Soils, sludges and treated bio-waste – Organic constituents – Dioxins and furans (PCDD/F and DL-PCB)"

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Foreword

The European project HORIZONTAL is focused on the standardisation of analytical methods for the analyses of various inorganic and organic contaminants in soil, sludge and bio waste. During the preparation of the project, several desk studies have been started to elaborate the possibility of horizontal standardisation on specific subjects. One of these subjects was the horizontal standardisation of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans (PCDD/F) together with the Dioxinlike Polychlorinated Biphenyls (DL-PCB).

This document has been developed in the framework of the project 'Horizontal-ORG'. based on the results of a desk study. Numerous established test methods published in literature, available CEN and ISO standards and various guidelines from official bodies have been reviewed, compiled and described in this study. After discussion with the project partners and other interested parties the draft-standard has been developed as an modular horizontal method.

This standard is applicable for the determination of PCDD/F and dioxin.like PCBs in soil, sludge and treated biowaste. It may also be applicable for other sample categories of plant origin and mineral origin.

Introduction

Two groups of related chlorinated aromatic ethers are known as polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs); they consist of a total of 210 individual substances (congeners): 75 PCDDs and 135 PCDFs.

A group of chlorinated aromatic compounds similar to polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) is known as polychlorinated biphenyls (PCBs) which consist of 209 individual substances.

PCDDs and PCDFs can form in the combustion of organic materials; they also occur as undesirable byproducts in the manufacture or further processing of chlorinated organic chemicals. PCDDs/PCDFs enter the environment via these emission paths and through the use of contaminated materials. In fact, they are universally present at very small concentrations. The 2,3,7,8-substituted congeners are toxicologically significant. Toxicologically much less significant than the tetrachlorinated to octachlorinated dibenzodioxins/dibenzofurans are the 74 monochlorinated to trichlorinated dibenzodioxins/dibenzofurans.

PCBs have been produced over a period of approx. 50 years until the end of the 1990s for the purpose of different use in open and closed systems, e.g. as electrical insulators or dielectric fluids in capacitors and transformers, as specialised hydraulic fluids, as a plasticizer in sealing material etc. World-wide more than one million tons of PCBs were produced.

PCDD/F as well as PCBs are emitted during thermal processes as e.g. waste incineration. PCB can contribute considerably to the total WHO-TEQ. In 1997 a group of experts of the World Health Organisation (WHO) fixed toxicity equivalent factors (TEFs) for PCDDs/PCDFs and 12 PCBs, known as dioxin-like PCBs. These 12 dioxin-like PCBs consist of four non-ortho PCBs and eight mono-ortho PCBs (no or only one chlorine atoms in 2-, 2'-, 6- and 6'-position), having a planar or mostly planar structure.

Only skilled operators who are trained in handling highly toxic compounds should apply the method described in this Standard.

1 Scope

This European standard specifies a method for quantitative determination of 17 2,3,7,8-chlorine substituted Dibenzo-p-dioxins and Dibenzofurans and dioxin-like Polychlorinated Biphenyls in soil, sludge, sediments and biowaste using liquid column chromatographic clean up methods and GC/HRMS.

The limit of detection is dependant on the kind of sample, the congener, the used equipment, the quality of chemicals used for extraction and clean-up. Under the quality requirements specified in this standard, limits of detection better than 1 ng/kg should be achieved.

This method is „performance based“. It is permitted to modify the method if all performance criteria given in this method are met.

2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

The following normative documents contain provisions which, through reference in this text, constitute provisions of this European standard.

ISO 14507 Soil quality - Guidance for sample pretreatment for the determination of organic contaminants in soil.

ISO/DIS 16720 Soil quality - Pretreatment of samples by freeze drying for subsequent analysis

EN 1948-2 Stationary source emissions - Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs - Part 2: Extraction and clean-up of PCDDs/PCDFs

EN 1948-3 Stationary source emissions - Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs - Part 3: Identification and quantification of PCDDs/PCDFs

3 Definitions

For the purposes of this European Standard, the following terms and definitions apply.

dioxin-like PCBs

non- and mono-ortho PCB having a affinity to the Ah-receptor, showing similar toxical effects as the 2,3,7,8-substituted PCDDs/PCDFs according to WHO [5].

marker PCBs

The seven PCBs 28, 52, 101, 118, 138, 153, 180

spiking

addition of 13C12-labelled PCDD/F or PCB standards

operational performance characteristics

measures which deal with the influence of the physical and chemical environment and maintenance problems, for example; mains voltage, temperature, supply of certain substances, set-up time, period of unattended operation (ISO 6879:1995) [7]

statistical performance characteristics

measures which quantify, for measured values, the possible deviations resulting from the random part of the measuring process; these are, for example, repeatability or instability (ISO 6879:1995) [7]

analytical blank

a blank sample covering the complete analytical procedure including extraction, clean-up, identification and quantification including all the relevant reagents and materials

extraction standard

13C12-labelled PCDD/Fs and PCBs, added before extraction and used for calculation of results

recovery standard

13C12-labelled PCDD/Fs and PCBs, added before injection into the GC and used for calculation of recovery rates of extraction standards

keeper

high boiling point solvent added to the sampling standard solution

congener

any one of the 210 individual PCDD/Fs or any one of the 209 individual PCBs

PCDD/PCDF isomers

PCDDs or PCDFs with identical chemical composition but different structure

PCB isomers

PCBs with identical chemical composition but different structure

pattern

defined as a chromatographic print of any series of PCDD, PCDF or PCB isomers.

profile

graphic representation of the analysed concentrations.

Limit of detection (LOD)

The limit of detection is expressed as the mean sample blank value plus three times the standard deviation (3s) of the blank. (EUROCHEM Guide)

Limit of quantification (LOQ)

The limit of quantification is expressed as the mean sample blank value plus, either, five, six or ten times the standard deviation of the blank. (EUROCHEM Guide)

4 Symbols and abbreviations

WHO-TEF

Toxic equivalent factor proposed by WHO in 1997 (for detailed description, see Annex A)

I-TEF

International toxic equivalent factor proposed by NATO-CCMS in 1988 (for detailed description, see Annex A)

WHO-TEQ

Toxic equivalent obtained by multiplying the mass determined with the corresponding WHO-TEF including

PCDDs, PCDFs and PCBs (for detailed description, see Annex A). WHO-TEQ $_{PCB,}$ WHO-TEQ $_{PCDD/F,}$ should be used to distinguish different compound classes.

I-TEQ

International toxic equivalent obtained by multiplying the mass determined with the corresponding I-TEF including PCDDs and PCDFs (for detailed description, see Annex A). Should only be used for comparison with older data

HRGC

High resolution gas chromatography

HRMS

High resolution mass spectrometry

PCDD/PCDF or PCDD/F

Polychlorinated dibenzo-p-dioxins/dibenzofurans

TCDD

Tetrachlorodibenzo-p-dioxin

PeCDD

Pentachlorodibenzo-p-dioxin

HxCDD

Hexachlorodibenzo-p-dioxin

HpCDD

Heptachlorodibenzo-p-dioxin

OCDD

Octachlorodibenzo-p-dioxin

TCDF

Tetrachlorodibenzofuran

PeCDF

Pentachlorodibenzofuran

HxCDF

Hexachlorodibenzofuran

HpCDF

Heptachlorodibenzofuran

OCDF

Octachlorodibenzofuran

PCB

Polychlorinated biphenyl

TCB

Trichlorobiphenyl

TeCB

Tetrachlorobiphenyl

PeCB

Pentachlorobiphenyl

HxCB

Hexachlorobiphenyl

HpCB

Heptachlorobiphenyl

PTFE

Polytetrafluoroethylene

5 Principle

This Standard is based on the use of the gas chromatography/mass spectrometry combined with the isotope dilution technique to enable the separation, detection and quantification of PCDD/PCDF and DL-PCB in soil, sludge and biowaste. For the isotope dilution method 17 labelled PCDD/F and 12 labelled PCB cleanup standards are used. The extracts for the GC/MS measurements contain one or two recovery standards. The gas chromatographic parameters offer information which enables the identification of isomers (position of Cl substituents) whereas the mass spectrometric parameters enable the differentiation between congeners with different numbers of chlorine substituents and between dibenzo-p-dioxins, furans and PCB.

Soil, sludge or biowaste is sampled according to EN yyyy: (Horizontal standard module(s) for sampling of sludge, soil and waste). $^{13}C_{12}$-labelled PCDD/F and PCB congeners are added prior to extraction and HRGC/HRMS measurement. Losses during extraction and clean-up are detected and compensated by using these added congeners as internal extraction standards for quantification together with recovery standards which are added just before the HRGC/HRMS analysis. For the determination of these substances it is necessary to separate PCBs from PCDDs/PCDFs and vice versa.

The main purpose of the clean-up procedure of the raw sample extract is the removal of sample matrix components, which may overload the separation method, disturb the quantification or otherwise severely impact the performance of the identification and quantification method and the separation of PCDD/F from DL-PCB. Furthermore, an enrichment of the analytes in the final sample extract is achieved. Extraction procedures are normally based on soxhlet or equivalent extraction methods of dried preferable freezedried samples. Sample clean-up is usually carried out by multi-column liquid chromatographic techniques using different adsorbents. The determination of PCDD/F and PCBs is based on quantification by the isotope-dilution technique using HRGC/HRMS.

6 Reagents

6.1 Chemicals:

Solvents used for extraction and clean-up have to be of pesticide grade or equivalent quality and checked for blanks. Adsorbents like alumina oxide, silica gel, celite and ohters used for clean-up have to be of p.a. qualtity or better and precleaned and activated if necessary.

A specific list of solvents and chemicals can be found in the example methods in Annex A

6.2 Standards

^{13}C-spiking solution for PCDD/F (Extraction Standard)

^{13}C-spiking solution for PCB (Extraction Standard)

Calibration solution PCDD/F

Calibration solution PCB

Syringe standard PCDD/F

Syringe standard PCB

An example for concentrations of the above mentioned standard solutions can be found in the example method in Annex A

7 Apparatus and materials

The apparatus and materials listed below are meant as minimum requirements for “conventional” sample treatment with soxhlet extraction and column chromatographic clean-up. Additional apparatus and materials may be necessary due to different methods of sample extraction and clean-up methods.

7.1 Equipment for sample preparation

Laboratory fume hood, of sufficient size to contain the sample preparation equipment listed below.

Desiccator

Balances, consisting of an analytical type capable of weighing 0,1 mg and a top-loading type capable of weighing 10 mg.

7.2 Extraction apparatus

Soxhlet extractor consisting of:

a) Soxhlet, 50 mm ID, 200 ml capacity with 500 ml round bottom flask;

b) thimble, 43 x 123 to fit Soxhlet;

c) hemispherical heating mantle, to fit 500 ml round-bottom flask.

7.3 Clean-up apparatus

Disposable pipettes, either disposable Pasteur pipettes, or disposable serological pipettes

Glass chromatographic columns of the following sizes:

150 mm long x 8-mm ID, with coarse-glass frit or glass-wool plug and 250 ml reservoir;

200 mm long x 15 mm ID, with coarse-glass frit or glass-wool plug and 250 ml reservoir;

300 mm long x 25 mm ID, with 300 ml reservoir and glass or fluoropolymer stopcock.

Oven, capable of maintaining a constant temperature (± 5 °C) in the range of 105°C to 250 °C for baking and storage of adsorbents.

7.4 Concentration Apparatus

Rotary evaporator, equipped with a variable temperature water bath and:

a) vacuum source for rotary evaporator equipped with shutoff valve at the evaporator and vacuum gauge;

b) recirculating water pump and chiller (use of tap water for cooling the evaporator wastes large volumes of water and can lead to inconsistent performance as water temperatures and pressures vary);

c) round-bottom flask, 100 ml and 500 ml or larger, with ground-glass fitting compatible with the rotary evaporator.

Nitrogen blowdown apparatus, equipped with water bath controlled in the range of 30°C to 60 °C, installed in a fume hood.

Sample vials, of the following types:

a) amber glass 2 ml to 5 ml with fluoropolymer-lined screw-cap;

b) glass, 0.3 ml, conical, with fluoropolymer-lined screw or crimp cap.

7.5 Other equipment

Gas chromatograph, with a splitless or on-column injection port for capillary column, temperature program with isothermal hold.

GC column for PCDDs/PCDFs and for isomer specificity for 2,3,7,8-TCDD (e.g., 60 m long x 0,32 mm ID; 0,25 µm; 5 % phenyl, 94 % methyl, 1 % vinyl silicone bonded-phase fused-silica capillary column).

Mass spectrometer, 28 eV to 80 eV electron impact ionization, capable of repetitively selectively monitoring 12 exact masses minimum at high resolution (>6000) during a period of approximately one second.

The mass spectrometer (MS) shall be interfaced to the GC such that the end of the capillary column terminates within 1 cm of the ion source but does not intercept the electron or ion beams.

Data system, capable of collecting, recording, and storing MS data.

8 Sampling and sample pre-treatment

8.1 Sampling

Sampling should be carried out in accordance with EN yyyy: (Horizontal standard module(s) for sampling of sludge, soil and waste). See Annex A for the specific information assuring the coherence and linkage between the different steps of measurement.

In addition to this standard the following requirements apply. Samples should be stored in suitable containers with an appropriate closure material such as PTFE. Samples to be frozen may be stored in aluminium containers pre-cleaned by heating to 450°C for minimum 4 hours or by rinsing with a non-chlorinated solvent.

Samples should be kept cold (< 8°C) and in the dark. The sample pre-treatment should take place within 24 hours of sampling. Alternatively, samples may be frozen (-18 °C) directly after sampling and kept frozen for a maximum of one month before sample pre-treatment.

8.2 Sample pre-treatment

Drying and homogenization should be carried out according to EN wwww: (Horizontal standard module(s) for pre-treatment of solid materials

Store the ground material in a desiccator or a tightly closed glass container.

9 Extraction and Clean-up

9.1 General

The determination of PCDDs/PCDFs is based on quantification by the isotope-dilution technique using HRGC/HRMS. $^{13}C_{12}$-labelled 2,3,7,8-chlorine substituted PCDD/PCDF congeners are added at different stages of the whole method. Losses during extraction and clean-up can be detected and compensated by using these added congeners as internal standards for quantification together with recovery standards which are added just before the HRGC/HRMS analysis. However, due to possible differences in the binding and adsorption characteristics between the native PCDDs/PCDFs and the $^{13}C_{12}$-labelled congeners, which are added during analysis, complete substantiation of the extraction efficiency and compensation of losses during clean-up is not guaranteed. Therefore, in addition the applied methods have to be validated thoroughly. Examples of well-proven extraction and clean-up methods are given in Annex A.
The main purpose of the clean-up procedure of the raw sample extract is the removal of sample matrix components, which may overload the separation method, disturb the quantification or otherwise severely impact the performance of the identification and quantification method and to separate DL-PCB from PCDD/F. Furthermore, an enrichment of the analytes in the final sample extract is achieved. Extraction procedures are normally based on soxhlet extraction of the <2mm fraction of the dry and sieved solid sample. Sample clean-up is usually carried out by multi-column liquid chromatographic techniques using different adsorbents.
In principle any clean-up method can be used which recovers the analytes in sufficient quantities. Furthermore, the final sample extract shall not affect adversely the performance of the analytical system or the quantification step. However, all applied methods have to be tested thoroughly and have to pass a set of method validation requirements before they can be employed for emission surveillance. In addition, the verification of the method performance for each single sample has to be part of the applied quality assurance protocol. This Standard describes a framework of method validation and quality control requirements which have to be fulfilled by any applied method.

In the present Standard the minimum requirements for extraction and clean-up to be met are described as well as examples of operation. The analyst may use any of the example procedures below and in Annex A or any suitable alternative procedures.

9.2 Extraction

Sample amount used for extraction may vary from 5 to 50 g depending on the expected level of contamination.

The $^{13}C_{12}$-labelled 2,3,7,8-chlorine substituted congeners listed in Table XX shall be added before extraction.

The extraction procedure is carried out using Soxhlet extraction with toluene for at least 8 hours.

Other methods like pressurized liquid extraction can also be used but shall be of proven equal performance.

9.3 Clean-up

Clean-up methods shall prepare the sample extract in an appropriate manner for the subsequent quantitative determination. Clean-up procedures have to concentrate PCDDs/PCDFs and DL-PCBs in the extracts and to remove interfering matrix components present in the raw extract.

Proven clean-up procedures shall be used containing normally two or more of the following techniques which can be combined in different orders. A detailed description of some of the procedures is given in Annex A.

Other methods can also be used but shall be of proven equal performance as the techniques described below:

9.3.1 Gel permeation chromatography.

The interesting molecular weight range for PCDDs/PCDFs and DL-PCBs of 200 g/mol to 500 g/mol can be isolated from larger molecules and polymers which might overload other clean-up methods.

9.3.2 Multilayer column

Multilayer column liquid chromatography using silica with different activity grades and surface modifications. Compounds with different chemical properties than PCDDs/PCDFs and DL-PCBs can be removed. A direct treatment of the sample extract with sulphuric acid shall be carried out very carefully to avoid losses of PCDDs/PCDFs and DL-PCBs on the formed carboniferous surfaces.

9.3.3 Activated carbon column

Column adsorption chromatography using activated carbon may be used to separate planar PCDD/PCDF and coplanar PCB molecules from monoortho PCB and other interfering non-planar molecules.

9.3.4 Alumina column

Column liquid chromatography on alumina of different activity grade and acidity/basicity.
Interfering compounds with small differences in polarity or structure compared to PCDDs/PCDFs and DL-PCBs can be removed.
Additionally alumina columns can be used to separate PCDDs/PCDFs from DL-PCBs

9.4 Final concentration of cleaned sample extract

To achieve sufficient detection limits, the cleaned sample extract shall be concentrated to a volume in the order of 25 µl to 100 µl before quantification. (Though PCDDs/PCDFs have rather high boiling points (> 320 °C) vapour phase transfer mechanisms and aerosol formation during solvent evaporation might lead to substantial losses when concentrating volumes below 10 ml). Depending on the method to be used for solvent volume reduction the following precautions have to be taken into consideration:

a) Rotary evaporators

Losses might be substantial when reducing solvent volumes below 10 ml. Counter measures are the use of controlled vacuum conditions according to the vapour pressure and boiling point of the solvent, addition of a high-boiling solvent as a keeper as well as the use of specially shaped vessels (e.g. V-shaped).

b) Counter gas flow evaporators (e.g. TurboVap®)

Volumes should not be reduced to less than 1 ml.

c) Nitrogen flow

An excessive flow of nitrogen which disturbs the solvent surface should be avoided. The vial shape has also some influence on possible losses. V-shaped vials or vial inserts shall be used for volume reductions below around 200 µl.

9.5 Addition of syringe standard

The very last step before quantification is the addition of the syringe standards to measure the recovery rates of the extraction standards. The syringe standards according shall be added under following conditions:

Syringe standards shall be added just prior to the quantification procedure. Samples with the recovery standard added which could not be analysed due to operational reasons (instrument failure), should be stored as briefly as possible and any further uncontrolled solvent evaporation shall be avoided.

Syringe standards shall be added after the final volume reduction. Any further direct volume reduction shall be avoided. A slow evaporation at room temperature from the open sample vial to a volume of about 25 µl is acceptable.

10 HRGC/HRMS analysis

10.1 Equipment

GC/MS analyses of PCDDs/PCDFs and DL-PCBs were usually carried out on a high resolution GC/MS instrument equipped with a high resolution gas chromatograph, an autosampler, a high resolution mass spectrometer and a data system for instrument control, data acquisition and processing.

10.2 Gas chromatographic analysis

Gas chromatographic separation has to be carried out in such a way, that sufficient separation of all PCDD/F and DL-PCB congeners is achieved.

For PCDD/F there is no capillary column available at present, which allows the separation of all 2,3,7,8-substituted congeners from all other non-2,3,7,8-substituted congeners. Complete separation can only be achieved by analysing a sample on different capillary columns of different polarity.

For DL-PCB analysis similar problems exist for the separation of all coplanar and monoortho congeners. There is no column available at present, which is able to separate all 12 DL-PCB congeners from all other non DL-PCB congeners.

The following conditions can be used as a starting point for optimizing a method. With the given specifications the complete separation of all 2,3,7,8-substituted PCDD/F congeners can be achieved. For DL-PCB the sufficient separation of all congeners of interest except for PCB-123 can be achieved. Different columns and parameters can be used if all quality requirements are fulfilled.

Injector temperature:

Split/splitless: 270 °C to 320 °C

PTV: 40 °C, Injection

2 °C/s to 60 °C

60 °C, 90s, solvent vent

12 °C/s to 320 °C

320 °C, 10min

Separation columns:

a) Total PCDDs/PCDFs and DL-PCBs:

DB-5 [1)] fused silica capillary column, length 60 m x 0,25 mm inner diameter with a film thickness of 0,25 µm.

b) Isomer specific PCDD/PCDF analysis:

DBDIOXIN [1)] fused silica capillary column, length 60 m x 0,25 mm inner diameter with a film thickness of 0,25 µm.

Oven temperature programmes:

PCDD/F:

DB5: 60 °C, 5 min

20 °C/min to 200 °C

1 °C/min to 220 °C

220 °C, 16min

3 °C/min to 320 °C

320 °C, 3 to 10min (depending on matrix load)

DBDIOXIN: 60 °C, 5 min

20 °C/min to 220 °C

220 °C, 40min

5 °C/min to 270 °C

270 °C, 57min

DL-PCB:

DB5: 60 °C, 5 min

20 °C/min to 190 °C

1 °C/min to 220 °C

220 °C, 16min

3 °C/min to 300 °C

300 °C, 3 to 10min (depending on matrix load)

Carrier gas: Helium, 1.7 ml/min, „constant flow“

MS-Interface temperature: 270 °C (DBDIOXIN), 320 °C (DB5)

NOTE: Fused silica capillary columns DB-5 and DBDIOXIN are trade-names of products supplied by J&W, USA. This information is given for the convenience of users of this Standard and does not constitute an endorsement by CEN of the product named. Equivalent products may be used if they can be shown to lead to the same results.

10.3 Mass spectrometric detection:

A high resolution mass spectrometer at a resolution of 9000 to 11000 is used for the detection of PCDD/F and PCB. This allows the use of $^{13}C_{12}$-labelled congeners as extraction standards for all 17 PCDD/F congeners and 12 DL-PCB congeners of interest. A mass resolution of 6000 to 9000 is possible if any interferences are absent.

The mass spectrometer is used in the MID-Mode (Multiple Ion Detection), the GC column is directly coupled to the MS. The Ion source temperature should be between 250 °C to 270 °C depending on type of instrument. To achieve appropriate sensitivity the detection capability should be at least 200 fg for 2,3,7,8-TCDD.

For identification and quantification the masses given in the following table have to be recorded in MID mode. For each PCDD/F or PCB congener of interest at least two ions of the molecular isotope cluster have to be recorded for both the native and the added $^{13}C_{12}$-labelled congeners.

In addition masses for quality control of the mass calibration have to be measured depending on the type of instrument, e.g. lock mass, calibration mass, lock mass check, etc.

The time slots for the MID windows have to be defined by a calibration standard in a way that all congeners of interest elute within the related MID-window. In the case the sum of the concentrations of isomer groups are needed the retention time window for all isomers of an isomer group have to be defined by measuring a standard mixture containing the first and last eluting isomers of each isomer group corresponding to the used GC column. As an alternative a fly ash extract or any other solution containing all native PCDD/F congeners can be used.

	Dibenzofurans		Dibenzo-p-dioxins	
	^{12}C	^{13}C	^{12}C	^{13}C
MID-Window 1 (Tetras)	303.9016	315.9419	319.8965	331.9368
	305.8987	317.9389	321.8937	333.9339
MID-Window 2 (Pentas)	339.8598	351.9000	355.8547	367.8949
	341.8569	353.8970	357.8518	369.8919
MID-Window 3 (Hexas)	373.8208	385.8610	389.8157	401.8559
	375.8179	387.8580	391.8128	403.8529
MID-Window 4 (Heptas)	407.7818	419.8220	423.7767	435.8169
	409.7789	421.8190	425.7738	437.8140
MID-Window 5 (Octas)	441.7428	453.7830	457.7377	469.7779
	443.7399	455.7801	459.7348	471.7750

Table 1 Masses for the detection of PCDD/F

	Homolog groups	^{12}C	^{13}C
MID-Window 1	Trichloro-PCB	255,9613	268,0016
		257,9584	269,9986
	Tetrachloro-PCB	289,9223	301,9626
		291,9194	303,9597
MID-Window 2	Tetrachloro-PCB	289,9223	301,9626
		291,9194	303,9597
	Pentachloro-PCB	325,8804	337,9207
		327,8775	339,9177
MID-Window 3	Pentachloro-PCB	325,8804	337,9207
		327,8775	339,9177
	Hexachloro-PCB	359,8415	371,8817
		361,8385	373,8788
MID-Window 4	Hexachloro-PCB	359,8415	371,8817
		361,8385	373,8788
	Heptachloro-PCB	393,8025	405,8427
		395,7995	407,8398
MID-Window 5	Heptachloro-PCB	393,8025	405,8427
		395,7995	407,8398
	Octachloro-PCB	427,7635	439,8038
		429,7606	441,8008
MID-Window 6	Octachloro-PCB	427,7635	439,8038
		429,7606	441,8008
	Nonachloro-PCB	461,7245	473,7648
		463,7216	475,7618
MID-Window 7	Decachloro-PCB	497,6826	509,7229
		499,6797	511,7199

Table 2 MID - Masses for the detection of PCB

10.4 Minimum requirements for identification of PCDF/PCDD and PCB

a) The isotope ratio between the two ions of the molecular isotope cluster which are recorded shall match the theoretical value within ± 15 % (see table 3).

	Isotope Ratio	**Isotope Ratio theoratical value**	**Isotope Ratio**

	Lower Limit	theoratical value	Upper Limit
TCDD/F	0,65	0,77 (M/M+2)	0,88
PeCDD/F	0,55	0,64 (M+4/M+2)	0,75
HxCDD/F	0,69	0,81 (M+4/M+2)	0,94
HpCDD/F	0,83	0,96 (M+4/M+2)	1,13
OCDD/F	0,74	0,89 (M+2/M+4)	1,009

Table 3 Limits of isotope ratios

b) The retention time of a native 2,3,7,8-chlorine substituted isomer (Cl_4-Cl_6-congeners) shall be within a time window of +3 s to -3 s based on the retention time of the corresponding $^{13}C_{12}$-labelled isomer in the sample. For the identification of low concentrations (S/N<10) a time window of ±10 s is acceptable. Alternatively, relative retention times based on the injection standard ($^{13}C_{12}$-1,2,3,4-TCDF) can be calculated. The difference shall not be more than 0,3 % compared with the calibration standard.

c) The signal-to-noise ratio of the raw data shall be at least 3:1 for the signal used for identification. The base line noise shall be measured in front of the signal of the native congener within a signal-free window corresponding to 10 times the signal width at half height. Peak-to-peak values are taken.

10.5 Minimum requirements for quantification of PCDF/PCDD and PCB

a) For PCDD/F analysis there is no chromatographic column available at present, that is able to separate all 2,3,7,8-chlorine substituted congeners from all other, non-2,3,7,8-chlorine substituted congeners. Complete separation can only be achieved by multi-analysis of the sample on different columns of different nature (polarity).
Single column data may therefore be reported by this method, however in cases where a regulatory limit is exceeded or congener specific data are needed, a confirmatory analysis should be performed on a second column.

For DL-PCB analysis similar problems exist for the separation of all coplanar and monoortho congeners. There is no column available at present, which is able to separate all 12 DL-PCB congeners from all other non DL-PCB congeners. The use of one weak polar column (e.g. DB-5) is the common technique. The separation of congener PCB-123 is the crucial point of the gas chromatographic separation. But due to the minor contribution to the overall TEQ this leads to an inessential increase of the uncertainty of the method.

b) The peak shape of the gas chromatographic signal of a congener shall contain ten or more sampling points (scanning units).

c) 2,3,7,8-TCDD shall be separated from all other interfering isomers within a 25 % valley below the top of the minor peak with respect to the height of that peak.

d) The recovery rate of each individual 2,3,7,8-chlorine substituted PCDD/PCDF of the extraction standards in each sample shall be within:

1) 50 % to 130 % for the tetra- to hexa-chlorinated congeners
2) 40 % to 130 % for the hepta- and octa-chlorinated congeners.

If the above ranges are exceeded for one or more congeners, then the ranges given below are

acceptable for congeners with recoveries not within these ranges, if the sum of the concentrations of those congeners contribute less than 10 % to the total TEQ in the sample.

3) 30 % to 150 % for the tetra- to hexa-chlorinated congeners
4) 20 % to 150 % for the hepta- and octa-chlorinated congeners.

e) The signal-to-noise ratio of the signal of the $^{13}C_{12}$-labelled congeners used for quantification shall be > 20 : 1.

f) The measuring range shall be linear (at least over a concentration range of a factor of a 100). The standard deviation of the relative response factor shall not exceed 15 % and shall be based on a minimum of five measuring points over the whole range.

10.6 Calibration of the HRGC/HRMS

10.6.1 General

The calibration is carried out with at least five calibration solutions. These solutions contain all native congeners of interest in different precisely defined amounts and all $^{13}C_{12}$-labelled standards (extraction and recovery standards) in the same concentrations as expected in the spiked sample solutions assuming 100 % recovery. The calibration range should encompass the concentrations of the sample.

10.6.2 Calibration for 2,3,7,8-congeners

The calibration curve is used to calculate the relative response factors for each congener of interest. The relative response factors are used together with the $^{13}C_{12}$-labelled congeners added to the sample to quantify the mass of the native congeners of interest by the isotope dilution method.

Calibration frequency depends on the stability of the instrument. Daily calibration checks shall be run. In addition a full calibration shall be repeated after major changes such as:

a) use of new or repaired equipment

b) replacement of GC columns

c) after cleaning of the separation and detection systems

d) if the deviation of an injected calibration standard exceeds 20 %.

The relative response factor for congener i is defined and calculated as follows:

$$rrf_i = \frac{A_{i[^{12}C]}}{A_{i[^{13}C]}} * \frac{c_{i[^{13}C]}}{c_{i[^{12}C]}}$$

where:

rrfi is the relative response factor of native congener i relative to $^{13}C_{12}$-labelled congener i

$A_{i[^{12}C]}$ is the area of native congener i

$A_{i[^{13}C]}$ is the area of $^{13}C_{12}$-labelled congener i

$c_{i[^{12}C]}$ is the concentration of native congener i in the calibration solution

$c_{i[^{13}C]}$ is the concentration of $^{13}C_{12}$-labelled congener i in the calibration solution

10.6.3 Calibration for sum of homologue groups

The calibration of the MS is done in the same way and with the same calibration solutions than for single congeners. The relative response factors for each homologue group is calculated by addition of all peak areas of all native congeners of the same homologue group which are included in the calibration solution relative to one $^{13}C_{12}$-labelled congener. The following table 4 shows the relations between native congenes and $^{13}C_{12}$-labelled congeners.

	Calibration of PCDD-Homologues		Calibration of PCDF-Homologues	
Parameter	**native Isomere**	**^{13}C-Isomer**	**native Isomere**	**^{13}C-Isomer**
Tetrachlorohomologues	2,3,7,8	2,3,7,8	2,3,7,8	2,3,7,8
Pentachlorohomologues	1,2,3,7,8	1,2,3,7,8	1,2,3,7,8 2,3,4,7,8	1,2,3,7,8
Hexachlorohomologues	1,2,3,4,7,8 1,2,3,6,7,8 1,2,3,7,8,9	1,2,3,7,8,9	1,2,3,4,7,8 1,2,3,6,7,8 1,2,3,7,8,9 2,3,4,6,7,8	2,3,4,6,7,8
Heptachlorohomologues	1,2,3,4,6,7,8	1,2,3,4,6,7,8	1,2,3,4,6,7,8 1,2,3,4,7,8,9	1,2,3,4,6,7,8

Table 4 Relations for Calibration of Homologuegroups

10.7 Quantification of HRGC/HRMS results

10.7.1 Quantification of concentrations of 2,3,7,8-congeners

The concentration of congener i in the sample is calculated as follows:

$$c_{i[^{12}C]} = \frac{A_{i[^{12}C]}}{A_{i[^{13}C]}} * \frac{c_{i[^{13}C]}}{rrf_i}$$

where:

rrfi is the relative response factor of native congener i relative to $^{13}C_{12}$-labelled congener i

$A_{i[^{12}C]}$ is the area of native congener i

$A_{i[^{13}C]}$ is the area of $^{13}C_{12}$-labelled congener i

$c_{i[^{12}C]}$ is the concentration of native congener i in the sample

$c_{i[^{13}C]}$ is the concentration of $^{13}C_{12}$-labelled congener i in the sample

The concentrations of all congeners of interest in the samples shall be within the linear range of the method. High concentrations of native congeners will cause overlapping in the mass window between high isotopic ions (i.e. M+12, M+14) of the native congeners with the lower isotopic ions (M, M+2) of the $^{13}C_{12}$-labelled standards especially for higher chlorinated congeners. This will result in a significant deviation from linearity beyond a mass ratio of 10. An overestimation of the recovery rate and an underestimation of the amount of the native congener caused by this should be avoided

10.7.2 Quantification of recovery rates of ^{13}C-labeled standards

The extraction standards are quantified against the recovery standard.

$$R_i = \frac{A_{i[E]}}{A_{[R]}} * \frac{c_{[R]}}{rrf_i} * \frac{100}{c_{i[E]}}$$

where:

R_i is the recovery rate of the extraction standard in percent

rrfi is the relative response factor of extraction standard i relative to $^{13}C_{12}$-labelled recovery standard

$A_{[R]}$ is the area of the recovery standard

$A_{i[E]}$ is the area of extraction standard i

$c_{[R]}$ is the concentration of the recovery standard

$c_{i[E]}$ is the concentration of extraction standard i

10.7.3 Quantification of sum of homologue groups

The sum of concentrations of all congeners of a homologue group in the sample is calculated as follows:

$$c_{h[^{12}C]} = \frac{\Sigma A_{i[^{12}C]}}{A_{i[^{13}C]}} * \frac{c_{i[^{13}C]}}{rrf_i}$$

where:

rrfi is the relative response factor of native congener i relative to $^{13}C_{12}$-labelled congener i

$\Sigma A_{i[^{12}C]}$ is the sum of areas of all native congeners of a hmologue group

$A_{i[^{13}C]}$ is the area of $^{13}C_{12}$-labelled congener i

$c_{h[^{12}C]}$ is the sum of concentrations of all native congeners of a homologue group in the sample

$c_{i[^{13}C]}$ is the concentration of $^{13}C_{12}$-labelled congener i in the sample

10.7.4 Calculation of the Toxic Equivalent

The total TEQ concentration of PCDD/F is calculated by the addition of the concentrations of the 17 individual 2,3,7,8-chlorine substituted PCDD/Fs multiplied by the appropriate TEF.

The total TEQ concentration of DL-PCB is calculated by the additioin of the concentrations of the 12 individual coplanar and monoortho PCB congeners multiplied by the appropriate TEF.

$$TEQ = \Sigma (c_{i[^{12}C]} * TEF_i)$$

where:

TEQ.....is the sum of the concentrations of all individual congeners of interest multiplied by the appropriate toxic equivalency factor

$c_{i[^{12}C]}$...is the concentration of native congener i in the sample

$TEF_{i.....}$ is the toxic equivalency factor of congener I

For PCDD/Fs currently two different TEF-concepts are in use. The first one the I-TEF concept was created by NATO-CCMS in 1988 and the second one the WHO-TEF concept was published in 1998 by WHO. For DL-PCBs only the WHO-TEF concept includes toxic equivalency factors. The TEF values for both schmese are given in table

CONGENER	TEF WHO_{Humans}	I-TEF Nato-CCMS
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	**1**	**0.5**
1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	**0.0001**	**0.001**
2,3,7,8-TCDF	0.1	0.1
1,2,3,7,8-PeCDF	0.05	0.05
2,3,4,7,8-PeCDF	0.5	0.5
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01
OCDF	**0.0001**	**0.001**
3,4,4',5-TCB (81)	**0.0001**	---
3,3',4,4'-TCB (77)	**0.0001**	---
3,3',4,4',5-PeCB (126)	**0.1**	---
3,3',4,4',5,5'-HxCB (169)	**0.01**	---
2,3,3',4,4'-PeCB (105)	**0.0001**	---
2,3,4,4',5-PeCB (114)	**0.0005**	---
2,3',4,4',5-PeCB (118)	**0.0001**	---
2',3,4,4',5-PeCB (123)	**0.0001**	---
2,3,3',4,4',5-HxCB (156)	**0.0005**	---
2,3,3',4,4',5'-HxCB (157)	**0.0005**	---
2,3',4,4',5,5'-HxCB (167)	**0.00001**	---
2,3,3',4,4',5,5'-HpCB (189)	**0.0001**	---

Table 5 TEF values 2,3,7,8 PCDD/F congeners and dioxin-like PCB congeneres according I-TEF and WHO scheme

11 Test report

The test report shall contain the following information:

a) a reference to this European Standard including its date of publication;

b) sampling report including precise identification of the sample;

c) pre-treatment report

d) The analytical results should contain the levels of the individual PCDD/F and PCB congeners

e) The report should include a short description of the method used for extraction and sample clean-up.

f) The recoveries of the individual internal standards must be made available

g) any deviation from this standard, and any facts which may have influenced the result. Where the test is not carried out in accordance with this standard, reference may only be made to EN xxxx in the report in case all deviations from the procedures prescribed in this standard are indicated in the report stating the reason for deviation.

Annex A
(informative)

Examples of operation of extraction and clean-up methods

A.1 Example A (Umweltbundesamt GmbH)

A.1.1 General

This method is applicable for the determination of PCDD/F and DL-PCB in dry solid samples with particle size of <2mm.

Sample volumes used for analysis have to be adapted in such a way that the expected amount of analyte lies between detection limit and upper end of calibration range. Samples exceeding the upper limit of the calibration range have to be repeated with smaller amounts of sample.

The described method is also applicable for the determination of PCDD/ or PCBs solely. In this case clean-up steps can be reduced accordingly.

A.1.1.1 Chemicals

Aceton

Benzol

Celite 545 Roth 0011.1

Dichloromethane

Ethanol absolut, p.A.

Extraction thimbles, pure cellulose

Glasballs, 5 mm LG 9.012.405

n-Hexan

Basic alumina

Silica gel 63-200 mesh, activ

Sodiumchloride, p.A.

Sodiumsulfate, p.A.

Sodium hydroxide solution, 1N

Sulfuric acid, p.A. 95-97 %

Seasand, p.A.

Toluene

A.1.2 Procedure

A.1.2.1 Spiking of the sample

Weigh an exact amount of 10g to 25g (+/-0,1g) of the freeze-dried and grounded clearing sludge or compost sample into an Erlenmeyer flask with a ground neck.

The sample will be spiked with 100µl of ^{13}C-solution “sewage sludge” and 100µl of ^{13}C-solution “WHO” (PCB). The compositions of these spiking solutions are listed in the following tables.

After spiking close the flask and agitate the sample for 1h using a mechanical shaker.

^{13}C- spiking solution „sewage sludge“	
	pg /100 µl
2378-$^{13}C_{12}$-TCDD	20
12378-$^{13}C_{12}$-PeCDD	40
123478-$^{13}C_{12}$-HxCDD	40
123678-$^{13}C_{12}$-HxCDD	140
123789-$^{13}C_{12}$-HxCDD	80
1234678-$^{13}C_{12}$-HpCDD	2500
$^{13}C_{12}$-OCDD	8500
2378-$^{13}C_{12}$-TCDF	60
12378-$^{13}C_{12}$-PeCDF	40
23478-$^{13}C_{12}$-PeCDF	40
123478-$^{13}C_{12}$-HxCDF	40
123678-$^{13}C_{12}$-HxCDF	40
234678-$^{13}C_{12}$-HxCDF	80
123789-$^{13}C_{12}$-HxCDF	20
1234678-$^{13}C_{12}$-HpCDF	500
1234789-$^{13}C_{12}$-HpCDF	40
$^{13}C_{12}$-OCDF	800

Table1: spiking solution „sewage sludge“

^{13}C-spiking solution„WHO“	
	pg /100 µl
$^{13}C_{12}$-PCB - 77	500
$^{13}C_{12}$-PCB - 81	500
$^{13}C_{12}$-PCB - 126	500
$^{13}C_{12}$-PCB - 169	500
$^{13}C_{12}$-PCB - 105	1000
$^{13}C_{12}$-PCB - 114	1000
$^{13}C_{12}$-PCB - 118	1000
$^{13}C_{12}$-PCB - 123	1000
$^{13}C_{12}$-PCB - 156	1000
$^{13}C_{12}$-PCB - 157	1000
$^{13}C_{12}$-PCB - 167	1000
$^{13}C_{12}$-PCB - 189	1000

Table2: spiking solution „WHO“

A.1.2.2 Extraction

Depending on sample volume use 150ml or 250ml soxhlet devices for extraction.

The right size of core is needed consisting of cellulose (33x130mm for 150ml adaptor and 33x205mm for 250ml adaptor).

The core will be set in a right dimensioned beaker.

The spiked and homogenised sample of clearing sludge or compost is filled into the core and some flask resisting particles will be flushed with a small amount of toluene and also put into the core. Flushing the flask will be repeated 3 times.

Afterwards the core will be closed with some cellulose drapery and fibreglass and put into the glass adaptor. Some resisting toluene in the beaker will be also flushed and filled into the glass adaptor.

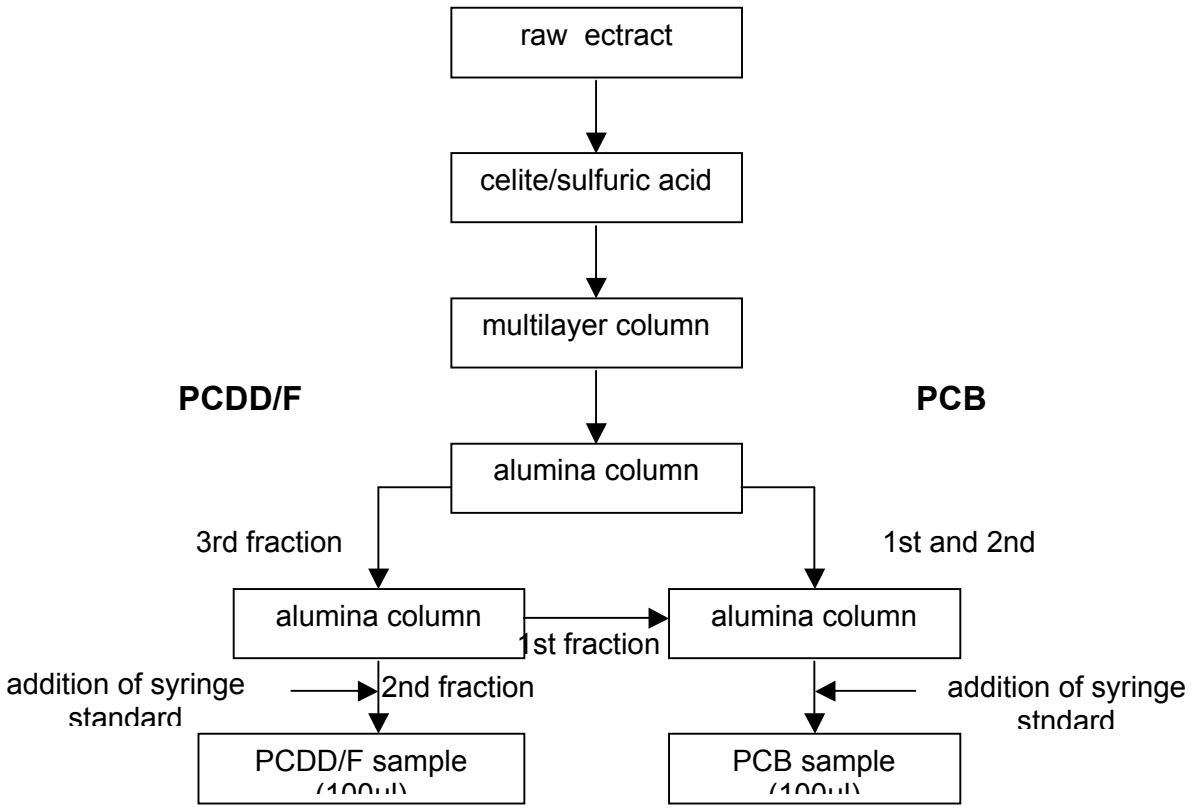
Now the glass adaptor is set on the right 500ml round bottomed flask filled with some zeolite and the whole equipment in set in a heater rounded by a isolation cover.

Now the adaptor is filled with toluene until all is flooding.

After completely running into the

A.1.2.3 Clean up

A.1.2.3.1 Schematics of Clean-up procedure



A.1.2.3.2 Preparation of adsorbents

A.1.2.3.2.1 Celite/sulphuric acid (1/1)

For preparing 200g clean-up material weigh 100g of celite and the same amount of sulphuric acid into a conical flask of 1000ml volume. Close the flask and shake briefly by hand until everything is mixed up steady.

Afterwards extract it for 1h using mechanical shaking.

For keeping leave it in closed position.

For preparing big amounts watch out for undersized conical flasks because of optimal stirring.

A.1.2.3.2.2 silica gel/ sulphuric acid (44%)

For preparing 100g clean-up material weigh 56g silica gel and 46g sulphuric acid (95-97%) into a conical flask, close it and extract it for 1h using mechanical shaking.

A.1.2.3.2.3 silica gel/ sodium hydroxide (33%)

For preparing 100g clean-up material weigh 67g silica gel and 33g 1N sodium hydroxide into a conical flask , close it and extract it for 1h using mechanical shaking.

A.1.2.3.3 Preparation of the clean-up columns

A.1.2.3.3.1 Celite-column

The column consisting of glass (20mm diameter, 300mm length, glasfrit, 250ml reservoir) is filled with (top down):

5g silica gel

30g celite/sulphuric acid (1/1)

5g silica gel

The column will be conditioned with 70ml of n-Hexane/Dichloromethane (80/20). Add the sample to the column and after infiltration, rinse the flask, where the sample was kept with a small amount of n-hexane and add this too.

Repeat the washing for 3 times and elute the sample with 200ml of n-hexane.

The eluate will be concentrated on a rotating evaporator at 40-50°C under vacuum down to app. 5ml.

A.1.2.3.3.2 multilayer column

The column consisting of glass (20mm diameter, 300mm length, glasfrit, 250ml reservoir) is filled with (top down):

2g silica gel

5g silica gel/ sodium hydroxide (33% 1N)

2g silica gel

10g silica gel/ sulphuric acid (44%,conc.)

2g silica gel

10g anhydrous sodium sulphate

The column will be conditioned with 150ml of n-Hexane. Add the sample to the column and after infiltration, rinse the flask, where the sample was kept with a small amount of n-hexane and add this too.

Repeat the washing for 3 times and elute the sample with 250ml of n-hexane.

The eluate will be concentrated on a rotating evaporator at 40-50°C under vacuum down to app. 5ml.

A.1.2.3.3.3 large aluminium oxide column

The column consisting of glass (20mm diameter, 300mm length, glasfrit, 250ml reservoir) is filled with (top down):

25g basic aluminium oxide

20g anhydrous sodium sulphate

The column will be conditioned with 150ml of n-Hexane. Add the sample to the column and after infiltration, rinse the flask, where the sample was kept with a small amount of benzene and add this too.

.

Repeat the washing for 3 times.

Elute the sample with:

80ml of benzene

20ml n-hexane/Dichloromethane (98/2)

150ml n-hexane/Dichloromethane (1/1)

The first and second fraction contains the PCBs, whereas the third fraction contains the PCDD/F. The Eluates will be concentrated on a rotating evaporator at 40-50°C under vacuum down to app. 5ml.

A.1.2.3.3.4 small aluminium oxide column

The column consisting of glass (7mm diameter, 180mm length, glasfrit, 50ml reservoir) is filled with (top down):

2,5g basic aluminium oxide

2g anhydrous sodium sulphate

The column will be conditioned with 40ml of n-Hexane. Add the sample (3rd fraction of A.1.2.3.3.3) to the column and after infiltration, rinse the flask, where the sample was kept with a small amount of n-hexane/Dichloromethane (98/2) and add this too

Repeat the washing for 3 times. Eluting of column with: it

-40ml of n-hexane/Dichloromethane (98/2)

-25ml n-hexane/Dichloromethane (1/1)

The first fraction contains PCB and is combined with the first and second fraction of A.1.2.3.3.3. The combined eluates are concentrated on a rotating evaporator at 40-50°C under vacuum down to app. 5ml.

The second fraction contains PCDD/F and will be concentrated on a rotating evaporator at 40-50°C under vacuum down to app. 5ml

A.1.2.3.4 Midi aluminium oxide column

The column consisting of glass (14mm diameter, 250mm length, glasfrit, 50ml reservoir) is filled with (top down):

6g basic aluminium oxide

4g anhydrous sodium sulphate

The column will be conditioned with 60ml of n-Hexane. Add the sample (combined PCB eluates from of A.1.2.3.3.4) to the column and after infiltration, rinse the flask, where the sample was kept with a small amount of n-hexane and add this too.

Repeat the washing for 3 times. Eluting of column with: it too.

-60ml of n-hexane

-40ml n-hexane/Dichloromethane (7/3)

The second fraction contains PCB and will be concentrated on a rotating evaporator at 40-50°C under vacuum down to app. 5ml.

A.1.2.4 Preparation of sample solution for measurement

A.1.2.4.1 PCDD/F

The concentrated eluate from the clean-up procedure, see schematics, is quantitatively transferred to a graduated conical vial (e.g. Suppelco Receiving Vessel Cat.No. 64723). Rinse the larger vial with toluene and add the rinse to the conical vial.. Concentrate the sample by applying a gentle N_2-stream down to 100 µl and add 25 µl 1,2,3,4-$^{13}C_{12}$-TCDF (concentration = 100 ng/ml). Adjust the endvolume to 100 µl. Transfer the sample to an autosampler vial with conical 100µl insert and seal it with a teflon lined crimp cap. The vial should be labeld with sample ID and type of analyte. The sample can be stored in the dark at room temparature until meaurement. For longer period of time the sample has to be stored in a regrigerator at app +5°C.

A.1.2.4.2 PCB

The concentrated eluate from the clean-up procedure, see schematics, is quantitatively transferred to a graduated conical vial (e.g. Suppelco Receiving Vessel Cat.No. 64723). Rinse the larger vial with toluene and add the rinse to the conical vial.. Concentrate the sample by applying a gentle N_2-stream down to 100 µl and add 25 µl $^{13}C_{12}$-PCB-209 (concentration = 100 ng/ml). Adjust the endvolume to 100 µl. Transfer the sample to an autosampler vial with conical 100µl insert and seal it with a teflon lined crimp cap. The vial should be labeld with sample ID and type of analyte. The sample can be stored in the dark at room temparature until meaurement. For longer period of time the sample has to be stored in a regrigerator at app +5°C.

A.2 Example B to …

The following table gives a non comprehensive list of available international standard methods, which contain descriptions of approved clean-up methods. Due to the modular design of the described methods laboratories may chose an appropriate combination of these clean-up steps according to need of the sample matrix and their available equipment.

Method	Analyte	Matrix	Origin
EN 1948 – 2,3	PCDD/F	Emission	EU
JIS K 0311	PCDD/F coplanar PCBs	Emission	Japan
EPA Method T0 9A	PCDD/F	Ambient Air	USA
EPA Method 1613	PCDD/F	Soil, water, ash, waste, chemical products, food, feeds, biota and other matrices	USA
EPA Method 8280	PCDD/F	Soil, water, ash, waste, chemical product, distillation residue, fuels, sludge	USA
EPA Method 8290	PCDD/F	Soil, water, ash, waste, chemical product, distillation residue, fuels, sludge, biota	USA
EPS 1/RM/19	PCDD/F	Paper industry products	Canada
EPA Method 1668	Coplanar PCBs	Soil, water, sludge, sediment, biota and other samples	USA
Guideline „Determination of Polychlorinated dioxins and Furansin Soil" BUWAL, 2001	PCDD/F	Soil	CH
ISO/DIS 18073	PCDD/F	Water	INT

Annex B
(informative)
Validation

To be undertaken after consultation of draft standard

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EN 1948-2,3: Stationary Source Emissions – Determination of the mass concentration of PCDDs/PCDFs. Part 2: Extraction and clean up, Part 3: Identification and quantification (May 1997)

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