

SLOVENSKI STANDARD SIST-TS CEN/TS 1948-5:2015

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Emisije nepremičnih virov - Določevanje masne koncentracije PCDD/PCDF in dioksinom podobnih PCB - 5. del: Dolgotrajno vzorčenje PCDD/PCDF in PCB

Stationary source emissions - Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs - Part 5: Long-term sampling of PCDDs/PCDFs and PCBs

Emissionen aus stationären Quellen - Bestimmung der Massenkonzentration von PCDD/PCDF und dioxin-ähnlichen PCB - Teil 5: Langzeitprobenahme von PCDD/PCDF and PCB (standards.iten.al)

Emissions de sources fixes. Détermination de la concentration massique en PCDD/PCDF et PCB de type dioxine. Partie 5: Echantillonnage à long-terme de PCDD/PCDF et PCB

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Stationary source emissions - Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs - Part 5: Long-term sampling of PCDDs/PCDFs and PCBs

Emissions de sources fixes - Détermination de la concentration massique en PCDD/PCDF et PCB de type dioxine - Partie 5: Prélèvement à long-terme de PCDD/PCDF et PCB

Emissionen aus stationären Quellen - Bestimmung der Massenkonzentration von PCDD/PCDF und dioxinähnlichen PCB - Teil 5: Langzeitprobenahme von PCDD/PCDF und PCB

This Technical Specification (CEN/TS) was approved by CEN on 29 December 2014 for provisional application.

The period of validity of this CEN/TS is limited initially to three years. After two years the members of CEN will be requested to submit their comments, particularly on the question whether the CEN/TS can be converted into a European Standard.

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CEN-CENELEC Management Centre: Avenue Marnix 17, B-1000 Brussels

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Foreword

This document (CEN/TS 1948-5:2015) has been prepared by Technical Committee CEN/TC 264 "Air quality", the secretariat of which is held by DIN.

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According to the CEN-CENELEC Internal Regulations, the national standards organizations of the following countries are bound to announce this Technical Specification: 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.

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Introduction

EN 1948-1, EN 1948-2, EN 1948-3 and EN 1948-4 describe reference methods for the determination of PCDD/PCDF/PCB, whereas this Technical Specification gives requirements for long-term sampling measurements in connection with the appropriate analytical methods (equivalent method). In contrast to the standard reference method (EN 1948-1) which refers to monitoring the limit value for compliance with emission limit values (ELVs) in Directives, such as Industrial Emission Directive (IED) [10], the long-term sampling is intended to determine the average concentration level during a longer period (see e.g. [12], [13]). CEN/TS 1948-5 provides a method for measuring long term average mass concentrations but it does not specify its potential use by the competent authority for demonstrating compliance with long term ELVs.

Long-term sampling methods are not automatic measurement methods and do not provide continuous emission monitoring data (real time display).

This Technical Specification in connection with EN 1948-2 and EN 1948-3 (extraction and analysis) are necessary for the performance of long-term sampling of PCDDs/PCDFs/ PCBs.

In some European Union countries PCDD/PCDF/PCB long-term sampling is an obligatory measurement for some incineration processes. In other countries of the European Union this may be obligatory in the future.

The European Organization for Standardization (CEN) draws attention to the fact that it is claimed that compliance with this document may involve the use of patents concerning the use of PCDD/PCDF/PCB long-term sampling systems, described in this document. This is valid for

- a) the filter/condenser method (see 5.2) and PREVIEW
- b) the cooled probe method (see 5.4).

CEN takes no position concerning the evidence, validity and scope of these patent rights.

The holder of this patent right has ensured CEN and CENELEC that he is willing to negotiate licenses under reasonable and non-discriminatory terms and conditions with applicants throughout the world. In this respect, the statement of the holder of this patent right is registered with CEN and CENELEC. Information may be obtained from:

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94134 Fontenay sous Bois

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d) Environment S.A

111, bd Robespierre

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http://www.cencenelec.eu/ipr/Patents/Pages/default.aspx maintains online databases of patents relevant to its documents. Users are encouraged to consult the databases for the most up to date information concerning patents.

It should be mentioned that also a patent right existed for the dilution method (see 5.3). This patent was phased out in September 2014.

In Reference [1] the results of a round robin test for long-term sampling are presented.

WARNING All relevant national safety regulations shall be observed. The 2,3,7,8-chlorine substituted PCDDs/PCDFs belong to the most toxic of chemicals. In addition working at the sampling site may include exposure to a range of hazards such as poisonous/asphyxiating flue gases and working at heights. Appropriate measures shall be taken to minimize exposure to such hazards. Care shall be taken when transporting samples to avoid their breakage both to prevent contamination and to avoid sample losses.

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1 Scope

This Technical Specification specifies the long-term sampling of PCDDs, PCDFs and PCBs. There are three different sampling methods, which use the three different principles described in EN 1948-1 modified for long-term sampling requirements:

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

Each sampling method is illustrated in detail in Annex D. The sampling methods described in this document are designed for a sampling duration of typically four weeks.

Additionally this document specifies a framework of quality control requirements for any long-term sampling method to be applied (see Annex C and Annex F).

With the methods described experiences were gained for a concentration range from typically 0,003 ng I-TEQ/m³ up to 4,0 ng I-TEQ/m³ and 0,003 ng WHO-TEQ/m³ up to 4,0 ng WHO-TEQ/m³ respectively at different stationary sources (e.g. waste incinerators, sinter plants, cement kilns).

For the complete measurement method the use of EN 1948-2 and EN 1948-3 describing extraction and cleanup and identification and quantification, respectively, is necessary in order to determine PCDDs/PCDFs. Also EN 1948-4 is necessary for the analyses of dioxin-like PCBs. R F V F W

2 Normative references (standards.iteh.ai)

The following documents, in whole or in part, are 4 normatively referenced in this document and are indispensable for its application. For idated 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 1948-4:2010+A1:2013, Stationary source emissions - Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs - Part 4: Sampling and analysis of dioxin-like PCBs

EN 13284-1:2001, Stationary source emissions - Determination of low range mass concentration of dust - Part 1: Manual gravimetric method

EN 15259:2007, Air quality - Measurement of stationary source emissions - Requirements for measurement sections and sites and for the measurement objective, plan and report

EN 15267-1, Air quality - Certification of automated measuring systems - Part 1: General principles

EN 15267-2, Air quality - Certification of automated measuring systems - Part 2: Initial assessment of the AMS manufacturer's quality management system and post certification surveillance for the manufacturing process

EN 15267-3:2007, Air quality - Certification of automated measuring systems - Part 3: Performance criteria and test procedures for automated measuring systems for monitoring emissions from stationary sources

EN ISO 16911-1:2013, Stationary source emissions - Manual and automatic determination of velocity and volume flow rate in ducts - Part 1: Manual reference method (ISO 16911-1:2013)

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1

sampling unit

different media including adsorber, absorber and filter in order to collect the PCDDs/PCDFs/PCBs

Each sampling system may use different collection systems to collect PCDD/PCDF and PCBs in the gaseous and particulate form (e.g. filter, cartridge with sorbent). In this standard the whole collection system is considered as the sampling unit which is send to the laboratory for analysis.

3.2

long-term sampling system

system to sample up to typically four weeks

3.3

standard reference method

SRM

sampling according to EN 1948-1 and extraction/clean-up/analysis according to EN 1948-2 and EN 1948-3

3.4

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stand by

interruption of the measurement period due to plant shut down or during the changing of sampling support https://standards.iteh.ai/catalog/standards/sist/ad789362-225d-4bf4-b3 (filters and adsorbant) 1325c956aa13/sist-ts-cen-ts-1948-5-2015

3.5

yearly PCDD/PCDF/PCB surveillance

several repeated long-term PCDD/PCDF/PCB measurements during 1 year

3.6

standard flue gas sample volume

flue gas sample volume expressed at standard conditions of temperature (273,15 K) and pressure (101,3 kPa) 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 (amount and direction) of the gas entering the sampling nozzle are the same as the velocity of the gas in the duct at the sampling point

3.8

sampling standard

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

3.9

extraction standard

¹³C₁₂-labelled 2,3,7,8-chlorine substituted PCDDs/PCDFs/PCB, added before extraction

Note 1 to entry: These standards are also used for calculation of results.

3.10

recovery standard

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

3.11

type performance test

test to be performed by an independent test house in a laboratory and on site to test the conformity of the automatic samplers according to the defined performance criteria corresponding to the concerned application

Note 1 to entry: This step, in analogy to automated measuring systems (AMS), provides the information to perform the step QAL (see also introduction).

Note 2 to entry: The type performance testing is part of the certification process described, by analogy with AMS described in EN 15267–3.

Note 3 to entry: The test laboratory should have accreditation to EN ISO/IEC 17025 for the dioxin SRM. The analytical lab should have accreditation to EN ISO/IEC 17025 for the analysis (see 7.1. i), 8)).

[SOURCE: EN 14181 [2]]

3.12

validation of the installation and calibration in the field

Validation performed for each plant by an independent test house to check the defined performance criteria

Note 1 to entry: This step in analogy to AMS (automated measurement systems), corresponds to the QAL2 (see also introduction).

Note 2 to entry: The test laboratory should have accreditation to EN ISO/IEC 17025 for the dioxin SRM. The analytical lab should have accreditation to EN ISO/IEC 17025 for the analysis (see 7.1. i), 8)).

[SOURCE: EN 14181 [2]] <u>SIST-TS CEN/TS 1948-5:2015</u>

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field blank value

value determined by a blank sample

Note 1 to entry: The described measurement procedure is employed 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.

3.14

accuracy

closeness of agreement between a measured quantity value and a true quantity value of a measurand

[SOURCE: VIM:2012 [3]]

3.15

maintenance interval

maximum admissible interval of time for which the performance characteristics will remain within a pre-defined range without servicing – cleaning, calibration or adjustment

3.16

measurement section

region of the flue gas duct which includes the measurement plane(s)

[SOURCE: EN 15259:2007; 3.12]

3.17

measurement cross section

plane normal to the centre line of the duct at the sampling position

Note 1 to entry: Measurement plane is also known as sampling plane.

[SOURCE: EN 15259:2007; 3.13]

3.18

availability

fraction of the total monitoring time for which data/sample material of acceptable quality has been collected

3.19

reference quantity

specified physical or chemical quantity which is needed for conversion of the measurand to standard conditions

Note 1 to entry: Reference quantities are e.g. temperature ($T_{\text{ref}} = 273,15 \text{ K}$), pressure ($p_{\text{ref}} = 101,325 \text{ kPa}$), water vapour volume fraction ($h_{\text{ref}} = 0$ %) and oxygen volume fraction (o_{ref} .)

3.20

purging

operation carried out to keep the probe clean during the stand-by modus

Note 1 to entry: Using oil-free instrument compressed air.

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Note 2 to entry: The purging flow is in the direction of the nozzle (countercurrent if compared to the sampling flow, passing in the whole probe and nozzle). The aim of the purging is to prevent contamination of the nozzle while the instrument is in stand-by mode. Purging is not related to the standby cause. Probe's temperature is the one selected for stand-by mode.

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rinsing

solvent based operation at least once a year

Note 1 to entry: See 7.1, i). and Annex B.

Note 2 to entry: Rinsing is carried out at the end of sampling run on all parts being in contact with the flue gas. Solvents are the same described in EN 1948–1:2006, 6.3 and they can be considered as part of the sample.

3.22

cleaning

operation requiring a complete removal and cleaning of the parts of the sampling train which can be affected e.g. by contamination

Note 1 to entry: Solvents used for cleaning of external parts of the sampling train are not to be considered part of the sample.

3.23

thermal desorption of the probe and sampling line

operation carried out at the end of the sampling run

Note 1 to entry: Temperature of the probe when heated, increases up to 200 °C to remove trace organic compounds which can be settled in the probe after a long-term sampling. The direction of the flow is from the nozzle to the sampling unit. Duration of the process is typically 15 min to 30 min.

3.24

substitute

value programmed in the memory of the control unit

Note 1 to entry: This substitute is used to continue the run of the sampling even in case of defect or missing of parameters of the system. For instance, if the external oxygen analyser is out of use, it is possible to switch to the substitute value for oxygen and to continue the run of the sampling. The value is calculated taking into account the mean value of the parameters since the last maintenance. In the case of e.g. oxygen analyser maintenance the last valid value is taken as long as the "Analyser Maintenance" signal applies. Attention is drawn to the fact that it should be reported, if values are substituted (see 7.2.4.4).

4 Symbols and abbreviations

For the purposes of this document the following symbols apply.

4.1 General

ELV emission limit value

I-TEF international toxic equivalent factor (for a detailed description see EN 1948–1)

I-TEQ international toxic equivalent obtained by weighting the mass determined with the

corresponding I-TEF (for a detailed description, see EN 1948–1)

LOQ lower limit of quantification

PU foam polyurethane foam used as adsorbent PREVIEW

ULOQ upper limit of quantification

WHO-TEF toxic equivalent factor proposed by WHO (for detailed description see EN 1948–1)

WHO-TEQ toxic equivalent obtained by multiplying the mass determined with the corresponding

WHO-TEF including PCDDs, PCDFs, PCBs (for detailed description see EN 1948-1)

XAD-2 used as adsorbent 5c956aa13/sist-ts-cen-ts-1948-5-2015

4.2 Polychlorinated biphenyls, polychlorinated dibenzodioxins and polychlorinated dibenzofuranes

HpCDDheptachlorodibenzo-p-dioxinHpCDFheptachlorodibenzofuraneHxCDDhexachlorodibenzo-p-dioxinHxCDFhexachlorodibenzofuraneOCDDoctachlorodibenzo-p-dioxinOCDFoctachlorodibenzofurane

PCDD/PCDF polychlorinated dibenzo-p-dioxin/dibenzofurane

PCB polychlorinated biphenyl

PeCDDpentachlorodibenzo-p-dioxinPeCDFpentachlorodibenzofuraneTCDDtetrachlorodibenzo-p-dioxinTCDFtetrachlorobenzofurane