



SLOVENSKI STANDARD
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Stationary source emissions - Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs - Part 1: Sampling of PCDDs/PCDFs

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Emissionen aus stationären Quellen - Bestimmung der Massenkonzentration von PCDD/PCDF und dioxin-ähnlichen PCB - Teil 1: Probenahme von PCDD/PCDF

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Emissions de sources fixes - Détermination de la concentration massique en PCDD/PCDF et PCB de type dioxine - Partie 1: Prélèvement des PCDD/PCDF

Ta slovenski standard je istoveten z: EN 1948-1:2006

ICS:

13.040.40 Ò{ ã ã Á ^] ! ^ { ã } ã ã [ç Stationary source emissions

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EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 1948-1

March 2006

ICS 13.040.40

Supersedes EN 1948-1:1996

English Version

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

Emissions de sources fixes - Détermination de la
concentration massique en PCDD/PCDF et PCB de type
dioxine - Partie 1: Prélèvement

Emissionen aus stationären Quellen - Bestimmung der
Massenkonzentration von PCDD/PCDF und dioxin-
ähnlichen PCB - Teil 1: Probenahme 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.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
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Foreword

This European Standard (EN 1948-1:2006) 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 1948-1:1996.

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 E).

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 1948-4¹ 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 1948-1:

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.

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- 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 B "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. **Introduction:** New hint that only skilled operators who are trained in handling highly toxic compounds should apply the method described in this European Standard (identical to EN 1948-2 and EN 1948-3)
4. **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
5. **Normative references:**
- Update of the references to EN 1948-2:2006, EN 1948-3:2006
 - Reference to EN 13284-1:2001 regarding determination of low range mass concentration of dust instead of ISO 9096, therefore deletion of all references to ISO 9096 and replacement by EN 13284-1:2001
 - Additional normative reference to EN ISO/IEC 17025:2005
 - Deletion of reference to ISO 4793:1980
6. **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"
 - Additional definition of "flue gas sample volume"
 - Additional definition of "measurement series" resp. "sampling campaign"

- 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
7. **Clause 5.1 Sampling:**
- Addition of a hint, that a higher temperature than 20°C/40°C (depending of the chosen sampling method) can be used for the sample gas if it is demonstrated that the results obtained are equivalent.
 - Corrected clarification regarding the temperature falling below the dew point resp. regarding the increase of the relative humidity
8. **Clause 6.1 General sampling device:**
- Extension of the general sampling devices, deletion of the old subclauses 5.1.1 to 5.1.4 dealing with the single compilation of the devices for the different sampling methods, because all details are listed in Annex B
 - Additional note regarding oxygen concentration and its influence on the performance characteristics
 - Harmonisation of the sampling device requirements with other existing standards EN 13284-1, EN 14790, EN 14789
9. **Clause 6.2 Materials:** Enlargement of the requirements for materials
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10. **Clause 6.3 Cleaning the sampling device:** New subclause 6.3
11. **Clause 7.1 Method validation criteria:**
- a) Requirements for the plane filter efficiency according to EN 13284-1:2001
 - c) Correction of the validation requirement regarding the flue gas sample volume
 - c) Additional validation requirements with regard to the mean adsorber temperature
12. **Clause 7.2 Requirements for sampling:**
- Maximum sampling time of 8 h was deleted
 - d) The field blank must be carried out according to the new subclause 7.3
 - e) Addition of the requirement regarding quantification limit according to EN 1948-3, addition of formula for calculation of the quantification limit according to EN 1948-3, addition of notes regarding minimum flue gas sample volume and regarding minimum sampling time according 2000/76/EG
 - f) Addition of the spiked parts of the equipment
13. **Clause 7.3 Field blank requirements:** Additional section dealing with a completed and corrected compilation of all field blank requirements

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14. **Clauses 7.4, 7.5, 7.6 Additional sampling minimum requirements for the 3 different methods:**
- Addition of a footnote, that a temperature limit of 125 °C is required for the filter of the filter/condenser method to avoid chemical reactions on activated surfaces.
 - Deletion of the requirement to connect the sampling device according to figures in Annex B
 - Deletion of the requirement to cool des sample gas temperature with a maximum of 20 °C resp. 40 °C
15. **Clause 9.3.4.2 Changing sampling line:** Additional requirement of leak check when changing sampling
16. **Clause 9.3.5.1 Sample recovery from the sampling train:** Additional requirements with regard to rinsing the equipment, the rinsing solution becomes part of the sample
17. **Clause 9.3.5.2 Sample storage:** Deletion of the requirement to store the samples below 4 °C. Additional requirement to use screw-caps with aluminium-lined seals for storing
18. **Clause 9.4 Calculation of flue gas volume:** Correction of the formula for conversion to standard conditions
19. **Clause 9.5 Sampling report:**
- Addition of the content and the relevance of the sampling report
 - e) Addition of requirement regarding the identification of the used parts of the sampling equipment
 - g) Harmonisation of the requirement regarding isokinetic sampling according to EN 13284-1:2001
20. **Annex A:** Revision/update of the Toxicity of PCDD/PCDF according to the requirements of the WHO
21. **Annex B:** Addition of bibliography references
22. **Annex B 1.5b:** Correction of filter position
23. **Annex E / F:** Deletion of annexes dealing with humidity and oxygen content determination
24. **Annex E:** 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
25. **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 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 tetrachlorinated to octachlorinated dibenzodioxins/dibenzofurans are the 74 monochlorinated to trichlorinated dibenzodioxins/dibenzofurans (for toxicity equivalent factors, see Annex A).

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

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EN 1948-1:2006 (E)**1 Scope**

This European Standard specifies the sampling of PCDDs/PCDFs. It is an integral part of the complete measurement procedure. The use of the other two parts EN 1948-2 and EN 1948-3 describing extraction and clean-up and identification and quantification, respectively, is necessary for the determination of the PCDDs/PCDFs.

This European Standard has been developed to measure PCDD/PCDF concentrations at about 0,1 ng I-TEQ/m³ 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 sampling.

The user has the possibility to choose between three different methods:

- "filter/condenser method"
- "dilution method"
- "cooled probe method"

Each sampling method is illustrated by some sampling systems described in detail in Annex B as examples of proven procedures.

During comparison measurements of the three sampling methods on municipal waste incinerators at the level of about 0,1 ng I-TEQ/m³ 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/m³ and a dust loading of from 1 mg/m³ to 15 mg/m³. 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 specifies requirements which shall be met in order to measure the 17 congeners necessary to calculate the total I-TEQ (see Table A.1).

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 1948-2:2006, *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*

EN 14789, *Stationary source emissions — Determination of volume concentration of oxygen (O₂) — Reference method — Paramagnetism*

EN 14790, *Stationary source emissions - Determination of the water vapour in ducts*

EN ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories (ISO/IEC 17025:2005)*

3 Terms and definitions

For the purposes of this European Standard, the terms and definitions given in 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 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

¹³C₁₂-labelled 2,3,7,8-chlorine substituted PCDDs/PCDFs, added before extraction. These standards are also used for calculation of 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 the measurement and to check that the operator can achieve a quantification level adapted to the task

3.6

flue gas sample volume

expressed at standard conditions of temperature and pressure on a dry basis and if required corrected to the reference concentration of oxygen

3.7

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]

3.8

keeper

high boiling point solvent added to the sampling standard solution

3.9

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.

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

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).

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

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.

3.10**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.

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

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.

3.11**measurement series****sampling campaign**

several successive measurements carried out at the same sampling site and at the same process operating conditions (in this European Standard often the wording sampling campaign is used)

3.12**pattern**

chromatographic print of any series of PCDD/PCDF isomers

3.13**PCDD/PCDF isomers**

PCDDs or PCDFs with identical chemical composition but different structure

3.14**profile**

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

3.15**recovery standard**

¹³C₁₂-labelled 2,3,7,8-chlorine substituted PCDDs, added before GC injection

3.16**sampling standard**

¹³C₁₂-labelled 2,3,7,8-chlorine substituted PCDFs, added before sampling

3.17**spiking**

addition of ¹³C₁₂-labelled PCDDs and PCDFs standards

3.18**standard pressure**

101,3 kPa

3.19**standard temperature**

273,15 K

3.16**WHO-TEF**

toxic equivalent factor proposed by WHO [iii] (for detailed description see 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 Annex A)

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

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4 Symbols and abbreviations**4.1 General****HRGC**

high resolution gas chromatography

HRMS

high resolution mass spectrometry

I-TEF

international toxic equivalent factor (for a detailed description, see Annex A)

I-TEQ

international toxic equivalent obtained by weighting the mass determined with the corresponding I-TEF (for a detailed description, see Annex A)

LOD

limit of detection

LOQ

limit of quantification

PCB

polychlorinated biphenyl

EN 1948-1:2006 (E)**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

TCDF

Tetrachlorodibenzofuran

PeCDF

Pentachlorodibenzofuran

HxCDF

Hexachlorodibenzofuran

HpCDF

Heptachlorodibenzofuran

OCDF

Octachlorodibenzofuran

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5 Principle of the complete PCDD/PCDF measurement procedure**5.1 Sampling****5.1.1 General**

Gas is sampled isokinetically in the duct. The PCDDs/PCDFs, both adsorbed on particles and in the gas phase, are collected in the sampling train. The collecting parts can be a filter, a condensate flask and a solid

or liquid adsorbent appropriate to the sampling system chosen. There is the choice between three different sampling systems:

- filter/condenser method;
- dilution method;
- cooled probe method.

Schematic representations of the sampling methods are given in Figures 1 to 3.

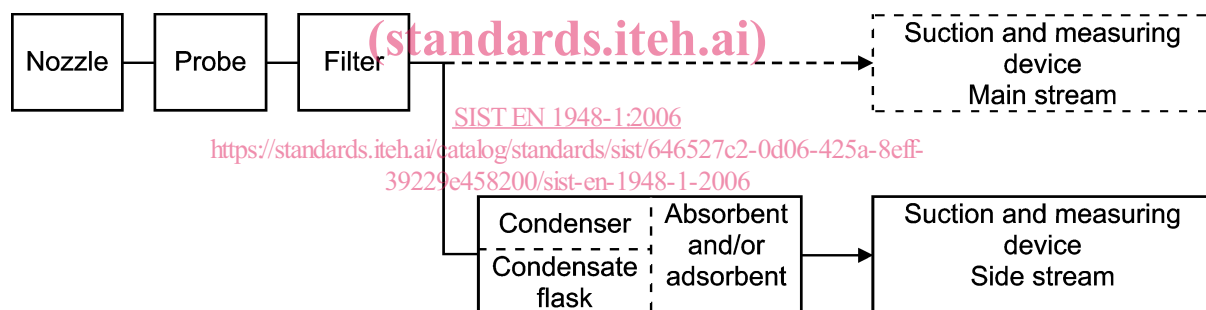
The main collecting parts are spiked with $^{13}\text{C}_{12}$ -labelled PCDDs/PCDFs before sampling to determine the sampling recovery rate of the congeners. The sample gas is brought to a temperature specific to the sampling system and the gaseous and particulate PCDDs/PCDFs are trapped.

Sampling shall be carried out according to EN 13284-1. Exceptions with their justification shall be reported.

The minimum requirements of the sampling procedure to be met are described in this European Standard. Examples of operation are listed in Annex B. The described systems meet the minimum requirements of Clause 7, but differ in their approach.

5.1.2 Filter/condenser method

The principle of the method is shown in Figure 1. Different variants for this system are possible (see Figures B.1, B.2 and B.5).



- - - optional

Figure 1 — Schematic representation of the filter/condenser method

The filter is placed downstream of the nozzle (in the stack) or after the probe (out of the stack). The filter shall be kept below 125 °C^2 , but above the flue gas dew point. When a high dust loading is expected, a quartz wool filter or a cyclone may be incorporated into the sampling train before the filter to prevent the filter from being overloaded. Downstream, a condenser is attached to cool the sample gas below 20 °C . An upper temperature can be used if it is demonstrated that the results obtained are equivalent. The gaseous and aerosol parts of the PCDDs and PCDFs are captured by impingers and/or solid adsorbents.

In a variant of this sampling system the solid adsorbent unit can be linked between condenser and condensate flask (see Figure B.5).

²⁾ In order to avoid chemical reactions on activated surfaces the temperature limit of 125 °C is required.