SLOVENSKI STANDARD
SIST EN 1948-3:2006

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Nadomeġļa:
SIST EN 1948-3:1999

Emisije nepremiļnih virov ï Doloļevanje masne koncentracije PCDD/PCDF in dioksinu podobnih PCB ï 3. del: Identifikacija in kvantifikacija PCDD/PCDF

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

Emissionen aus stationären Quellen - Bestimmung der Massenkonzentration von PCDD/PCDF und dioxin-ähnlichen PCB - Teil 3: Identifizierung und Quantifizierung von PCDD/PCDF

Emissions de sources fixes - Détermination de la concentration massique en PCDD/PCDF et PCB de type dioxine - Partie 3: Identification et quantification de PCDD/PCDF

Ta slovenski standard je istoveten z: **EN 1948-3:2006**

ICS:

13.040.40 Emisije nepremiļnih virov Stationary source emissions

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EUROPEAN STANDARD

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English Version

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

Emissions de sources fixes - Détermination de la concentration massique en PCDD/PCDF et PCB de type dioxine - Partie 3: Identification et quantification de PCDD/PCDF

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This European Standard was approved by CEN on 23 January 2006.

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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 Central Secretariat has the same status as the official versions.

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Foreword

This European Standard (EN 1948-3:2006) 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of an identical text or by endorsement, at the latest by September 2006, and conflicting national standards shall be withdrawn at the latest by September 2006.

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 European Standard supersedes EN 1948-3:1996.

This European Standard has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association to support Essential Requirements of EU Directive 94/67/EC of 16 December 1994 [i] on the incineration of hazardous waste. This directive is now replaced by EU Directive 2000/76/EC of 4 December 2000 on the incineration of waste [ii] and this European Standard also supports the Essential Requirements of the new EU Directive 2000/76/EC (see also Annex G).

The precision and the performance characteristics were determined between 1992 and 1995 in four comparative and validation trials at waste incinerators sponsored by the European Commission, the European Free Trade Association and the German Federal Environment Agency.

The revision of this EN between 2001 and 2004 only refers to the normative part. The information given in the informative annexes as examples of operation are kept unchanged, as they represent the state of the art at the time of the validation measurements of EN 1948:1996 between 1992 and 1995.

This European Standard EN 1948:2006 consists of three parts dealing with the determination of the mass concentration of PCDDs and PCDFs 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.

All three parts are necessary for the performance of the dioxin measurements.

In addition for the sampling, extraction and analyses of dioxin-like PCBs the Technical Specification CEN/TS 1948-4[1] is developed and will be transferred to a European Standard after corresponding validation measurements or after an approval time of three years respectively.

Important changes made in the revision of EN 1948-3:

1. **Title:** Broadening of the title with regard to the future EN 1948-4 for the determination of dioxin-like PCBs

2. **Foreword:**

[1]) To be published.

- Deletion of all precursor documents which were basis for elaboration of EN 1948 as well as the names of the standardisation bodies involved in the elaboration of EN 1948

- Update of the hint regarding mandate of the standardisation project and regarding fulfilment of the Essential Requirements of EU Directives 94/67/EC and 2000/76/EC

- Addition of a hint, that the revision only refers to the normative parts of the standard. The Informative Annex A “Examples of operation” is kept unchanged and represents the state of the art at time of the validation measurements of EN 1948:1996 between 1992 and 1995

- Addition of hint with regard to the future document EN 1948-4 dealing with the analyses of dioxin-like PCBs.

3. **Scope**:

   - Addition of a hint, that EN 1948 can be applied for wide concentration ranges and various emission sources

   - Addition of a hint, that the described measurement methods are suitable for determination of other low-volatile substances, e.g. of dioxin-like PCBs

4. **Normative references**: Update of the references to EN 1948-1:2006, EN 1948-2:2006

5. **Clause 3 Terms and definitions:**

   - Distinction between Clause 3 "Terms and definitions" and Clause 4 "Symbols and abbreviations" resulting in a different numbering of the following chapters

   - Corrected definition of "field blank" for clarification

   - Corrected definition of "analytical blank" for clarification

   - Corrected definition of "sampling standard": only furans

   - "Syringe standard" renamed to read "recovery standard"

   - Corrected definition of "recovery standard": only dioxins

   - Additional definition of "dioxin-like PCBs"

   - Corrected definition and requirement of isokinetic sampling according to EN 13284-1:2001

   - Additional definition and calculation of limit of detection

   - Additional definition and calculation of limit of quantification

   - Additional definition of WHO-TEF/WHO-TEQ

6. **Clause 8.1 Minimum requirements for identification of PCDF/PCDD congeners:**

   - Deletion of the permission that resolution in the range of 6 000 to 10 000 might be acceptable if the absence of interferences is documented.

   - Deletion of the permission that other techniques which show that they meet the requirements described in this Standard may be used for identification.

- Uniform specification of retention times for all native congeners of +3 s to 0 s relative to the ^{13}C-labelled congeners.

- Clarification of the requirement, that the signal-to-noise ratio of the raw data as documented in Figure 1 shall be at least 3 : 1 for the native signal used for identification.

- Correction of the measurement of the base line noise

7. **Clause 8.3 Minimum requirements for quantification:**

   - Correction of the requirements for quantification in 8.3.a, c, e, f, g, h, i

   - h) Calculation of the quantification limit according to new definition

   - i) Additional requirement to carry out quantification based on two isotopes

8. **Clause 11 Quantification of HRGC/HRMS results:**

   - Correction of the quantification scheme (Table 1): Quantification of dioxins with ^{13}C-labelled dioxins, quantification of furans with ^{13}C-labelled furans

   - Correction of calculation scheme for recovery rate of the sampling standards (Table 3): ^{13}C-labelled furan sampling standards are related to ^{13}C-labelled furan extraction standards

9. **Clause 12 Calculation of measurement results:** Combination of formerly two formulas to one formula for calculating the concentration of the emitted PCDD/PCDF and adaptation of the formula caption

10. **Annex B:** Additional Annex B for estimation of the measurement uncertainty and the accuracy of polychlorinated PCDD/PCDF determination

11. **Annex G**: Update of the hint regarding mandate of the standardisation project and regarding fulfilment of basic requirements of EU Directives 94/67/EC and 2000/76/EC

12. **Bibliography**: Update

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

Introduction

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

PCDDs and PCDFs can form in the combustion of organic materials; they also occur as undesirable by-products 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 (for toxicity equivalent factors, see Annex A of EN 1948-1:2006).

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

1 Scope

This European Standard specifies the identification and quantification procedures of the sampled PCDDs/PCDFs. It is an integral part of the complete measurement procedure. The use of the other two parts of this standard, EN 1948-1:2006 and EN 1948-2:2006, describing sampling and extraction and clean-up, respectively, is necessary for the determination of the PCDDs/PCDFs.

This European Standard has been designed to measure PCDD/PCDF concentrations at about 0,1 ng I-TEQ/m^3 in stationary source emissions.

This European Standard specifies both method validation and a framework of quality control requirements which shall be fulfilled by any PCDD/PCDF identification and quantification methods to be applied. Some methods are described in detail in Annex A as examples of proven procedures.

Each of the three sampling methods (Part 1) can be combined with the extraction and clean-up (Part 2) and the identification and quantification (Part 3) to complete the measurement procedure.

During comparison measurements of the three sampling methods on municipal waste incinerators at the level of about 0,1 ng I-TEQ/m^3 these methods have been deemed comparable within the expected range of uncertainty. Validation trials were performed on the flue gas of municipal waste incinerators at the level of about 0,1 ng I-TEQ/m^3 and a dust loading of from 1 mg/m^3 to 15 mg/m^3. Although this European Standard is primarily developed and validated for gaseous streams emitted by waste incinerators, the practical experience shows that it can be applied for wide concentration ranges and various emission sources.

The procedure described in the three parts of EN 1948:2006 specifies requirements in order to measure every 2,3,7,8-chlorine substituted PCDD/PCDF congener required to calculate the total I-TEQ (see Table A.1 of EN 1948-1:2006).

Besides the determination of PCDDs/PCDFs the described measurement methods are suitable for determination of other low-volatile substances, e.g. of dioxin-like PCBs (details for sampling and analyses see CEN/TS 1948-4), although no validated performance characteristics are available yet.

2 Normative references

The following referenced documents are indispensable for the application of this European Standard. 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*

3 Terms and definitions

For the purposes of this European Standard, the terms and definitions given in EN 1948-1:2006, EN 1948-2:2006 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 210 individual PCDDs/ PCDFs

3.3
dioxin-like PCBs
any PCB showing similar toxicity as the 2,3,7,8-substituted PCDDs/PCDFs according to WHO [iii]

3.4
extraction standard
$^{13}C_{12}$-labelled 2,3,7,8-chlorine substituted PCDD/PCDF, added before extraction and used for the calculation of results

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

3.6
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 [iv]]

3.7
keeper
high boiling point solvent added to the sampling standard solution

3.8
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 limit of detection, 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.

[prEN ISO 9169:2004, definition 3.2.6 [v]]

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 European Standard 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.

3.9
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 European Standard 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 using the requirement of Clause 8.3e.

3.10
pattern
defined as a chromatographic print of any series of PCDD/PCDF isomers

3.11
PCDD/PCDF isomers
PCDDs or PCDFs with identical chemical composition but different structure

3.12
profile
graphic representation of the sums of the isomer concentrations of the PCDDs and the PCDFs

3.13
recovery standard
$^{13}C_{12}$-labelled 2,3,7,8-chlorine substituted PCDD, added before injection into the GC

3.14
sampling standard
$^{13}C_{12}$-labelled 2,3,7,8-chlorine substituted PCDF, added before sampling

3.15
spiking
addition of $^{13}C_{12}$-labelled PCDD/PCDF standards

3.16
WHO-TEF
toxic equivalent factor proposed by WHO [iii] (for detailed description see EN 1948-1:2006, Annex A)

3.17
WHO-TEQ
toxic equivalent obtained by multiplying the mass determined with the corresponding WHO-TEF including PCDDs, PCDFs, and PCBs (for detailed description see EN 1948-1:2006, Annex A)

NOTE $WHO\text{-}TEQ_{PCB}$, $WHO\text{-}TEQ_{PCDD/PCDF}$ 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 obtained by weighting the mass determined with the corresponding I-TEF (for detailed description, see Annex A of EN 1948-1:2006)

LOD
limit of detection

LOQ
limit of quantification

PCB
polychlorinated biphenyl

PCDD/PCDF
polychlorinated dibenzo-p-dioxin/dibenzofuran

PTFE
polytetrafluoroethylene

WHO-TEF
toxic equivalent factor of the World Health Organisation

WHO-TEQ
toxic equivalent of the World Health Organisation

4.2 Congeners of PCDD/PCDF

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

5 Principles of identification and quantification

This European 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 in the extracts of emission samples. These extracts are prepared in accordance with EN 1948-2 and contain the 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 and furans.

6 Reagents, materials and equipment

See examples of operation in Annex A.

7 Safety measures

All relevant national safety regulations shall be observed. The 2,3,7,8-chlorine substituted PCDDs/PCDFs are among the most toxic of chemicals. All work with PCDDs/PCDFs requires therefore the utmost care; the national safety measures which correspond to those for toxic substances shall be strictly adhered to.

8 Quality control requirements for identification and quantification

8.1 Minimum requirements for identification of PCDF/PCDD congeners

High resolution gas chromatography/high resolution mass spectrometry at a resolution of greater or equal to 10 000 is at present required to achieve adequate sensitivity, selectivity and to allow the use of all the $^{13}C_{12}$-labelled standards.

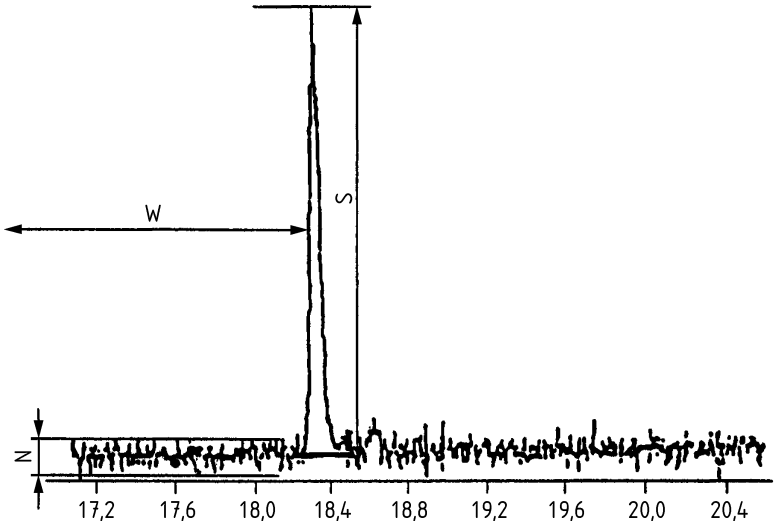
For each 2,3,7,8-chlorine substituted congener at least two ions of the molecular isotope cluster shall be recorded for both the native and the added $^{13}C_{12}$-labelled congeners (see Annex C). A positive identification of a congener is made if all the following requirements are met:

a) the isotope ratio between the ions monitored shall match the theoretical value within ± 20 % (see Annex D);

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 0 s based on the retention time of the corresponding $^{13}C_{12}$-labelled isomer in the sample. Alternatively, relative retention times based on 1,2,3,7,8-PeCDF can be calculated. The difference shall not be more than 0,25 % compared with the calibration standard.

c) The signal-to-noise ratio of the raw data as documented in Figure 1 shall be at least 3 : 1 for the native 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.



Key

S signal height

N peak-to-peak-noise

W 10 × signal width at half height

Figure 1 — Determination of the signal-to-noise ratio

8.2 Isomer sums of PCDD/PCDF congeners

If the sum of the concentrations of isomer groups are needed the following requirements shall be met:

a) The retention time window for all isomers of an isomer group shall be measured by a solution containing all native PCDDs/PCDFs. A fly ash extract can be used for this purpose. Each group of isomer (tetra to octa) should be defined via relative retention times (of the central isomer first). The pattern of overlapping windows (tetra/penta) should be "constant" during one series of measurements; the changes in the relative retention times shall not be greater than ± 10 %.

b) The retention times of all congeners attributed to an isomer group shall be within the time window of the first and last eluting isomer.

8.3 Minimum requirements for quantification

In addition to the requirements for identification, the following points shall be fulfilled as quantification requirements:

a) At present, there is no chromatographic column available 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 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 emission limit value is exceeded, a confirmatory analysis should be performed on a second column.

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, then provided the sum of the contributions to the total I-TEQ in the sample from all the congeners with recoveries not within these ranges does not exceed 10 %, the acceptable ranges shall be:

3) 30 % to 150 % for the tetra- to hexa-chlorinated congeners;

4) 20 % to 150 % for the hepta- and octa-chlorinated congeners.

e) For quantification the signal-to-noise ratio of the native congeners shall be 10 : 1. The signal-to-noise ratio 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.

g) An analytical blank shall be taken. The blank of all 2,3,7,8-chlorine substituted congeners shall be equal or less than the detection limit of the method. Alternatively, the levels found shall be at least a factor of 10 below the lowest measured concentrations in the series of samples.

NOTE In case of monitoring dioxin emissions significantly lower than 0,1 ng I-TEQ/m³, the analytical blank may be in the same range as the measured concentration.

h) The permissible limits of quantification (LOQs) for the individual congener *i* shall be as follows:

$$LOQ_i \leq \frac{0{,}5\ \text{pg/m}^3}{\text{I-TEF}_i} \tag{3}$$

where

LOQ is the limit of quantification;

I-TEF is the international toxic equivalency factor.

i) Quantification is based on two isotope ions. If quantification is possible only with one single ion in case of interferences on the second trace (e.g. by PCB), this has to be reported.

9 Quality assurance criteria for extraction/clean-up/quantification procedure blanks

The analytical blank value of all 2,3,7,8-chlorine substituted congeners shall be measured in a blank sample covering the complete analytical procedure including extraction, clean-up, and quantification when one of the following situations occurs:

a) after a series of no more than 10 samples;