SLOVENSKI STANDARD
SIST EN 1948-2:2006

01-maj-2006

Nadomeģļ a:
SIST EN 1948-2:1999

Emisije nepremiļ nih virov ï Doloļ evanje masne koncentracije PCDD/PCDF in dioksinu podobnih PCB ï 2. del: Ekstrakcija in ļ iģļ enje PCDD/PCDF

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

Emissionen aus stationären Quellen - Bestimmung der Massenkonzentration von PCDD/PCDF und dioxin-ähnlichen PCB - Teil 2: Extraktion und Reinigung von PCDD/PCDF

Emissions de sources fixes - Détermination de la concentration massique en PCDD/PCDF et PCB de type dioxine - Partie 2: Extraction et purification des PCDD/PCDF

Ta slovenski standard je istoveten z: **EN 1948-2:2006**

ICS:

13.040.40 Emisije nepremiļ nih virov Stationary source emissions

SIST EN 1948-2:2006 **en,fr,de**

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 1948-2

March 2006

ICS 13.040.40

Supersedes EN 1948-2:1996

English Version

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

Emissions de sources fixes - Détermination de la concentration massique en PCDD/PCDF et PCB de type dioxine - Partie 2: Extraction et purification de PCDD/PCDF

Emissionen aus stationären Quellen - Bestimmung der Massenkonzentration von PCDD/PCDF und dioxinähnlichen PCB - Teil 2: Extraktion und Reinigung von PCDD/PCDF

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

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

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.

CEN members are the national standards bodies of 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.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: rue de Stassart, 36 B-1050 Brussels

Ref. No. EN 1948-2:2006: E

Contents

Page

Foreword

This European Standard (EN 1948-2:2006) 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 1948-2:1996.

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 B).

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 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 1948-2:

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 1948-3:2006
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"
   - "Sampling volume" renamed to read "volume of the sampling extract"
   - 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 5 Principle of the extraction and clean-up procedure**: Additional subclause 5.2 "Minimum information prior to analyses"
7. **Clause 7.2 Sample pre-treatment:** Correction of the requirements regarding sample pre-treatment for better comprehensibility

8. **Clause 8.1 Addition of extraction standards**: Correction for better comprehensibility

9. **Clause 8.2 Sample storage**: Requirement to store the samples < 4 °C was deleted and replaced by "in the dark not higher than room temperature (approximately 25 °C)."

10. **Clause 8.3 Extraction:** Requirement to carry out principally a sample pre-treatment with HCL was placed at first position.

11. **Annex A.2.1.4.4:** Correction of title "Check of adsorbent activity"

12. **Annex A.4.3:** Correction: the dioxin-like (not the planar) PCB are separated from PCDD/F

13. **Figure A.4 Caption:** Correction: dioxin-like PCB (not planar PCB) are adsorbed

14. **Annex B**: 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

15. **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 the 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 may 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 in very small concentrations. The 2,3,7,8-chlorine 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 extraction and clean-up procedures of the sampled PCDDs/PCDFs. It is an integral part of the complete measurement procedure. The use of the other two parts EN 1948-1:2006 and EN 1948-3:2006 describing sampling or identification and quantification, 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 extraction and clean-up 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 which shall be met in order to measure the 17 congeners necessary 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 1948-3:2006, *Stationary source emissions — Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs — Part 3: Identification and quantification of PCDDs/PCDFs*

3 Terms and definitions

For the purposes of this European Standard, the terms and definitions given in EN 1948-1:2006, 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 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 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 EN 1948-3:2006, 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 EN 1948-3:2006, 8.1 using the requirement of EN 1948-3:2006, 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 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

PU foam
polyurethane foam

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