SLOVENSKI STANDARD
SIST EN 1948-4:2011+A1:2014

01-julij-2014

Nadomešča:
SIST EN 1948-4:2011

Emisije nepremičnih virov - Določevanje masne koncentracije PCDD/PCDF in dioksinom podobnih PCB - 4. del: Vzorčenje in analiza dioksinom podobnih PCB (vključno z dopolnilom A1)

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

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

Ta slovenski standard je istoveten z: **EN 1948-4:2010+A1:2013**

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13.040.40 Emisije nepremičnih virov Stationary source emissions

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

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This European Standard was approved by CEN on 28 August 2010 and includes Amendment 1 approved by CEN on 23 October 2013.

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This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN-CENELEC Management Centre has the same status as the official versions.

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Foreword

This document (EN 1948-4:2010+A1:2013) has been prepared by Technical Committee CEN/TC 264 “Air quality”, the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by June 2014, and conflicting national standards shall be withdrawn at the latest by June 2014.

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.

This document includes Amendment 1 approved by CEN on 21 October 2013.

This document supersedes ⟨A1⟩ EN 1948-4:2010 ⟨A1⟩.

Annex H provides details of significant technical changes between this European Standard and the previous document CEN/TS 1948-4:2007.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association, and supports essential requirements of EU Directive.

For relationship with EU Directive(s), see informative Annex ZA, which is an integral part of this document.

The start and finish of text introduced or altered by amendment is indicated by tags ⟨A1⟩ ⟨A1⟩.

EN 1948 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*

The first three parts are necessary for the performance of the PCDD/PCDF measurements. In addition this document EN 1948-4 describes the sampling, extraction and analyses of dioxin-like PCBs and requires references to EN 1948-1, −2, −3.

The precision and the performance characteristics of the measurement of PCBs were determined between 2006 and 2008 in a comparison and validation trial at both a waste incinerator and a shredder plant sponsored by the European Commission and the European Free Trade Association. The basic requirements of the determination of PCBs were first published as CEN/TS 1948-4, which served as a basis for these mandated validation measurements. This document EN 1948-4 additionally includes important guidance for sampling and analysis over a broad concentration range gained during the mandated validation measurements.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

Introduction

Polychlorinated biphenyls (PCBs) are a group of chlorinated aromatic compounds similar in structure to polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) which consist of 209 individual substances (see Figure 1 for the basic structure).

PCBs have been produced intentionally 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. Worldwide, more than one million tons of PCBs were produced.

PCBs as well as PCDD/PCDF are emitted from thermal and other processes. PCB can contribute 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 12 PCBs, known as dioxin-like PCBs [9, 10] (see Annex A). 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, see Figure 1. In the meanwhile these toxicity equivalent factors were revised (see Annex A).

This document deals with the determination of these *dioxin-like* PCBs in emissions from stationary sources. Additionally informative annexes are provided, describing the analyses of the marker PCBs and hexachlorobenzene (HCB) in the same sample (Annex F and Annex G).

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

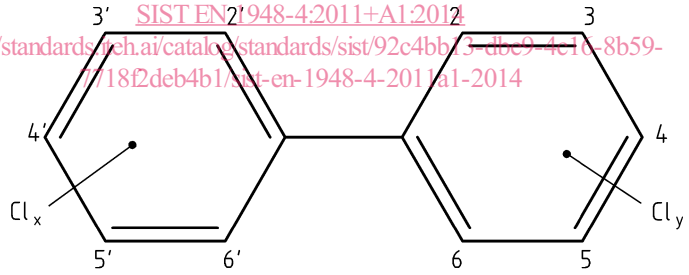

Figure 1 —Structure of PCB

1 Scope

This European Standard 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 12 non- and mono-ortho PCB designated by the WHO. It is optimised to measure PCB concentrations of about 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 “marker PCB” 28, 52, 101, 138, 153, 180 (see Annex F).

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

As a result of their similar chemical behaviour PCBs, as shown in the validation campaign, can be sampled from stationary sources together with the PCDDs/PCDFs. Therefore, it is possible to measure PCBs together with PCDDs/PCDFs by applying EN 1948-1, −2, −3 and −4. The complete sampling procedure is described in 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.

The analyses of the following PCB congeners is described in this European Standard and is validated in the validation campaign:

a) Non-ortho substituted PCBs

   1) 3,3’,4,4’-TeCB(77)

   2) 3,4,4’,5-TeCB (81)

   3) 3,3’,4,4’,5-PeCB (126)

   4) 3,3’,4,4’,5,5’-HxCB (169)

b) Mono-ortho substituted PCBs

   1) 2,3,3’,4,4’-PeCB (105)

   2) 2,3,4,4’,5-PeCB (114)

   3) 2,3’,4,4’,5-PeCB (118)

   4) 2’,3,4,4’,5-PeCB (123)

   5) 2,3,3’,4,4’,5-HxCB (156)

   6) 2,3,3’,4,4’,5’-HxCB (157)

   7) 2,3’,4,4’,5,5’-HxCB (167)

   8) 2,3,3’,4,4’,5,5’-HpCB (189)

c) Marker PCBs

   1) 2,4,4'- TriCB (28)

2) 2,2',5,5'-TeCB (52)

3) 2,2',4,5,5'- PeCB (101)

4) 2,2',3,4,4',5'- HxCB (138)

5) 2,2',4,4',5,5'- HxCB (153)

6) 2,2',3,4,4',5,5'- HpCB (180)

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 13284-1:2001, *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
any one of the 209 individual PCBs

3.3
dioxin-like PCB
WHO-PCB
non- and mono-ortho PCB with an affinity to the Ah-receptor, showing similar toxic effects as the 2,3,7,8-substituted PCDDs/PCDFs according to WHO [9]

3.4
extraction standard
quantification 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 suitable for the task

3.6
I-TEF
international toxic equivalent factor defined by NATO/CCMS in 1988 [11]

NOTE 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

NOTE 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, 3.5]

3.9
keeper
solvent of high boiling point added to the sample in order to avoid evaporation losses

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.

[Adapted from EN ISO 9169:2006, 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. 10.5 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 five to ten times the standard deviation of the analytical blank

NOTE 1 The factor *F* depends on the accepted measurement uncertainty.

$$LOQ = b_{ave} + F\ s_b \tag{2}$$

where

LOQ	is the quantification limit;
b_{ave}	is the mean analytical blank value;
s_b	is standard deviation of the analytical blank.

NOTE 2 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 or see 10.5 of this document using the requirement of 8.3, e) of EN 1948–3:2006 or 10.6, d) of this document.

NOTE 3 In practice, the Factor *F* = 10 corresponds to a reasonable measurement uncertainty of approximately 20 %.

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

3.13
PCB isomers
PCBs with identical chemical composition but different structure

3.14
recovery standard
$^{13}C_{12}$-labelled PCBs, added before injection into the GC

3.15
sampling standard
$^{13}C_{12}$-labelled PCBs, added before sampling

3.16
spiking
addition of $^{13}C_{12}$-labelled PCB standards

3.17
WHO-TEF
toxic equivalent factor first proposed by WHO in 1997 [9; 10]

NOTE For detailed description, see Annex A.

3.18
WHO-TEQ
toxic equivalent obtained by multiplying the mass determined with the corresponding WHO-TEF including PCDDs, PCDFs and PCBs

NOTE 1 For detailed description, see Annex A.

NOTE 2 WHO-TEQPCB, WHO-TEQPCDD/PCDF and WHO-TEQPCDD/PCDF/PCB should be used to distinguish different compound classes. In this document WHO-TEQPCDD/PCDF/PCB is also defined as Total WHO-TEQ.

4 Symbols and abbreviations

4.1 General

GC
gas chromatography

HCB
hexachlorobenzene

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 in the duct or stack according to the methods described in EN 1948-1 taking into account the requirements of isokinetic sampling according to EN 13284-1. 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 E).

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 12 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. The reagents shall be of high purity to meet the criteria of blank analysis to have a low PCB and PCDD/PCDF background concentration.

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 before extraction ▌A1⟩ (see EN 1948-1) ⟨A1▐. These $^{13}C_{12}$-labelled congeners behave in the same way as 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 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 PCB concentration level of 0,01 ng WHO-TEQ_{PCB}/m^3 and 10 m^3 sampling volume (dry gas) are given in Table 1. If a considerably higher mass of native PCBs is expected in the sample, the masses of the $^{13}C_{12}$-labelled standards to be added shall be enhanced accordingly taking into account the calibration range.

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 microlitres: (e.g. toluene, n-nonane)	**Sampling** sampling standard 100	**Extraction** extraction standard 100	**GC Injection** recovery standard [a] at least 10
Congeners added	**Total amount in picograms added before:**		
$^{13}C_{12}$-2,3,4,4'-TeCB (60)	1 000		
$^{13}C_{12}$-3,3',4,5,5'-PeCB (127) [b]	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) [b]		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	

Solution: Total volume in microlitres: (e.g. toluene, n-nonane)	**Sampling** sampling standard 100	**Extraction** extraction standard 100	**GC Injection** recovery standard [a] at least 10
Congeners added	**Total amount in picograms added before:**		
$^{13}C_{12}$-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
[a] **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. [b] **Sampling Standards:** Attention should be paid to possible co-elution problems of PCB 127 and PCB 105 on certain commercially available columns. [A1] If the co-elution problems cannot be avoided, the sampling standard PCB 127 may be omitted. [A1]			

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 amongst 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 shall be strictly adhered to.

8 Measurement procedure

8.1 Sampling

The sampling and storage shall be performed according to 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.

For sample storage the use of screw caps with aluminium-lined seals is recommended to avoid losses. Alternatively the use of non-greased glass ground necks is recommended. If using plastic sealings, losses have to be expected due to adsorption on the sealing materials.

8.2 Extraction

Before extraction the extraction standards shall be added to the sample following EN 1948-2. Pre-treatment of all 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]). 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: