SLOVENSKI STANDARD

SIST-TS CEN/TS 1948-4:2008

01-marec-2008

Emisije nepremiļnih virov - Doloļevanje masne koncentracije PCDD/PCDF in dioksinu podobnih PCB - 4. del: Vzorļenje in analiza dioksinu podobnih PCB

Stationary source emissions - Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs - Part 4: Sampling and analysis of dioxin-like PCBs

Emissionen aus stationären Quellen - Bestimmung der Massenkonzentration von PCDD/PCDF und dioxin-ähnlichen PCB - Teil 4: Probenahme und Analyse dioxin-ähnlicher PCB

Emissions de sources fixes - Détermination de la concentration massique en PCDD/PCDF et PCB de type dioxine - Partie 4 : Prélèvement et analyse de PCB de type dioxine

Ta slovenski standard je istoveten z: **CEN/TS 1948-4:2007**

ICS:

13.040.40

SIST-TS CEN/TS 1948-4:2008 **en,fr,de**

TECHNICAL SPECIFICATION

SPÉCIFICATION TECHNIQUE

TECHNISCHE SPEZIFIKATION

CEN/TS 1948-4

July 2007

ICS 13.040.40

English Version

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This Technical Specification (CEN/TS) was approved by CEN on 16 June 2007 for provisional application.

The period of validity of this CEN/TS is limited initially to three years. After two years the members of CEN will be requested to submit their comments, particularly on the question whether the CEN/TS can be converted into a European Standard.

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Ref. No. CEN/TS 1948-4:2007: E

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Foreword

This document (CEN/TS 1948-4:2007) has been prepared by Technical Committee CEN/TC 264 "Air quality", the secretariat of which is held by DIN.

The European Standard EN 1948:2006 consists of several parts dealing with the determination of the mass concentration of PCDDs, PCDFs and PCBs in stationary source emissions:

Part 1: Sampling of PCDDs/PCDFs

Part 2: Extraction and clean-up of PCDDs/PCDFs

Part 3: Identification and quantification of PCDDs/PCDFs

Part 4: Sampling and analysis of dioxin-like PCBs (Technical Specification CEN/TS)

The first three parts are necessary for the performance of the dioxin measurements. In addition this Technical Specification, CEN/TS 1948-4, describes the sampling, extraction and analyses of dioxin-like PCBs and will be transferred to a European Standard after corresponding validation measurements.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

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Introduction

A group of chlorinated aromatic compounds similar to polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) is known as polychlorinated biphenyls (PCBs) which consists of 209 individual substances (see Figure 1 for the basic structure).

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

PCDD/PCDF as well as PCBs are emitted during thermal processes. PCB can contribute considerably to the total WHO-TEQ as reported for Germany;[1] [2], Great Britain [3], Poland [4], Spain [5], Japan [6]; [7], Korea [8].

In 1997 a group of experts of the World Health Organisation (WHO) defined toxicity equivalent factors (TEFs) for PCDDs/PCDFs and twelve PCBs, known as dioxin-like PCBs [9;10] (see Annex A). These twelve 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, see Figure 1.

This document deals with the determination of these *dioxin-like* PCBs in emissions from stationary sources.

Only skilled operators who are trained in handling highly toxic compounds should apply this document.

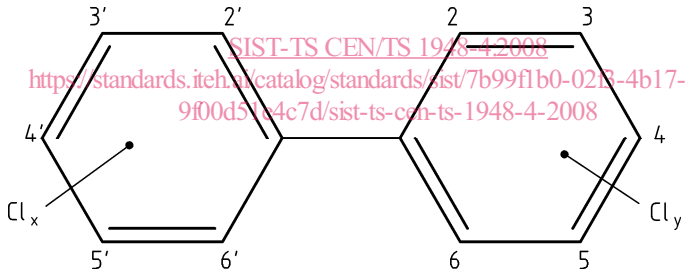

Figure 1 —Structure of PCB

1 Scope

This document specifies sampling from stationary sources, extraction, clean-up, identification and quantification procedures of the dioxin-like PCBs. The procedure described lays down requirements to measure the PCB congeners given in Annex A (see Table A.1). It is applicable to the twelve non- and mono-ortho PCB designated by the WHO. It is optimised to measure PCB concentrations in the range of 0,01 ng WHO-TEQ_{PCB}/m^3.

In addition to the 12 non- and mono-ortho-PCB the present document is also applicable to measure further PCB-congeners like the so-called "marker PCB" 28, 52, 101, 138, 153, 180 (see Annex D).

This document specifies a framework of quality control requirements which have to be fulfilled by any PCB sampling, extraction, clean-up, identification and quantification methods to be applied.

It is assumed that due to their similar chemical behaviour PCBs may be sampled from stationary sources together with the PCDDs/PCDFs by the same methods. The complete sampling procedure is described in the EN 1948-1. Each of the three sampling methods of EN 1948-1 can be combined with the methods described

in this document to complete the measurement procedure. EN 1948-1 is an integral part of the complete measurement procedure and is necessary for the determination of PCBs.

In addition it is possible to measure PCBs together with PCDDs/PCDFs by applying EN 1948 Part 1, Part 2, Part 3 and CEN/TS 1948 Part 4.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 1948-1:2006, *Stationary source emissions - Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs - Part 1: Sampling of PCDDs/PCDFs*

EN 1948-2:2006, *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 1948-3:2006, *Stationary source emissions - Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs - Part 3: Identification and quantification of PCDDs/PCDFs*

EN 13284-1, *Stationary source emissions – Determination of low range mass concentration of dust – Part 1: Manual gravimetric method*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 1948-1:2006, EN 1948-2:2006, EN 1948-3:2006 and the following apply.

3.1
analytical blank value
value determined by a blank sample covering the complete analytical procedure including extraction, clean-up, identification and quantification including all the relevant reagents and materials

3.2
congener
one of the 209 individual PCBs

3.3
dioxin-like PCBs
non- and mono-ortho PCB with an affinity to the Ah-receptor, showing similar toxical effects as the 2,3,7,8-substituted PCDDs/PCDFs according to WHO [**Error! Bookmark not defined.**]

3.4
extraction standard
$^{13}C_{12}$-labelled PCBs, added before extraction and used for calculating results

3.5
field blank value
value determined by a blank sample covering a specific procedure to ensure that no significant contamination has occurred during all steps of measurement and to check that the operator can achieve a quantification level adapted to the task

3.6
I-TEF
international toxic equivalent factor defined by NATO/CCMS in 1988 [11] (for detailed description, see EN 1948-1:2006, Annex A)

3.7
I-TEQ
international toxic equivalent obtained by weighting the mass determined with the corresponding I-TEF (for a detailed description, see EN 1948-1:2006, Annex A)

3.8
isokinetic sampling
sampling at a flow rate such that the velocity and direction of the gas entering the sampling nozzle are the same as the velocity and direction of the gas in the duct at the sampling point

[EN 13284-1:2001, definition 3.5]

3.9
keeper
solvent of high boiling point added to the sampling standard solution

3.10
Limit of detection (LOD)
minimum value of the measurand for which the measuring system is not in the basic state, with a stated probability

NOTE 1 The detection limit, also referred to as capability of detection, is defined by reference to the applicable basic state. But it may be different from "zero", for instance for oxygen measurement as well as when gas chromatographs are used.

[EN ISO 9169:2006, definition 2.2.10 [12]]

NOTE 2 The measurement value can be distinguished from the analytical blank value with a confidence of 99 %. The limit of detection is expressed as the mean analytical blank value (b_{ave}) plus three times the standard deviation of the analytical blank (s_b).

$$LOD = b_{ave} + 3\,s_b \qquad (1)$$

where

LOD is the detection limit;

b_{ave} is the mean analytical blank value;

s_b is standard deviation of the analytical blank.

NOTE 3 In this document the limit of detection should preferably be calculated from the analytical blank b_{ave}. If this is not possible, the limit of detection can be calculated from the signal to noise ratio according to 8.1 of EN 1948-3:2006 (resp. 10.3 of this document).

3.11
limit of quantification (*LOQ*)
limit above which a quantification of the measurand is possible, expressed as the mean analytical blank value plus, either, five to ten times the standard deviation of the analytical blank. The factor F depends to the accepted measurement uncertainty

$$LOQ = b_{ave} + F\,s_b \qquad (2)$$

where

LOQ is the quantification limit;

b_{ave} is the mean analytical blank value;

s_b is standard deviation of the analytical blank

NOTE In this document the limit of quantification should preferably be calculated from the analytical blank b_{ave}. If this is not possible, the limit of quantification can be calculated from the signal to noise ratio according to 8.1 of EN 1948-3:2006 (resp. 10.3 this document) using the requirement of Clause 8.3 e) of EN 1948-3:2006 (resp. 10.4 e) of this document).

3.12
marker PCBs
six PCBs 28, 52, 101, 138, 153, 180

3.13
PCB isomers
PCBs with identical chemical composition but different structure

3.14
PCB profile
graphic presentation of the analysed PCB concentrations

3.15
recovery standard
$^{13}C_{12}$-labelled PCBs, added before injection into the GC

3.16
sampling standard
$^{13}C_{12}$-labelled PCBs, added before sampling

3.17
spiking
addition of $^{13}C_{12}$-labelled PCB standards

3.18
WHO-TEF
toxic equivalent factor proposed by WHO in 1997 **[Error! Bookmark not defined.]** (for detailed description, see Annex A)

3.19
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)

NOTE WHO-TEQ $_{PCB,}$ WHO-TEQ $_{PCDD/PCDF,}$ should be used to distinguish different compound classes.

4 Symbols and abbreviations

4.1 General

HRGC
high resolution gas chromatography

HRMS
high resolution mass spectrometry

I-TEF
international toxic equivalent factor (for detailed description, see Annex A of EN 1948-1:2006)

I-TEQ
international toxic equivalent (for detailed description, see Annex A of EN 1948-1:2006)

LOD
limit of detection

LOQ
limit of quantification

PCBs
polychlorinated biphenyls

PCDDs/PCDFs
polychlorinated dibenzo-p-dioxins/dibenzofurans

PTFE
polytetrafluoroethylene

PU foam
polyurethane foam

TDI
tolerable daily intake

WHO-TEF
toxic equivalent factor of the World Health Organisation

WHO-TEQ
toxic equivalent of the World Health Organisation

4.2 Polychlorinated biphenyls

TriCB
Trichlorobiphenyl

TeCB
Tetrachlorobiphenyl

PeCB
Pentachlorobiphenyl

HxCB
Hexachlorobiphenyl

HpCB
Heptachlorobiphenyl

5 Principle of the measurement procedure

Gas is sampled isokinetically in the duct or stack according to the methods described in EN 1948-1. PCBs in the gas phase and adsorbed on particles are collected in the sampling train together with the PCDDs/PCDFs. Minimum requirements for PCDD/PCDF sampling are described in EN 1948-1 and have also to be met for PCB sampling. There is the choice between three different sampling systems:

— filter/condenser method;

— dilution method;

— cooled probe method.

$^{13}C_{12}$-labelled PCB congeners are added at different stages of the whole method (before sampling, extraction and HRGC/HRMS-measurement). Spiking with $^{13}C_{12}$-labelled PCBs according to 6.2 before sampling is necessary to determine the sampling recovery rate of the PCB congeners. 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 PCBs it is useful to separate them from PCDDs/PCDFs and vice versa (interferences see Annex C).

The main purpose of the clean-up procedure of the raw sample extract is removal of sample matrix components, which can overload the separation method, disturb the quantification or severely impact the performance of the identification and quantification method. Furthermore, enrichment of the analytes in the final sample extract is achieved. Extraction procedures are normally based on soxhlet extraction of filters and adsorbents and liquid extraction of the condensate. Sample clean-up is usually carried out by multi-column liquid chromatographic techniques using different adsorbents.

The method specified in this document is based on using gas chromatography/mass spectrometry combined with the isotope dilution technique to enable the separation, detection and quantification of PCB in the extracts of emission samples. These extracts are prepared in accordance with EN 1948-2 and contain at least one of the recovery standards mentioned in Table 1. The combination of gas chromatography and mass spectrometry enables the differentiation of twelve dioxin-like PCB congeners and marker PCB congeners by either retention time and/or mass.

6 Device, materials and $^{13}C_{12}$-labelled standards

6.1 Device and materials

For determining dioxin-like PCBs in emission samples the same devices and materials for sampling, extraction, clean-up, identification and quantification may be used as for determining PCDDs/PCDFs. For a description, see EN 1948-1, EN 1948-2 and EN 1948-3.

6.2 $^{13}C_{12}$-labelled standards

The sampling standards (see Table 1) shall be added to the different sampling media before sampling and the extraction standards shall be added to the samples after their arrival in the laboratory. These $^{13}C_{12}$-labelled congeners behave in the same way to the native PCBs during sampling and clean-up due to their similar chemical and physical properties. The sampling standards are only used to verify the sampling quality by determining their recovery rates versus extraction standard. The extraction standards are used for quantification. The recovery standards are added just before the injection to measure the recovery rates of the extraction standards. Table 1 shows a selection of available $^{13}C_{12}$-labelled PCBs suitable as recovery standards. At least one shall be added for each dioxin-like PCB containing fraction.

The quantities of the $^{13}C_{12}$-labelled congeners to be added per sample for sampling at a medium PCB concentration level of 0,01 ng WHO-TEQ_{PCB}/m³ and 10 m³ sampling volume (dry gas) are given in Table 1. If a considerably higher or lower mass of native PCBs is expected in the sample, the masses of the $^{13}C_{12}$-labelled standards to be added shall be adapted accordingly.

Table 1 — $^{13}C_{12}$-labelled PCBs congeners to be added to the sample at different stages of the procedure for measurement of about 0,01 ng WHO-TEQ_{PCB}/m^3 assuming 10 m^3 of sampling volume

Solution: Total volume in µl: (eg. toluene, n-nonane)	**Sampling** sampling standard 100	**Extraction** extraction standard 100	**GC Injection** recovery standard *) at least 10
Congeners added	**Total amount in pg added before:**		
$^{13}C_{12}$-2,3,4,4'-TeCB (60)	1 000		
$^{13}C_{12}$-3,3',4,5,5'-PeCB (127) **)	1 000		
$^{13}C_{12}$--2,3,3',4,5,5'-HxCB (159)	1 000		
$^{13}C_{12}$-3,3',4,4'-TeCB (77)		1 000	
$^{13}C_{12}$-3,4,4',5-TeCB (81)		1 000	
$^{13}C_{12}$-2,3,3',4,4'-PeCB (105) **)		1 000	
$^{13}C_{12}$-2,3,4,4',5-PeCB (114)		1 000	
$^{13}C_{12}$-2,3',4,4',5-PeCB (118)		1 000	
$^{13}C_{12}$-2',3,4,4',5-PeCB (123)		1 000	
$^{13}C_{12}$-3,3',4,4',5-PeCB (126)		1 000	
$^{13}C_{12}$-2,3,3',4,4',5-HxCB (156)		1 000	
$^{13}C_{12}$-2,3,3',4,4',5'-HxCB (157)		1 000	
$^{13}C_{12}$-2,3',4,4',5,5'-HxCB (167)		1 000	
$^{13}C_{12}$-3,3',4,4',5,5'-HxCB (169)		1 000	
$^{13}C_{12}$-2,3,3',4,4',5,5'-HpCB (189)		1 000	
$^{13}C_{12}$-2,3',4',5-TeCB (70)			1 000
$^{13}C_{12}$-2,3,3',5,5'-PeCB (111)			1 000
$^{13}C_{12}$-2,2',3,3',4,4',5-HpCB (170)			1 000
Recovery standards: *) Table 1 shows a selection of available $^{13}C_{12}$-labelled PCBs suitable as recovery standards. At least one shall be added for each dioxin-like PCB containing fraction. **Sampling Standards:** **) Attention should be paid to possible co-elution problems of PCB 127 and PCB 105 on certain commercially available columns.			

7 Safety measures

All relevant national safety regulations shall be observed. The dioxin-like PCBs as well as the 2,3,7,8-chlorine substituted PCDDs/PCDFs, which can usually be present in emission samples together with PCBs, are among the most toxic chemicals. All work with PCBs and PCDDs/PCDFs therefore requires the utmost care; the national safety measures which correspond to those for toxic substances should be strictly adhered to.

8 Measurement procedure

8.1 Sampling

Sampling and storing see EN 1948-1.

The sampling train is spiked with $^{13}C_{12}$-labelled PCBs (see Table 1) as described for PCDD/PCDF in EN 1948-1.

During sample storage, the use of screw-caps with PTFE-lined seals is recommended to avoid contamination.

8.2 Extraction

The extraction procedure is carried out using the following materials and techniques. Detailed descriptions of some procedures are given in Annex A of EN 1948-2:2006. Other methods can also be used but shall be of proven equal performance to the techniques below:

a) Pre-treatment of sampled particles with hydrochloric acid shall be part of any extraction procedure (examples of procedures are given in Annex A of EN 1948-2:2006 see also [13]).

b) Particle collecting media (glass fibre filters, thimbles, glass wool etc.): Soxhlet extraction with toluene or a comparable method.

c) Solid adsorbents (Polyurethane foam, XAD-2): Soxhlet extraction for 20 h with toluene or comparable validated method. (Water shall be removed, e.g. via a Dean-Stark water separator or by sodium sulphate.)

d) Aqueous liquids (condensate and bubbler/impinger solution): Liquid/liquid extraction with toluene or dichloromethane. The water/toluene volume ratio should not be greater than 20:1. Three consecutive extractions shall be carried out.

e) Inner surfaces of tubes, vessels or other parts of the sampling device in contact with the sample: Rinsing with a water-miscible solvent (acetone, methanol) followed by toluene. Reflux boiling with toluene is an alternative for the second step.

f) When sampling with flow division is performed, the filter part and the condenser/adsorber part may be analyzed separately. The measured concentrations shall be added at the final stage of calculation.

g) Alternatively an aliquot of the filter extract, corresponding to the proportion of side stream to main stream gas volume, is combined for analysis with the condenser/adsorber part. In this case, the quantity of extraction standard solution added to the filter is increased in proportion to the ratio of main stream to side stream gas volume.

h) If coke or activated carbon is used in the gas cleaning system of the incinerator suitable methods, including freeze drying or Dean-Stark extraction or the addition of water miscible solvents to the extraction medium, shall be taken to remove water. Attention shall be paid to the method validation of this step.

After extraction, the organic solvents containing water shall be dried before the concentration procedure. After combination of all extraction and rinsing solutions any volume reduction shall be carefully carried out to avoid evaporation losses of PCBs. In case evaporation to nearly dryness is necessary, use of a small amount (e.g. 50 µl) of a keeper (usually a high-boiling solvent such as tetradecane) is strongly recommended.

8.3 Clean-up

Clean-up methods shall prepare the sample extract in an appropriate manner for subsequent quantitative determination (see also 8.8). Clean-up procedures have to concentrate PCBs in the extracts and to remove interfering matrix components present in the raw extract.