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

EVS **EESTI STANDARDIKESKUS**

EESTI STANDARDI EESSÕNA

NATIONAL FOREWORD

Käesolev Eesti standard EVS-EN 1948-3:2006 sisaldab Euroopa standardi EN 1948-3:2006 ingliskeelset teksti. Käesolev dokument on jõustatud 28.04.2006 ja selle kohta on avaldatud teade Eesti standardiorganisatsiooni ametlikus väljaandes. Standard on kättesaadav Eesti standardiorganisatsioonist.	This Estonian standard EVS-EN 1948-3:2006 consists of the English text of the European standard EN 1948-3:2006. This document is endorsed on 28.04.2006 with the notification being published in the official publication of the Estonian national standardisation organisation. The standard is available from Estonian standardisation organisation.

Käsitlusala: 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.	**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.

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Võtmesõnad:

EUROPEAN STANDARD

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EN 1948-3

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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

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

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Ref. No. EN 1948-3:2006: E

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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:**

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[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