in Table 4.

Total Toxicity Equivalency Quantity (TEQ) shall be the total of TEQ of all the congeners. Japan Industrial Standards (JIS) present the following three methods to calculate the TEQ of each congener.

1) The values equal to or greater than the QL are handled as they are, and those falling between QL and DL and those lower than the DL are handled as zero.
2) The values equal to or greater than the QL and those falling between QL and DL are handled as they are, and the DL values are used for those lower than the DL.
3) The values equal to or greater than the DL and those falling between QL and DL are handled as they are, and one-half the DL is used for those lower than the DL.

This manual has adopted the method 3) to calculate the total TEQ.

Table 5 shows an example of the representation of concentration of dioxins .

Table 4 Toxicity Equivalency Factor (TEF) of Dioxins

PCDD/PCDF Congener	WHO-TEF (1998)	Coplanar PCB Congener	IUPAC No.	WHO-TEF(1998) for Humans/Mammals
PCDDs		Non-*ortho* PCBs		
2,3,7,8-TeCDD	1	3,4,4',5-TeCB	#81	0.0001
1,2,3,7,8-PeCDD	1	3,3',4,4'-TeCB	#77	0.0001
1,2,3,4,7,8-HxCDD	0.1	3,3',4,4',5-PeCB	#126	0.1
1,2,3,6,7,8-HxCDD	0.1	3,3',4,4',5,5'-HxCB	#169	0.01
1,2,3,7,8,9-HxCDD	0.1			
1,2,3,4,6,7,8-HpCDD	0.01			
1,2,3,4,6,7,8,9-OCDD	0.0001			
PCDFs		Mono-*ortho* PCBs		
2,3,7,8-TeCDF	0.1	2',3,4,4',5-PeCB	#123	0.0001
1,2,3,7,8-PeCDF	0.05	2,3',4,4',5-PeCB	#118	0.0001
2,3,4,7,8-PeCDF	0.5	2,3,3',4,4'-PeCB	#105	0.0001
1,2,3,4,7,8-HxCDF	0.1	2,3,4,4',5-PeCB	#114	0.0005
1,2,3,6,7,8-HxCDF	0.1	2,3',4,4',5,5'-HxCB	#167	0.00001
1,2,3,7,8,9-HxCDF	0.1	2,3,3',4,4',5-HxCB	#156	0.0005
2,3,4,6,7,8-HxCDF	0.1	2,3,3',4,4',5'-HxCB	#157	0.0005
1,2,3,4,6,7,8-HpCDF	0.01	2,3,3',4,4',5,5'-HpCB	#189	0.0001
1,2,3,4,7,8,9-HpCDF	0.01			
1,2,3,4,6,7,8,9-OCDF	0.0001			
Other PCDDs, PCDFs	0	Other Co-PCBs		0

(3) Significant Figure

Following rules are applied to control the significant figures of data, unless specifically indicated.

a) Significant figures of the concentration should be 2 digits according to the rounding procedure defined in JIS-Z8401. If the concentration is lower than the DL, it should be noted. Digits of the concentration should be limited to the DL of the air sample, and lower figures than the DL shall not be represented.

b) The significant figure of the DL should be 1 digit by rounding the value according to JIS-Z8401.

c) Toxicity Equivalency Quantity should be the total of all the congeners determined. The significant figure should be 2 digits by the same procedure as a). This means that the TEQ of each congener should not be rounded.

Table 5 Example of Representation of Dioxins (2,3,7,8-chlorine substituted PCDDs/PCDFs and coplanar PCBs)

a) PCDDs and PCDFs

	Measured Item	Concentration (pg/m^3)	TEF	TEQ ($pg\text{-}TEQ/m^3$)
For congener				
Dibenzo-*p*-dioxin	2,3,7,8-TeCDD	<0.003	x 1	<0.0015>
	1,3,6,8-TeCDD	0.080	-	-
	1,3,7,9-TeCDD	0.040	-	-
	1,2,3,7,8-PeCDD	0.010	x 1	0.01
	1,2,3,4,7,8-HxCDD	(0.010)	x 0.1	0.001
	1,2,3,6,7,8-HxCDD	0.020	x 0.1	0.002
	1,2,3,7,8,9-HxCDD	0.020	x 0.1	0.002
	1,2,3,4,6,7,8-HpCDD	0.14	x 0.01	0.0014
	OCDD	0.60	x 0.0001	0.00006
Dibenzofuran	2,3,7,8-TeCDF	0.010	x 0.1	0.001
	1,2,7,8-TeCDF	0.040	-	-
	1,2,3,7,8-PeCDF	0.040	x 0.05	0.002
	2,3,4,7,8-PeCDF	0.040	x 0.5	0.02
	1,2,3,4,7,8-HxCDF	0.040	x 0.1	0.004
	1,2,3,6,7,8-HxCDF	0.040	x 0.1	0.004
	1,2,3,7,8,9-HxCDF	<0.007	x 0.1	<0.00035>
	2,3,4,6,7,8-HxCDF	0.050	x 0.1	0.005
	1,2,3,4,6,7,8-HpCDF	0.13	x 0.01	0.0013
	1,2,3,4,7,8,9-HpCDF	0.020	x 0.01	0.0002
	OCDF	0.10	x 0.0001	0.00001
For homologue				
Dibenzo-*p*-dioxin	TeCDDs	0.19	-	-
	PeCDDs	0.20	-	-
	HxCDDs	0.33	-	-
	HpCDDs	0.26	-	-
	OCDD	0.60	-	-
	Total PCDDs	1.6		0.018 [1)]
Dibenzofuran	TeCDFs	0.76	-	-
	PeCDFs	0.51	-	-
	HxCDFs	0.41	-	-
	HpCDFs	0.23	-	-
	OCDF	0.10	-	-
	Total PCDFs	2.0		0.038 [2)]
	Total (PCDDs＋PCDFs)	3.6		0.056 [3)]

[1)] The TEQ of total PCDDs is calculated by summing up TEQ of each congener and rounded to two significant figures as defined in JIS-Z8401.

[2)] The TEQ of total PCDFs is calculated by summing up TEQ of each congener and rounded to two significant figures as defined in JIS-Z8401.

[3)] The TEQ of total PCDDs and PCDFs is calculated by summing up TEQ of each congener and rounded to two significant figures as defined in JIS-Z8401.

b) Coplanar PCBs

	Measured Item		Concentration (pg/m^3)	TEF	TEQ ($pg\text{-}TEQ/m^3$)
Non-*ortho* PCB	3,3',4,4'-TeCB	(#77)	1.2	x 0.0001	0.00012
	3,4,4',5-TeCB	(#81)	1.4	x 0.0001	0.00014
	3,3',4,4',5-PeCB	(#126)	1.4	x 0.1	0.14
	3,3',4,4',5,5'-HxCB	(#169)	1.6	x 0.01	0.016
	Total non-*ortho* PCBs		5.6		0.16 [1)]
Mono-*ortho* PCB	2,3,3',4,4'-PeCB	(#105)	1.2	x 0.0001	0.00012
	2,3,4,4',5-PeCB	(#114)	1.5	x 0.0005	0.00075
	2,3',4,4',5-PeCB	(#118)	2.5	x 0.0001	0.00025
	2',3,4,4',5-PeCB	(#123)	<0.007	x 0.0001	$<3.5 \times 10^{-7}>$
	2,3,3',4,4',5-HxCB	(#156)	0.36	x 0.0005	0.00018
	2,3,3',4,4',5'-HxCB	(#157)	0.36	x 0.0005	0.00018
	2,3',4,4',5,5'-HxCB	(#167)	<0.007	x 0.00001	$<3.5 \times 10^{-8}>$
	2,3,3',4,4',5,5'-HpCB	(#189)	0.98	x 0.0001	0.000098
	Total mono-*ortho* PCBs		6.9		0.0016 [2)]
Total Coplanar PCBs			13		0.16 [3)]
Total TEQ			-		0.21

[1)] The TEQ of total non-*ortho* PCBs is calculated by summing up TEQ of each congener and rounded to two significant figures as defined in JIS-Z8401.
[2)] The TEQ of total mono-*ortho* PCBs is calculated by summing up TEQ of each congener and rounded to two significant figures as defined in JIS-Z8401.
[3)] The TEQ of total coplanar PCBs is calculated by summing up TEQ of each congener and rounded to two significant figures as defined in JIS-Z8401.

Number with # in brackets indicates IUPAC No.
The value in the round brackets ( ) indicates that it is equal to or greater than the DL and lower than the QL.
The value in the triangle brackets < > means an estimated value as it is lower than the DL.
The QL and the DL of the congeners are shown below.

Congener	Quantification Limit (pg/m^3)	Detection Limit (pg/m^3)
TeCDD/CDF, PeCDD/CDF	0.01	0.003
HxCDD/CDF, HpCDD/CDF	0.02	0.007
OCDD/CDF	0.04	0.01
Co-PCBs	0.02	0.007

6. Quality Control

Quality control should be properly performed to assure the reliability of the determination. The following Chapter describes detailed procedures of quality control. Quality control procedures are illustrated in Figure 2.

<Note for Figure 2>

*1 Target Quantification Limit means the minimum sensitivity to quantify dioxins at 1/10 of the ambient air quality standard value expressed in TEQ concentrations, in principle.

*2 Fluctuation in sensitivity of the instruments throughout a series of determination should be within 20% of the sensitivity recorded at the calibration. The ratio of the peak areas of the two monitor ions of each chlorinated congener should be almost the same as that of the standard solution. The difference between the ratio of the peak areas and the natural existence ratio of the corresponding isotope should be within ±15%.

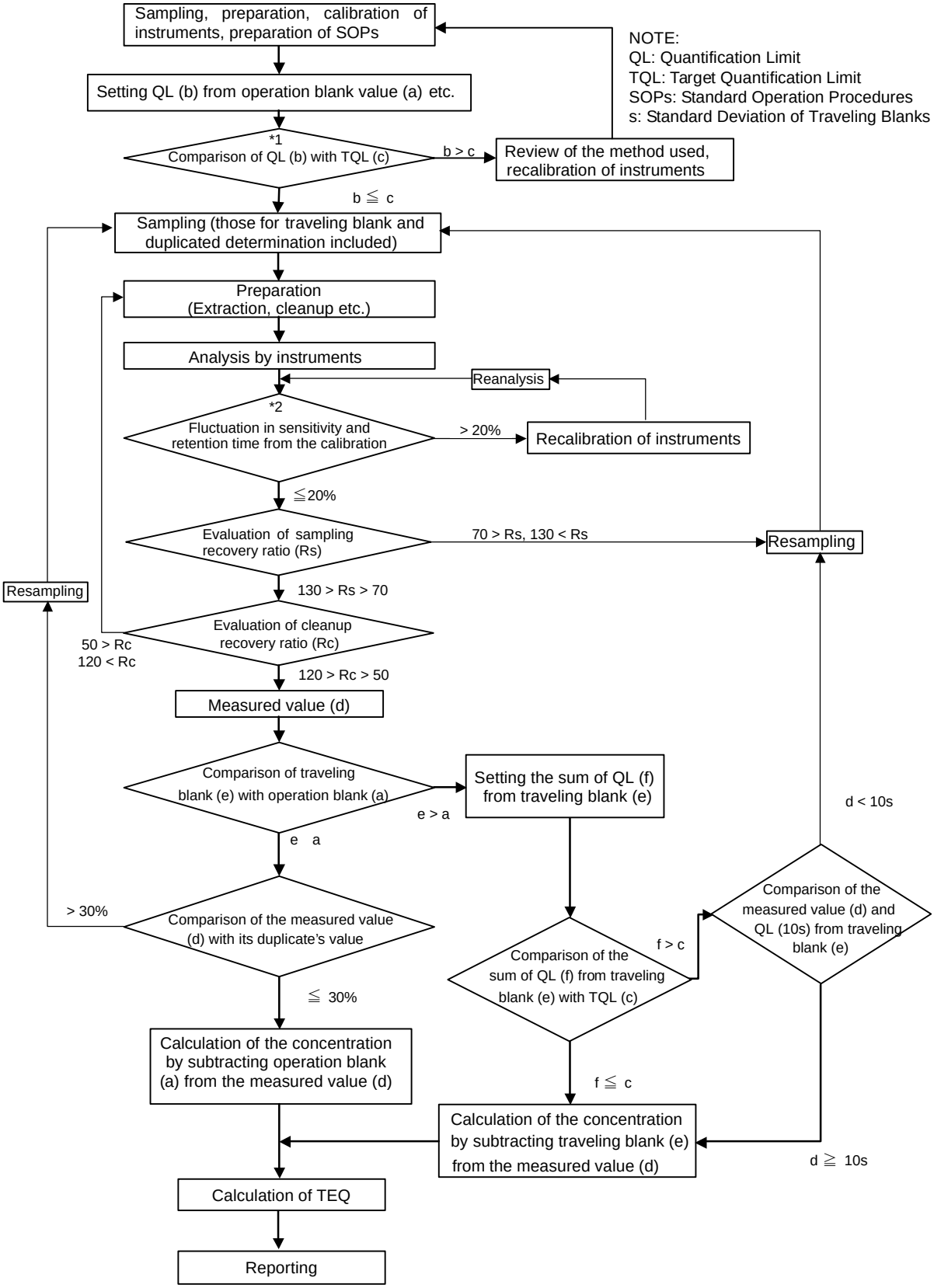


Figure 2 Overview of Quality Control

7. Criteria for Selecting Determination Methods

Among determination methods developed for dioxins, this manual presents the determination methods which have been verified by actual experiments. However, newly developed methods or the methods which are generally employed but not presented in this manual should also be adopted if they have the same performance as the methods presented in this manual.

Should new method be adopted with careful examination of the following.

(1) Sample Collection

a) Can representative samples be obtained constantly?
b) Does NOT the method lose compounds with low boiling point?
c) Can samples thoroughly be collected from sampling apparatus?
d) Are NOT samples contaminated by apparatus, atmospheric deposition or dust on site?

(2) Sample Preparation (Extraction)

a) Can target compounds be efficiently extracted from various samples? Can it be preformed constantly?
b) Can ^{13}C or ^{37}Cl- labeled internal standards be recovered sufficiently or extracted with sufficient recovery? Can target compounds be extracted efficiently from samples?

(3) Preparation (Cleanup)

a) Can blank value of reagents and apparatus be verified?
b) Can eluting condition in each cleanup procedure be verified?
c) Can samples be cleaned up stably and efficiently?
d) Can interfering matrices be separated and removed which may be found in actual samples?

(4) GC/MS Analysis

a) Can congener specific analysis be performed?
b) Can a capillary column separate congeners clearly? Is there a method (or guideline) to validate the coeluted congeners?
c) Are GC/MS calibration and calibration curve of standard reference materials suitable for various concentrations of samples?
d) Is absolute sensitivity of instruments high enough? Can fluctuation in sensitivity be controlled within acceptable range?
e) Is resolution of high resolution mass spectrometry, M/ÄM, greater than 10,000?

(5) Identification and Quantification

a) Can operation blank value and traveling blank value be obtained properly?
b) Can the detection limit (DL) and the quantification limit (QL) be established properly?
c) Can reproducibility of determination be assured?
d) Can actual samples and blank samples be preserved stably?

A new method, if adopted, should satisfy the appropriate acceptance criteria for the quality control presented in this manual, and data variation should range within 50% throughout the whole procedure of the determination. It is desirable that the new method is recognized widely as a proper analytical method of dioxins by results of verification tests at numbers of laboratories being open to the public.

8. Safety Control

8.1 Controlled Area

As dioxins are highly toxic, they should be handled only in the designated area of a laboratory of which the building design is complying with the following conditions. Inhalation of dioxins and their direct contact with human skin should be prevented. A preparation room and an analysis room should be sufficiently ventilated, and wastewater and solid waste should be properly managed.

(1) Laboratory

The laboratory should be divided into two or three rooms according to purposes such as preparation, and determination. Indoor air pressure should be kept lower than atmospheric pressure of -2 to -5 mmAq to prevent leakage of indoor air to outside.

(2) Entrance to and Exit from the Laboratory

Admission to the laboratory should be limited only to analysts. “No admittance except for the analysts” should be indicated on the doors of the laboratory.

(3) Ventilation and Wastewater Management

The laboratory should be ventilated through a ventilation system or draft chambers. Exhaust gas must be treated with an air treatment system, for example, an activated carbon filter, before emitted.

Wastewater from the laboratory should be treated with the activated carbon column to remove toxic substances before discharged.

8.2 Safety Operation Standard

Reagents and solvents used for the determination of dioxins as well as that of other substances must be handled carefully as some of them may harm the health of analysts if being inhaled or swallowed.

(1) Work in Laboratory

Analysts should wear special clothes for experiments in a laboratory and also wear safety glasses and gloves during experiments.

(2) Handling of Standard reference materials

A list of all standards and solution should be prepared. All containers of the standards and solution should be double-sealed and stored in a refrigerator.

(3) Handling of Samples

Samples for analysis must be stored in airtight containers. Concentrated extracts should be stored in airtight containers and kept in a refrigerator.

(4) Treatment and Storage of Waste

Wastes generated during the determination of hazardous chemicals should not be taken out from the controlled area except for those proved to be harmless. Hazardous solid wastes (gloves, masks, paper wipers, activated carbon filters, etc.) should be stored in airtight containers, and hazardous liquid waste (waste solvents, waste oil from vacuum pump, etc.) should be stored in special airtight containers.

(5) Work Record

The following information should be recorded.

1) Names of analysts who entered the laboratory
2) Work time and duration of analysts
3) Name, quantity, concentration, origin, destination and usage of standards
4) Storage and treatment of wastes
5) Other necessary information

(6) Health Check

Since organic solvents are used, periodical health check on effects of designated chemicals provided by the Labor Safety and Health Law should be conducted. In addition, concentrations of triglyceride, cholesterol in serum, etc. should be checked to detect effects of dioxins.

Chapter 2 Quality Control

For the dioxin determination in this manual, high precision and accuracy as well as high resolution is required because homologues of the chlorinated congeners need to be separated and quantified, and quality of the analysis must be controlled carefully.

Quality control includes preparation of the standard operation procedure (SOP), method validation (evaluation of validity of the method, and function and maintenance of equipment and apparatus) and examination of system adequacy (evaluation of reliability of data). It is desirable that they are conducted periodically (normally everyday) to verify the adequacy of the method prior to the daily monitoring operation.

1. Standard Operation Procedure

The standard operation procedure (SOP) of the following points should be prepared at the testing laboratory. It should be specific and easy to understand, and should be disseminated to all who are involved in the analytical procedure.

1) Sampling method and preparation, purification, storage and handling of reagents for preparation.
2) Preparation, storage and handling of the reagents for analysis, standard reference materials and standard solution.
3) Preparation of sampling equipments, and calibration and operation of the instruments and apparatus.
4) Calibration and establishment of operating conditions and procedures of analytical instruments.
5) Records of all the procedures of the determination including those of hard- and soft-ware of the computer used.

2. Evaluation and Maintenance of Instruments and Apparatus

2.1 Sampling

The apparatus, materials and reagents used for the sampling should be verified as being not to interfere the determination. Blank value should be lowered to the extent possible in order not to exceed the value equivalent to the Target Quantification Limit (as shown in Table 1).

Maintenance procedures of the apparatus, materials and reagents should be standardized so as to keep the quality of the sampling constant. The standard should be accountable.

2.1.1 Preparation and Storage of Sampling Apparatus

Glass fiber filter should be used after the blank value being lowered by preheating, and so should be polyurethane foam by being cleaned by the Soxhlet extraction or ultra-sonic

extraction.

The filters and polyurethane foam should be stored in airtight containers so as not to get contaminated by ambient air during the time after the cleansing to the sampling.

2.1.2 Storage and Transportation of Sampling Apparatus and Samples

Sampling apparatus and their parts must be cleansed to minimize contamination from them. Being assembled and fixed, the apparatus should be proved to be air-tight without any leakage before sampling. The filter should be shielded from sunlight. Collected samples should be stored in tightly sealed containers to prevent from being contaminated by the ambient air and not leaking out. The samples should be also shielded from sunlight during storage and transportation.

2.1.3 Assurance of the Reliability of Sampling

A sampling method must achieve obtaining the representative sample. It is important that PCDDs/PCDFs and coplanar PCBs should be collected sufficiently from obtained samples.

For obtaining a 24-hour average concentration, sample should be collected at a high flow rate of 700 L/min for 24 hours; the volume of the sample should be about 1,000 m^3. For obtaining a weekly average concentration, samples should be collected 7 times at a high flow rate of 700 L/min for 24 hours or collected continuously at a medium flow rate of 100 L/min for consecutive 7 days; the total volume of the samples should be about 1,000 m^3. A flow meter used for sampling should be calibrated periodically by using a reference gas flow meter. A calibration curve of flow volume should be developed, when necessary.

2.2 Reliability of the Preparation

The samples should be sufficiently cleaned up so that neither color nor matrices is observed visually after preparation. Any pigment or solid residue may disturb separation in the capillary columns, lower resolution due to degradation or fluctuation in sensitivity caused by contamination of ion sources of the MS, or interfere an accurate tuning of the PFK by the standard reference materials for mass calibration.

2.2.1 Soxhlet Extraction

Moisture should be removed from the filter paper by rinsing with acetone, as water disturbs efficient sample extraction. This acetone solution is mixed with the extract also. An extractor with a function of dehydration, Soxhlet-Deanstark Extractor, for example, is suitable for efficient removal of water.

2.2.2 Sulfuric Acid Treatment

The extract should be treated until no color is observed.

2.2.3 Silica Gel Column Chromatography

The condition for elution differs depending on the type and activity of agent, or the type/combination and volume of used solvents. The condition should be determined by conducting preliminary elution tests using the standard solution.

2.2.4 Multi-layered Silica Gel Column Chromatography

Elution position of each congener should be identified by preliminary elution tests using those containing all the congeners such as fly ash extract.

2.2.5 Alumina Column Chromatography

Alumina may change the polarity due to its production lot, and storing condition and duration. Coplanar PCBs (especially #81), 1,3,6,8-TeCDD and 1,3,6,8-TeCDF, etc, may be eluted into the first fraction if the activity of an alumina column is degraded. On the other hand, octa-chlorinated congeners may not be eluted enough into a standard volume of 50% (v/v) dichloromethane-hexane. The activity grade should also be checked by preliminary elution tests.

2.2.6 High Performance Liquid Chromatography with Activated Carbon Column

The injection port should be cleaned carefully to prevent contamination at a time of sample injection. Detailed conditions should be determined by preliminary elution tests.

2.2.7 Activated Carbon- Impregnated Silica Gel Column Chromatography

It should be verified that interfering substances are removed with dichloromethane-hexane. It should also be tested whether PCDDs/PCDFs and non-*ortho* PCBs can be eluted efficiently with toluene by preliminary elution tests.

2.3 Determination by the Instruments

High Resolution Gas Chromatograph-High Resolution Mass Spectrometer is used to identify and quantify each congener with high sensitivity and selectivity, as there are many congeners of PCDDs/PCDFs and coplanar PCBs.

2.3.1 Standard Reference Materials and Internal Standards

Traceability of the standard reference materials should be required as much as possible to assure the reliability of data, as the data is calculated by comparing measured concentration of samples with those of the standards.

Table 6 lists examples of the standard reference materials and the internal standards required for identifying and quantifying PCDDs/PCDFs and coplanar PCBs by the internal standard method[5].

The internal standards are used for the following objectives:

1) Sampling spike to verify validity of sampling
2) Cleanup spike to verify validity of preparation
3) Syringe spike to verify validity of sample injection to GC/MS

Different isotopically labeled congeners should be used for each of the sampling spike, the cleanup spike and the syringe spike.

For example, $^{13}C_{12}$-1,2,3,4-TeCDD is used for the sampling spike among the tetra-chlorinated isotopically labeled congeners whose volatility is relatively high because its toxicity is low.

For the cleanup spike, it is desirable that all the isotopically labeled congeners are added correspondingly to each congener to be determined. At least one isotopically labeled congener must be added to each congener group having the same number of chlorine.

$^{13}C_{12}$-2,3,7,8-chlorine substituted PCDDs and PCDFs are used for PCDDs/PCDFs determination. As to coplanar PCBs, all of the four isotopically labeled congeners are used for non-*ortho* PCBs, while at least one isotopically labeled congener should be added to each homologue of mono-*ortho* PCBs.

Table 6 Standard Reference Materials and Internal Standards

a) Standard Reference Materials of PCDDs and PCDFs

Homologue	PCDD	PCDF
Tetra-CDD/F	2,3,7,8-TeCDD	2,3,7,8-TeCDF
Penta-CDD/F	1,2,3,7,8-PeCDD	1,2,3,7,8-PeCDF 2,3,4,7,8-PeCDF
Hexa-CDD/F	1,2,3,4,7,8-HxCDD 1,2,3,6,7,8-HxCDD 1,2,3,7,8,9-HxCDD	1,2,3,4,7,8-HxCDF 1,2,3,6,7,8-HxCDF 1,2,3,7,8,9-HxCDF 2,3,4,6,7,8-HxCDF
Hepta-CDD/F	1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,8-HpCDF 1,2,3,4,7,8,9-HpCDF
Octa-CDD/F	1,2,3,4,6,7,8,9-OCDD	1,2,3,4,6,7,8,9-OCDF

b) Internal Standards of PCDDs and PCDFs

Homologue	PCDD	PCDF
Tetra-CDD/F	$^{13}C_{12}$-1,2,3,4-TeCDD $^{13}C_{12}$-1,3,6,8-TeCDD $^{13}C_{12}$-2,3,7,8-TeCDD $^{37}C1_4$-2,3,7,8-TeCDD	$^{13}C_{12}$-2,3,7,8-TeCDF $^{13}C_{12}$-1,3,6,8-TeCDF $^{13}C_{12}$-1,2,7,8-TeCDF
Penta-CDD/F	$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDF $^{13}C_{12}$-2,3,4,7,8-PeCDF
Hexa-CDD/F	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD $^{13}C_{12}$-1,2,3,6,7,8-HxCDD $^{13}C_{12}$-1,2,3,7,8,9-HxCDD	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF $^{13}C_{12}$-1,2,3,6,7,8-HxCDF $^{13}C_{12}$-1,2,3,7,8,9-HxCDF $^{13}C_{12}$-2,3,4,6,7,8-HxCDF
Hepta-CDD/F	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF
Octa-CDD/F	$^{13}C_{12}$-1,2,3,4,6,7,8,9-OCDD	$^{13}C_{12}$-1,2,3,4,6,7,8,9-OCDF

c) Standard Reference Materials and Internal Standards of Coplanar PCBs

Homologue	Standard Reference Material	Internal Standard	IUPAC NO.
	Non-*ortho* PCBs		
Tetra-CB	3,3',4,4'-TeCB	$^{13}C_{12}$-3,3',4,4'-TeCB	#77
	3,4,4',5-TeCB	$^{13}C_{12}$-3,4,4',5-TeCB	#81
Penta-CB	3,3',4,4',5-PeCB	$^{13}C_{12}$-3,3',4,4',5-PeCB	#126
Hexa-CB	3,3'4,4',5,5'-HxCB	$^{13}C_{12}$-3,3',4,4',5,5'-HxCB	#169
	Mono-*ortho* PCBs		
Penta-CB	2,3,3',4,4'-PeCB	$^{13}C_{12}$-2,3,3',4,4'-PeCB	#105
	2,3,4,4',5-PeCB	$^{13}C_{12}$-2,3,4,4',5-PeCB	#114
	2,3',4,4',5-PeCB	$^{13}C_{12}$-2,3',4,4',5-PeCB	#118
	2,3,4,4',5-PeCB	$^{13}C_{12}$-2,3,4,4',5-PeCB	#123
Hexa-CB	2,3,3',4,4',5-HxCB	$^{13}C_{12}$-2,3,3',4,4',5-HxCB	#156
	2,3,3',4,4',5'-HxCB	$^{13}C_{12}$-2,3,3',4,4',5'-HxCB	#157
	2,3',4,4',5,5'-HxCB	$^{13}C_{12}$-2,3',4,4',5,5'-HxCB	#167
Hepta-CB	2,3,3',4,4',5,5'-HpCB	$^{13}C_{12}$-2,3,3',4,4',5,5'-HpCB	#189

For the syringe spike, the congeners that are not used for the sampling spike or the cleanup spike should be adopted. For example, $^{37}Cl_4$-2,3,7,8-TeCDD or $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF is used for PCDDs/PCDFs. For coplanar PCBs, $^{13}C_{12}$-2,3,4,4',5-PeCB is generally used, but the same congeners for PCDDs /PCDFs can be adopted.

The isotopically labeled congeners may interfere the determination depending on the resolution of the mass spectrometer; the conditions that avoid the interference should be checked before using the isotopically labeled congeners for internal standards.

2.3.2 Calibration of Instruments

Conditions for the determination should be established according to its purpose, and the instruments should be calibrated so that samples can be measured. Magnitude of interference resulting in quantification error, its calibration method, the linearity and stability of the sensitivity should be examined so as to assure the reliable quantification.

(1) Tuning of Mass Spectrometer

The MS is calibrated by the perfluorokerosene for mass calibration so as to verify mass pattern and resolution (greater than 10,000, 10 % valley) through its calibration program; the sensitivity of the MS should be also verified. Tuning process and results should be recorded.

(2) Tuning of Gas Chromatography

Set the conditions such as the temperature of capillary columns and injection port and flow volume of carrier gas. Then check whether response is stable, retention time of each chlorinated congener is in a proper range, and the peak is separated enough to be identified. Set adequately the splitless time and flow volume of purge gas.

The capillary column should be replaced with new one if the substance to be determined cannot be separated clearly enough from other substances. The separation may be recovered by cutting off one or both ends of the capillary column for about 300 mm. The capillary column need not be replaced if the sensitivity and separation are recovered by the cutting.

(3) Operating Conditions of GC/MS

Peak duration generated by the capillary column ranges between 5 and 10 seconds, while the sampling frequency of the SIM (Selected Ion Monitoring) method should be less than 1 second so that a sufficient number of determination points for each peak is plotted. The number of monitor channels available for one circuit of determination is restricted by the sensitivity required; the balance between them should be examined carefully.

Considering the retention time of each peak on the chromatograph, the mass channel for analysis can be grouped by time sharing, if the GC/MS can be properly conditioned so as to detect clearly the peak of the corresponding internal standards.

3. Evaluation of Reliability of the Determination

3.1 Fluctuation in Sensitivity

More than once a day, the sensitivity of the instruments should be verified as a periodical check to show no large fluctuation when compared with that at the calibration by using the standard solution whose concentration is in the middle of a range of the calibration curve. If the fluctuation in comparative sensitivity between each chlorinated congener of dioxins and

the internal standard is beyond ±20 % range, identify the cause and correct the sensitivity. After the correction, the samples quantified before the adjustment should be quantified again.

The retention time may change generally due to the degradation of separation capillary columns. In this case, it is necessary to take measures. If changes are drastic, for example, the retention time fluctuates greater than ±5 % or comparative retention ratio of the sample to the internal standards varies greater than ±2 % in a day, identify the causes and correct the sensitivity. The samples measured prior to the adjustment should be quantified again.

3.2 Verification of Calibration Curve

Plot a calibration curve based on the ratios of the concentration and the peak area of each standard reference material for each chlorinated congener to those of the internal standard. Calculate the Relative Response Factor (RRF) with the following equation.

$$RRF = \frac{Cis}{Cs} \times \frac{As}{Ais}$$

where

Cis: Concentration of the corresponding internal standard in the standard solution

Cs: Concentration of the target congener in the standard solution

Ais: Peak area of the characteristic mass in the internal standard solution

As: Peak area of the target congener in the standard solution

The calibration of response factor requires at least 3 times of analyses for each concentration, and total of 15 data points should be obtained to plot a calibration curve covering the whole range of the analysis. The instruments should be conditioned and adjusted so that the RRF derived from these data has small variation for all the concentrations, that is, coefficient of variation is less than 5 %.

An intercept of a linear regression line by the least square method should be as close to zero as possible.

A calibration curve should be routinely verified at the same time of quantifying target samples by quantifying the actual samples used for the development of the calibration curve. If the result shows an error, the instruments should be checked, and the calibration should be performed again. A calibration curve should be developed, and the samples must be quantified again.

3.3 Detection Limit and Quantification Limit

The following three types of detection limit and quantification limit should be measured.

(1) Apparatus Detection Limit and Apparatus Quantification Limit

Inject the standard solution with the lowest concentration (near the detection limit)6) used for development of the calibration curve into GC/MS and quantify it. Calculate the concentration of each congener of PCDDs/PCDFs and coplanar PCBs in air sample by using the quantification results, the final concentration volume of the solution, suction gas volume for a regular sample, and the measured values obtained from the former step. Repeat this five or more times.

Apparatus Detection Limit (ADL) and Apparatus Quantification Limit (AQL) of each congener of PCDDs/PCDFs and coplanar PCBs are calculated by the following equation in which the standard deviation (s_a) of the concentrations obtained from the above steps is applied.

Measure the operation blank if it is available, and calculate the ADL and AQL by using the greater standard deviation among those of the operation blank and the standard solution. Verification of the ADL and AQL should be performed more than once when quantification conditions are changed.

Apparatus Detection Limit (ADL) = $3s_a$ (pg/m^3)
Apparatus Quantification Limit (AQL) = $10s_a$ (pg/m^3)

(2) Method Detection Limit and Method Quantification Limit

To the extract solution from the filter and the polyurethane foam, which is the same amount for the determination of samples, add the standard reference materials equivalent to Qs (ng) that is calculated back by substituting AQL into the concentration of air sample in the equation for each computation of congener concentration shown in the section 7.1 of Chapter 3, and perform GC/MS measurement after cleanup procedure. Repeat the measurement five or more times.

Calculate the concentration of each congener of PCDDs/PCDFs and coplanar PCBs in air sample, by using the final concentration volume and the suction gas volume for a regular sample and the measured values obtained from the former step.

Method Detection Limit (MDL) and Method Quantification Limit (MQL) of each congener of PCDDs/PCDFs and coplanar PCBs are calculated by the following equation in which the standard deviation (s_a) of the concentrations obtained from the former steps is applied.

Since the MDL and MQL derived from this measurement method may fluctuate by the preparation procedures and the conditions of the determination, it is necessary to verify them at regular intervals. The MDL and MQL should be verified for every change in the preparation procedures and the quantification conditions.

Method Detection Limit (MDL) = $3s_m$ (pg/m^3)
Method Quantification Limit (MQL) = $10s_m$ (pg/m^3)

(3) Sample Detection Limit and Sample Quantification Limit

Noise level (N) should be determined as either

1) Twofold of the standard deviation of baseline noise around the peak (tenfold range of one-half the peak height) on the chromatogram of the sample determination, or
2) 2/5 of the difference between the maximum and the minimum noise levels, as the difference is almost fivefold of the standard deviation in the past experiments.

Peak height (S) should be a top height of the peak from the baseline that is determined at median of the noise level.

Estimate the peak area, whose height is threefold of the noise level (S/N=3), from the chromatogram of the standard solution. Calculate Qs based on the peak area by using the quantification equation. Sample Detection Limit (SDL) can be calculated by substituting the Qs for the quantity in the sample in the equation for the computation of congener concentration defined in the section 7.1 of Chapter 3 (where Qt = 0) [45].

Similarly, estimate the peak area whose height is tenfold of the noise level (S/N=10), and calculate sample quantification limit (SQL) from the peak area.

When some of 2,3,7,8-chlorine substituted congeners do not show the peaks on the chromatogram, the noise bands shall be determined by measuring baseline noise around the peak, and then the SDL and SQL can be calculated in the same way as above.

Because SDL and SQL vary by instrument and determination condition, they should be determined more than once for every change in quantification conditions. It should be verified that SQL is lower than TQL (see Table 1). For the samples regulated by high criteria, the SQL should be minimized regardless of the TQL value so that the concentration is determined as low as possible in order to observe change in the concentration in the future. The SDL and the SQL should be determined for every sample, as they vary by the volume of samples and the preparation procedure, for example, the concentration scale.

3.4 Determination of Operation Blank Value

Operation blank test is performed to check the contamination occurred during the preparation of the testing solution and the injection into the instruments and to assure the quantification condition without interference.

High operation blank value lowers not only the sensitivity but also the reliability of measured data due to greater QL. Therefore, it is desirable to minimize the operation blank as low as possible so that the sample concentration presented in TEQ becomes lower than TQL (see Table 1).

Operation blank need not be determined for every determination if properly managed.

For assuring the reliability of sampling, however, operation blank should carefully be examined, and the relevant data should be presented when necessary.[7)]

3.5 Determination of Traveling Blank Value

Traveling blank test is performed to check the contamination occurred during the preparation of the sampling until the determination. Traveling blank is the blank sample that is handled and transported in the same way as the actual samples except sample collection.

The number of the traveling blanks should be 10 % of the total number of the samples, and at least 3 traveling blanks should be analyzed. The average value (e) and standard deviation (s) of the traveling blanks should be calculated, and the measured value should be corrected as follows (see Figure 2):

1) If the average of traveling blank values (e) (hereinafter referred to as traveling blank value) is equal to or smaller than the operation blank value (a) (e a), the contamination during the transport can be ignored; the concentration is calculated by subtracting the operation blank value (a) from the measured value (d).
2) If the traveling blank value is greater than the operation blank value due to the contamination during the transport, and if the sum (f) of the Toxicity Equivalency Quantity of the Quantification Limit (10s) derived from the standard deviation of the traveling blanks is lower than the TQL (c) ($f \leqq c$), the concentration is calculated by subtracting the traveling blank value (e) from the measured value (d).
3) Even if the sum (f) of the QL derived from traveling blank values is greater than the TQL (c) ($f > c$), when the measured value (d) is greater than the QL (10s) derived from traveling blank values ($d \geqq 10s$), the concentration is calculated by subtracting the traveling blank value (e) from the measured value (d).
4) However, if the sum (f) of the QL derived from traveling blank values is greater than the TQL (c) ($f > c$) due to the contamination during the transport ($e > a$), and if the measured value (d) is smaller than the QL (10s) derived from traveling blank values ($d < 10s$), the measured value should be omitted because of low reliability. Remove the contamination source and collect samples again.

The traveling blank values need not be determined for every determination if controlled in advance. To assure the reliability, however, traveling blank values should be examined, and the relevant data should be presented when necessary.

Determination of the traveling blank value must be performed if there is a possibility of contamination during the transport, for example, by ash from an electrostatic precipitator.

3.6 Duplicate Determination

In order to assure overall reliability of the determination process including sampling,

preparation and analysis, more than two aliquots should be taken from the samples and analyzed. The difference in total TEQ between the two aliquots should be equal to or less than 30 % of the average. If the difference is greater than the criteria (< 30 %), the data should be omitted because they are not reliable[8].

If the data do not meet the criteria, the determination should be started from the preparation again. If the new data meet the criteria, they can be adopted. Otherwise, whole process of sampling must be reviewed as it might have some problems. The volume of vacuumed air, leakage from the apparatus, stability of analysis instruments etc. should be checked and improved, and then the samples should be taken again.

The duplicate determination can be omitted if duplicate sampling is impossible. The sampling method, however, should be examined, and the relevant data should be presented when necessary. Though determination does not have to be duplicated for every determination if the sampling method is well controlled, duplicate analysis should be conducted for 10 % of total samples.

3.7 Recovery

Add known amount of syringe spikes for measuring recovery right before GC/MS analysis, quantify and calculate the recovery of cleanup spikes used in the internal standard method. If the recovery does not fall between 50 to 120 %, the samples should be cleaned up again from the crude extraction step.

If the recovery of newly prepared samples does not meet the criteria, the data should be omitted because the cleanup procedure may be incomplete.

Based on the cleanup spikes, determine the recovery of sampling spikes. If the recovery ratio does not fall between 70 to 130 %, the data should be omitted due to its low reliability. Improve the cause(s), and then collect samples again.

4. Data Management and Evaluation

4.1 Requirements for Sampling

Samples should be those representing the environment monitored and fulfilling the purpose of the determination. Therefore, the sampling procedure might be modified depending on the characteristics of the samples.

For obtaining a 24-hour average concentration, sample should be collected at a high flow rate of 700 L/min for 24 hours; the volume of the sample should be about 1,000 m^3. For obtaining a weekly average concentration, samples should be collected 7 times at a high flow rate of 700 L/min for 24 hours or collected continuously at a medium flow rate of 100 L/min for consecutive 7 days; the total volume of the samples should be about 1,000 m^3.

4.2 Evaluation of Error and Data Omission

As already mentioned, when measured values are not reliable as in the following cases, the sample should be determined again:

- Large fluctuation in sensitivity of the instruments
- Large traveling blank value due to contamination of the samples
- Large difference in measured values between duplicated aliquots

If the data are omitted due to their low reliability, samples should be collected again.

The error and data omission not only require additional labors, costs and time but also spoil the reliability of data. Therefore, the error and the data omission should be minimized by close check prior to the determination. If the error or data omission is observed, their causes should be examined carefully and recorded to prevent the same problem in the future.

4.3 Record of Operational Procedure

The following information should be recorded and stored.

(1) Procedures of adjustment, calibration and testing operation of the instruments and apparatus for sampling.
(2) Preparation, handling and storing conditions of the sample containers, sampling filters, polyurethane foam, etc.
(3) Conditions of sampling such as the sampling method, location, date and time, temperature, humidity, wind direction and wind speed at the sampling point, etc.
(4) Sampling condition such as flow rate, duration and sampled air volume.
(5) Calibration and operation of the analytic instruments.
(6) Raw data and other reference parameters used for the determination.

5. Reporting on Quality Control

The following information concerning quality control should be recorded and reported together with data.

(1) Compliance with the SOP (Standard Operational Procedure).
    a) Records of daily maintenance and check of instruments, such as calibration.
    b) Producer’s name of the standard reference materials and its traceability, and determination condition of the instruments.
(2) Results of the detection limit (DL) and quantification limit (QL).
(3) Results of the operation blank test and traveling blank test.
(4) Verification of the recovery from the sampling and preparations.
(5) Fluctuation in sensitivity of the instruments.
(6) Records of the whole analytical procedures from sampling to analysis.

Chapter 3 Determination Method of Dioxins in Ambient Air

1. Outline of the Determination Method

Dioxins in ambient air are collected in the glass fiber filters and the polyurethane foams. The samples to be determined are extracted and prepared, and then dioxins are quantified by the HRGC-HSMS.

2. Reagents and Materials

All the reagents and materials used must show no interference on the determination of dioxins, which should be verified by the blank tests with the reagents and materials.

(1) Hexane, methanol, acetone, toluene and dichloromethane

Used for the detection of pesticide residues or residual PCBs. When 1ìl of these solvents concentrated in accordance with the concentration scale of reference samples is injected into the GC/MS, they must show no interference on the chromatogram overlapping the standard reference material and internal standard of dioxins.

(2) Nonane, decane and iso-octane

Should be of excellent grade. They must show no interference on the chromatogram overlapping the standard reference material and internal standard of dioxins when 1 ìl of those reagents concentrated in accordance with the concentration scale of determination samples is injected into the GC/MS.

(3) Water treated by hexane rinsing

Distilled water cleansed with hexane.

(4) Sulfuric acid and hydrochloric acid

Should be of excellent or better grade.

(5) Sodium sulfate anhydrous

Used for the detection of pesticide residues or residual PCBs.

(6) Potassium hydroxide, silver nitrate

Should be of excellent grade.

(7) Silica gel

Silica gel for column chromatography (Wako-Gel S-1 for PCB determination with a

diameter of 0.063 to 0.200 mm, 70 to 230 mesh) [Remark 1] is washed with methanol, then put into a beaker, spread with less than 10 mm in thickness, activated by being dried at 130 °C for 18 hours and finally cooled down in a desiccator for 30 minutes.

(8) 2% potassium hydroxide impregnated silica gel (hereinafter referred to as potassium hydroxide silica gel)

Put 1 mol/L potassium hydroxide water solution to silica gel with a volume necessary to make 2 % (w/w) mixture and dehydrate the mixture by decompression at 50 °C in a rotary evaporator. After water is mostly removed from the mixture, grind it into powder form at 80 °C for an hour. Store the powder in an airtight container after preparation and place it in a desiccator.

(9) 44 % and 22 % sulfuric acid impregnated silica gel (hereinafter referred to as sulfuric acid silica gel)

Put sulfuric acid into silica gel to make 44 % or 22 % (w/w) mixture and then shake the mixture until it becomes powder form. Store the powder in an airtight container and place it in a desiccator.

(10) 10 % silver nitrate impregnated silica gel (hereinafter referred to as silver nitrate silica gel)

Put 0.25 ml of 40 % (w/w) silver nitrate (excellent grade) water solution into 1g of silica gel and dehydrate it completely by a rotary evaporator. Use a brown colored flask to shield sunlight during the preparation. Store the mixture in an airtight container and place it in a desiccator.

(11) Alumina for alumina column chromatography

Aluminum oxide 90 (basic, activity grade 1) with 70 to 230 mesh (Merck) [Remark 1] is an example. Pre-activated alumina can be used as it is, but it is better to reactivate since its activity may be degraded depending on storing period and conditions. To activate, put alumina into a beaker, spread it with less than 10 mm in thickness, dry it at 130 °C for 18 hours, and cool it down in a desiccator until its temperature reaches the room temperature. In another way, put alumina into a laboratory dish, spread it with about 5 mm in thickness, heat it at 500 °C for 8 hours and cool it down in a desiccator until its temperature reaches the room temperature. Store the alumina in an airtight container and place it in a desiccator.

Remark 1 These commercially available chemicals mentioned here are not those recommended to use but referred for the convenience of the readers of the manual. The chemicals of higher quality are also recommendable.

(12) Standard reference materials

Standard reference materials for the identification and quantification of dioxins by the internal standard method are listed in Tables 1 to 4 in Chapter 1.

(13) Standard solution

According to the calibration range, purchase and prepare a set of standard solution by diluting with those commercially available mixed solution with certification.

(14) Internal standard materials

PCDDs/PCDFs and coplanar PCBs labeled with stable isotopes such as ^{13}C or ^{37}Cl should be purchased and used (see Table 4)[9].

(15) Internal standard solution

Prepare a set of internal standard solution by diluting with those commercially available mixed solutions with certification according to the calibration range and volume to be added as an internal standard.

3. Instruments and Apparatus

All the instruments and apparatus to be used for the analysis must show no interference on the determination of dioxins. It should be verified by performing blank tests with the instruments and apparatus. Grease must be avoided to assemble the instruments.

(1) Apparatus for Sampling

As shown as an example in Figure 3, a high volume air sampler with 2 pieces of polyurethane foam set in a filter holder and a piece of glass fiber filter is used for sampling.

The high volume air sampler (hereinafter referred to as the HV) is composed of a filter holder, a vacuum pump, a flow meter and a protective cover.

a) Filter Holder

The filter holder must keep a piece of filter of 20 x 25 cm inserted without leakage and also attach a holder for polyurethane foam of 84 mm in internal diameter and 200 mm in length.

Glass fiber filter should be heated at 600°C for 6 hours before being used. Polyurethane foam should be washed with water and acetone, cleaned by the Soxhlet extraction for 16 to 24 hours or the ultrasonic extraction (3 times for 30 minutes) with acetone, and then dried10). It should be stored in an airtight container. Two pieces are set in the filter holder.

Specifications of polyurethane foam are;

Material: Polyether type; 0.016 g/cm3 in density; 9 to 10 cm in diameter; 5 cm in thickness

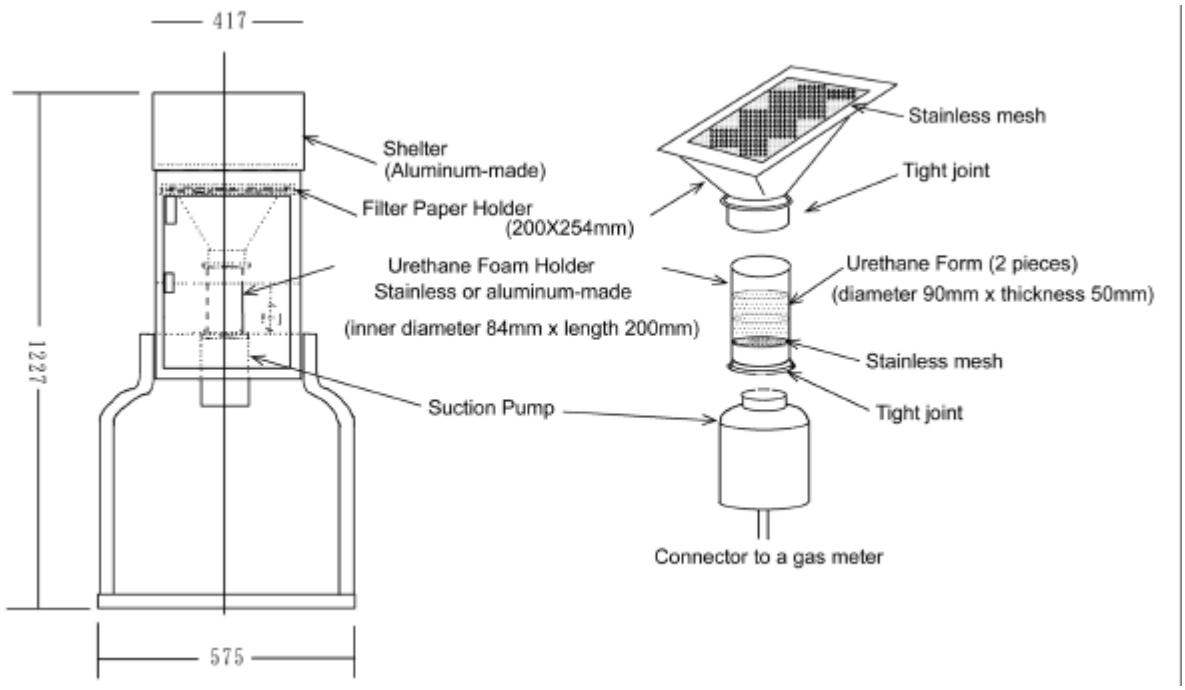


Figure 3 Example of Air Sampler

b) Vacuum Pump

For sampling at a high flow rate during 24 hours, the pump should have suction capacity with a rate of 700 L/min when the filter is set, can control flow volume and can be operated continuously for more than 24 hours. For continuous sampling at a medium flow rate for 7 days, the pump should have suction capacity with a rate of 100 L/min when the filter is set, can control flow volume and can be operated continuously for more than 7 days.

c) Flow Meter

A pressure detector type, heat sensor type or float type flow meter is used. The flow meter should be able to accurately measure 50 L/min at a rate of 700 L/min for high volume air sampling for 24 hours or 5 L/min at a rate of 100L/min for a medium volume air sampling for consecutive 7 days.

The flow meter should be calibrated by a reference gas flow meter under a normal working condition of HV.

d) Protection Case

The case should have the structure that a HV can be fixed horizontally with a collector facing up and that sampling filter can be protected from wind and rain. It should be made of corrosion resistant materials.

(2) Apparatus for Preparation

a) Glass Column for Silica Gel

The size of a column is 10 mm in internal diameter and 300 mm in length. The column is filled with 3g of activated silica gel with hexane. A layer of anhydrous sodium sulfate with 10 mm in thickness is laminated in head and bottom of the activated silica gel[11]. Wash the reagents with hexane.

b) Glass Column for Multilayered Silica Gel

As shown in Figure 4, the column with an internal diameter of 15 mm and length of 300 mm is composed of the layers[11] in the following order from the bottom. Wash the reagents with hexane.

Silica gel	0.9 g
2% potassium hydroxide impregnated silica gel	3 g
Silica gel	0.9 g
44 % sulfuric acid impregnated silica gel	4.5 g
22 % sulfuric acid impregnated silica gel	6 g
Silica gel	0.9 g
10 % silver nitrate impregnated silica gel	3 g
Anhydrous sodium sulfate	6 g

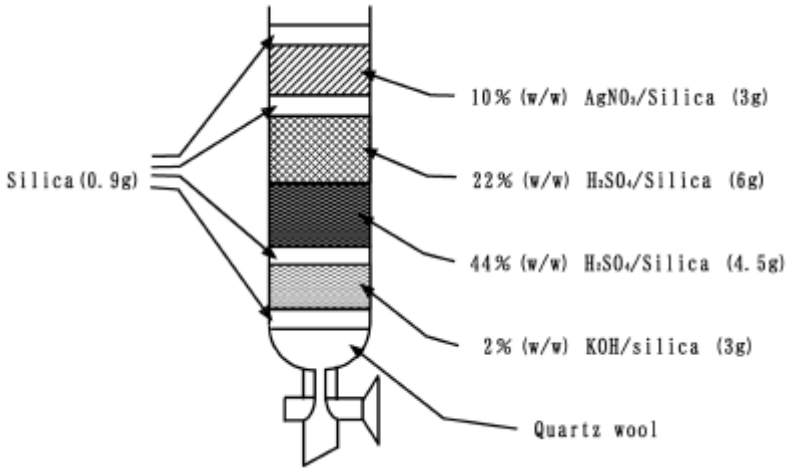


Figure 4 Multilayered Silica Gel Column

c) Glass Column for Alumina

The size of the column is 10 mm in internal diameter and 300 mm in length. The column is filled with 10g of activated alumina with hexane. Anhydrous sodium sulfate with 10 mm in thickness is layered over it[11]. Wash the reagents with hexane.

d) Activated Carbon Impregnated Silica Gel Column

The size of the column is 10 mm in internal diameter and 300 mm in length. The column is filled with layers of sodium sulfate anhydrous with 10 mm in thickness, 1g of activated carbon impregnated silica gel (for dioxins determination, Wako Pure Chemicals (Remark 1)), and again anhydrous sodium sulfate with 10 mm in thickness[11]. Wash the reagents with hexane.

e) Concentrator r or Evaporator

Kuderna-Danish concentrator or a rotary evaporator.

(3) High Performance Liquid Chromatography with an Activated Carbon Column

a) Separation Column

The column filled with porous graphite carbon[12].

b) Fraction Solution

Flow rate of eluate is set at 2 ml/min.

c) Flow Switching Valve

The valve can change the direction of moving beds in the separation column.

d) Detector

Absorptiometry detector which can take the fraction at the outlet.

(4) Gas Chromatograph-Mass Spectrometer

High resolution gas chromatography combined with a double-focusing high resolution mass spectrometer (HRGC-HRMS) is used. The sensitivity required is 0.1 pg for tetra- and penta- compounds, 0.2 pg for hexa- and hepta-compounds, 0.5 pg for octa-compound and 0.2 pg for coplanar PCBs[13].

a) GC Oven

The GC oven covering 50 to 350 °C to set optimal temperature program of the target compounds.

b) Capillary Column

The capillary column is made from fused silica with 0.25 to 0.32 mm in internal diameter and 25 to 60 m in length, of which inside is coated with strong-polarity liquid of cyanopropyl compound for PCDDs/PCDFs determination. For coplanar PCBs, non-polarity or semi-polarity column of methylsilicone is generally used; recently the column with siloxane-carborane is also used[14].

c) Mass Spectrometer

Double-focusing type is used. The resolution required is greater than 10,000.

The machine can keep ion source temperature at 250 to 350 °C, which ionizes with electron impact ionization (EI) by 35 to 70 V of the ionization voltage.

Selected ion monitoring (or SIM) should be adopted as a detection method. The frequency of the SIM can be adjusted to be less than 1 second. Lock-mass method is adopted to detect ions.

d) Sample Injection Port

Injection port should be able to inject the total volume of sample with high reproducibility. For example, splitless type and on column type meet the criteria.

e) Carrier Gas

Helium gas with a purity of greater than 99.999 %.

f) Standard reference materials for Calibration

Compounds for mass spectrometry with high boiling point such as perfluorokerosene (PFK).

4. Sampling and Preparation

4.1 Collection of Samples

Internal standard for sampling spike is added on the filter paper before sampling[9), 15)].

(1) Air sampling should be performed using an air sampler as specified in the section 3 (1) of Chapter 3.

For obtaining a 24-hour average concentration, sample should be collected at a high flow rate of 700 L/min for 24 hours; the volume of the sample should be about 1,000 m^3. For obtaining a weekly average concentration, samples should be collected 7 times at a high flow rate of 700 L/min for 24 hours or collected continuously at a medium flow rate of 100 L/min for consecutive 7 days; the total volume of the samples should be about 1,000 m^3.

Flow rate at start (Fs) is adjusted and recorded five minutes after sampling is started. Flow rate at end (Fe) is recorded right before the end of sampling. Total volume of vacuumed air can be recorded if the accumulative flow meter is installed.

The collected sample should be kept in an airtight container to prevent contamination by the atmospheric air and leakage.

The sample should be shielded from sunlight during storage and transportation.

(2) For the traveling blank test, the glass fiber filter and the polyurethane foam, which have the same production lot as those for sample collection, are carried and handled in the same manner as for the sample collection, except when they are used for actual sampling. The traveling blank should be prepared for more than 3 samples and 10 % of total samples throughout a series of sampling. Besides, the glass fiber filter and the polyurethane foam for the operation blank test are prepared, which have the same production lot as those for sample collection [16)].

(3) More than two samples should be collected at one sampling point for duplicate determination. The duplicate sampling should be conducted for 10 % of total number of samples[17].

4.2 Sample Extraction

The filter paper and the polyurethane foam after sampling should be handled separately. After spiking internal standard as the cleanup spike, the samples are extracted from each of sampling devices.

(1) Put the polyurethane foam into a Soxhlet extractor and add internal standards [9), 18)]. Extract the sample with 300 ml of acetone for 16 to 24 hours. If there are several polyurethane foams used during a series of high volume air sampling for 24hours, the samples can be extracted together in the extractor.

(2) Put the glass fiber filter into a Soxhlet extractor and add internal standards [9), 18)]. Extract the sample with 300 ml of toluene for 16 to 24 hours. If there are several glass fiber filters used during a series of high volume air sampling for 24 hours, the samples can be extracted together in the extractor.

(3) Concentrate the extracts from each extractor by evaporators and mix them together. Adjust the volume of the extracts to 100 ml, and accurately fractionate a half of the volume[19]. Concentrate the aliquot until its volume becomes about 5 ml. Remove almost all solvent carefully under a gentle stream of nitrogen with the concentrator tube [20], and then dissolve it in hexane to make 0.5 ml of a final volume. This solution is used for sulfuric acid treatment or multilayered silica gel chromatography.

(4) Extract the samples from the glass fiber filter and polyurethane foam for operation blank, traveling blank, and duplicate determination in the same way as mentioned above[16), 17)].

4.3 Cleanup

The interfering matrices should be removed from the extracts by the sulfuric acid treated-silica gel column chromatography or by the multilayered silica gel column chromatography[21]. The solution obtained is divided into two aliquots: one for PCDDs/PCDFs determination and the other for coplanar PCBs. The aliquot is used for separation of PCDDs/PCDFs from coplanar PCBs by the alumina column chromatography. HPLC with activated carbon column or activated carbon impregnated silica gel chromatography is used for further cleanup if the GC/MS analysis is disturbed by interferences. They are also used as the substitution of alumina column chromatography. The HPLC is especially effective when separating PCDDs/PCDFs from non-*ortho* PCBs.

4.3.1 Sulfuric Acid Treatment

(1) Transfer the extract prepared in 4.2 (3) into a separate funnel (300 ml) while rinsing the extract with 50 to 150 ml of hexane. Add proper amount of sulfuric acid, gently shake the mixture, leave it for a while, and then remove the sulfuric acid portion. This procedure should be repeated until the color in the sulfuric acid cannot be observed[22].

(2) Wash the hexane layer with 50 ml of hexane rinsed water for 3 or 4 times until it becomes neutralized. Dehydrate it with anhydrous sodium sulfate, and concentrate it until its volume is reduced to 5 ml. Then, evaporate it under a gentle stream of nitrogen until its volume becomes 100 ìl as a final volume. Dissolve it in 2 ml of hexane. This solution is used in the silica gel chromatography.

(3) The extract prepared for operation blank test, traveling blank test and duplicate determination can be prepared for silica gel chromatography in the same way as mentioned above[16), 17)].

4.3.2 Silica Gel Column Chromatography

(1) After washing the filler and reagent of the silica gel column with hexane, adjust liquid volume to the surface level of anhydrous sodium sulfate.

(2) Gently transfer the concentrated extract prepared in 4.3.1 (2) to the column by using a Pasteur pipette. Adjust the sample liquid volume to the top of the column.

(3) Rinse the concentrator tube with 5 ml of hexane. The hexane should be poured in a way to rinse inside of the column. Repeat the rinse one more time.

(4) Pour 3 ml of hexane into the column, connect the separation funnel as a column head, and drip 150 ml of hexane at a rate of 2.5 ml/min (approximately one drop/sec).

(5) Concentrate the extract until its volume is reduced to 5 ml, and divide it into two portions, of which one is for the alumina column chromatography for dioxins and non-*ortho* coplanar PCBs, and the other is for the coplanar PCBs other than non-*ortho* PCBs[21]. If the colorization of the silica gel at filler part is significant, repeat the procedure (1) through (4) to clean up.

(6) The extracts prepared for operation blank test, traveling blank test and duplicate determination can be prepared for alumina column chromatography in the same way as mentioned above[16), 17)].

4.3.3 Multilayered Silica Gel Column Chromatography[23)]

(1) After washing the filler and reagent of the multilayered silica gel column with hexane, adjust the liquid volume to the surface level of anhydrous sodium sulfate.

(2) Gently transfer the concentrated extract prepared in 4.2 (3) into the column by using a Pasteur pipette. Adjust the liquid volume to the top of the column.

(3) Rinse the concentrator tube with 5 ml of hexane. The hexane should be poured in a way to rinse inside of the column. Repeat rinsing one more time.

(4) Pour 3 ml of hexane into the column, connect the separation funnel as a column head, and drip 120 ml of hexane at a rate of 2.5 ml/min (approximately one drop/sec).

(5) Concentrate the extract until its volume becomes 5 ml, and divide it into two portions, of which one is for the alumina column chromatography for dioxins and non-*ortho* coplanar PCBs, and the other is for the coplanar PCBs but non-*ortho* PCBs[22)]. If the colorization of the silica gel at filler part is significant, repeat the procedure (1) through (4) to clean up.

(6) The extracts prepared for operation blank test, traveling blank test and duplicate determination can be prepared for alumina column chromatography in the same way as mentioned above[16), 17)].

A. PCDDs and PCDFs

4.3.4-A Alumina Column Chromatography[24)]

(1) Adjust the liquid volume in the alumina column to the surface level of anhydrous sodium sulfate. Gently pour the sample solution prepared in 4.3.2 or 4.3.3 into the column. Rinse the column with a small volume of hexane several times and adjust the liquid volume to the surface level of anhydrous sodium sulfate again. The first fraction is eluted by dropping 100 ml of 2% (v/v) dichloromethane-hexane at a rate of 2.5 ml/min (approximately one drop/sec). This fraction contains PCBs. Store the fraction until the determination is completed.

(2) The second fraction can be eluted by dropping 150 ml of 50% (v/v) dichloromethane-hexane at a rate of 2.5 ml/min. This fraction contains PCDDs/PCDFs.

(3) Concentrate the second fraction until its volume becomes 5 ml, and evaporate the hexane under a gentle stream of nitrogen until the volume becomes 0.5 ml. The extract is used

for the GC/MS determination or used as the cleanup for the further procedure cited in 4.3.5-A or 4.3.6-A[25].

Add the syringe spike to the sample for PCDDs/PCDFs determination at the same concentration as used in the calibration[26]. Put 0.5 ml of nonane[27], and evaporate the solvents under a gentle stream of nitrogen again until the sample reaches a certain volume (20 to 100 ìl). Use this sample for the determination of PCDDs/PCDFs by the GC/MS analysis.

(4) The extracts prepared for operation blank test, traveling blank test and duplicate determination according to 4.3.2 or 4.3.3 can also be prepared for the GC/MS analysis in the same way as mentioned above[16), 17)].

4.3.5-A High Performance Liquid Chromatography with Activated Carbon Column[28]

(1) Connect the activated carbon column to the HPLC[12], wash the column completely with toluene first, and then replace the toluene with hexane. Inject the concentrated extract of the second fraction (0.1 ml) prepared in 4.3.4-A (3), or those in 4.3.2 (5) or 4.3.3 (5) for PCDDs/PCDFs determination into the HPLC column. Pour 30%(v/v) toluene-hexane for 20 minutes as a carrier phase, and then take 40 ml pf the aliquot from the eluate as the first fraction. The aliquot from the extract according to 4.3.2 and 4.3.3 contains PCBs.

(2) Heat the oven to 50°C, pour the toluene as a carrier in a reversed flow mode for 15 minutes, then take 30 ml of the aliquot from the eluate as the second fraction. This aliquot contains PCDDs/PCDFs.

(3) Concentrate the second fraction until its volume becomes 5 ml, and evaporate the hexane under a gentle stream of nitrogen until the volume becomes 0.5 ml[20]. Add the syringe spike for PCDDs/PCDFs to the extract at the same concentration used as in the calibration[26]. Put 0.5 ml of nonane[27], and evaporate the solvents under a gentle stream of nitrogen again until the sample reaches a certain volume (20 to 100 ìl). This sample is used for the determination of PCDDs/PCDFs by the GC/MS analysis.

(4) The extracts prepared for operation blank test, traveling blank test and duplicate determination in 4.3.4-A (4), 4.3.2 or 4.3.3 can also be prepared for the GC/MS analysis in the same way as mentioned above[16), 17)].

4.3.6-A Activated Carbon Impregnated Silica Gel Column Chromatography [28]

(1) Completely wash the column with toluene and then replace the toluene with the hexane.

Transfer the concentrated extract (0.1 ml) of the second fraction prepared in 4.3.4-A (3), (or the concentrated sample solution prepared for PCDDs/PCDFs determination in 4.3.2 (5) or 4.3.3 (5)) into the column. The first fraction can be eluted by dropping 150 to 200 ml of 25% (v/v) dichloromethane-hexane at a rate of 2.5 ml/min. The fraction contains PCBs when the sample solution prepared in 4.3.2 or 4.3.3 is used.

(2) The second fraction can be eluted with 200 ml of toluene. The fraction contains PCDDs/PCDFs.

(3) Concentrate the second fraction until its volume becomes 5 ml and evaporate the hexane under a gentle stream of nitrogen until the volume becomes 0.5 ml[20]. Add the syringe spike for PCDDs/PCDFs to the extract at the same concentration used as in the calibration[26]. Put 0.5 ml of nonane[27], and evaporate the solvents under a gentle stream of nitrogen again until the sample reaches a certain volume (20 to 100 ìl). This sample is used for the determination of PCDDs/PCDFs by the GC/MS analysis.

(4) The extracts prepared for operation blank test, traveling blank test and duplicate determination according to 4.3.4-A (4), 4.3.2 or 4.3.3 can also be prepared for the GC/MS analysis in the same way as mentioned above[16), 17)].

B. Coplanar PCBs

4.3.4-B Alumina Column Chromatography [24)]

(1) Adjust the liquid volume in the alumina column to the surface level of anhydrous sodium sulfate. Gently pour the extract prepared according to 4.3.2 or 4.3.3 into the column. Rinse the column with a small volume of hexane several times, and adjust the liquid volume to the surface level of anhydrous sodium sulfate again. The first fraction is eluted by dropping 40 ml of hexane at a rate of 2.5 ml/min (approximately one drop/sec). This fraction contains aliphatic hydrocarbons.

(2) The second fraction is eluted by dropping 120 ml of 5% (v/v) dichloromethane-hexane at a rate of 2.5 ml/min. This fraction contains coplanar PCBs.

(3) Concentrate the second fraction until its volume becomes 5 ml, and evaporate the hexane under a gentle stream of nitrogen until the volume becomes 0.5 ml. The extract is used for the GC/MS determination or the further cleanup for the procedure cited in 4.3.5-B or 4.3.6-B[25)].

Add the syringe spike for coplanar PCBs to the sample at the same concentration used as in the calibration[26)]. Put 0.5 ml of nonane[27)], and evaporate the solvents under a gentle

stream of nitrogen again until the sample reaches a certain volume (20 to 100 ìl). This sample is used for the determination of coplanar PCBs by the GC/MS analysis.

(4) The third fraction is eluted by dropping 160 ml of 50% (v/v) dichloromethane-hexane at a rate of 2.5 ml/min. This fraction contains PCDDs/PCDFs. Generally this fraction is not used for the determination but should be stored until the determination is completed.

(5) The extracts for operation blank test, traveling blank test and duplicate determination prepared according to 4.3.2 or 4.3.3 can also be prepared for the GC/MS analysis in the same way as mentioned above[16), 17)].

4.3.5-B High Performance Liquid Chromatography with Activated Carbon Column [28)]

(1) Connect the activated carbon column to the HPLC[12)], wash the column completely with toluene first and then replace the toluene with hexane. Inject the concentrated extract of the second fraction (0.1 ml) prepared according to 4.3.4-B (3) or the sample solution prepared for coplanar PCBs determination in 4.3.2 (5) or 4.3.3 (5) into the HPLC column. Pour hexane for 4 minutes as a carrier phase, and then take 8 ml of aliquot from the eluate as the first fraction. The aliquot contains PCBs other than non-*ortho* and mono-*ortho* PCBs.

(2) Pour 50% (v/v) dichloromethane-hexane as a carrier phase for 20 minutes, and then take 40 ml of aliquot from the eluate as the second fraction. This fraction contains mono-*ortho* PCBs.

(3) Pour 30% (v/v) toluene-hexane as a carrier phase for 20 minutes, and then take 40 ml of the aliquot from the eluate as the third fraction. This fraction contains non-*ortho* PCBs.

(4) Heat the oven to 50°C, pour the toluene as a carrier in a reversed flow mode for 15 minutes, then take 30 ml of aliquot from the eluate as the fourth fraction. This aliquot contains PCDDs/PCDFs.

(5) Concentrate each of the first, the second and the third fractions until each volume becomes 5 ml and evaporate the aliquots under a gentle stream of nitrogen until the volume becomes 0.5 ml[20)]. The syringe spike for coplanar PCBs is added to the extract at the same concentration used as in the calibration[26)]. Put 0.5 ml of nonane[27)], and evaporate the solvents under a gentle stream of nitrogen again until the sample reaches a certain volume (20 to 100 ìl). This sample is used for the determination of coplanar PCBs by the GC/MS analysis.

(6) The extracts prepared for operation blank test, traveling blank test and duplicate determination according to 4.3.4-B (4), 4.3.2 or 4.3.3 can also be prepared for the GC/MS analysis in the same way as mentioned above[16), 17)].

4.3.6-B Activated Carbon Impregnated Silica Gel Column Chromatography [28)]

(1) Completely wash the column with toluene and then replace the toluene with hexane. Transfer the concentrated extract (0.1 ml) of the second fraction prepared according to 4.3.4-B (3), or the concentrated sample solution for coplanar PCBs determination prepared according to the 4.3.2 (5) or 4.3.3 (5) into the column. The first fraction can be eluted by dropping 150 to 200 ml of 25% (v/v) dichloromethane-hexane at a rate of 2.5 ml/min. The aliquot contains PCBs when the sample solution prepared in 4.3.2 and 4.3.3 is used.

(2) Concentrate this fraction until its volume becomes 5 ml and evaporate the hexane under a gentle stream of nitrogen until the volume becomes 0.5 ml[20)]. The syringe spike for coplanar PCBs is added to the extract at the same concentration used as in the calibration[26)]. Put 0.5 ml of nonane[27)], and evaporate the solvents under a gentle stream of nitrogen again until the sample reaches a certain volume (20 to 100 ìl). This sample is used for the determination of coplanar PCBs by the GC/MS analysis.

(3) The extracts prepared for operation blank test, traveling blank test and duplicate determination according to 4.3.4-B (4), 4.3.2 or 4.3.3 can also be prepared for the GC/MS analysis in the same way as mentioned above[16), 17)].

5. Testing Operation

5.1 Setting Conditions for GC/MS Analysis and Calibration

The following conditions of the instruments have been verified through the experiments for preparing this manual. Actual conditions of the instruments should be set referring the following[14)].

(1) GS/MS condition

a) Homologues of TeCDDs, TeCDFs, PeCDFs and their 2,3,7,8-chlorine substituted congeners

[GC]

Capillary Column	SP-2331, 0.32 mm ID x 60 m long Film thickness: 0.2 ìm
Column Temperature	Initial temperature at 100 °C hold for 1.5 min. → heat up to 180 °C at 20 °C/min. → heat up to 260 °C at 3 °C/min. → hold at 260 °C for 25 min.
Injector Temperature	260 °C

Injection Method	Splitless (Split retention time is 90 seconds)

[MS]

Resolution (M/ÄM)	Equal to or greater than 10,000
Ionization Voltage	25 to 70 V
Ionization Current	500 to 1,000 ìA
Temperature of Ion Source	280 to 300 °C
Ion Accelerating Voltage	8 kV

b) Homologues of PeCDDs, HxCDDs, HxCDFs and their 2,3,7,8-chlorine substituted congeners

[GC]

Capillary Column	SP-2331, 0.32 mm ID x 60 m long Film thickness: 0.2 ìm
Column Temperature	Initial temperature at 100 °C hold for 1.5 min. → heat up to 210 °C at 20 °C/min. → heat up to 260 °C at 3 °C/min. → hold at 260 °C for 25 min.
Injector Temperature	260 °C
Injection Method	Splitless (Split retention time is 90 seconds)

[MS]

Resolution (M/ÄM)	Equal to or greater than 10,000
Ionization Voltage	25 to 70 V
Ionization Current	500 to 1,000 ìA
Temperature of Ion Source	280 to 300 °C
Ion Accelerating Voltage	8 kV

c) Homologues of HpCDDs, HpCDFs, OCDD, OCDF and their 2,3,7,8-chlorine substituted congeners

[GC]

Capillary Column	DB-17, 0.32 mm ID x 30 m long, Film thickness: 0.15 ìm
Column Temperature	Initial temperature at 100 °C hold for 1.5 min. → heat up to 200 °C at 20 °C/min. → heat up to 280 °C at 10 °C/min. → hold at 280 °C for 5 min.
Injector Temperature	280 °C
Injection Method	Splitless (Split retention time is 90 seconds)

[MS]

Resolution (M/ÄM)	Equal to or greater than 10,000
Ionization Voltage	25 to 70 V
Ionization Current	500 to 1,000 ìA
Temperature of Ion Source	280 to 300 °C
Ion Accelerating Voltage	8 kV

d) Homologues of TeCB, PeCB, HxCB, HpCB and their congeners

[GC]

Capillary Column	DB-5MS, 0.32 mm ID x 60 m long, Film thickness: 0.25 ìm

Column Temperature	Initial temperature at 150 °C hold for 1 min. → heat up to 180 °C at 20 °C/min. → heat up to 245 °C at 2 °C/min. → hold at 245 °C for 3 min. → heat up to 290 °C at 6 °C/min. → hold at 290 °C for 3 min.
Injector Temperature	290 °C
Injection Method	Splitless (Split retention time is 60 seconds)

[MS]

Resolution (M/ÄM)	10,000 to 15,000
Ionization Voltage	35 to 40 V
Ionization Current	600 ìA
Temperature of Ion Source	290 °C
Ion Accelerating Voltage	8 kV

e) Homologues of coplanar PCBs and their congeners

[GC]

Capillary Column	HT-8, 0.22 mm ID x 50 m long , Film thickness: 0.25 ìm
Column Temperature	Initial temperature at 130 °C hold for 1 min. → heat up to 220 °C at 20 °C/min. → heat up to 320 °C at 5 °C/min. → hold at 320 °C
Injector Temperature	280 °C
Injection Method	Splitless (Split retention time is 60 seconds)

[MS]

Resolution (M/ÄM)	10,000 to 15,000
Ionization Voltage	30 to 50 V
Ionization Current	600 ìA
Temperature of Ion Source	335 °C
Ion Accelerating Voltage	7 to 8 kV

(2) Detection

SIM detection method (lock mass method)

Inject the reference compound (such as PFK) for mass calibration into the mass spectrometer and tune mass pattern and resolution (equal to or greater than 10,000, 10 % valley) depending on the purpose of the determination. Calibration condition should be recorded.

5.2 SIM Measurement

(1) A capillary column should be selected according to the target compounds to be determined. For PCDDs/PCDFs determination, select the most appropriate columns for the target compounds among a), b), and c) specified in the section 5.1(1). For coplanar PCBs determination, use column d) or e) specified in the section 5.1(1). The capillary column should be pre-run in high temperature prior to determination.

(2) Set the mass numbers for monitoring ion and lock mass of each homologue of the target

compounds, as well as the corresponding internal standards (see Table 7) [29].

(3) Flow standard reference gas for the mass tuning until lock mass response becomes stable, and then inject 1 or 2 ìl of the samples.

(4) Record the chromatogram for each of the mass numbers of each homologue of PCDDs/PCDFs, coplanar PCBs and the internal standard set according to the item (2) above.

(5) After measurement and prior to the quantification, verify the presence of the fluctuation of lock mass monitor channels of the standard reference materials for the mass tuning[30], the interfering substances, and the separation of each 2,3,7,8-chlorine substituted congener and coplanar PCBs[31] for each sample.

5.3 Calibration Curve

(1) For PCDDs/PCDFs, a series of standard solution with about five levels of concentrations covering the range from 0.2 ng/ml to 1 ìg/ml including zero should be prepared for each homologue[32]. Prior to the determination, an appropriate quantity of the internal standards should be added to the standard solution as the cleanup spike and the syringe spike so that the concentration falls between 10 to 50 ng/ml for TeCDDs, PeCDDs, HxCDDs, HpCDDs, TeCDFs, PeCDFs, HxCDFs and HpCDFs, and 20 to 100 ng/ml for OCDD and OCDF.

For coplanar PCBs, similarly, a series of standard solution with about five levels of concentrations covering the range from 0.2 ng/ml to 1 ìg/ml including zero should be prepared for each homologue[32]. Prior to the determination, an appropriate quantity of the internal standards should be added to the standard solution as the cleanup spike and syringe spike so that the concentration falls between 20 to 100 ng/ml.

(2) Inject 1 ìl of each of standard solution of PCDDs/PCDFs and coplanar PCBs prepared according to (1) above into the corresponding column of the GC/MS, and record the chromatogram of each chlorinated congener by selected ion monitoring mode (SIM) mentioned in the section 5.2. Verify the presence of the lock mass monitor channel[30] and peak separation of each congener[31] for every series of standard solution.

Table 7 Example of Mass Number of Dioxins for Monitoring Ion

a) PCDDs/PCDFs

	Homologue	M^+	$(M+2)^+$	$(M+4)^+$
Unlabeled PCDD/PCDF	TeCDDs	319.8965	321.8936	
	PeCDDs	353.8576	355.8546	357.8516*
	HxCDDs		389.8157	391.8127*
	HpCDDs		423.7766	425.7737
	OCDD		457.7377	459.7348
	TeCDFs	303.9016	305.8987	
	PeCDFs		339.8597	341.8567
	HxCDFs		373.8207	375.8178
	HpCDFs		407.7818	409.7789
	OCDF		441.7428	443.7399
Internal Standards	$^{13}C_{12}$TeCDDs	331.9368	333.9339	
	$^{13}C_{12}$PeCDDs	365.8978	367.8949	369.8919
	$^{13}C_{12}$HxCDDs		401.8559	403.8530
	$^{13}C_{12}$HpCDDs		435.8169	
	$^{13}C_{12}$OCDD		469.7779	471.7750
	$^{13}C_{12}$TeCDFs	315.9419	317.9389	
	$^{13}C_{12}$PeCDFs		351.9000	353.8970
	$^{13}C_{12}$HxCDFs		385.8610	387.8580
	$^{13}C_{12}$HpCDFs		419.8220	421.8191
	$^{13}C_{12}$OCDF		453.7830	455.7801

* May receive interference from PCBs.

b) Coplanar PCBs

	Homologue	M^+	$(M+2)^+$	$(M+4)^+$
Unlabeled PCB	TeCBs	289.9224	291.9194	
	PeCBs		325.8804	327.8776
	HxCBs		359.8415	361.8385
	HpCBs		393.8025	395.7995
Internal Standards	$^{13}C_{12}$TeCBs	301.9626	303.9597	
	$^{13}C_{12}$PeCBs		337.9207	339.9178
	$^{13}C_{12}$HxCBs		371.8817	373.8788
	$^{13}C_{12}$HpCBs		405.8428	407.8398

c) Lock Mass

Type of M/Z	330.9792	(for the determination of 4,5-chlorinated congeners)
	380.9760	(for the determination of 5,6-chlorinated congeners)
	430.9729	(for the determination of 7,8-chlorinated congeners)
	442.9729	(for the determination of 7,8- chlorinated congeners)

(3) Measure the peak area of each ion of congeners of PCDDs/PCDFs and coplanar PCBs and that of the internal standards[33] with respect to the mass numbers. Plot the calibration curve based on the ratio of the peak areas and the ratio of the concentration of each congener in the standard solution injected to that of its corresponding internal standard for the cleanup spike.

According to the equation below, the relative response factor (RRFcs) (refer to the section 3.2 of Chapter 2) can be calculated from the ratios of the peak area and the concentration of each congener in the standard solution to those of its corresponding internal standard for the cleanup spike in the standard solution[34].

Similarly, the relative response factor (RRFrs) can be calculated from the ratios of the peak area and the concentration of each internal standard for the cleanup spike to those for the syringe spike, according to the equation below.

Also, the relative response factor (RRFss) can be calculated from the ratios of the peak area and the concentration of each internal standard for the sampling spike to those for the cleanup spike, according to the equation below.

$$RRFcs = \frac{Ci(cs)}{Cs} \times \frac{As}{Ai(cs)}$$

where

Cs: Concentration of the congener to be determined in the standard solution

Ci(cs): Concentration of the corresponding internal standard for the cleanup spike in the standard solution

As: Peak area of the congener to be determined in the standard solution

Ai(cs): Peak area of the corresponding internal standard for the cleanup spike in the standard solution

$$RRFrs = \frac{Ci(rs)}{Ci(cs)} \times \frac{Ai(cs)}{Ai(rs)}$$

where

Ci(rs): Concentration of the corresponding internal standard for the syringe spike in the standard solution

Ai(rs): Peak area of the corresponding internal standard for the syringe spike in the standard solution

$$RRFss = \frac{Ci(cs)}{Ci(ss)} \times \frac{Ai(ss)}{Ai(cs)}$$

where

Ci(ss): Concentration of the corresponding internal standard for the sampling spike in the standard solution

Ai(ss): Peak area of the corresponding internal standard for the sampling spike in the standard solution

5.4 Determination and Quantification

5.4.1 Identification and Quantification

(1) For PCDDs/PCDFs determination, inject 1 to 2 ìl of the determination samples for GC/MS analysis prepared according to 4.3.4-A (3), 4.3.5-A (3) or 4.3.6-A (3) into the column a), b) or c) attached to the GC/MS and record the chromatogram of each congener by SIM (Selected Ion Monitoring) mentioned in the section 5.2.
For coplanar PCBs determination, inject 1 to 2 ìl of the determination samples for GC/MS analysis[21] prepared according to 4.3.4-B (3), 4.3.5-B (3) or 4.3.6-B (3) into the column d) or e) attached to the GC/MS and record the chromatogram of each congener by SIM.

(2) Check the lock mass monitor channel[30] for each sample.

(3) Measure the peak area of each ion of the congeners of PCDDs/PCDFs or coplanar PCBs and that of the internal standards[33] with respect to the mass numbers. Confirm that the sample solution is injected into the GC/MS by comparing the peak area of the internal standard for the syringe spike in the sample and that of the standard solution[35].

(4) Confirm that relative intensity of the peak area between two monitor ions of different mass numbers of each congener of PCDDs/PCDFs or coplanar PCBs is similar to the relative intensity of the peak area in the standard solution and the natural existence ratio (see Table 8)[31].

(5) Calculate the ratio of the peak area of each congener of PCDDs/PCDFs or coplanar PCBs to that of corresponding internal standard for the cleanup spike with respect to the mass numbers[33], then each congener (Qs in ng) in the whole extract using the following equation and relative response factor (RRF) defined in the section 5.3[18].

$$Qs = \frac{As}{Acsi} \times \frac{Qcsi}{RRFcs}$$

where

Qs:	Quantity of each congener to be determined in the whole extract (ng)
As:	Peak area of each congener to be determined in the extracts
Acsi:	Peak area of the corresponding internal standard for the cleanup spike in the extracts
Qcsi:	Quantity of the corresponding internal standard for the cleanup spike added to the extracts (ng)
RRFcs:	Relative response factor of the congener to the cleanup spike

Table 8 Natural Existence Ratio of Isotope by Number of Chlorine Atom

a) PCDDs and PCDFs

	M	M+2	M+4	M+6	M+8	M+10	M+12	M+14
TeCDDs	77.43	100.00	48.74	10.72	0.94	0.01		
PeCDDs	62.06	100.00	64.69	21.08	3.50	0.25		
HxCDDs	51.79	100.00	80.66	34.85	8.54	1.14	0.07	
HpCDDs	44.43	100.00	96.64	52.03	16.89	3.32	0.37	0.02
OCDD	35.54	88.80	100.00	64.48	26.07	6.78	1.11	0.11
TeCDFs	77.55	100.00	48.61	10.64	0.92			
PeCDFs	62.14	100.00	64.57	20.98	3.46	0.24		
HxCDFs	51.84	100.00	80.54	34.72	8.48	1.12	0.07	
HpCDFs	44.47	100.00	96.52	51.88	16.80	3.29	0.37	0.02
OCDF	34.61	88.89	100.00	64.39	25.98	6.74	1.10	0.11

b) Coplanar PCBs

	M	M+2	M+4	M+6	M+8	M+10
TeCBs	76.67	100.00	49.11	10.83	0.93	
PeCBs	61.42	100.00	65.29	21.43	3.56	
HxCBs	51.22	100.00	81.48	35.51	8.75	1.17
HpCBs	43.93	100.00	97.67	53.09	17.38	3.43

Note: M is an isotope with the minimum mass number.
The numbers in the table are ratios of ions in percentage that show the maximum strength for each homologue.

5.4.2 Percent Recovery

(1) Based on the result obtained in the section 5.4.1, percent recovery of the cleanup spike (Rc) can be calculated by using the ratio of the peak area of the internal standard for the cleanup spike to that for the syringe spike, and the corresponding relative response factor (RRFrs)[18), 36)].

Following equation can be used.

$$Rc(\%) = \frac{Acsi}{Arsi} \times \frac{Qrsi}{RRFrs} \times \frac{V \times F}{V'} \times \frac{100}{Qcsi}$$

where

Acsi: Peak area of the internal standard for the cleanup spike in the extracts
Qcsi: Quantity of the internal standard for the cleanup spike added to the extracts (ng)
Arsi: Peak area of the internal standard for the syringe spike in the extracts
Qrsi: Quantity of the internal standard for the syringe spike added to the extracts (ng)
RRFrs: Relative response factor of the cleanup spike to the syringe spike
V: Quantity of crude extracts (ml)
V': Fraction quantity of crude extracts (ml)
F: Factor ratio between the samples for PCDDs/PCDFs and that for

coplanar PCBs (usually 2 fractions, F=2)

(2) Similarly, percent recovery of the sampling spike (Rs) can be calculated according to the following equation by using the ratio of the peak area of the internal standard for the sampling spike to that of the internal standard for the cleanup spike, and the corresponding relative response factor (RRFss) [18), 37)].

$$Rs(\%) = \frac{Assi}{Acsi} \times \frac{Qcsi}{RRFss} \times \frac{100}{Qssi}$$

where

Assi: Peak area of the internal standard for the sampling spike in the extracts

Qssi: Quantity of the internal standard for the sampling spike added to the extracts (ng)

Acsi: Peak area of the corresponding internal standard for the cleanup spike in the extracts

Qcsi: Quantity of the corresponding internal standard for the cleanup spike added to the extracts (ng)

RRFss: Relative response factor of the sampling spike to the cleanup spike

5.5 Calibration Curve

With the calibration curve of the standard solution determined by the selective ion monitoring (SIM) referred in the section 5.2, calculate relative response factor (RRFcs) of each congener to the corresponding cleanup spike. Then, calculate relative response factor (RRFrs) of the cleanup spike to the corresponding syringe spike. Procedure should be referred to the section 5.3. The calibration curve should be verified more than once a day[38)].

5.6 Sensitivity of Gas Chromatography-Mass Spectrometer

It should be verified that the sensitivity of the GC/MS is kept constant by determining the standard solution with the middle concentration among a series of the standard solution according to the procedure referred in the section 5.4.1. The sensitivity should be verified more than once a day[39)].

5.7 Determination of Operation Blank Value

Operation blank value of each congener of PCDDs/PCDFs or coplanar PCBs should be determined by the procedures referred in the section 5.4.1 using the testing solution prepared according the section 4[16), 40), 41)].

5.8 Determination of Traveling Blank Value

Each congener of PCDDs/PCDFs or coplanar PCBs should be quantified by the procedure referred in the section 5.4.1 using the travel blank testing solution prepared in the section 4. More than three samples should be determined for this purpose, and the average value is adopted as the traveling blank value (Qt in ng)[16), 41), 42)].

5.9 Duplicate Determination of the Testing Solution

Each congener of PCDDs/PCDFs or coplanar PCBs should be quantified by the procedure referred in the section 5.4.1 using the solution for duplicate determination prepared in the section 4[17), 43)].

6. Detection Limit and Quantification Limit

The following three types of detection limit and quantification limit should be determined.

(1) Apparatus Detection Limit and Apparatus Quantification Limit

Inject 1 μl of the standard solution with the lowest concentration near the detection limit (0.2 – 0.5 ng/ml) used for preparing the calibration curve into the GC/MS [44)], and quantify each congener of PCDDs/PCDFs and coplanar PCBs. Repeat five or more times.

Calculate the concentration of each congener of PCDDs/PCDFs and coplanar PCBs in air sample by using the final concentration volume and the suction gas volume for a regular sample and the measured values obtained from the former step[45)]. Apparatus detection limit (ADL) and apparatus quantification limit (AQL) of each congener of PCDDs/PCDFs and coplanar PCBs are calculated by the following equation in which the standard deviation (s_a) of the concentrations obtained from the former steps is applied.

Measure the operation blank if it is available, and calculate the ADL and AQL by using the greater standard deviation between those of the operation blank and the standard solution.

The ADL and AQL should be verified more than once for every modification of quantification conditions[46)].

$$\text{Apparatus Detection Limit} = 3s_a \ (\text{pg/m}^3)$$
$$\text{Apparatus Quantification Limit} = 10s_a \ (\text{pg/m}^3)$$

(2) Method Detection Limit and Method Quantification Limit

To the extract solution from the filter and the polyurethane foam, which is the same quantity for the determination of samples, add the standard reference materials equivalent to Qs (ng) that is calculated back by substituting AQL into the concentration of air sample (C) in the equation for each computation of congener concentration shown in the section 7.1 of Chapter 3, and perform GC/MS measurement after cleanup procedure. Repeat the

measurement five or more times.

Calculate the concentration of each congener of PCDDs/PCDFs and coplanar PCBs in air sample by using the final concentration volume and the suction gas volume for a regular sample and the measured values obtained from the former step[45].

Method detection limit (MDL) and method quantification limit (MQL) of each congener of PCDDs/PCDFs and coplanar PCBs are calculated by the following equation in which the standard deviation (s_m) of the concentrations obtained from the former steps is applied.

Since the MDL and MQL derived from this measurement method may fluctuate by the preparation procedures and the conditions of the determination, it is necessary to verify them at regular intervals. The MDL and MQL should be verified for every change in the preparation procedures and the quantification conditions.

Method Detection Limit = $3s_m$ (pg/m^3)
Method Quantification Limit = $10s_m$ (pg/m^3)

(3) Sample Detection Limit and Sample Quantification Limit

Noise level (N) should be determined as either;

1) Twofold of the standard deviation of the baseline noise around the peak (tenfold range of one-half the peak height) on the chromatogram of the sample determination, or
2) 2/5 of the difference between the maximum and the minimum noise levels, as the difference is almost fivefold of the standard deviation in the past experiments.

Peak height (S) should be a top height of the peak from the baseline that is the median of the noise level.

Estimate the peak area whose height is threefold of the noise level (S/N=3), from the chromatogram of the standard solution, and calculate Qs based on the peak area by using the quantification equation. Sample detection limit (SDL) can be calculated by substituting the Qs into the equation for the computation of congener concentration defined in the section 7.1 of Chapter 3 (where Qt = 0)[45].

Similarly, estimate the peak area whose height is tenfold of the noise level (S/N=10), and calculate sample quantification limit (SQL) from the peak area.

When some of 2,3,7,8-chlorine substituted congeners do not show the peaks on the chromatogram, the noise levels shall be determined by measuring the baseline noise around the peak, and then the SDL and SQL can be calculated in the same way as above.

The sample detection limit (SDL) and the sample quantification limit (SQL) must be lower than the method detection limit (MDL) and the method quantification limit (MQL), respectively. If the SDL/SQL are greater than the MDL/MQL, review the procedures of the preparation and the determination, and then measure the samples again. The SDL and the SQL should be determined for every sample series, as they change depending on the volume

of samples and the preparation procedure (e.g., the condensation ratio)[47].

7. Notation of Concentration

7.1 Calculation

The concentration of each congener of PCDDs/PCDFs and coplanar PCBs in ambient air can be calculated by the following equation, based on the determination data according to the section 5.4.1.

$$C = \frac{(Qs - Qt) \times 1{,}000}{V \times 293/(273 + t) \times P/101.3}$$

where

C: Concentration of each congener at 20 °C in ambient air (pg/m^3)

Qs: Quantity of each congener in the whole crude extract (ng)

Qt: Quantity of each congener in the crude solution for traveling blank test (ng). If neither traveling blank test nor operation blank test is conducted, the traveling blank value or the operation blank value determined beforehand should be applied.

V: Sample quantity (m^3) = (Fs+Fe) × St/2. Where, Fs: Flow rate at starting (m^3/min), Fe: Flow rate at the end (m^3/min), and St: Duration of sample collection (min). An indicated value should be the sample quantity if a cumulative flow meter is used.

t: Average air temperature (°C) at the time and place of sampling, or average water temperature (°C) if a wet type cumulative flow meter is used[48].

P: Average atmospheric pressure at the time and place of sampling (kPa)[48].

The concentration of PCDDs/PCDFs is represented as the concentration of each homologue from tetra-chlorinated to octa-chlorinated and that of all the homologues. The concentration of each homologue should be represented as a total of the concentration of 2,3,7,8-chlorine substituted congeners and those of other congeners. The concentration of each 2,3,7,8-chlorine substituted congener (17 congeners, see Table 2) should also be represented. The concentration of 1,3,6,8-TeCDD, 1,3,7,9-TeCDD, 1,2,7,8-TeCDF, etc. is determined in order to trace the origin of the contaminants, if necessary.

For coplanar PCBs, the concentrations of the following congeners should be represented.

- Each congener (4 non-*ortho* congeners and 8 mono-*ortho* congeners)
- Total of non-*ortho* congeners
- Total of mono-*ortho* congeners
- Total of all the coplanar PCBs

The concentration of each congener should be represented as:

- Determined value, when the concentration is equal to or greater than the quantification limit (QL).
- Determined value with a note indicating less reliability (e.g. putting the determined value in brackets), when the concentration is equal to or greater than the detection limit (DL) and lower than the quantification limit (QL).
- "< DL (value)", when the concentration is equal to or lower than the detection limit (DL).

Total of the determined values should be calculated by summing the determined values when the concentration is equal to or greater than the DL, or one-half the DL value when the concentration is lower than the DL.

The congeners to be represented are shown in Table 3. Table 5 shows an example of the representation of dioxins determination results.

7.2 2,3,7,8-TeCDD Toxicity Equivalency Quantity (TEQ)

The determined concentration should be represented as the Toxicity Equivalency Quantity (pg-TEQ/m^3) by using 2,3,7,8-TeCDD Toxicity Equivalency Factor (TEF). The TEQ is calculated by multiplying the determined value by the corresponding TEF when the determined value is equal to or greater than the DL. If the determined value is lower than the DL, TEQ is calculated by multiplying one-half the DL by the corresponding TEF. Total TEQ is represented as the total of TEQ of each congener. TEFs of dioxins are listed in Table 4.

7.3 Significant Figure

Following rules are applied to control the significant figures of data, unless specifically indicated.

1) Significant figures of the concentration should be 2 digits according to the rounding procedure defined in JIS-Z8401. If the concentration is lower than the DL, it should be noted. Digits of the concentration should be limited to the DL of the air sample and lower figures shall not be represented.
2) The significant figure of the DL should be 1 digit by rounding the value according to JIS-Z8401.
3) Toxicity Equivalency Quantity should be the total of all the congeners determined. The significant figure should be 2 digits by the same procedure as 1). This means that the TEQ of each congener should not be rounded.

Notes

[1] Dioxins have many kinds of toxicity such as animal carcinogenicity, teratogenicity, and the like. It is reported that dioxins are carcinogenic to humans though there are some uncertainties. Therefore, the determination of dioxins should be conducted at the laboratory which can completely protect analysts from inhalation of, ingestion of or direct contact with dioxins and which can strictly control emissions or effluent from preparation rooms or analytical laboratories in order to prevent adverse effects on human health.

[2] It is necessary to take appropriate measures if detection limit (DL) or quantification limit (QL) of the actual samples around the peak does not satisfy those of the standard reference materials.

[3] For analyzing only coplanar PCB in the sample without interfering substances, the sample solution can be analyzed by the GC/MS; the sample should be transferred into nonane solution with syringe spike after being concentrated by silica gel column chromatography or multilayered silica gel column chromatography. In this case, the capillary column which can clearly separate all the congeners of PCBs, such as HT-8 (8 % Phenyl (equiv.) poly carborane-siloxane), DB-5MS (Phenyl (5 %) methyl (95 %) silicone bonded), and so on, should be employed.

[4] It is not necessary to achieve this level of resolution for all the congeners if the target quantification limit (TQL) is assured.

[5] Mixed solution as standard solution and internal standard solution is available in the market. The commercially available chemicals mentioned here are not those recommended to use but just listed for the convenience of readers of the manual. The chemicals of equal or higher quality are also recommended.

For PCDDs/PCDFs,
- Cambridge Isotope Laboratories (CIL), U.S.A. provides
  - EDF-949 Native Quantifying Cocktail (2,3,7,8-PCDD/PCDF Isomers) for mixed standard solution (50 ± 5 ìg/ml nonane solution) and
  - EDF-957 Carbon-13 Quantifying Cocktail (2,3,7,8-PCDD/PCDF Isomers) for internal standard solution (50 ± 5 ìg/ml nonane solution).
- Wellington Laboratories, Canada provides
  - NK-ST-E; Native Stock E (Native PCDDs and PCDFs) for mixed standard solution equivalent to EDF-949 of CIL, and
  - NK-LCS-H; Labeled Compound Solution H (Labeled PCDDs and PCDFs) for internal standard solution equivalent to EDF-957 of CIL.

For coplanar PCBs,
- AccuStandard, U.S.A. provides
  - Standard solution for each congener (100 ìg/ml iso-octane solution).
- CSL/Wellington provides
  - Internal standard solution for each congener (50 ìg/ml nonane solution).

In Japan, it may take several months to purchase PCBs as the Ministry of Economy, Trade and Industry's permission is required because PCBs are the class 1 designated chemicals listed in the Law concerning the Examination and Regulation of Manufacture etc. of Chemical Substances.

[6] For Coplanar PCBs, the QL may fluctuate, especially when the blank value is high and unstable. It would be better to set the stable QL but somewhat higher than the normal QL by using the standard solution with slightly higher concentration.

[7] If contamination is detected for some specific congeners, measured values should not be adopted unless the difference between the measured values including and excluding the contaminated congeners is lower than 30 % of the measured values excluding the contaminated congeners.

[8] When they are higher than the QL, it should be confirmed for all congeners that the difference in TEQ between the duplicated aliquots is equal to or less than ±30 % of the average.

[9] Different stable isotopically labeled congeners should be used for each of the sampling spike, the cleanup spike and the syringe spike. For example, $^{13}C_{12}$-1,2,3,4-TeCDD, whose volatility is relatively high and toxicity is low, is used for the sampling spike among the tetra-chlorinated stable isotopically labeled

congeners. For the cleanup spike, it is desirable that stable isotopically labeled congeners are added correspondingly to each congener to be determined. At least one isotopically labeled congener must be added to each homologue. $^{13}C_{12}$-2,3,7,8-chlorine substituted PCDDs and PCDFs are used for the determination of PCDDs/PCDFs. As to coplanar PCBs, all of the four isotopically labeled congeners are used for non-*ortho* PCBs, while at least one isotopically labeled congener should be added to each homologue of mono-*ortho* PCBs.

For the syringe spike, the internal standards which are not used for the sampling spike or the cleanup spike should be adopted. For example, $^{37}Cl_4$-2,3,7,8-TeCDD or $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF is used for PCDDs/PCDFs. For coplanar PCBs, $^{13}C_{12}$-2,3,4,4',5-PeCB is generally used, but the same internal standards for PCDDs /PCDFs can be adopted. The internal standards may interfere the determination depending on the resolution of the mass spectrometer; the conditions that avoid the interference should be identified before the internal standards are used.

[10] A vacuum dryer can be used instead. If the solvent remains in the polyurethane foam, the foam might get softened, which would lead loss of the vacuum pressure and consequently result in loss of the vacuumed air volume.

[11] Types and quantity of the filler or solvents used for preparation of the columns should be determined by preliminary separation tests of standard reference materials.

[12] Hypercarb S (porous graphitized carbon, produced by Shandon Co.) is one of the commercially available columns (see Remark 1). The size is 4.6 mm in internal diameter and 100 mm in length.

[13] This level of resolution is not necessarily required for all congeners if the target quantification limit (TQL) is assured.

[14] The standard capillary column is the one that can separate all the congeners clearly and for which their eluted positions on the chromatography are identified. Considering various factors, it is desirable to use two or more types of capillary columns with different polarity.

For separation of PCDDs/PCDFs, SP-2331 (Supelco, USA), HP-5 (Hewlett-Packard, USA), DB-5 and DB-17 (J&W Scientific, USA), and CP-Si188 (Varian - Chrompack International, Netherlands) are the representative capillary columns. For separation of coplanar PCBs, DB-1, DB-5 and DB-5MS (J&W Scientific), Ultra #1 and Ultra #2 (Hewlett-Packard), SPB-1 and SPB-5 (Supelco), and HT-8 (SGE, Australia) are generally used. (see Remark 1).

[15] Sampling spike is an operation to add corresponding internal standards to samples at the time of sampling; the internal standards are added onto the filters before the air sampling is started. Quantity of the internal standards to be added should be adjusted so that their concentration in the samples can be covered by the calibration curve. Usually 0.2 to 4 ng of the internal standards is added on the assumption that the solution will be divided into two fractions. When a small volume of aliquot is taken from the extract, additional internal standards should be added according to the number of fractions. When the extract contains high concentration of PCDDs/PCDFs or coplanar PCBs, dilution of the extract is expected because addition of the regular amount of the internal standards to the extract would make the concentration beyond the quantification limit. If it is clear that the extract is to be diluted for quantification, the internal standards can be added more than 0.2 ~ 4 ng.

[16] Blank tests need not be carried out for every batch of samples if the blank values are controlled in advance. To assure the reliability of sampling, however, operation blank and traveling blank should be examined, and the relevant data should be prepared for the future reporting when necessary. Generally the traveling blank test is conducted 3 times a year so as to make data statistically significant**.** However, when the sample is possibly contaminated during transportation for example by the ash from the electrostatic precipitator, the traveling blank test must be conducted for every sampling.

[17] The duplicate determination can be omitted if duplicate sampling is not possible. The determination need not be duplicated for every batch of samples if the sampling method is well controlled. The sampling method, however, should be examined to assure the reliability of sampling, and relevant data should be prepared for the future reporting when necessary.

[18] Quantity of the internal standards to be added as the cleanup spike should be adjusted so that the total concentration of those added at each cleanup process can be covered by the calibration curve. On the assumption that the solution will be divided into two fractions, 0.4 to 2 ng of the internal standards is usually added for TeCDDs, PeCDDs, HxCDDs, HpCDDs, TeCDFs, PeCDFs, HxCDFs and HpCDFs, and 0.8 to 4 ng for OCDD, OCDF and coplanar PCBs. If a small volume of aliquot is taken from the extract, additional internal standards should be added according to the number of fractions. When the extract

contains high concentration of PCDDs/PCDFs or coplanar PCBs, dilution of the extract is expected because addition of the regular amount of the internal standards to the extract would make the concentration beyond the quantification limit. If it is clear that the extract is to be diluted for quantification, the internal standards can be added more than 0.2 ~ 4 ng. The cleanup spike can be added to the aliquot of crude extract, if the sample preparation is to be started again from the beginning, that is, addition of the internal standards, because the concentration of PCDDs/PCDFs or coplanar PCBs in the sample could not be estimated beforehand. In this case, it is necessary to confirm the percent recovery of the extract in advance; the volume of the spike should be reduced according to the number of aliquot. In addition, the quantification equation shown in 5.4.1 (5) and the equation for sampling spike recovery shown in 5.4.2 (2) should be multiplied by (V/V'), and on the other hand, (V/V') should be deleted from the equation for cleanup spike recovery shown in 5.4.2 (1).

[19] Store the crude extract for a certain period for possible duplicate determination. Even if the sample volume is smaller than a half of total volume, the sample can be also analyzed if the extraction was performed all at once.

[20] Be careful not to blow or dry up the solvent with nitrogen stream.

[21] When only coplanar PCBs are determined in the samples showing no interference on gas chromatogram, the concentration can be calculated based on the measurement of the nonane solution after the samples being added with syringe spike for coplanar PCBs, concentrated and transferred into nonane. In this case, it is necessary to use the capillary column of the gas chromatography that can clearly separate all the PCB congeners. HT-8 and DB-5MS are those commercially available.

[22] When adding concentrated sulfuric acid, be careful about bumping of the solvents due to the reaction of the sulfuric acid with organic matters. Start from several milliliter of sulfuric acid and increase its amount gradually, while observing colorization. Wear protective gears such as a mask and gloves.

[23] Sulfuric acid (22 %) impregnated silica gel chromatography can be performed instead of the multilayered silica gel column chromatography depending on the sample conditions, because the sulfuric acid impregnated silica gel can also remove the organic matrices as the sulfuric acid does.

[24] Polarity of alumina may vary by its production lot and storing condition and duration. If activity of an alumina column is degraded, mono-*ortho* PCBs, 1,3,6,8-TeCDD, 1,3,6,8-TeCDF, and the like may be eluted to the first fraction while octa-chlorinated congeners may not be eluted to the second fraction by the standard volume of 50 % (v/v) dichloromethane-hexane. The activity should be verified by preliminary elution tests.

[25] High performance liquid chromatography with activated carbon column or activated carbon impregnated silica gel column chromatography is employed if interference in GC/MS analysis is found or if further cleanup process is needed. The HPLC is useful to separate PCDDs/PCDFs from non-*ortho* PCBs.

[26] Syringe spike is added to adjust the injection volume. Volume of the spike is 0.2 to 1 ng for TeCDDs, PeCDDs, HxCDDs, HpCDDs, TeCDFs, PeCDFs, HxCDFs and HpCDFs, and 0.4 to 2 ng for OCDD, OCDF and coplanar PCBs.

[27] Toluene, decane or iso-octane can be used instead.

[28] The determination condition should be examined by the preliminary separation tests using extracts from fly ash because it depends on the instruments and column conditions.

[29] Peak duration generated by the capillary column ranges from 5 to 10 seconds, while the sampling frequency of the SIM should be less than one (1) second so as to plot a sufficient number of determination points for each peak. The number of monitor channels available for one circuit of determination is restricted by the sensitivity required. The balance between them should be carefully examined.
Considering the retention time of each peak on the chromatogram, the data can be grouped for analysis by time-sharing, if the GC/MS can be properly conditioned so as to detect the peak of the corresponding internal standards.

[30] If the chromatogram of the locked mass channel swings, especially at the peak position of the target compounds to be determined, the peak might not be detected satisfactorily due to the loss of the resolution, and the target compounds should not be quantified. This might, mainly, be attributed to the insufficient preparation of the sample. The fluctuation in the locked mass should be minimized by careful preparation of the sample.

[31] Each congener can be quantified if the ratio of the peak areas of two or more monitor ions on the chromatogram is similar to that of the corresponding standard reference material, and if the difference between the ratio of the peak areas and the natural existence ratio of corresponding isotope is within

±15 % (±25 % if the concentration is less than the detection limit) (see Table 8).

2,3,7,8-chlorine substituted PCDDs/PCDFs and coplanar PCB congeners can be identified if the retention time of the congeners is almost the same as that of the standards on the chromatogram by the SIM on which the peaks are clearly separated, and if the relative retention time of the corresponding internal standard is the same as that of the standards. The congener for which the standard reference material is not available should be determined by referring the literature. For coplanar PCBs, especially, during the retention time of the congeners, no significant peak of highly chlorinated PCBs should be observed, and no influence of fragmented ion of [M-Cl] or [M-2Cl] can be detected.

The column and the ion sources should be kept clean by using the guarded column or cleaning the ion sources when tailing or absorption occurs for non-*ortho* PCBs due to the contamination of the column or the ion sources.

[32] Calibration range should include the concentration close to the detection limit and be within the dynamic range of the GC/MS.

[33] 2,3,7,8-chlorine substituted PCDD/PCDF congeners should be quantified by using corresponding standard reference materials. Other congeners of PCDDs/PCDFs should be calculated on the assumption that they show the same sensitivity as 2,3,7,8-chlorine substituted congeners in corresponding homologues; so should be coplanar PCBs as corresponding chlorine substituted congeners.

[34] The calibration curve should be verified by comparing the RRFcs with the relative resolution factor (RRF) in ordinary determination and by simultaneously quantifying a standard sample of known concentration.

[35] If the peak area of the syringe spike in the sample is equal to or greater than 70 % of that of the standard solution, it means that the whole sample solution is injected to the GC/MS. If not, check and correct the causes, and then repeat the measurement.

[36] If the percent recovery of the cleanup spike does not fall between 50 and 120 %, the sample should be prepared from crude extraction and measured again. If the percent recovery of the newly prepared sample does not meet the criteria, the data should be omitted because the extraction procedure may be incomplete.

[37] If the percent recovery of the sampling spike does not fall between 70 and 130 %, the data should be omitted because of the low reliability. Correct the causes and then collect samples again.

[38] Fluctuation in the RRFcs and the RRFrs should be within ±20 % compared to those at the calibration. If the fluctuation exceeds the value, correct the causes and analyze the sample again.

[39] The sensitivity of the internal standard should not change from the time of calibration. Fluctuation in the relative response to the internal standard should be within ±20 % comparing to the time of calibration. If the fluctuation exceeds the value, correct the causes and analyze the sample again.

If the retention time changes within a fairly short duration -- for example, the retention time fluctuates over ±5% within a day, and the relative retention ratio to the internal standard fluctuates over ±2% -- correct the causes and analyze the sample again.

[40] Operation blank value should be determined prior to the sample determination. If the converted operation blank value expressed as the concentration in ambient air exceeds the target quantification limit (TQL, Table 1), determine the samples again after minimizing the operation blank value by cleaning and calibrating the instruments and apparatus.

[41] If the contamination is occurred for some specific congeners, the data cannot be adopted, unless the difference between the data including and excluding those contaminated congeners is less than 30 % of the former.

[42] If the traveling blank value is equal to or smaller than the operation blank value, contamination during the transportation can be ignored, and the concentration is calculated by subtracting the operation blank value from the measured value.

Even if the samples are contaminated during the transportation, the concentration can be calculated by subtracting the traveling blank value from the measured value when the sum of the QLs in TEQ (10s) derived from the standard deviation (s) of the traveling blanks of more then three samples is equal to or smaller than the TQL. Similarly, even if the sum of the QLs derived from the traveling blank value is larger than the TQL, the concentration can be calculated by subtracting the traveling blank value from the measured value when the measured value obtained according to Section 5.4 is equal to or greater than the QL.

However, if the sum of the QLs derived from the traveling blank value is greater than the TQL due to the contamination during the transportation, and if the measured value obtained according to Section 5.4 is

smaller than the QL derived from the traveling blank value, the measured value should be omitted because they are not reliable. Correct the causes of the contamination and collect samples again. Refer to Figure 2.

[43] The difference in the concentrations expressed in TEQ between the duplicated aliquots should be equal to or less than 30 % of the average of the two. If the difference is greater than the criteria (=30 %), the sample should be determined again starting from the preparation. If the new data meet the criteria, it should be adopted. Otherwise, the data should be omitted. Correct the causes and collect samples again. Duplicative verification should be conducted at a rate of 10 % of a total number of samples throughout a series of samplings.

It should be confirmed for all congeners that the difference in measured values between the duplicated aliquots should be within ±30 % of the average of the two that are higher than the QL.

[44] For coplanar PCBs, the QL might fluctuate especially when the blank value is high and unstable. It may be better to set the stable QL even if it is slightly higher than the normal QL which can be calibrated by using the standard solution with slightly high concentration.

[45] It should be calculated under the normal conditions, but if the samples to be determined show the quite different conditions, sample conditions are used.

[46] If the AQL in TEQ derived from each congener of PCDDs/PCDFs and coplanar PCBS is greater than the TQL shown in Table 1, the instruments and apparatus should be checked and adjusted in order to lower the AQL below the TQL. Regardless of the TQL, the AQL should be minimized so that the concentration can be quantified even if the concentration is changed in the future.

[47] Especially in the case of the samples with low concentrations, the SQL should be lower than the TQL. If the SQL is greater than the TQL, the sample should be prepared again from cleanup of the extracts.

[48] Data from appropriate institutions such as the nearest meteorological observatory can be used.