PD CEN/TS 1948-5:2015

BSI Standards Publication

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

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National foreword

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A list of organizations represented on this committee can be obtained on request to its secretary.

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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

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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.

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.

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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

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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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.

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/m^3 up to 4,0 ng I-TEQ/m^3 and 0,003 ng WHO-TEQ/m^3 up to 4,0 ng WHO-TEQ/m^3 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 clean-up 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.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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*

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

Note 1 to entry: 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
stand by
interruption of the measurement period due to plant shut down or during the changing of sampling support (filters and adsorbant)

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
$^{13}C_{12}$-labelled 2,3,7,8-chlorine substituted PCDFs/PCB added before sampling

3.9
extraction standard
$^{13}C_{12}$-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
$^{13}C_{12}$-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]]

3.13
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_{ref} = 273,15 K), pressure (p_{ref} = 101,325 kPa), water vapour volume fraction (h_{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.

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.

3.21
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	**i**nternational 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
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

4.2 Polychlorinated biphenyls, polychlorinated dibenzodioxins and polychlorinated dibenzofuranes

HpCDD	heptachlorodibenzo-p-dioxin
HpCDF	heptachlorodibenzofurane
HxCDD	hexachlorodibenzo-p-dioxin
HxCDF	hexachlorodibenzofurane
OCDD	octachlorodibenzo-p-dioxin
OCDF	octachlorodibenzofurane
PCDD/PCDF	polychlorinated dibenzo-p-dioxin/dibenzofurane
PCB	polychlorinated biphenyl
PeCDD	pentachlorodibenzo-p-dioxin
PeCDF	pentachlorodibenzofurane
TCDD	tetrachlorodibenzo-p-dioxin
TCDF	tetrachlorobenzofurane

5 Principle of long-term PCDD/PCDF/PCB sampling

5.1 General

For patent rights see Introduction.

The sampling is done isokinetically in the duct for a long time period usually from 24 h up to several weeks, typically four weeks. The sample gas flow rate is automatically controlled. The PCDDs/PCDFs/PCBs, both adsorbed on particles and in the gas phase, are collected in the long term sampling system. Dependent on the sampling system, the sampling unit can consist of different compartments, e.g. filter, condensate flask unit, solid or liquid adsorbent. The systems are based on the following sampling methods, described in EN 1948-1:

— filter/condenser method;

— dilution method;

— cooled probe method.

Schematic representations of the sampling methods according to EN 1948-1 including the modifications for long-term sampling are given in Figure 1, Figure 2 and Figure 3.

The sampling unit is spiked with $^{13}C_{12}$-labelled PCDFs/PCBs 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/PCBs are trapped.

The minimum requirements of the long-term sampling procedure to be met are described in this part of EN 1948. Examples of operation are listed in Annex D. The described systems meet the minimum requirements of Clause 7 and Annex A, but differ in their approach.

After sampling, the sampling unit and the data storage device has to be sent to the analytical laboratory for the sample analysis. The necessary safety precautions, e.g. for transport, have to be fulfilled.

5.2 Long-term sampling based on the filter/condenser method

Long-term sampling systems based on the filter/condenser method filter the dust at a temperature above the flue gas dew point but below 125 °C and cool down the sampling gas to a temperature of about 20 °C as described in EN 1948-1. A higher temperature can be used if it is demonstrated that the minimum requirements for adsorption efficiency are fulfilled (see 7.1, e) and f) and 7.2.1, d)) The PCDDs/PCDFs/PCBs passing the filter are collected in an adsorption medium, e.g. XAD-2. The complete sampling unit comprises a filter and the cartridge with the adsorbent. The condensate is filtered through the adsorption cartridge and discarded via the condensate flask unit.

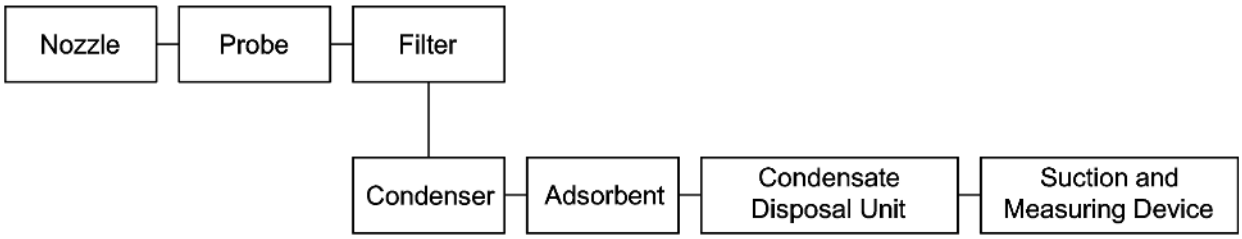


Figure 1 — Scheme of long-term sampling system based on filter/condenser method

5.3 Long-term sampling based on the dilution method

Long-term sampling systems based on the dilution method extract the flue gas from the stack and dilutes the flue gas with cleaned air to a temperature of about 40 °C as described in EN 1948-1 before filtering the dust and adsorption of the gaseous PCDD/PCDF/PCBs in a cartridge. A higher temperature can be used if it is demonstrated that the minimum requirements for adsorption efficiency are fulfilled (see 7.1, e) and f) and 7.2.1, d)).The long-term sampling using the dilution method adds dilution air to the sample in order to avoid the relative humidity of the sampling gas to reach 100 %.

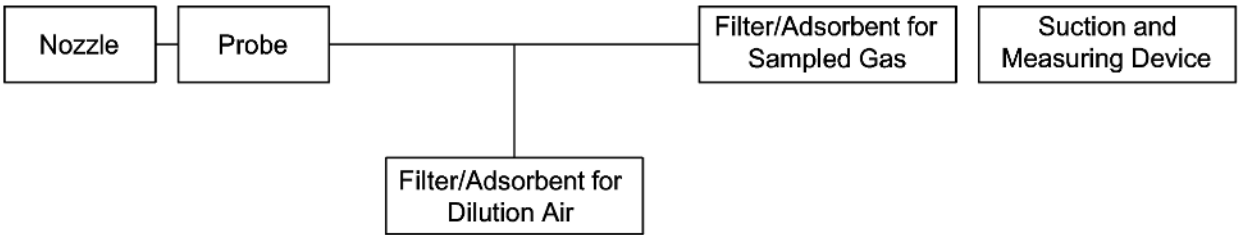


Figure 2 — Scheme of long-term sampling system based on dilution method

5.4 Long-term sampling based on the cooled probe method

Long-term sampling systems based on the cooled probe method extract the sample from the gas stream continuously through a probe, which is cooled to below 20 °C as mentioned in EN 1948-1. The wet sample is drawn through a sampling unit, which consists of a filter and a suitable adsorption medium, e.g. XAD-2. An upper temperature can be used if it is demonstrated that the minimum requirements for adsorption efficiency are fulfilled (see 7.1,e) and f) and 7.2.1,d)). The condensate is filtered through the adsorption cartridge and discarded via the condensate flask unit.

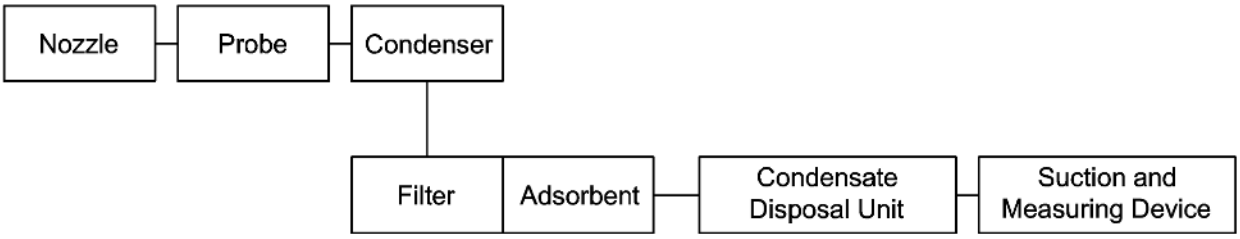


Figure 3 — Scheme of long-term sampling system based on cooled probe method

6 Sampling device and materials

6.1 General sampling device

a) sampling train

b) devices for measuring the flue gas parameters

c) automatic controller

d) measurement data storage system

6.2 Components for the sampling train

a) nozzle with defined shape

b) probes (cooled or heated)

c) flue gas velocity measurement device: e.g. Pitot tube or zero pressure probe

d) condenser, if part of the method

e) tempered filter holder

f) insulated and tempered adsorber cartridge

g) volume measurement device

h) pump to suck in the sample gas

6.3 Automatic controller

The automatic controller should be protected by a password to prevent inadvertent and unauthorized access or adjustment and shall have the following automatic functions:

a) maintenance of the isokinetic sampling condition;

b) leak test at the start and end of the sampling (or can be performed manually as an option);

c) restart after power loss; (after start-up procedures are completed);

d) automatic start and stop following the operation condition of the plant; the start and stop functions are also under control of the operators; the controller functions themselves are sufficiently described by demanding the functionality of reacting upon suitable external control signals, e.g. from oxygen measurement system.

6.4 Devices for measuring the flue gas parameters

Dependent on the type of plant, there are different components and flue gas parameters needed.

a) flue gas velocity in accordance with EN ISO 16911-1 barometer and pressure gauge, if necessary;

b) temperature of the flue gas, if necessary;

c) flue gas composition, if necessary (e.g. taken by the plant data system);

d) O_2 measurement device (e.g. taken by the plant data system);

e) humidity measurement device (e.g. taken by the plant data system).

6.5 Materials

a) All parts of the system in contact with the flue gas: nozzle, probe, glass tubes, filter holder, filter casing, condenser, bubbler, sampling unit etc. shall be made of non-PCDD/PCDF/PCB-adsorbing materials as titanium, quartz or glass.

b) Sealings coming in direct contact with the flue gas shall be made of PTFE furthermore, filter supporting parts made of PTFE can be used if validated by the manufacturer.

c) Particle filter shall be made of quartz or glass fibre, meeting the minimum requirements (see 7.1, e)).

d) Solid adsorbent, XAD-2[1)], polyurethane foam (PU foam), other solid adsorbents (e.g. Porapak PS[1]) meeting the minimum requirements (see 7.2.1, e)). See EN 1948-2:2006, Annex A, for examples on material specification.

7 Minimum requirements for long-term PCDD/PCDF/PCB sampling methods

7.1 Certification of the sampling system

The minimum requirements and method validation criteria shall be fulfilled by the manufacturer of the long-term sampling system and documented and checked during the type performance test which is part of the certification process (see EN 15267-1). For this the following criteria shall be fulfilled.

a) A validation trial shall be carried out at least once with each design of sampling equipment for the specified maximum sampling volume and the specified maximum sampling period (usually 2 weeks or 4 weeks). This trial has to be performed in order to validate the sampling efficiency and the long-term behaviour of the system for the specified measurement periods.

b) Sufficient sample mass shall be collected during all tests of the validation trial so that the quantification limit is less than 5 % of the total amount collected (expressed in I-TEQ or WHO-TEQ).

c) In the case of using two or more probes, it shall be ensured that the unused probes are protected against contamination or cleaned before use, if exposed for long time to stack atmosphere.

d) In case, XAD-2 is used, the XAD-2 cartridge shall be mounted in a vertical direction in order to avoid channelling. Additionally, the flue gas shall flow from top to bottom of the XAD-2 cartridge.

e) The filter efficiency shall be higher than 99,5 % on a test aerosol with a mean particle diameter of 0,3 µm, at the maximum flow rate anticipated (or 99,9 % on a test aerosol of 0,6 µm mean diameter). This efficiency shall be certified by the filter supplier.

f) The overall deposits in the sampling train shall be determined at the end of the intended sampling duration (typically 4 weeks). More than 90 % of the total I-TEQ and WHO-TEQ respectively shall be found in the analysed compartments of the sampling train. This means that less than 10 % of total I-TEQ/WHO-TEQ are acceptable to be found in the sum of the breakthrough sample (see also 7.2.1) and in all compartments not analysed in routine measurements. The breakthrough test shall be performed covering the intended sampling duration using a second sampling unit in series.

g) If the maximum temperature of the sampling gas mentioned in 5.2, 5.3 and 5.4 (filter/condenser method: 125 °C; dilution method: 40 °C; cooled probe method: 20 °C) is exceeded it shall be validated. This validated temperature shall not be exceeded during sampling.

h) A leak check shall be performed before and after each sampling procedure according to 7.2.4.1 (see also D.3.4).

i) A validation trial shall be carried out to demonstrate the comparability of the long-term method against the standard reference methods and shall be performed as follows:

   1) The sampling points of the two methods shall be as close as possible without any interference.

   2) For this validation trial the requirement of grid measurements according to EN 1948-1 are not required.

[1)] XAD-2 and Porapak PS are examples of suitable commercially available products. This indication is only made for information of the user of this European Technical Specification and does not constitute an endorsement by CEN of the product named. Equivalent products may be used.

3) The conditions for the validation of the long-term method and the standard reference methods shall be identical according to the specifications of the long-term measurements system apart from the sampling duration specified in 3.2).

4) Long-term sampling and standard reference sampling according to EN 1948-1:2006, 7.2, a) and 7.2, b) shall be performed in parallel during a specified time period (at least 40 h). The long-term sampling as well as the standard reference sampling is performed for 6 h to 8 h. The sampling unit including the filter of the standard reference methods are exchanged, whereas the sampling unit including the filter of the long-term method are kept for the specified time period. This results in one sample for the long-term method and a mean value of multiple, at least five samples for the standard reference methods.

5) During interruption of the sampling, the sampling probe of the long-term sampling system shall be secured against any contamination. This should be done in the same way as during regular interruptions in the sampling process, e.g. by thermal desorption and reverse flow purging or by closing the nozzle, if appropriate after having removed the probe.

6) At the end of this validation trial the probes of both systems shall be rinsed.

7) The difference between the mean value of the multiple samples of the standard reference methods and the single long-term sample shall be within ± 35 % of the value determined by the standard reference methods based on the corresponding I-TEQ/WHO-TEQ value. This data refers to measurement results in the range of 0,1 ng I-TEQ/m^3 (or WHO-TEQ) values at standard conditions (dry). If the measurement results are much lower than 0,1 ng I-TEQ/m^3 (or WHO-TEQ) the relevance of deviations between SRM result and the long-term sampling systems will be checked according to the normative Annex I.

8) These comparison measurements shall be performed by laboratories fulfilling the requirements of EN ISO/IEC 17025 [4].

Additional minimum requirements for individual systems are given to avoid increase of uncertainty.

j) Filter/condenser method

1) The probe temperature shall be adjusted to a temperature higher than the water dew point.

2) The filter shall adjusted to a temperature below 125 °C in order to avoid chemical reactions on activated surfaces and shall be kept over the dew point to avoid condensation.

3) The condensate shall pass through the adsorbent.

k) Dilution method

1) Dilution air shall be filtered using a filter system with 99,5 % efficiency for 0,3 µm particulates and with efficiency > 90 % for PCDDs/PCDFs/PCB. The filter system has to be exchanged at least once a year.

2) The probe temperature shall be adjusted to a temperature higher than the dew point.

l) Cooled probe method

1) The condensate shall pass through the sampling unit.

7.2 Validation of the installation/functioning on each plant to be fulfilled by the plant operator

7.2.1 Long-term PCDD/PCDF/PCB sampling systems using sampling units which have to be prepared in the laboratory

a) Before use, the sampling unit has to be cleaned carefully to avoid any contamination (see EN 1948-1).

b) The sampling standard shall be added to the filter and/or the adsorbents of the sampling unit.

c) The prepared sampling unit shall be securely sealed against contamination and placed in clean containers for transport.

d) The filter efficiency shall be higher than 99,5 % on a test aerosol with a mean particle diameter of 0,3 µm, at the maximum flow rate anticipated (or 99,9 % on a test aerosol of 0,6 µm mean diameter). This efficiency shall be certified by the filter supplier.

e) The overall deposits in the sampling train shall be determined at each installation. More than 90 % of the total I-TEQ and WHO-TEQ respectively shall be found in the analysed compartments of the sampling train. This means that less than 10 % of total I-TEQ/WHO-TEQ are acceptable to be found in sum in the breakthrough sample (as determined during the type performing test) and in the deposit of the probe.

f) The O_2 measurement data can be taken from the plant (measured by a certified measurement device). In this case the O_2 probe should be situated near to the PCDD/PCDF/PCB sampling probe or representative O_2 comparative measurements shall be performed.

7.2.2 Minimum requirements for set-up

a) All available information on the plant relevant to estimate the emission behaviour shall be considered to configure the long-term sampling system. The requirements of EN 15259 shall be considered.

b) The measurement section shall allow the sampling and execution of measurements at a suitable measurement cross section and shall be selected according to EN 15259:2007, Clause 6.

c) The system shall be assembled and set-up according to the manufacturer's installation instructions.

d) Deposits in the probe should be minimized by the following measures:

   1) minimization of the probe length in dependency of the sampling point (see Annex F);

   2) for dust concentrations > 10 mg/m^3 the minimum flow velocity in the probe should be at least 10 m/s and the inner diameter of the probe shall be adapted accordingly.

e) All relevant parameters listed in 7.3.2 shall be recorded as a reference basis for the upcoming maintenance.

7.2.3 Minimum requirements for selecting the sampling point

a) Sampling should be done at representative position(s) in the duct. The measurement for identifying the representative sampling point(s) shall be performed during normal plant operating conditions. EN 15259:2007, 7.2.2 (see Annex F) shall be considered.

b) The determination of the representative sampling point(s) shall be performed depending on the dust concentration of the plant.

c) If the dust concentration in the flue gas is below 10 mg/m^3 (reference conditions) and the requirements of EN 15259:2007, 6.2.1 c), are fulfilled, the determination of the representative sampling point(s) shall be performed according to EN 15259:2007, 8.4 for gaseous components (e.g. O_2 or NO_x) (see Annex H).

d) Any existing data of flow velocity and the oxygen profile from the plant may be used for selecting the sampling point.

e) If the dust concentration in the waste gas exceeds 10 mg/m^3 (reference conditions) or the requirements of EN 15259:2007, 6.2.1, c) are not fulfilled, the representative sampling point(s) determined according to 7.2.3, c) shall be confirmed by a minimum of three comparison measurements of dust. These dust comparison measurements shall be performed simultaneously as a single point measurement at the selected representative sampling point(s) and as a grid measurement according to EN 13284-1. The acceptable deviation Δ between the two average measurements (average value of the measurement at the representative sampling point and the average value of the three comparison measurements) shall be below or equal to the uncertainty of the method for the determined concentration.

f) In order to confirm the selected sampling point(s) and the proper configuration of the long-term sampling system, comparison measurements of PCDD/PCDF with the standard reference methods according to EN 1948-1:2006, 7.2, a) and 7.2, b) shall be performed for 6 h to 8 h.

   The difference between the mean value of the multiple samples of the standard reference methods and the single long-term sample shall be within ± 35 % of the value determined by the standard reference methods based on the corresponding I-TEQ/WHO-TEQ value. This data refer to measurement results in the range of 0,1 ng I-TEQ/m^3 (or WHO-TEQ) values. If the measurement results are much lower than 0,1 ng I-TEQ/m^3 (or WHO-TEQ) the relevance of deviations between SRM result and the long-term sampling systems will be checked according to the normative Annex I.

g) The nozzle(s) should be placed as close as possible to the selected sampling point(s). If several representative points are identified, the point which corresponds to the shortest probe should be selected in order to minimize dust deposits in the probe. Nozzle positioning close to the sampling point for O_2 and flanges for reference measurements of the plant is preferable.

7.2.4 Minimum requirements for sampling

7.2.4.1 Leak test

The integrity of the all connections and the tightness of the system shall be tested by a leak check after set-up, before and after each sampling procedure. The leak check is performed in the following way:

a) For set-up and maintenance the complete sampling train shall be assembled including the nozzle and shall be checked by a leak check according to EN 1948-1:2006, 7.2, c). The leak rate shall be less than 5 % of the normal flow rate.

b) A leak check before and after each sampling procedure shall be performed. The leak test should include the complete assembled train including the nozzle and the sampling probe. The leak rate shall be less than 5 % of the normal flow rate.

If it is not possible to include the nozzle and the sampling probe into the leak check it can be accepted that the leak check only needs to include all parts, which are installed newly before the start (e.g. sampling unit), and all parts downstream of the sampling unit, adsorbent and/or filter. The leak rate shall be less than 5 % of the normal flow rate. In this case the tightness of the complete system should be checked according to a) at least once a year.

During the sampling it is recommended to monitor the tightness of the system by continuously measuring oxygen, humidity and/or pressure.

7.2.4.2 Isokinetic sampling

a) Isokinetic sampling shall be performed. To ensure isokinetic sampling an alarm system shall be installed to indicate if the isokinetic rate differs by more than −5 % to +15 % from the ideal isokinetic condition. If the deviation of the isokinetic rates cannot be kept between these limits for more than 15 min, then the system should stop the sampling and the stop should be indicated by an alarm signal. The alarm should be included in the sampling protocol.

b) Preferably, the isokinetic sampling should be done according to EN 13284-1:2001 using a nozzle with minimum diameter of 6 mm.

c) If the use of a 6 mm nozzle is not possible, the nozzle diameter can be reduced to a minimum of 3 mm under the following prerequisites:

   1) Particle concentration < 10 mg/m^3 under normal plant operating conditions (demonstrated e.g. by online particle monitoring systems of the plant).

   2) This deviation from the requirements described in EN 13284-1 has to be validated, explained and reported.

d) According to EN 13284-1:2001, 6.2.4 (see also Annex E), the uncertainty of the effective sampling area of the nozzle should be less than 10 % in order to fulfil isokinetic sampling.

e) The nozzle diameters used and the corresponding sampling volume shall be validated in the method validation tests (see 7.1).

f) Any deposition on the nozzle entry shall be minimized in order to ensure isokinetic sampling. Depending on the plant emissions the cleaning frequencies of the nozzle shall be increased with regard to the normal maintenance frequencies (see 7.1, f)).

7.2.4.3 Further minimum requirements for sampling

a) The sampling train is spiked with $^{13}C_{12}$-labelled standards specified in Table 3 and Table 4. The spiked parts of the equipment depend on the method used and are specified in EN 1948-1:2006, 7.2 f).

b) The recovery rate of each sampling standard shall be greater than 50 % calculated on the basis of the relevant extraction standard (see EN 1948-3).

c) In case that XAD-2 is used, the XAD-2 cartridge shall be mounted in a vertical direction in order to avoid channels. Additionally, the flue gas shall flow from top to bottom of the XAD-2 cartridge.

d) The maximum adsorber temperature of the long-term sampling system during normal operation shall not exceed the maximum adsorber temperature tested during the method validation.

e) The permissible limit of quantification (LOQ_i) for the individual congener *i* shall be as follows:

   The field blank shall be less than 10 % of the limit value; if emission values are far below the limit value (e.g. 5 % to 10 % of the limit value) are less or in the same order than the field blank value, the result shall be reported as less or equal to the blank. For the particular case of the field blanks it is not allowed to aliquote the field blank extracts.

If analysing an aliquot as recommended in 9.1 it should be considered that the LOQ_i is increased by the factor of dilution. A field blank shall be performed twice a year for the plant in the following way:

— The blank sample comprises the complete sampling unit consisting of the dust filter and adsorber.

— A new adsorbent unit is inserted as blank sample.

— No gas is drawn through the sampling train.

— A leak check is performed.

— The sampling unit is dismounted and analysed.

If only PCDD/PCDF have to be measured the results are reported as I-TEQ and in case of PCDD/PCD/PCB measurements the result has to be reported as WHO-TEQ.

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

$$LOQ_i \leq \frac{0{,}5\ pg/m^3}{I-TEF_i} \quad (1)$$

where

LOQ_i is the limit of quantification for congener *i*;

I-TEF_i is the international toxic equivalency factor of congener *i*

f) After exceptional plant conditions (e.g. high dust load in flue gas due to maintenance work) the parts of the sampling train coming into contact with the exhaust gas shall be cleaned according to Annex B. An additional rinsing shall be performed and stored. If the following sample gives abnormal results the rinsing solution can be analysed to prove the cleanness of the sampling train.

g) For long-term sampling systems rinsing of the sampling train upstream of the first sampling unit after each sampling is not mandatory but shall be performed once a year according to EN 1948-1:2006, 9.3.5.1, and the rinsing solution shall be analysed. If the rinsing is performed more often than once a year the rinsing solutions shall be combined and analysed. More than 90 % of the total annual mass in I-TEQ and WHO-TEQ respectively shall be found in the analysed compartments of the sampling train. This means that less than 10 % of total I-TEQ and WHO-TEQ respectively is acceptable to be found in sum in the breakthrough sample and in all compartments not analysed in routine measurements.

h) The deposits in the probe can be minimized by the following measures:

   — reduction of the length of the probe;

   — enhancement of flow velocity;

   — rinsing (solution is to be added to the analysed sample);

   — thermal desorption (mass to be included in the sample).

   The deposits in the sampling line upstream the first sampling unit should be determined at least once a year. The mass of the PCDDs/PCDFs/PCBs in the rinsing solution shall be documented in every measurement report as absolute mass value and in terms of the percentage of the corresponding total mass I-TEQ and WHO-TEQ respectively. The loss shall be lower than 10 % (see 7.2.1, e)). If this requirement is not fulfilled, the sampling train shall be checked. A correction of measured values by the quantified loss of less than 10 % is not performed.

i) The PCDD/PCDF/PCB sampling system shall be able to be operated at a minimum velocity of 3 m/s. (or differential pressure of 5 Pa, as specified by EN ISO 16911-1).

j) Depending on the application and the operating conditions which were defined before for this specific application the sampling system should be able to stop or break the sampling if limit values (e.g. velocity

and/or temperature of flue gas, static pressure in stack, O_2 and/or CO_2 content of flue gas, temperature of the adsorption cartridge, etc.) are exceeded.

Each of these breaks has to be registered in the sampling protocol with reason of the break and the total period of how long the break applied.

7.2.4.4 Minimum requirements for data storage system

The measurement data storage system shall store all necessary information regarding sampling, sampling conditions, plant conditions and identification of plant and sample at a suitable data registration rate.

For quality assurance the long-term PCDD/PCDF/PCB sampling system shall record relevant measurement parameters at least every 30 min as 30 min mean values. Shorter record periods can be used, whereby then the mean value calculation should be adapted to the record period (e.g. 15 min mean value if record period is 15 min). Interruptions, events and standby periods have to be recorded at the time they occur. All other parameters are recorded in addition then for the time period since the last record.

As minimum the following parameters shall be recorded and reported:

a) flue gas velocity (mean value);

b) mean flue gas temperature during the last period;

c) maximum adsorber temperature during the last period;

d) flue gas pressure;

e) total sampled volume in standard conditions dry;

f) identifiers for the different kind of records (start/end of sampling, interruptions, events);

g) maximum filter temperature during the last period, if appropriate, depending on sampling technique;

h) temperature of the sampling probe, if appropriate;

i) flue gas humidity, if appropriate;

j) O_2 content of the flue gas;

k) dilution factor, if appropriate.

Additional parameters could be stored if necessary or helpful, e.g.

l) minimum/maximum flue gas temperature during the last period;

m) temperature at the gas meter (or volume measurement device);

n) total pressure at the gas meter (or volume measurement device);

o) density factor of gas meter (or volume measurement device);

p) collected condensate value;

q) CO_2 content.

If substitute values are used for any of the above mentioned parameters it shall be also reported in the sampling protocol (see 3.24). The recording should be done in record sets suitable for automatic processing

during data evaluation and reporting. This means the structure of each record set has to be equal. Changes in the data structure within the same recording table should be avoided. Data processing shall be possible by using normal database programs.

The long-term PCDD/PCDF/PCB sampling system shall have an interface to download the recorded data, e.g. to a computer and/or external storage device.

7.3 Minimum requirements for on-going operations on each plant to be fulfilled at regular time intervals by the plant operator

7.3.1 Regular check-up

During the exchange procedure of the sampling unit a plausibility check of the following parameters shall be performed.

a) Check of the volume measurement device (i.e. gas meter, flow meter, flow-control unit) is still functional.

b) Visual inspection of the adsorption cartridge i.e. colour, dust content, contamination.

c) Check the proper operation of the adsorption cartridge sealing, when the cartridge is changed.

d) Visual inspection of the complete system in relation of contamination, tightness of connections and hoses.

e) A field blank shall be performed twice a year in the following way:

   1) The blank sample comprises the complete sampling unit consisting of the dust filter and adsorber. (apart from the sampling device upstream of the first sampling unit).

   2) A new adsorbent unit is inserted as blank sample.

   3) No gas is drawn through the sampling train.

   4) A leak check is performed.

   5) The sampling unit is dismounted.

7.3.2 Maintenance

a) A maintenance procedure shall be performed once per year.

b) The system shall be dismantled and all parts upstream of the sampling unit coming into contact with the flue gas shall be cleaned. But the requirements of 7.2.4.3, g) shall be fulfilled.

c) The integrity of the nozzle to probe connection shall be checked.

d) The maintenance procedure shall also include the following devices and parameters, to be calibrated where appropriate:

   1) device(s) for monitoring and controlling the isokinetic conditions, i.e. zero point of differential pressure sensor, static pressure sensor, plugs and wires of temperature sensors,

   2) volume measurement device,

   3) temperature sensor at the sampling unit,

   4) vacuum pump,

5) velocity measurement system,

6) status values (plausibility check),

7) if appropriate, sample gas cooler,

8) if appropriate, calibration of the gas meter (validation check),

9) if appropriate, flow meter or flow controller (validation check).

e) Additionally any manufacturer's recommendation shall be taken into account.

f) A leak test shall be performed according to 7.2.4.1.

g) At the end of maintenance, all devices and the long-term sampling system shall meet the performance after the first installation.

h) The maintenance procedure, any service and repair shall be documented.

i) All measurement relevant devices with respect to Table A, e.g. volume meters, shall be checked at least every 12 months.

Table 1 — Overview of general requirements for design and performance

Parameter	Criterion	Description
filtration efficiency	> 99,5 %	7.1, e) tested once by design
collection efficiency	> 90 %	7.2.1 and 7.2.4.3, f)
Quantification limit	For validation the quantification limit is < 5 % of the total masses LOQ_i < (0,5 pg /m^3)/ I-TEF$_i$	7.1, b) and 7.2.4.3, e)
Overall deposit and breakthrough	< 10 % of the total mass in TEQ	7.1, f)
Temperature of the sorbents	5 °C < to ≤ 50 °C	5.2, 5.3, 5.4
Leak check	< 5 %	7.2.4.1
Comparability with SRM	Deviation < 35 %	7.1, i) 4), 7.1, i) 7) duration > 40 h
Minimum velocity in the probe	> 10 m/s	7.2.2, d)
Isokinetic sampling	Deviation between −5 % and +15 %	7.2.4.2
Nozzle diameter Nozzle area	≥ 4 mm or ≥ 3 mm if particle concentration < 10 mg/m^3 Uncertainty on area < 10 %	7.2.4.2
Recovery rate of spiking components	> 50 %	7.2.4.3, b)
Blank sample	see 7.2.4.3, e)	7.2.4.3, e) at least twice a year

8 Quality assurance

8.1 General

Quality assurance refers to a recurring planned and systematic activity so that quality requirements can be fulfilled.

Systematic measures in correspondence to the standard should basically be a helpful tool to prevent errors. Quality assurance measures should be documented in order to trace the performances in time.

8.2 Quality assurance for the sampling unit

8.2.1 Leak check

A leak check shall be performed and documented before and after each sampling procedure according to 7.2.4.1.

8.2.2 Field blank

A field blank shall be performed according to 7.2.4.3 e) to check the absence of contamination of the sampling cartridge and the sampling line at least twice a year. The last field blank value is divided by the same volume as the actual sample volume. A field blank control shall be implemented in the measurement procedure.

The concentration of the blank sample shall be performed according to 7.2.4.3 e). If this value is exceeded, the previous results and the significance of the blank value should be re-assessed. All field blanks shall be reported referring to the measurement results and any measure in order to increase the quality of the field blanks of the future measurements shall be taken.

8.3 Quality assurance for sampling volume

8.3.1 Initial quality assurance

If a gas meter is used to measure total volume and volume flow, the calibration certificate of the gas meter producer can be used. It is usually valid for 1 year.

If volume measuring devices are used, where the output reading is influenced by the gas density, there is the need to evaluate the calibration function, starting from zero to the maximum flow rate using typical flue gas composition of the plant. The evaluation of the calibration function shall be done by comparison measurement with a reference gas meter and a silica gel absorber to subtract the water vapour.

In addition to the dry volume reading, the calibration function of the humidity measurement shall be measured. Evaluated calibration function shall be used to calculate the wet volume reading, necessary to adjust the isokinetic sampling.

8.3.2 Ongoing quality assurance on site

The leak check is an important precondition for accurate sampling volume and accurate sampling flow. The leak check shall be done before each start and at the end of the measurement according 7.2.4.1.

The sampling flow shall be measured by comparison of the total flow with silica gel dryer and a reference volume meter with temperature and pressure compensation, including the influence of the humidity. Comparison measurements shall be done at least once a year.

The quality assurance of the wet volume measurement shall be done by calibration of the humidity measurement device, in the operation range. Calibration shall be done at least once a year.

8.4 Quality assurance of isokinetic sampling

The sampling flow rate shall be adjusted in such way that the velocity vector, direction and magnitude of the gas entering the sampling nozzle is the same as the velocity vector of the gas in the duct at the sampling point [EN 13284-1:2001, definition 3.5].

The deviation of the isokinetic rate shall be limited to the interval: −5 %; +15 % on the average sampling time [EN 13284-1:2001, requirement 8.4].

8.5 Quality assurance of flue gas conditions (O_2 content, temperature, pressure, humidity)

The calculation of the stack gas velocity from differential pressure measurements made with a pitot tube requires the knowledge of the stack gas density, which is calculated from these five parameters:

— temperature,

— pressure,

— humidity,

— O_2 content,

— CO_2 content.

These flue gas data may be obtained from calibrated automated monitoring instruments installed on the stack or directly monitored by the sampling system.

If the flue gas parameters are monitored by the sampling system directly the devices need to be calibrated. The calibration intervals of Table 2 shall be met. Methods specified in EN ISO 16911-1 shall be used for calibration.

Table 2 — Parameters for quality assurance of flue gas conditions

Parameter	Calibration interval	Drift tolerance
Temperature	12 months	1 °C
Pressure	6 months	10 mbar
Humidity	12 months	1 Vol%
O_2 content	24 h	0,5 Vol%
Carbon dioxide	24 h	0,5 Vol%

9 Analytical procedure

9.1 General

The sampling train is spiked with $^{13}C_{12}$-labelled PCDD/PCDF standards and/or $^{13}C_{12}$-labelled PCB-standards before sampling according to Table 3 and Table 4. The set of the labelled standards shall be identical to the composition of EN 1948-1, EN 1948-2, EN 1948-3 and EN 1948-4. The total masses of the sampling standard and the extraction standards have to be adapted to the expected concentration in the flue gas and to the expected sampling volume. Table 3 gives an example for a PCDD/PCDF of 0,05 ng I-TEQ/m^3 assuming 250 m^3 of sampling volume (approximately 4 weeks sampling duration). Table 4 gives an example for a PCB concentration of 0,005 ng WHO-TEQ/m^3 assuming 250 m^3 of sampling volume (approx. 4 weeks sampling duration).

The measured concentration shall be within the calibration range. It is recommended to perform the analyses only with an aliquot of the sample extract (5 % to 50 %). For the calculation of the recovery rate of the extraction standards it is necessary to consider the aliquot within the masses of the extraction standards.

The amount of recovery standards have to be adapted to the amount of the extraction standard. In the example of Table 3 and Table 4 it is assumed that an aliquot of 5 % of the sample extract is taken for the analysis.

9.2 Extraction of the sample

After sampling, extraction is necessary to separate the PCDDs/PCDFs/PCBs from the matrix in an appropriate solvent volume. Extraction procedures are based on soxhlet extraction of filters and adsorbents and liquid extraction of condensates.

Extraction standards shall be added before the extraction procedure according Table 3 and Table 4. The total mass of the extraction standards have to be adapted to the expected concentration in the flue gas and to the expected sampling volume.

The amount of all standards specified in Table 3 and Table 4 mainly depends on the sampling volume and the expected concentration. Preliminary studies are necessary to decide the precise amount of standards, e.g. by applying the standard reference methods according to EN 1948-1. The extraction process applies to the requirements of EN 1948-2:2006, 8.3, and EN 1948-4:2010+A1:2013, 8.2.

9.3 Partitioning of the sample extract

The clean-up procedure of EN 1948-2 is suitable for a flue gas sample of 10 m^3 at a level of 0,1 ng I-TEQ/m^3. Long-term sampling shall collect e.g. a volume of 50 m^3 to 400 m^3. Depending on the sampled volume and the LOD target it is necessary to divide the extract in appropriate fractions (5 % to 50 %).

Aliquotation can be performed as follows: After extraction, the complete raw extract is transferred into a flask and filled up to a definite volume (10 ml, 50 ml or 100 ml). Defined aliquots are taken by volumetric division.

Table 3 —$^{13}C_{12}$-labelled 2,3,7,8-chlorine substituted PCDDs/PCDFs congeners to be added to the sample at different stages of the procedure for the long-term sampling

Example for a concentration of 0,05 ng I-TEQ/m^3 assuming 250 m^3 of sampling volume

	Total amount in pg added before:			
	Sampling	**Extraction**	**GC Injection**	**Example for final volume of 25 µl 5 % aliquot [a]**
Solution:	(sampling standard)	(extraction standard)	(recovery standard)	
Total volume in µl:	100	100	25	1 µl analysed
(e.g. toluene, n-nonane)				
Congeners added				
$^{13}C_{12}$-2,3,7,8-TCDF		4 000		8
$^{13}C_{12}$-1,2,3,4-TCDD			400	16
$^{13}C_{12}$-2,3,7,8-TCDD		4 000		8
$^{13}C_{12}$-1,2,3,7,8-PeCDF	4 000			8
$^{13}C_{12}$-2,3,4,7,8-PeCDF		4 000		8
$^{13}C_{12}$-1,2,3,7,8-PeCDD		4 000		8
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF		4 000		8
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF		4 000		8
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF		4 000		8
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	4 000			8
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD		4 000		8
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD		4 000		8
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD			400	16
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF		8 000		16
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	8 000			16
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD		8 000		16
$^{13}C_{12}$-OCDF		8 000		16
$^{13}C_{12}$-OCDD		8 000		16

[a] The masses given in column 5 are not used for calculation of concentrations and recovery rate. They only indicate the absolute concentrations of the labelled standards within the injected volume of 1 µl.

Table 4 — $^{13}C_{12}$-labelled PCBs congeners to be added to the sample at different stages of the procedure for the long-term sampling

Example for a concentration of 0,005 ng WHO-TEQ_{PCB}/m^3 assuming 250 m^3 of sampling volume

	Total amount in pg added before:			
Solution: Total volume in microlitres: (e.g. toluene, n-nonane)	**Sampling** sampling standard 100	**Extraction** extraction standard 100	**GC Injection** recovery standard [a] at least 10	**Example for final volume of 25 µl** **5 % aliquot**[c] 1 µl analysed
Congeners added				
$^{13}C_{12}$-2,3,4,4'-TeCB (60)	10 000			20
$^{13}C_{12}$-3,3',4,5,5'-PeCB (127) [b]	10 000			20
$^{13}C_{12}$-2,3,3',4,5,5'-HxCB (159)	10 000			20
$^{13}C_{12}$-3,3',4,4'-TeCB (77)		10 000		20
$^{13}C_{12}$-3,4,4',5-TeCB (81)		10 000		20
$^{13}C_{12}$-2,3,3',4,4'-PeCB (105) [b]		10 000		20
$^{13}C_{12}$-2,3,4,4',5-PeCB (114)		10 000		20
$^{13}C_{12}$-2,3',4,4',5-PeCB (118)		10 000		20
$^{13}C_{12}$-2',3,4,4',5-PeCB (123)		10 000		20
$^{13}C_{12}$-3,3',4,4',5-PeCB (126)		10 000		20
$^{13}C_{12}$-2,3,3',4,4',5-HxCB (156)		10 000		20
$^{13}C_{12}$-2,3,3',4,4',5'-HxCB (157)		10 000		20
$^{13}C_{12}$-2,3',4,4',5,5'-HxCB (167)		10 000		20
$^{13}C_{12}$-3,3',4,4',5,5'-HxCB (169)		10 000		20
$^{13}C_{12}$-2,3,3',4,4',5,5'-HpCB (189)		10 000		20
$^{13}C_{12}$-2,3',4',5-TeCB (70)			5 000	10
$^{13}C_{12}$-2,3,3',5,5'-PeCB (111)			5 000	10
$^{13}C_{12}$-2,2',3,3',4,4',5-HpCB (170)			5 000	10

[a] **Recovery standards:** Table 3 shows a selection of available $^{13}C_{12}$-labelled PCBs suitable as recovery standards. At least one shall be added for each dioxin-like PCB containing fraction.

[b] **Sampling Standards:** Attention should be paid to possible co-elution problems of PCB 127 and PCB 105 on certain commercially available columns. If the co-elution problems cannot be avoided, it is allowed to omit the sampling standard PCB 127.

[c] The masses given in column 5 are not used for calculation of concentrations and recovery rate. They only indicate the absolute concentrations of the labelled standards within the injected volume of 1 µl.

9.4 Clean-up

The clean-up procedure of EN 1948-2 and EN 1948-4 is suitable for a flue gas sample of 10 m^3 at a level of 0,1 ng I-TEQ/m^3. Long-term sampling shall collect a volume up to e.g. 400 m^3. Dependent on the sampled volume and the LOD target it is necessary to divide the extract in appropriate fractions (5 % to 50 %).

9.5 Identification and quantification

Identification and quantification follow the requirements of EN 1948-3 and EN 1948-4.

Apart from the calculation of the recovery rates of the extraction standards shall take into account the amount of the aliquot.

9.6 Calculation of the recovery rates of the extraction standards

The extraction standards are quantified against the recovery standards as given in Table 3 and Table 4 using Formula (2).

$$R_{\mathrm{i\,e}} = \frac{100}{Q_{\mathrm{i\,e}} \cdot f_{\mathrm{aliquot}}} \times \frac{Q_{\mathrm{i\,re}}}{rrf_{\mathrm{i}}} \times \frac{A_{\mathrm{i\,e}}}{A_{\mathrm{i\,re}}} \qquad (2)$$

where

$R_{\mathrm{i\,e}}$ is the recovery rate of the extraction standard *i,* in percent;

$Q_{\mathrm{i\,e}}$ is the mass of the extraction standard *i* added to the sample, in picogram;

$Q_{\mathrm{i\,re}}$ is the mass of the $^{13}C_{12}$-labelled recovery standard *i* added to the sample, in picogram;

$\frac{A_{\mathrm{i\,e}}}{A_{\mathrm{i\,re}}}$ is the response ratio of the extraction standard *i* and the relevant recovery standard *i* in the sample;

rrf_{i} is the relative response factor of extraction standard *i* relative to recovery standard *i*;

f_{aliquot} is the factor of the aliquot.

9.7 Calculation of results

PCDD/PCDF emissions are expressed as the mass per dry standard cubic meter of waste gas at reference oxygen (or carbon dioxide) content.

The total I-TEQ concentration is calculated by the addition of the concentrations of the 17 individual 2,3,7,8-chlorine substituted PCDDs/PCDFs when multiplied by the appropriate I-TEF according to Formula (3):

$$C_T = \frac{1}{V_{nr}} \sum \left(Q_{i^{12}C} \times \mathrm{I-TEF}_i \right) \qquad (3)$$

where

C_T is the concentration of the emitted PCDDs/PCDFs expressed as I-TEQ under standard conditions dry and reference conditions, in picogram per metre cube;

$Q_{i\ ^{12}C}$ is the mass of the emitted congener , *in picogram*;

V_{nr} is the waste gas volume of the sample under standard conditions dry and reference conditions calculated, in metre cubic;

I-TEF$_i$ I-TEF of congener *i*.

The calculation of the result referenced to standard conditions (273 K and 1013 hPa) and to the state dry and the oxygen content is performed according to Formula (H.1) and Formula (H.2).

If the PCB values shall be included in the result (WHO-TEQ values) the concentrations of all congeners (see EN 1948-4:2010+A1:2013, Table A.1) shall be multiplied by the respective toxic equivalent factors. Then the results of all congeners are summed up.

10 Estimation of uncertainty of the method

10.1 General

The informative Annex G gives an example of the calculation of the uncertainty budget established to demonstrate the compliance of the measuring system with the given uncertainty requirements of this standard. The compliance of the system will be checked at the level of 0,1 ng I-TEQ/m^3 (or WHO-TEQ/m^3). The manufacturer has to provide the uncertainty budget established during the type testing of its long term sampling system.

The procedure for calculating the measurement uncertainty is based on the law of propagation of uncertainty as described in EN ISO 14956 [5] or ENV 13005 [6]. The individual standard uncertainties, the combined standard uncertainty and the expanded uncertainty are determined according to the requirements of EN ISO 14956 or ENV 13005.

The manufacturers have to provide during the type testing information about the uncertainty budget.

10.2 Elements required for the uncertainty determinations

10.2.1 Model formula and parameters

In the first step, the model formula is established. The model formula describes the mathematical relationship between the measurand and all the parameters that influence the result of measurement. These parameters are called input quantities. It is necessary to clearly define the measurand and the input quantities.

The following parameters have been identified to establish the uncertainty budget according to Table 5.

Table 5 — Parameters identified to establish the uncertainty budget

Sampled gas volume: Uncertainty of calibration of the meter Drift between 2 calibrations Reading
Temperature at the gas meter: Uncertainty of calibration of the temperature sensor Drift
Static pressure: Maximal error permitted Reading
Atmospheric pressure
Absolute pressure
Relative pressure at the gas meter: Uncertainty of calibration of the sensor Resolution Lack of fit Drift between two calibration
Adsorption efficiency of the XAD-2 cartridge
Analysis: standard deviation of reproducibility of the analysis

The model function is used to calculate the result of measurement on the basis of the values assigned to the input quantities and to obtain the combined standard uncertainty of the result of measurement by application *of the law of propagation of uncertainty.*

The model formula for the PCDD/F concentration of each congener can be expressed according to Formula (4):

$$C_{t,0di} = \frac{m_{Xi}}{V_{0d}} \tag{4}$$

where

$C_{t,0di}$ is the concentration of the compound considered (one of the 17 PCDD/PCDF congeners) in the flue gas, at standard temperature and pressure and dry gas, in pictogram per metre cubic;

m_{Xi} is the mass of the gas fraction of the considered compound trapped by the sampling unit, in picogramg;

V_{0d} is the volume of dry gas under standard conditions of temperature and pressure,in metre cubic.

The variance related to each concentration of each congener according to Formula (5) is:

$$\frac{u^2(C_{t,0di})}{C_{t,0di}{}^2} = \frac{u^2(m_{Xi})}{(m_{Xi})^2} + \frac{u^2(V_{0d})}{V_{0d}{}^2} \tag{5}$$

where

u is the uncertainty.

The variance related to the global concentration is then according to Formula (6):

$$u^2\left(c_{t,0d}\right) = \left(\frac{1}{V_{0d}}\right)^2 \times \left(\sum_{i=1}^{n}\left(\left[I-TEF\right]_i^2 \times u^2\left(m_{Xi}\right)\right)\right) + \left(\frac{\sum_{i=1}^{n}\left(\left[I-TEF\right]_i \times \left(m_{Xi}\right)\right)}{V_{0d}{}^2}\right)^2 \times u^2\left(V_{0d}\right) \tag{6}$$

where

$\left[I-TEF\right]_i$ is the toxicological equivalency factor of congener i.

10.2.2 Expanded uncertainty

In general, the uncertainty associated to a result of measurement is expressed as an expanded uncertainty which corresponds to the combined standard uncertainty $u(C_{PCDD})$ multiplied by a coverage factor k. Since most of the values of the uncertainty components u_i are determined from test data, where the probability distribution of values is rectangular for most parameters and a normal distribution for a few parameters, a factor k = 2,0 is used for a level of confidence of approximately 95 % since the number of measurements to determine the uncertainty contributions and the associated number of degrees of freedom is sufficiently high or a rectangular distribution is assumed.

The expanded uncertainty $U\left(C_{PCDD}\right)$ of the PCDD mass concentration is determined using Formula (7):

$$U\left(C_{PCDD}\right) = 2{,}0\, u\left(C_{PCDD}\right) \tag{7}$$

where

C_{PCDD} is the PCDD mass concentration in picogram per metre cubic;

$u(C_{PCDD})$ is the combined standard uncertainty, in picogram per metre cubic.

11 Reporting

11.1 Sampling and analytical report

The sampling and analytical report should be generated according to EN 1948-1, EN 1948-2, EN 1948-3, EN 1948-4 and EN 15259. The data collected with an automated long-term sampling system as described in this document shall be integrated into the sampling report. If data are substituted the procedure is in detail explained in 3.24.

The following parameters and information shall be reported in order to demonstrate compliance with this document. This reporting has to be done in a format which is suitable for further processing. Parameters and information collected according to the following.

a) Basic information:

   1) identification of site and sampling location inside the plant;

   2) stack or duct transverse dimensions;

   3) actual software version of the system;

   4) sample number.

b) Sampling data:

   1) Sampling duration:

      — total amount of sampling time, h:min;

      — sampling start, Day/month/year hh:mm of sampling start;

      — sampling stop, Day/month/year hh:mm of sampling stop;

      — list of all relevant events including reasons;

      — availability of the long term sampling.

   2) Leak checks results before and after sampling;

   3) Total sampled volume, standard conditions:

      — dry related to 273,15 K and 101,3 kPa;

      — wet related to 273,15 K and 101,3 kPa.

c) Total collected condensate volume:

   1) total collected condensate volume if cooled probe or filter/cooler method is used;

   2) amount of dilution air if dilution method is used.

   3) mean O_2 value during sampling time;

   4) mean CO_2 value, if flue gas density needs to be calculated for isokinetics;

   5) mean humidity in flue gas, if flue gas density needs to be calculated for isokinetics;

   6) mean operating density factor if flue gas needs to be calculated for isokinetics;

   7) mean isokinetic ratio calculated in accordance with EN 13284-1, mean and maximum filter temperature;

   8) mean and maximum adsorber temperature.

d) Additional information for the methods

1) Filter/condenser method:

   — mean probe temperature;

   — mean condenser temperature;

   — total collected condensate volume.

2) Cooled probe method:

   — total collected condensate volume.

3) Dilution method:

   — mean probe temperature;

   — total dilution volume in standard conditions dry.

e) List of all relevant events (interruptions ≥ 15 min) during the sampling, including the reasons. Shorter interruptions can be listed in summarized form (x times interruption Y with single duration < 15 min).

11.2 Record keeping every half hour

For quality assurance the long-term PCDD/PCDF/PCB sampling system shall record relevant measurement parameter as 30 min mean values. If data are substituted the procedure is detailed explained in 3.24. As a minimum requirement following parameters shall be recorded:

a) Stack data:

   — temperature of the flue-gas;

   — O_2 content of the flue gas;

   — CO_2 content of the flue gas;

   — Flue gas humidity; if appropiate

   — velocity of the flue gas.

b) Sampling data:

   — sampled volume in standard conditions dry;

   — temperature of dry gas meter;

   — pressure of dry gas meter;

   — isokinetic ratio (calculated in accordance with EN 13284-1);

   — temperature of the sampling unit;

   — maximum temperature of the sampling unit.

c) Additional information for filter/condenser method:

   — probe temperature;

— filter temperature;

— condenser temperature;

— collected condensate volume.

d) Additional information for cooled probe method:

— collected condensate volume;

e) Additional information for dilution method:

— probe temperature;

— dilution volume, standard conditions dry.

The long-term PCDD/PCDF/PCB sampling system shall have an interface to download the recorded data to a computer.

11.3 Interruptions recording

For quality assurance, all the interruption of the sampling period shall be documented. As a minimum requirement following parameters shall be recorded:

— day/month/year, hh:mm of the stop of sampling;

— reason of the interruption;

— day/month/year, hh:mm of the re-start of sampling.

There are a lot of reasons of interruption of the sampling e.g.

— manual stop;

— alarm in sampling system (temperature, isokinetism);

— fire off;

— O_2 in flue gas too high;

— speed, if flue gas too low;

— temperature of flue gas too low.

11.4 Reporting of the method validation (from manufacturer and test house)

The results of the validation shall be reported in a report and shall include the following topics:

a) model name of tested device;

b) manufacturer;

c) test period;

d) date of report;

e) report number;

f) editor;

g) person in charge of technical matters;

h) scope of report;

i) application;

j) serial number and software version;

k) description of the validated system, specific used method (filter/condenser, dilution or cooled probe) incl. sequence of the used elements (e.g. filter, adsorption cartridge, pump etc.);

l) all performances which are described in Reference [7].

Additionally, the following topics should be reported:

— dimensions of adsorption cartridge incl. amount of adsorption material (if applicable);

— maximum validated sampling period;

— maximum validated concentration for maximum sampling period;

— results of break-through test;

— losses in the sampling line upstream of the adsorption cartridge;

— maximum adsorption cartridge temperature;

— flow range through sampling system;

— flue gas conditions of field test (e.g. temperature, humidity, dust concentration, etc.);

— description of the reference measurement system;

— results of the validation test as described in 7.1 i).

Annex A
(normative)

Overview of minimum requirements

The requirements listed in this Annex A are not fully described in this document but in Reference [7] and EN 15267-3.

Table A.1 — Overview on minimum requirements

Performance characteristic **In laboratory** **In the field**	**Criterion**	**Description and test procedure**	**To be considered in the uncertainty budget**
Response time to step changes to flue gas velocity under laboratory conditions,	300 s	MCerts Performance specification (see Reference [7, Chapter 6.3])	No
Accuracy of isokinetic sampling rate	−5 % and +15 %	7.2.4.2	No
Flow repeatability	5 %	MCerts Performance specification (see Reference [7, Chapter 6.3])	Yes
Linearity	5 %	MCerts Performance specification (see Reference [7,Chapter 6.3])	No
Short-term drift of flow under laboratory conditions	5 %	MCerts Performance specification (See Reference [7, Chapter 6.3])	Yes
Minimum operating (flue gas) velocity	No criterion: to be operated at a minimum velocity of 3 m/s. (in MCerts standard criterion is 2 m/s, but it was mentioned that the minimum velocity which can be measured by Pitot/Prandtl tube is 3 m/s)	MCerts Performance specification (See Reference [7, Chapter 6.3])	No
Influence of voltage variations	No criterion: functionality of the long-term PCDD/PCDF/PCB sampling system shall not be affected	C.3.2	Yes
Influence of vibration	No criterion: functionality of the long-	11.4	Yes

Performance characteristic **In laboratory** **In the field**	**Criterion**	**Description and test procedure**	**To be considered in the uncertainty budget**
	term PCDD/PCDF/PCB sampling system shall not be affected		
Accuracy of the long-term PCDD/PCDF/PCB sampling system against a standard reference method (SRM) under field conditions	< 0,035 ng WHO-TEQ/m^3 at concentrations in the range of 0,1 ng I-TEQ/m^3 (or WHO-TEQ/m^3) If the measurement results are much lower than 0,1 ng/I-TEQ the difference between the SRM result and the long-term sampling system results can be greater according to Annex I. Should be used only to validate the installation of the sampling system on each plant	7.2.3 f) and Annex I	No
Maintenance interval under field conditions	> 30 days	7.3.2	No
Availability under field conditions	> 95 %	C.4.4	No
Maximum losses of PCDD/PCDF/PCB in the sampling train under field conditions	10 %	7.1, f)	Yes
Reproducibility of sampled volume and flow under field conditions	5 % [7, Table 6.2 and 6.3]	8.3	Yes
Field blank value	< 10 % of ELV	7.2.4.3, e)	No

Annex B
(informative)

Cleaning of the probe

Long-term PCDD/PCDF/PCB sampling systems are using fixed installed probes, which have to be cleaned before start of the sampling. Long-term sampling systems are constructed also for the possibility to have a very easy operation which can be handled also by a trained plant operator. Therefore each additional handling creates risk of additional faults. Therefore there should be different criteria, that a probe rinsing before/after each sampling is not necessary, e.g. confirmed by a type performance test or similar. If the probe cleaning is necessary, then surely it has to be done after the sampling by e.g. rinsing of the probe and the rinsing solution has to be added to the cartridge. There are two possibilities for cleaning the probes:

a) Purging with compressed air at temperatures higher than 200 °C

   In 7.1, j) the maximum temperature of the filter shall be restricted to +125 °C with the argument to prevent chemical reactions on activated surfaces. This is also in compliance to EN 1948-1. If the probe is purged with compressed air at temperatures higher than +200 °C the risk of such chemical reactions is quite higher and surely depends additional very strong on the flue-gas conditions. It has to be taken into account that the purging direction is performed from the nozzle to the adsorption cartridge and that as many parts as possible (e.g. nozzle, probe, tubes etc.) which are upstream of the cartridge should be included. This will ensure, that any desorption of PCDDs/PCDFs/PCBs during this rinsing will be included in the sampling result. However, under the consideration of practice and possible technical realization it should be acceptable that the nozzle is excluded from this rinsing procedure. If a second probe is installed in parallel the same cleaning procedure has to be performed for this probe.

b) Field operations for probe cleaning (rinsing with solvents)

   Material needed:

   — tools for probe removal;
   — tools for probe disassembly;
   — solvents (one solvent miscible with water, e.g. acetone and toluene);
   — clean flasks (previously washed with the same solvents which will be used for cleaning the probe) to collect washing solution.

   Field operation:

   — Probe removal from the stack (according to the probe fixing and locking characteristics of the device). It is important that all the elements of the probe are removed from the stack to be checked and cleaned.
   — Probe disassembly in the single elements in order to clean all the parts and make a visual check.
   — Wash each single part with acetone and toluene and collect the washing solutions in a flask.
   — When rinsing equipment is wetted by condensate. It is important to use the water miscible solvent (acetone) as the first solvent in the washing sequence to remove water.
   — Reassemble all the equipment.

   For the determination of the deposition see 7.1 f).

Annex C
(normative)

Performance criteria and test procedure for certification

C.1 General relation to other standards

Performance testing of a long-term PCDD/PCDF/PCB sampling system should be consistent with the general approach of EN 15267. The requirements described in EN 15267-1 and EN 15267-2 are applicable completely with the exception that the term of AMS is replaced with the term long-term PCDD/PCDF/PCB sampling system.

Although long-term PCDD/PCDF/PCB sampling systems are not automatic isokinetic samplers, the requirements defined in Reference [7] are applicable.

Additional to this document the requirements of EN 15267-3 are partly applicable as listed below.

C.2 General requirements

C.2.1 Application of the minimum requirements

EN 15267-3:2007, 5.1 is completely applicable.

C.2.2 Certification ranges

In deviation to EN 15267-3:2007, 5.2 the certification range of the long-term PCDD/PCDF/PCB sampling system is:

— for PCDD/PCDF/PCB: twice the Emission Limit Value (ELV);

— for the velocity range: minimum 2 m/s to 20 m/s as listed in Reference [7].

EN 15267-3:2007, 5.3 and 5.4, is applicable.

C.3 Performance criteria common to all long-term PCDD/PCDF/PCB sampling systems for laboratory testing

C.3.1 Performance criteria for the automatic isokinetic control

The performance criteria for the automatic isokinetic control have to fulfil the requirements of Chapter 6, Table 6.1, of Reference [7].

C.3.2 Requirements of EN 15267-3

The requirements of the following chapters of EN 15267-3:2007 have to be fulfilled:

— 6.1, Long-term PCDD/PCDF/PCB sampling systems for the performance test

— 6.2, CE-marking

— 6.3, Unauthorized changes

— 6.6, Display of status signals

— 6.8, Degree of protection provided by enclosures

— 6.14, Influence of the ambient temperature and

— 6.17, Influence of voltage variations

C.4 Performance criteria common to all long-term PCDD/PCDF/PCB sampling systems for field testing

C.4.1 For the automatic isokinetic control

The performance criteria have to fulfil the requirements of those given in Reference [7, Chapter 6, Table 6.3].

C.4.2 Event of long-term sampling

Sampling may be also carried out in cycles, i.e. in regular alternating sampling and pause intervals. In each case at least 30 % of the total time of use shall be documented by measurements. In connection with this, various operating states of the plant shall be considered.

C.4.3 Status information

The sampling system shall be able to process status information about the operation of the plant.

C.4.4 Availability

During the suitability test the availability of the sampling system shall be at least 95 % (see EN 15267-3:2007, Table 5, 8.3; calculation according to 12.6).

C.4.5 Reproducibility

The reproducibility RD shall be determined on the basis of repeated measurements and shall be calculated according to the following Formula (C.1):

$$R_{\mathrm{D}} = \frac{\text{upper limit of the measuring range}}{S_{\mathrm{D}} \cdot t_{\mathrm{f};0,95}} \qquad \text{(C.1)}$$

where

S_{D} is the standard deviation from parallel measurements;

$t_{\mathrm{f};0,95}$ is the student factor; statistical confidence level 95 %.

The repeated measurements shall be carried out simultaneously by means of two identical, complete measuring systems at the same measuring point.

The reproducibility RD in justified individual cases may also be determined by means of a measuring system using a standard reference measuring method.

C.4.6 Automatic post-adjustment unit

In sampling systems with an automatic post-adjustment unit, the facilities envisaged for that shall be included in the suitability test. In the case of an automatic correction being made, the regulation range shall be determined. If the control range to be determined is exceeded, then a status signal shall be given.

C.4.7 Loss of PCDD/PCDF/PCB to be determined in the sampling line

The loss of PCDD/PCDF/PCB to be determined in the sampling gas line (e.g. due to deposition, sorption, diffusion) shall not exceed the value mentioned in 7.1 f) of this part of EN 1948. If necessary, there shall be the possibility for cleaning the sampling line.

C.4.8 Number of values to be determined

For the whole validation test period, at least 15 values per component shall be determined according to the standard reference measuring method.

C.4.9 Labelling

The measuring filters, cartridges etc. used shall be clearly labelled.

Information required are:

— marking of the measuring point/designation of the plant,

— date,

— sampling period,

— volume of extracted sample gas.

C.4.10 Storage life

The storage life of the measuring filters, cartridges etc. shall be tested during the certification test and shall be assessed according to the measurement task.

C.4.11 Blank value

The blank value for the filter and sorption materials shall not exceed 5 % of the limit to be checked relative to the respective sample volume (7.2.4.3).

C.4.12 Relation to the plant conditions

Starting time, duration of sampling and pauses shall be adjustable and adaptable to the operating conditions of the plant.

C.4.13 Isokinetic sampling

Isokinetic sampling shall be isokinetically carried out within an accuracy of −5 % and +15 % according to 7.2.4.2.

C.4.14 Essential characteristic data

Essential characteristic data shall be automatically documented in a printer log (e.g. the data according to 7.2.4.2, the effective sampling period and total period of use). Electronic data carriers may be also used.

Annex D
(informative)

Examples of devices and operation for long-term sampling systems

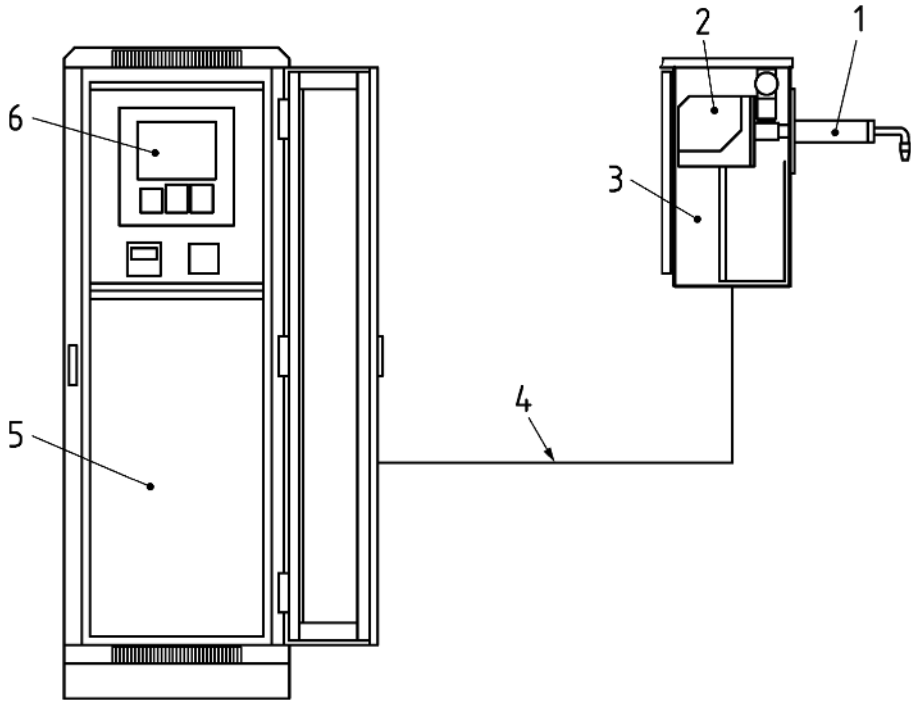
D.1 Filter/condenser method

D.1.1 Summary of apparatus design

D.1.1.1 General

For patent rights see Introduction.

The principle of the Dioxin Emission Control System (DECS)® sampling train is shown in Figure D.1. As it is a long-term sampling system, the device is composed by two main units, a sampling unit, permanently installed on the chimney and a control unit, placed at a variable distance according to the plant accessibility and characteristics.



Key

1 titanium heated sampling probe and Pitot tube

2 heated filter cartridge

3 XAD-2 cartridge

4 electric and pneumatic connection to control unit

5 control unit cabinet with sample gas conditioning and measurement of sucked gas

6 control panel, equipped with a LCD colour interface

Figure D.1 —Schematic presentation of the Dioxin Emission Control System® (filter/condenser method)

D.1.1.2 Sampling unit

It is the unit responsible for the sample collection and stack parameters measuring (gas velocity, pressure, temperature). The sample gas is sucked through the nozzle, probe and filter (t < 125 °C) and then through the condenser and the sorbent trap. The trap is working on the wet phase, following the scheme suggested in EN 1948-1:2006, B.4, variant with solid adsorbent upstream of the condensate flask.

D.1.1.3 Control unit

The control unit is placed on a secure area and communicates with the sampling unit by using a RS485 port. It is responsible for the data acquisition from the stack and the sampling unit parameters, regulation of the flow rate in accordance to the stack condition in order to kept isokinetic conditions, and volume measurement. The sample gas and the condensate are conditioned by a chiller in order to keep it below 10 °C and dry for volume measurement accuracy.

The sampling system is constructed on the basis of a flow rate of 10 l/min to 12 l/min in order to take into account the velocity in the XAD-2 trap (linear velocity smaller than 34 cm/s as specified in EN 1948-1:2006, Annex C), with a range of regulation from 5 l/min to 35 l/min according to the velocity variations

D.1.2 Spiking position

The filter is spiked by distributing portions of the standard solution at different places of the filter. Additionally, the XAD-2 adsorbent may be spiked too/or instead of.

D.1.3 Assembly procedure

As a fixed instrument, the only parts to assemble/disassemble are the titanium filter holder and the XAD-2 trap.

Filter holder: closed filter holder is open only before installation in the sampling position. It is screwed on its position inside the heated box.

XAD-2 trap: Brown glassware trap is sealed with caps. The upper part is plugged and sealed (cap fitted with a PTFE O-ring) to the bottom of the condenser, and the lower part screwed and sealed to the main sampling line.

D.1.4 Leak check procedure

The leak check is a key operation in order to increase sampling quality, to avoid external air to dilute sample from the stack. DECS has got an automated leak check procedure. Vacuum is set at 50 kPa. Measurement is stable, no valve is responsible for the depression, vacuum is set by constant rotation of the inverter driven pump.

Leak check includes all the elements which are moved or replaced (filter holder and XAD-2 trap).

D.1.5 Sampling

A sampling routine is programmed by the operator on the DECS user interface by the user. Parameters to set are the requested sampling time and the filter and XAD-2 cartridge in order to ensure traceability of the sample. Those values are stored in the report.

D.1.6 Sample gas flow control

Isokinetic flow rate is automatically controlled by a feedback regulation between stack measured velocity (Pitot tube) and nozzle velocity. Readings are lower than 1 s and regulations are in the same order. The flow rate is checked by the mass flow meter and modified to fit the condition.

D.1.7 Long-term sample automated features

All the parameters are checked and logged in order to keep sampling traceability. All of them are linked to an alarm with a working interval. If one of the parameters is out of the proper working range, the sampling run is stopped and the DECS switches from the sampling status to the alarm status. This situation secures the sample to contamination by closing the three-way valve and flushing oil-free compressed air inside the probe to prevent dust deposition. The sampling will automatically restart once the parameter in alarm is inside of the working range.

All those operations are reported on screen and logged in the report

Typical volumes for 4 weeks of a sample are about 500 m^3, and the isokinetic deviation is about ± 0,05 %.

D.2 Dilution method

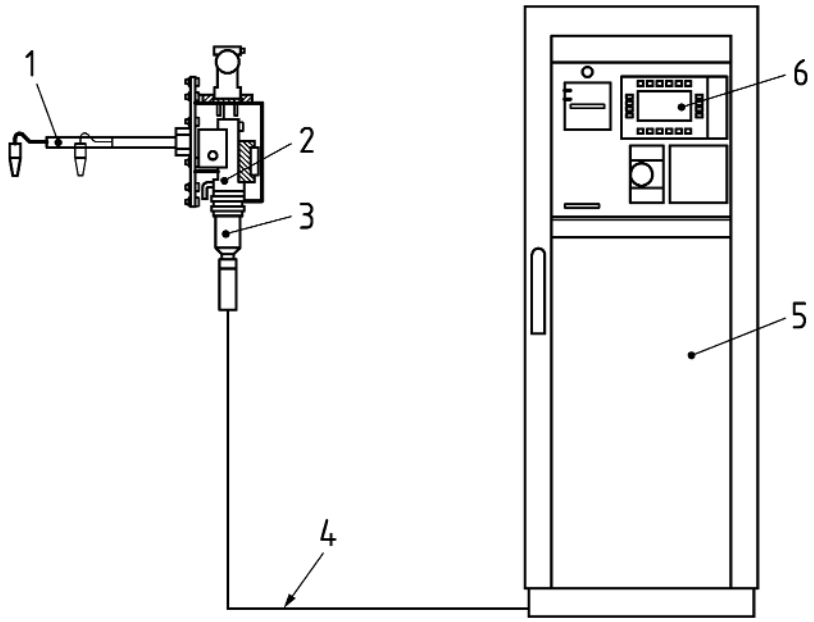
D.2.1 Summary of apparatus design

D.2.1.1 General

For patent rights see Introduction.

The principle of the DioxinMonitoringSystem® is shown in Figure D.2 (see also Reference [8]). Being a long-term sampling system, the device is composed in two main units, the extraction unit and the suction/measurement device.

The extraction unit is installed on the stack, using a flange. The suction and measurement unit is placed at a variable distance nearby in a measurement container. Both units are connected by tubes and cables.



Key

1 titanium heated sampling probe and Pitot tube
2 heated filter cartridge
3 XAD-2 cartridge
4 electric and pneumatic connection to control unit
5 control unit cabinet with sample gas conditioning and measurement of sucked gas
6 control panel, equipped with a LCD colour interface

Figure D.2 — Schematic presentation of the DioxinMonitoringSystem® (dilution method)

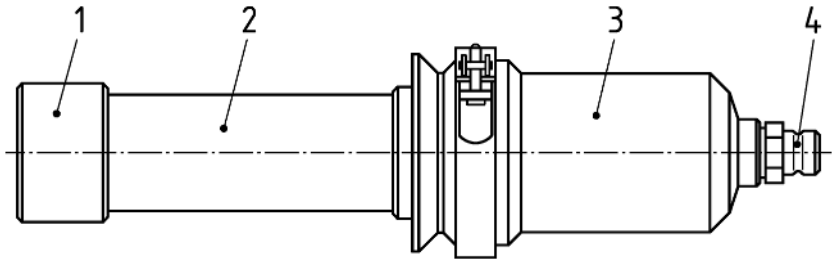
D.2.1.2 Extraction unit

It is the unit responsible for the sample collection and the measurement of the relevant stack parameters for isokinetic sampling. It can extract the sample at 1 or 2 positions in the stack.

The sample gas is sucked through a nozzle, a probe and a closing valve. Downstream it is mixed with dilution air, resulting in a mixing temperature of approx. 40 °C. In the sampling unit at the temperature of approx. 40 °C, the PCDD/PCDF and PCB are precipitated as a sample. It includes the mixing chamber, the filter and the adsorbent.

For isokinetic adjustment a zero pressure probe in combination with a differential pressure sensor is used. Isokinetic deviation is zero, if the differential pressure is zero.

The mixing chamber is designed to precipitate high portions of the dust in the case of high dust loading. Up to 200 g of dust can be precipitated in the mixing chamber. The filter consists of a glass fibre filter with a surface of 0,1 m^2, operated with a dry surface, fulfilling the requirement of 99,5 % precipitation efficiency for 0,3 µm particulates. Due to the low precipitation temperature of about 40 °C, the main mass of PCDD/PCDF and PCB is sampled together with the dust. To adsorb gaseous PCDD/PCDF and PCB, which are passing the filter, 2 polyurethane plugs are used (see Figure D.3).



Key

1 plugging cap for transport to laboratory

2 mixing chamber – dilution air with flue gas

3 chamber consisting dust filter and adsorbent

4 quick connector to heated tube

Figure D.3 — Sampling unit of the DioxinMonitoringSystem®

D.2.1.3 Sucking and measurement unit

This unit is designed to control up to 2 sampling units. This unit measures 2 volume flows, conditions the dilution air and controls the isokinetic sampling. The volume flow is measured by the use of 2 temperature compensated gas meters, a pressure sensor and a humidity sensor. The conditioning of dilution air is done with a 3 stage filter unit. Isokinetic control is done with 2 valves.

For communication with the plant, this unit has an interface to exchange analogue and digital signals. Communication with the plant means, to receive the order to interrupt the measurement or to tell the plant control system that the measurement is interrupted because a stand-by condition is active. Analogue signals like for oxygen can be received and the mean concentration related to the sampling period is calculated to be included in the measurement protocol.

To secure the sample this unit has the feature to connect uninterrupted power supply which allows to close the valves and to maintain the sampling temperature, when main power supply is interrupted.

D.2.2 Spiking position

The filter is spiked by distributing portions of the sampling standard solution at different places of the filter.

D.2.3 Assembly procedure

If the system is installed in a fixed installation only the sampling unit can be assembled/disassembled. It is mounted with a clamp and a quick connector. After the mixing chamber and the quick connector are disassembled the sampling unit is closed with a cap and are stored in a transport box (e.g. titanium) for the transport to the laboratory.

D.2.4 Leak test procedure

The DioxinMonitoringSystem® uses an automatic leak check, at start and at the end of the sampling procedure. Moderate vacuum is applied, afterwards all of the valves are closed and the loss of vacuum is detected. If required by the user the leak check will be repeated within a given interval.

D.2.5 Sampling

To start sampling, the user has to follow this procedure:

— to configure the filter units;

— to assemble the filter unit with the extraction unit;

— to zero the counters;

— to press “Start”.

Afterwards the measurement procedures start automatically. As cleaning measure to reduce blank values, nozzle, inner tube of the probe and closing valve are purged with dilution air in reverse mode for a given period. After purging, a leak check is initiated as described above.

If no stand-by condition is active, the isokinetic sampling is started. Flue gas flow is adjusted until the differential pressure is zero. Due to the use of the zero pressure probe the deviation to isokinetic sampling is calculated based on the measured differential pressure in the nozzle during sampling, without the need to calculate the flue gas density.

As long as the sampling is not stopped by an authorized user, the measurement proceeds. Dependent on active stand-by condition, the measurement is paused.

After automatic stop or manual stop by an authorized user, the system performs a thermal desorption using 200 °C desorption temperature. During thermal desorption the isokinetic sampling is maintained. After 30 min desorption time the thermal desorption is stopped, the pump stops sucking and the valves are closed to secure the sample.

The user prints the measurement protocol by pressing “report”. Together with the sampling unit the printed protocol is given to a transportation box. Sample and measurement protocol are ready for shipment to the laboratory. Sample gas flow control

The differential pressure information from the zero pressure probe and the result of the volume measurement control the isokinetic flow rate. The volume measurement unit measures flow rate of the flue gas and the amount of dilution air. The dilution rate can be in the range of 0 to 8, dependent on the stack velocity, temperature and the humidity.

D.2.6 Long-term sample automated features

All of the parameters for sampling are collected, processed, evaluated and used to extract the flue gas sample, without the need of operator control.

If there is a reason to pause the sampling, the reason is detected and the extraction of the sample is automatically stopped as long as this reason is still valid.

If the filter and adsorber temperature exceeds the configured maximum temperature, sampling is paused to allow the system to cool down below maximum temperature.

If the plant stops the flue gas emission, there are three possibilities to detect. If detected the measurement is paused, if the stack emissions proceed the system starts automatically.

The measurement report prints all pauses with start and end, it prints the sampling time, the stop time and the stand-by time.

Typical sampling volumes during the 4 weeks are in the range of 200 m^3 to 600 m^3, dependent on the flue gas velocity and the stack temperature.

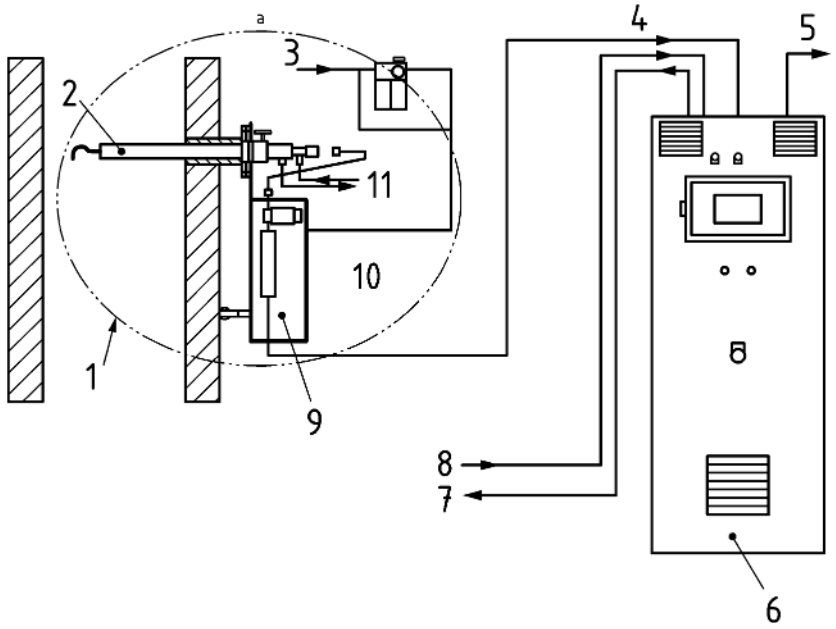
D.3 Cooled probe method

D.3.1 Summary of apparatus design

D.3.1.1 For patent rights see Introduction

The method is based on extraction of a part of the flue gas through a cooled probe and adsorption of PCDDs/PCDFs/PCBs on a XAD-2 adsorber cartridge with integrated dust filter.

The general design is illustrated in Figure D.4 (see also Reference [9]). The long-term sampling system consists of a cooled probe and a sampling unit, which are permanently installed on the stack or duct and a control cabinet. The control cabinet is placed on a variable distance according to the plant accessibilities and characteristics and is connected with the sampling unit by control and flue gas umbilicals.



Key

1	stack	7	condensate drain
2	probe	8	power supply, signal inputs
3	compressed air	9	XAD-2 cartridge
4	gas and condensate transfer line	10	sampling unit
5	option signal outputs	11	cooling water
6	control cabinet		

Figure D.4 — Schematic presentation of the Amesa system® (cooled probe method)

D.3.1.2 Sampling probe

A sample of the flue gas stream is extracted isokinetically through titanium nozzle which is connected to a water cooled probe. The nozzle diameter is variable to be able to adapt it to the different sampling applications. The probe is of titanium construction with a titanium inner liner. Quartz liners are available as an alternative option but they are considered less durable being more susceptible to accidental breakage. For leakage tests the nozzle can be closed automatically.

In the water-cooled probe the sampled gases are cooled down to a temperature below 50 °C, if the long term sampling is validated according to QAL1 [2] for this temperature. Otherwise the temperature of 20°C defined in 5.4 has to be met. The probe incorporates an L- or S-Pitot tube and a thermocouple or temperature sensor. The thermocouple or temperature sensor measures the temperature of the flue gas. The Pitot tube is used to receive the difference between the total pressure of the gas stream and the static pressure or 'wake' pressure (according to the Pitot tube type) to enable the determination of the stack gas velocity at the point of measurement.

D.3.1.3 Sampling unit

Downstream of the cooled probe a sampling unit is installed in which the sample gas and generated condensate pass through a brown glass XAD-2 cartridge where the PCDDs/PCDFs/PCBs are absorbed. The XAD-2 cartridge comprises an integrated dust filter and a bed of XAD-2 supported by porous glass frit (porosity grade 0). The sampling unit is equipped optional with trace heating and/or cooler to maintain the box temperature above 5 °C and/or below +50 °C.

Upstream of the XAD-2 cartridge is installed a valve which is used for the leakage tests, if the sampling probe is not equipped with a valve to close the nozzle.

Downstream of the sampling unit, the cooled, filtered flue gas sample is transported via a PTFE line (heated in case of outside installation) to the control cabinet.

D.3.1.4 Control cabinet

The control cabinet houses a gas cooler, a gas meter, a flow meter, a pump and a control system. In the control cabinet the sample gas is dried by passage through a jet stream heat exchanger reducing the temperature to 5 °C. The generated condensate is pumped away permanently or is optionally collected in a condensate tank.

The parts downstream of the gas cooler are protected by a filter/liquid sensor combination. The dried gas stream then passes through a gas meter to measure the sampled volume and a mass flow meter to determine the mass flow of the sampled gas. The output from the mass flow meter controls the sampling rate at the probe and it provides the isokinetic control for the system.

The gas meter, which is equipped with a thermocouple and a pressure sensor measures the integrated volume of the sampled gas and records it with a resolution of 10 m^3. The control system converts the measured operating volume with the use of the data of the thermocouple and the pressure sensor into standard volumes. The sampled gas is drawn through the system by a rotary vane pump, which is controlled by a frequency converter via a 4 mA to 20 mA signal from the control system.

The system operates fully automatically, collects data relating to both the sampler and other parameters such as plant temperature, duct O_2 and/or CO_2, flue gas humidity and flow. This data are collected via the control system and stored on a memory device (e.g. SRAM card, USB flash drives, etc.) that can be reviewed by using software. The rate of the data collection can be selected whereby a normal rate is half-hourly.

D.3.2 Spiking position

The XAD-2 adsorber cartridge is spiked by distributing portions of the standard solution at different places of the integrated dust filter and/or in the XAD-2 bed.

D.3.3 Handling procedure

After the sampling period (between 2 h and 8 weeks) only the adsorption cartridge has to be exchanged and sent to a laboratory for analysis.

D.3.4 Leak test procedure

At the start, the end and after each break of the sampling an automatic leak test is done. The leak test includes the complete sampling train from the nozzle until the gas pump. In case of no equipped nozzle valve, the leak test includes all parts which are exchanged, means the XAD-2 adsorber cartridge.

D.3.5 Sampling

A sampling routine is programmed by the operator on the control cabinet with the sampling system software. Parameters to set are the conditions to start and stop the sampling (e.g. manually, at fixed times, after fixed sampling period, etc.) sampling number and/or XAD-2 adsorber cartridge.

After the start of the sampling the system starts automatically with the leak test and all procedures to start a correct sampling.

Manual operations on the control cabinet:

— insert sampling number,

— start of sampling,

— stop of sampling,

— if necessary, confirm alarms, which stopped the sampling.

Automated operations by the automatic sampling system:

— leak test at the start, end and after each break,

— isokinetic control of the sampling,

— cooling of the sampled gas,

— purging of the pitot tube and/or sampling probe with oil free compressed air.

D.3.6 Isokinetic flow control

The flow rate through the sampling system is measured by a mass flow meter and with that is calculated the sampled gas velocity at the entrance of the nozzle. Together with the measured velocity of the stack gas (by Pitot tube or external signal) the isokinetic flow rate is automatically controlled, with a control cycle of less than 1 s, by controlling the velocity of the vacuum pump

D.3.7 Automatic features of long-term sampling system

The system operates fully automatically, collects data relating to both the sampler and other parameters such as plant temperature, duct O_2 and/or CO_2, flue gas humidity and flow. This data are collected via the control system and stored in the controller and/or a memory device (e.g. SRAM card, USB flash drives, etc.). If one of the parameters is out of the proper working range, the sampling is stopped and the system switches into the break status. The reason and the time of the break status are recorded. Once the parameter which generated the break was coming back to normal operating conditions the system will start automatically, whereby some alarms and/or breaks need to be confirmed by the operator.

All sampling conditions and events are stored in the sampling protocol. The rate of the data collection can be selected whereby a normal rate is half-hourly.

Typical sampling volumes of 4 weeks sampling are approx. 500 m^3 to 600 m^3 (at standard conditions).

Annex E
(informative)

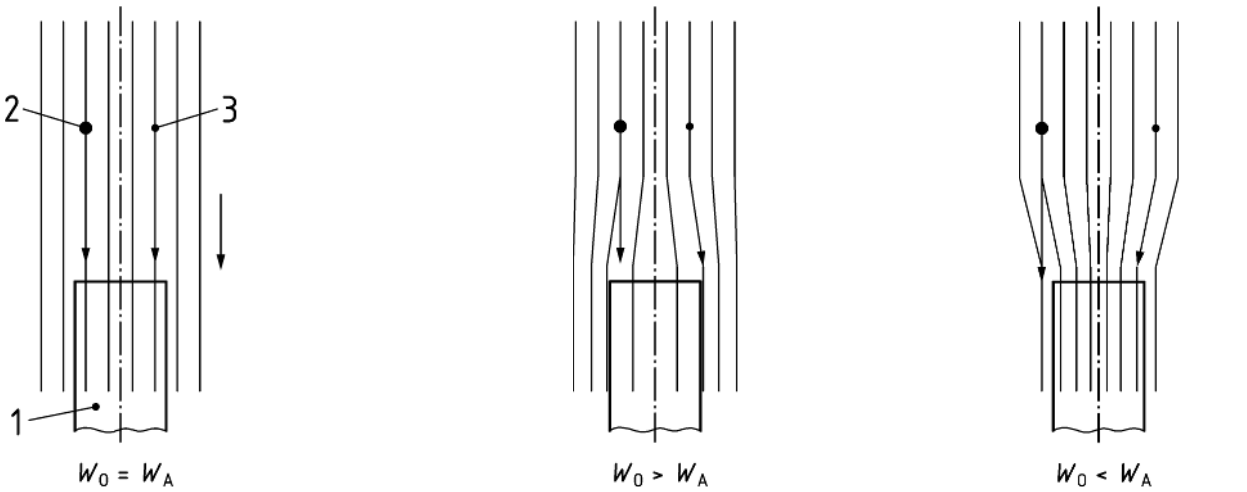
Fundamentals of isokinetic sampling

E.1 Isokinetic sampling

E.1.1 General

Very often the question is raised how big the influence on the accuracy of the isokinetic sampling is if the nozzle diameter is changing during a sampling of several months.

Reasons why isokinetic sampling is normally necessary.



Isokinetic sampling | Under-isokinetic sampling | Over-isokinetic sampling

Key

W_0 real flue gas velocity

W_A aspiration velocity

1 Nozzle

2 Big particles

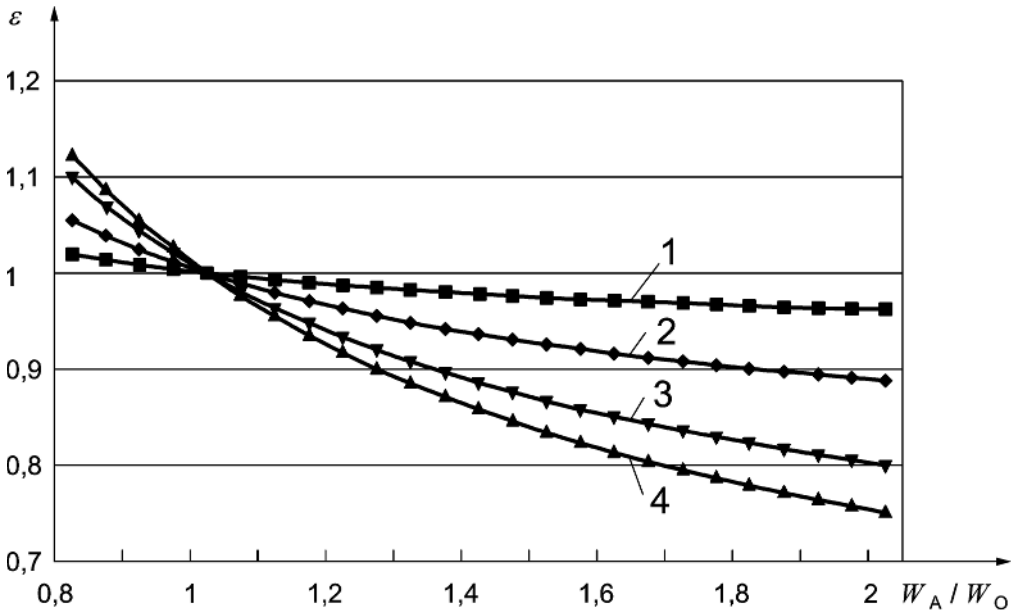
3 Small particles

Figure E.1 — Schemas for sub-isokinetic, over-isokinetic and isokinetic sampling

By under-isokinetic sampling ($W_0 > W_A$) relatively more bigger particle will enter the nozzle = > particle size distribution will be shifted to higher concentration of bigger particle sizes.

By over-isokinetic sampling ($W_0 < W_A$) relatively bigger particles will not enter the nozzle = > particle size distribution will be shifted to higher concentration of smaller particle sizes.

Error (ε) by non-isokinetic sampling depending on particle diameter.



Key

ε error by non-isokinetic sampling depending on particle diameter

W_A aspiration velocity

W_0 real flue gas velocity

1 2,5 µm

2 5 µm

3 8 µm

4 10 µm

Figure E.2 — Example for a degree of sampling ε by non-isokinetic sampling depending on the aerodynamic particle diameter in µm (VDI 2066 Part 10 [11]). E.g. for an aerodynamic diameter of 10 µm an over isokinetic sampling of factor 1.5 causes a sampling-loss of about 15 %

Figure E.2 shows, that sub-isokinetic sampling is more critical than over-isokinetic sampling. Therefore the isokinetic accuracy is defined according to EN 13284-1 as −5 % to +15 %.

E.1.2 Influence on the isokinetic sampling over several days and weeks

There exists an Influence on the isokinetic sampling over several days and weeks, if the nozzle cannot be cleaned automatically. Therefore the risk exists that due to the depositions of particles the nozzle diameter will shrink over the time. In the following tables are given examples how the aspiration velocity in the nozzle is changed depending on the different nozzle diameter, which are used for the different velocity ranges. The extraction flow rate is kept fixed according to the selected nozzle diameter.

Table E.1 —Aspiration) velocities by changing nozzle diameters and isokinetic control according to selected nozzle diameter

Flue gas velocity w_0 = 10 (m/s), nozzle diameter = 8 mm							
Nozzle diameter d in mm	8	7,8	7,6	7,2	7	6,5	6
w_A in m/s	10,0	10,5	11,1	12,3	13,1	15,1	17,8
Flue gas velocity w_0 = 20 (m/s), nozzle diameter = 6 mm							
Nozzle diameter d in mm	6	5,8	5,6	5,2	5	4,5	4
w_A in m/s	20,0	21,4	23,0	266	28,8	35,6	45,0
Flue gas velocity w_0 = 30 (m/s), nozzle diameter = 5 mm							
Nozzle diameter d in mm	5	4,8	4,6	4,2	4	3,5	3
w_A in m/s	30,0	32,6	35,4	42,5	46,9	61,2	83,3

According to Table E.1, the maximum allowed isokinetic deviation is reached, when the nozzle diameter was reduced by approx. 0,4 mm, which means a deposition layer of 0,2 mm inside the nozzle.

By a deposition layer of 0,75 mm to approximately 1 mm (depending on the nozzle diameter) the extraction velocity is already 2 times higher than the real flue gas velocity.

The sampling flow rate will be adjusted in such a way that the velocity and the 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).

The deviation of the isokinetic rate should be limited to the interval: -5 %; +15 % on the average sampling time (EN 13284-1:2001, requirement 8.4).

Perfect isokinetic condition is as follows:

$$w_0 = w_A \tag{E.1}$$

where

w_0 is the entering nozzle gas velocity, in metre per second,

w_A is the gas velocity at the sampling point, in metre per second.

Pitot tubes are used to received the difference Δp_i between the total pressure of the gas and the static pressure or wake pressure (according to the Pitot tube type) to enable the determination of the stack gas velocity

The gas velocity w_A at a sampling point is expressed according to Formula (E.2) as:

$$w_A = \alpha \cdot \sqrt{\frac{2 \cdot \Delta Pi}{\rho_g}} = 129 \cdot \alpha \cdot \sqrt{\frac{\Delta Pi \cdot \overline{T_c}}{\overline{p}_S \cdot \overline{M}}} \tag{E.2}$$

where

α	is the Pitot tube constant;
$\Delta P_i = p_t - p_s$	is the differential pressure of stack gas between total pressure p_t and static pressure p_s, in Pascal;
$\rho_g = \frac{\overline{M}_w \cdot \overline{p}_s}{R \cdot \overline{T}_c}$	is the density of the gas at actual sampling conditions, in kilogram per metre cubic;
$\overline{T}_c$	is the average temperature at actual sampling conditions, in Kelvin;
$\overline{M}_w$	is the molecular weight of the stack gas on a wet basis, in gram per mole;
$\overline{p}_s$	is the static pressure, in Pascal;
R	is the universal gas constant (= 8,314), in joule per mole and Kelvin.

The molecular weight of the stack gas can be calculated knowing the compounds of the stack gas, converted to a wet basis according to Formula (E.3):

$$\overline{M}_w = 18 \times x_\alpha + (1 - x_\alpha) \sum_g \left(M_{a'} \times x_g \right) \quad \text{(E.3)}$$

where

18	is the molecular weight of water, in gram per mole);
x_α	is the fraction of water vapour in the gas stream, in percent;
$M_{a'}$	is the molecular weight of dry gas component of the stack gas, in g per mol;
x_g	is the fraction of dry gas component in the stream, in percent.

It should be noticed that the average velocity according to Formula (E.4) is:

$$\overline{V} = \frac{\sum_i v_i}{N} \quad \text{(E.4)}$$

where

N	is the number of sampling points for short-term isokinetic sampling system.

When considering long term sampling systems, N is the number of values recorded during the average time, because of the fixed probe.

E.1.3 Parameters to be checked

E.1.3.1 α Pitot constant

It is outside of the square root in the formula. Its value has got a strong influence on the velocity value. This parameter, nearly constant on the range of application, needs to be determined and periodically (5 years) checked by an accredited lab. This constant should be reported with its calibration uncertainty. The calibration should be metrologically traceable to SI (Standard International) units. This can be achieved for example by the use of a flow facility with flow rates traceable to Laser Doppler Anemometry. The frequency of calibration of the Pitot will depend on its use. The user may demonstrate that the calibration function of a Pitot is still valid by periodic checks of the Pitot.

E.1.3.2 Δp_i differential pressure

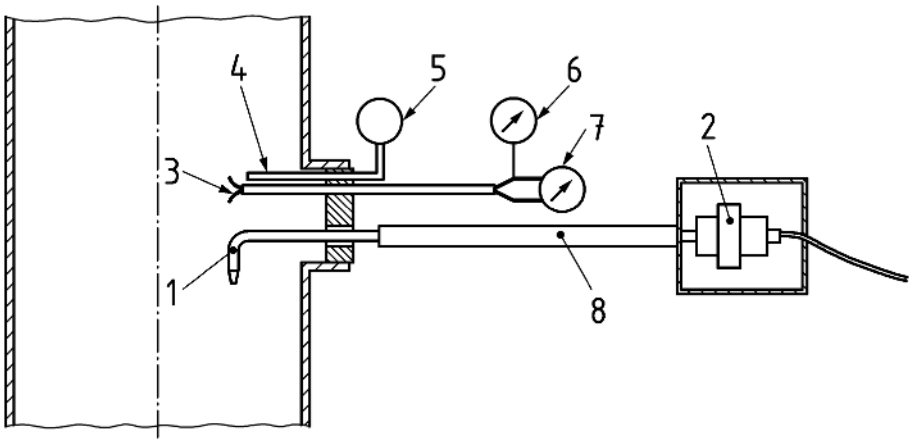
The values should not drift for internal deposition of dust in the Pitot tubes. This will be checked at least at each change of the cartridge. If problems occur, then a purging device should be installed to keep cleaned the Pitot tubes. The situation is acceptable if the reading of the Pitot tube before and after purging with pressurized air to clean pressure taps, are within 5 %.

The differential pressure gauge should be calibrated, at a range appropriate for the application. The calibration should be metrologically traceable to SI. The calibration range of the device should be no more than 3 times the maximum differential pressure required to be measured.

Differential pressure sensor should be checked and calibrated every year and the uncertainty in differential pressure will be lower than 1 % (cf. performance requirements Table 3 of EN ISO 16911-1:2013).

E.1.3.3 p_s static pressure

Following the scheme on EN 13284-1:2001, Figure 4:



Key

1 entry nozzle
2 filter holder
3 Pitot tube
4 temperature sensor
5 temperature indicator
6 static pressure measurement
7 dynamic pressure
8 suction tube (“out stack” device)

Figure E.3 — Schema for isokinetic sampling

Static pressure is taken by the Pitot tube. Static pressure sensor should be checked and calibrated on an appropriate operating range. The uncertainty in pressure should be below 1 %.

Thermocouple should be calibrated on the working range every year with an uncertainty calibration lower than ± 2,5 K or 1 % of the measured value.

All the parts referring to the gas density, composition and water vapour concentration, have got as raw data an input signal coming directly from the plant’s analysers.

Determination of w_n according to Formula (E.5) is

$$w_n = \frac{Q_{v,w}}{A_n} \quad \text{(E.5)}$$

where

A_n is the nozzle face area, in metre square;

$Q_{v,w}$ is the flow rate at the nozzle expressed in the actual sampling conditions, in metre cubic per second.

Further parameters to be checked:

— Devices to check flow rates are dry gas meter (DGM) and mass flow meter.

— DGM should be calibrated and the mass flow meter checked on the calibrated DGM.

— Temperatures and pressures, both at actual and measured conditions, should be checked and logged.

Annex F
(informative)

Example for the determination of the representative sampling point

The selection of the gaseous components depend on their concentration level in the flue gas, which should ensure a reliable measurement and evaluation according to EN 15259:2007, 8.4, or EN 15259:2007, Annex E.2. Here it is assumed that low dust concentration (<20 mg/m^3) in the flue gas show gaseous characteristics under standard conditions. This approach is not directly applicable to finding a representative point for long term dioxin sampling but provides a pragmatic approach based on temperature, velocity and gas concentrations (e.g. O_2 and NO_x).

EXAMPLE Table F.1 shows examples of working platform areas required for the following two measurement objectives:

a) small measurement plane and simple measurement objective (open width of the flue gas duct: 0,2 m diameter, measurement: total carbon);

b) acceptance testing in a waste incineration plant (open width of the vertical flue gas duct: 2 m width (measurement ports) and 1,5 m depth, wall thickness: 0,3 m, measurement: total dust, total carbon, hydrogen chloride, hydrogen fluoride, sulfur dioxide, nitrogen oxides, carbon monoxide, PCDD/PCDF, heavy metals, oxygen, flue gas volumetric flow rate, flue gas pressure, flue gas temperature, carbon dioxide, water vapour).

Table F.1 — Examples of working platform areas

Measurement objective	**Clearance area** m^2	**Minimum area required for instruments, operations or movement** m^2	**Minimum total area** m^2
a	not needed	4	4
b	6	12	18

Permanently installed long term measurement systems are usually restricted to sampling at a single point, or along a single line-of-sight. These sampling points or lines should be located such that a representative sample of the measurand is obtained. They should be positioned so as not to obstruct, or be affected by sampling probes used to perform grid measurements.

For long term measurement systems used for continuous monitoring of emissions, it is necessary that the measurement point is representative for the mass flow density and often also the oxygen volume fraction. Therefore, the best available sampling point for long term measurement systems should be determined according to the following procedure:

— determine the sampling points for the grid measurement according to EN 15259;

— install the probe of the measuring system for the grid measurement;

— install the probe of an independent measuring system (reference measurement) at a fixed point in the measurement section;

— adjust the sample flow in both systems in order to obtain equal response times;

— perform a grid measurement and in parallel measurements at a fixed point in the measurement section, with a sampling time of at least four times the response time of the measuring system but not less than three minutes at each sampling point;

— record for each grid point the observed reference gas temperature T_{ref}, flue gas velocity v_{ref}, oxygen volume fraction o_{ref} and the mass concentration c_{ref} and the observed values T_{grid}, v_{grid}, o_{grid} and c_{grid} of the profile measurement;

— calculate for each grid point i the factor $F_{rep,i}$ according to Formula (F.1):

$$F_{rep,i} = \frac{c_{grid,i} \times v_{grid,i}}{c_{ref,i} \times v_{ref,i}} \times \frac{T_{ref,i}}{T_{grid,i}} \times \frac{21\,\% - o_{ref,i}}{21\,\% - o_{grid,i}} \quad \text{(F.1)}$$

NOTE 1 The terms $(21\,\% - o_{ref,i})/(21\,\% - o_{grid,i})$ and $(T_{ref,i} / T_{grid,i})$ are only used if variations of temperature and/or oxygen content occur in the measurement plane (e.g. at waste incinerators, combustion plants).

The best available sampling point of the AMS for concentration measurements is the point where $F_{rep,i}$ is nearest to the average value F_{rep} of all the grid points. The long term measurement system probe should be placed as close as is practical to this point.

NOTE 2 The remaining deviation from representativeness is incorporated by the calibration of the long term measurement system with standard reference methods according to EN 14181 [2] and is therefore not subject for special attention in this framework.

EN 15259 gives an example of the determination of a suitable measurement point for long term measurement systems analogue to AMS (EN 15259:2007, Annex E.2: Permanently installed AMS).

Table F.2 — Example of finding the best available sampling point for permanently installed long term measurement systems

	NO_x		Oxygen content		Temperature		Velocity			Info profile 1
	c_{grid}	c_{ref}	o_{grid}	o_{ref}	T_{grid}	T_{ref}	v_{grid}	v_{ref}	F_{rep}	
Axis - depth	mg/m³	mg/m³	%	%	°C	°C	m/s	m/s	%	abs(deviation)
Axis 1 - 0,16 m	516	492	7,8	8,6	362	346	27,2	20,3	126,2	0,12
0,47 m	542	501	7,6	8,7	373	346	28,9	20,5	129,9	0,16
0,78 m	540	499	7,9	8,8	380	346	29,3	19,9	135,1	0,21
1,09 m	554	504	7,9	8,8	376	346	30,3	23,1	123,6	0,10
Axis 2 - 0,16 m	429	493	10,5	8,9	343	346	16,9	19,6	87,2	0,26
0,47 m	497	489	8,6	8,8	355	344	29,0	19,5	144,1	0,30
0,78 m	505	486	8,3	8,8	373	344	30,3	20,5	136,1	0,22
1,09 m	480	463	8,3	8,7	364	344	27,1	20,5	125,4	0,12
Axis 3 - 0,16 m	440	468	9,4	8,7	332	342	5,7	20,3	28,8	0,85
0,47 m	467	474	9,2	8,9	339	343	21,5	23,0	95,6	0,18
0,78 m	492	472	8,6	8,8	364	342	31,2	21,0	143,2	0,29
1,09 m	496	474	8,7	8,9	361	342	29,7	21,2	136,6	0,23
Axis 4 - 0,16 m	460	467	9,4	8,9	333	341	7,1	21,7	34,4	0,79
0,47 m	445	447	9,1	8,8	335	341	20,0	21,0	98,9	0,15
0,78 m	466	455	9,0	8,8	347	341	28,3	20,6	140,6	0,27
1,09 m	447	445	9,0	8,8	341	341	27,2	20,8	133,5	0,20
Mean value	486,0	476,8	8,7	8,8	354,9	343,4	24,4	20,8	113,7	0,10

Table F.3 — Calculation for the best available sampling point

Best available sampling point	Axis 1 - 1,09 m
F_{rep} at best available sampling point	123,6 %
Ratio of measured value at best available sampling point to mean value of all grid measurements for:	
NO_x	$c_{grid} / \overline{c_{grid}}$ = 114,0 %
oxygen	$o_{grid} / \overline{o_{grid}}$ = 90,7 %
temperature	$T_{grid} / \overline{T_{grid}}$ = 106,0 %
velocity	$v_{grid} / \overline{v_{grid}}$ = 124,4 %

Annex G
(informative)

Estimation of the uncertainty of measured PCDD/PCDF of the long-term sampling system

G.1 General

Three sampling methods are acceptable:

— filter/condenser method,

— dilution method,

— cooled probe method.

The method considered in this document is the filter/condenser method.

G.2 Analysis of the measurement process and mathematical modelling

G.2.1 Basic formula of the calculation of the concentration of each of the PCDD/PCDF congeners

In the case of a system without derivation and the concentration C_{0di} of each congener of particulate and gaseous phases of PCDD/PCDF is calculated according to Formula (G.1):

$$C_{0di} = \frac{m_i}{V_{0d}} \quad \text{(G.1)}$$

where

C_{0di} is the concentration of the compound i considered (one of the 17 PCDD/PCDF congeners) in the flue gas, at standard temperature and pressure and dry gas, in pictogram per metre cubic;

m_i is the mass of the gas fraction of the considered compound trapped by filtration, condensation and in the sampling unit, in picogram;

$\mathrm{V}_{0\mathrm{d}}$ is the volume of dry gas from the standard conditions of temperature and pressure, at standard temperature and pressure, in metre cubic;

with the indexes:

0 means standard temperature and pressure;

d means dry gas;

i characterize one of the relevant 17 PCDD/F congeners.

Total PCDD/PCDF concentration

In the case of the PCDD/PCDF, total concentration is expressed as toxic equivalents. It is equal to the sum of the concentrations of each of the 17 congeners weighted by their toxic equivalency factor according to Formula (G.2):

$$C_{0d} = \sum_{i=1}^{17} C_{0di} \times I - TEF_i \quad \text{(G.2)}$$

where

$I - TEF_i$ is the congener toxicological equivalency factor for congener i.

G.2.2 Determination of the sampled gas volume collected by a volumetric meter

G.2.2.1 Volume at the actual conditions of temperature and pressure of the gas meter

For a gas meter, the volume sampled is obtained from volumes read on the gas the meter before and after collection according to Formula (G.3) is:

$$V = V_{fin} - V_{ini} \quad \text{(G.3)}$$

where

V is the volume of gas at the conditions of temperature, pressure and humidity of the gas meter, in metre cubic;

V_{fin} is the volume read at the gas meter at the end of the sampling period, in metre cubic;

V_{ini} is the volume read at the gas meter at the beginning of the sampling period, in metre cubic.

G.2.2.2 Volume sampled at standard temperature and pressure conditions, on dry gas (in case of the volume measurement of dry gas)

The calculation of the volume of gas at normal temperature and pressure conditions is given by Formula (G.4):

$$V_{0d} = V_d \times \frac{P_{atm} + \overline{P}_{rel}}{P_0} \times \frac{T_0}{\overline{T}_d} \quad \text{(G.4)}$$

with:

$$\overline{T}_d = \frac{1}{m} \times \sum_{i=1}^{m} T_{d,i} \quad \text{(G.5)}$$

$$P_d = P_{atm} + \overline{P}_{rel} = P_{atm} + \frac{1}{m} \times \sum_{j=1}^{m} P_{rel,j} \quad \text{(G.6)}$$

where

m is the number of sampling points in the cross section;

V_{0d} is the volume of dry gas at standard conditions of temperature and pressure, in metre cubic;

V_d is the volume of dry gas at the actual conditions of temperature and pressure of the measuring device, in metre cubic;

P_0, T_0 is the standard condition of temperature and pressure equal to 273 K and 101 325 Pa, in Pascal and Kelvin;

$\overline{P_{rel}}$ is the average relative pressure at the pressure meter, in Pascal;

P_{atm} is the atmospheric pressure, in Pascal;

$\overline{T_d}$ is the average temperature measured at the level of the gas meter during the sampling period, in Kelvin

$T_{d,i}$ is the i^{th} observed temperature, in Kelvin;

P_d is the absolute pressure at the level of the measuring device, in Pascal;

$P_{rel,j}$ is the j^{th} measurement of the relative pressure at the volume measuring device, in Pascal.

G.2.3 Sources of errors

The mathematical modelling of the PCDD/PCDF concentration measurement is based on the basic formulas used to calculate the concentration.

In these formulas, all parameters have an uncertainty value that contributes to the overall uncertainty of the measured result.

But a more in-depth analysis of the implementation of the measure led to identify additional sources of uncertainty that does not explicitly appear in the expression used to calculate the concentration of the target compound. These sources are such:

— to the heterogeneity of the physicochemical characteristics of gas on the sampling section and to the representative of a sampling point;

— temporal fluctuations of the velocity in the duct leading, particularly in the case of measured compounds in particulate and gaseous form, to gaps of isokinetism;

— temporal fluctuations of concentration in the duct;

— sampling blank that may show a contamination of the adsorber material of the filter or glassware;

— to the efficiency of adsorption of the adsorber material which can be less than 100 %: the requirements in terms of minimum efficiency of collection are set at 90 % for PCDD/PCDF;

— loss of congener of PCDD/PCDF, resulting in a recovery rate of the added $^{13}C_{12}$-labelled sampling standards lower than the minimum requirements;

— to the assumption, that all isomers, are absorbed in the same manner and that the toxic effects are added;

— to a leak.

G.3 Application of the law of propagation of uncertainties

G.3.1 Total concentration of PCDD/PCDF

It is considered that toxic factors are constants; the uncertainty is therefore zero according to Formula (G.7).

$$u^2\left(C_{0d}\right)=\sum_{i=1}^{17}\left(\left(\frac{\partial C_{0d}}{\partial m_i}\right)^2\times u^2(m_i)\right)+\left(\frac{\partial C_{0d}}{\partial V_{0d}}\right)^2\times u^2(V_{0d}) \tag{G.7}$$

G.3.2 Determination of the gas volume collected by a volumetric meter

The application of the law of propagation of uncertainty to the Formula (G.3) leads according to Formula (G.8) to:

$$u^2\left(V\right)=\left(\frac{\partial V}{\partial V_{\text{fin}}}\right)^2\times u^2\left(V_{\text{fin}}\right)+\left(\frac{\partial V}{\partial V_{\text{ini}}}\right)^2\times u^2\left(V_{\text{ini}}\right) \tag{G.8}$$

In the case of a dry volume at standard conditions of temperature and pressure the application of the law of propagation of uncertainty in Formula (G.4) leads to:

$$u^2(V_{0d})=\left(\frac{\partial V_{0d}}{\partial V_d}\right)^2\times u^2(V_d)+\left(\frac{\partial V_{0d}}{\partial P_{atm}}\right)^2\times u^2(P_{atm})+\left(\frac{\partial V_{0d}}{\partial \overline{P_{rel}}}\right)^2\times u^2(\overline{P_{rel}})+\left(\frac{\partial V_{0d}}{\partial \overline{T_d}}\right)^2\times u^2(\overline{T_d}) \tag{G.9}$$

with:

$$u^2\left(\overline{T_d}\right)=u^2\left(\frac{1}{m}\times\sum_{i=1}^{m}T_{d,i}\right) \tag{G.10}$$

$$u^2(P_d)=\left(\frac{\partial P_d}{\partial P_{atm}}\right)^2\times u^2(P_{atm})+\left(\frac{\partial P_d}{\partial \overline{P_{rel}}}\right)^2\times u^2\left(\overline{P_{rel}}\right) \tag{G.11}$$

$$u^2(\overline{P_{rel}})=u^2\left(\frac{1}{m}\times\sum_{j=1}^{m}P_{rel,j}\right) \tag{G.12}$$

G.4 Calculation of type uncertainties

G.4.1 Calculation of the concentration of each of the PCDD/PCDF congeners considered

Sensitivity factors are:

$$\frac{\partial C_{0di}}{\partial m_i}=\frac{1}{V_{0d}}=\frac{C_{0di}}{m_i} \tag{G.13}$$

$$\frac{\partial C_{0di}}{\partial V_{0d}}=\frac{-m_i}{{V_{0d}}^2}=\frac{-C_{0di}}{V_{0d}} \tag{G.14}$$

Type uncertainty according to Formula (G.15) is:

$$\frac{u^2(C_{0di})}{C_{0di}^{\ 2}} = \frac{u^2(m_i)}{(m_i)^2} + \frac{u^2(V_{0d})}{V_{0d}^{\ 2}} \quad \text{(G.15)}$$

G.4.2 Total concentration of PCDD/PCDF

Sensitivity factors:

Formula (G.2) leads to the following sensitivity factors:

$$\frac{\partial C_{0d}}{\partial m_{p,i}} = \frac{[I - TEF]_i}{V_{0d}} \quad \text{(G.16)}$$

$$\frac{\partial C_{0d}}{\partial V_{0d}} = \frac{-\sum_{i=1}^{n}\left((m_i)\times[I - TEF]_i\right)}{V_{0d}^{\ 2}} \quad \text{(G.17)}$$

Type uncertainty:

$$u^2(C_{0d}) = \left(\frac{1}{V_{0d}}\right)^2 \times \left(\sum_{i=1}^{17}\left([I - TEF]_i^{\ 2} \times u^2(m_i)\right)\right) + \left(\frac{-\sum_{i=1}^{17}\left([I - TEF]_i \times (m_i)\right)}{V_{0d}^{\ 2}}\right)^2 \times u^2(V_{0d}) \quad \text{(G.18)}$$

G.4.3 Determination of the volume of gas by a volumetric meter

G.4.3.1 Volume at actual conditions of temperature, pressure and humidity

$$u^2(V) = u^2(V_{fin}) + u^2(V_{ini}) \quad \text{(G.19)}$$

where

$u(V_{ini})$ depends on the reading, function of the gas meter resolution, of the gas meter drift, of its calibration;

$u(V_{fin})$ depends on the reading.

G.4.3.2 Dry volume at standard conditions of temperature and pressure

G.4.3.2.1 Case of the measurement of a volume of dry gas V=V_d

$$\frac{u^2(V_{0d})}{V_{0d}^{\ 2}} = \frac{u^2(V_d)}{V_d^{\ 2}} + \frac{u^2(P_{atm})}{\left(P_{atm} + \overline{P_{rel}}\right)^2} + \frac{u^2\left(\overline{P_{rel}}\right)}{\left(P_{atm} + \overline{P_{rel}}\right)^2} + \frac{u^2\left(\overline{T_d}\right)}{\overline{T_d}^{\ 2}} \quad \text{(G.20)}$$

Standard uncertainty associated with atmospheric pressure depends on resolution of the sensor, calibration uncertainty of the sensor, drift of the sensor, hysteresis of the sensor, repeatability, lack of fit of the sensor.

Standard uncertainty associated with the pressure relative to the level of the sensor:

$$u^2(\overline{P_{rel}}) = \frac{\sigma_{\mathrm{Prel}}^{\ 2}}{m} + \sum_{f=1}^{r} u^2(Corr_f) \quad \text{(G.21)}$$

where:

$\frac{\sigma_{\mathrm{Prel}}}{\sqrt{m}}$ is the standard deviation of the mean of the relative pressure values measured;

$Corr_f$, $f = 1$ to r are the corrections on the relative pressure measurements.

with:

$\sigma_{\mathrm{Prel}} = s_{\mathrm{Pr}\,el}$ or, if the number m of repetitions is less than or equal to 10: $\sigma_{\mathrm{Prel}} = d_n \times \left(P_{rel,\max} - P_{rel,\min}\right)$

For a number of values n < 10, the estimate of the standard uncertainty $\sqrt{\frac{\sum_{i=1}^{n}(x_i - \overline{x_i})^2}{n-1}}$ is biased.

It is then preferable to estimate the standard deviation by correcting the range by a coefficient d_n depending on the size of the sample: $d_n \times range$ with the value of d_n given in the following Table G.1:

Table G.1 — Estimation of the standard deviation

Size of the sample n	**Multiplication factor** d_n	**Size of the sample** n	**Multiplication factor** d_n
2	0,885	12	0,307
3	0,591	15	0,288
4	0,486	20	0,268
5	0,430	25	0,254
6	0,395	30	0,245
7	0,370	40	0,227
8	0,351	50	0,222
9	0,337	60	0,216
10	0,325	80	0,206
11	0,315	100	0,199

The corrections on the relative pressure measurements are related to calibration uncertainty of the sensor, drift of the sensor, hysteresis of the sensor, lack of fit of the sensor.

Standard uncertainty associated with temperature:

The standard uncertainty associated with the measurement of temperature meter is given by Formula (G.22) as follows:

$$u^2(\overline{T_d}) = \frac{{\sigma_{Td}}^2}{p} + \sum_{f'=1}^{r'} u^2(Corr_{f'}) \qquad \text{(G.22)}$$

where

$\frac{\sigma_{Td}}{\sqrt{p}}$ is the standard deviation of the mean of the *p* values of the measured temperature;

$Corr_{f'}$ $f' = 1$ to r' are the corrections on temperature measurements.

with:

$\sigma_{Td} = s_{Td}$ or, if the number of repetitions is greater than 10: $\sigma_{Td} = d_n \times (T_{d,\max} - T_{d,\min})$.

G.4.3.2.2 Corrections on temperature measurements

Corrections on temperature measurements are linked to:

— the resolution of the display used,

— the uncertainty of calibration of the sensor and the display (respective uncertainties or uncertainty of the set if the two elements have been associated to the calibration),

— to the drift of the sensor and the display or complete measurement system,

— the hysteresis of the sensor and the display or full measurement system,

— the linearity of the sensor and the display or full measurement system.

G.5 Calculation of expanded uncertainty

The uncertainty in a measurement is generally expressed as absolute or relative expanded uncertainty. The absolute expanded uncertainty is calculated according to the Formula (G.23):

$$U(C_{t,0d}) = k \times u(C_{t,0d}) \quad \text{(G.23)}$$

where

$U(C_{t,0d})$ is the absolute expanded uncertainty associated with the measurement of the compound;

$u(C_{t,0d})$ is the combined type uncertainty associated with the measurement of the compound;

k is the coverage factor, usually 2.

NOTE The absolute expanded uncertainty is expressed in the same unit as the combined type uncertainty:

$$U(C_{t,0d})_{rel} = \frac{U(C_{t,od})}{C_{t,od}} \times 100 \quad \text{(G.24)}$$

G.6 Example of digital application: measurement of dioxin/furan-concentration

G.6.1 Specific conditions on site

Hypothesis: measurement in a duct where it is assumed homogeneous concentration on the section.

— Sampling system: sampling without bypass system; method to filter and condenser.

— The collection is provided by a pump and sampled gas volume is measured by a meter of dry type preceded by a silica gel cartridge.

The sampling line includes a filter holder and the filter, followed by a condensate bottle condenser, a solid, adsorbent cartridge and the sampling device.

Table G.2 — Measurement conditions

Specific conditions	**Value / range**
Study concentration of PCDD/PCDF: ELVS for the site in ng/m^3 toxic equivalents, at the reference oxygen concentration $O_{2,ref}$	Concentration close to: 0,1 ng/m^3 I-TEQ (or WHO-TEQ) at standard conditions
reference concentration of oxygen $O_{2,ref}$	11 % volume
Measured concentration of oxygen in the field O_2	10,8 % volume ± 6 % relative (k = 2)
Sampled gas volume : V_d	732 m^3
Average temperature at the gas meter: $\overline{T_d}$	296,2 K
Mean absolute pressure at the level of the volumetric meter: P_d	100281 Pa

Measurements of temperature at the gas meters:

Table G.3 — Temperature at the gas meter

Average $\overline{T_d}$	296,2 K
Standard deviation of the average σ_{Td}	3,23 K

Pressure measurements at the gas meter

Atmospheric Pressure: $P_{atm} = 100212$ Pa

Table G.4 — Relative Pressure and absolute pressure at the gas meter

average $\overline{P_{rel}}$ (Pa)	69,2 Pa
P_d	100281 Pa
Standard deviation of the average $\sigma_{\Pr el}$	1,27 Pa

Table G.5 — Analysis results

Isomer	**I-TEF (*)**	**Total mass collected** m_{Xi} ng	**Total mass collected** $m_{xi} \times I - TEF_i$ ng I-TEQ
2,3,7,8-TCDD	1	2,88	2,88
1,2,3,7,8-PentaCDD	0,5	8,1	4,05
1,2,3,4,7,8-HexaCDD	0,1	5,4	0,54
1,2,3,4,7,8-HexaCDD	0,1	7,02	0,72
1,2,3,7,8,9-HexaCDD	0,1	5,4	0,54
1,2,3,4,6,7,8-HeptaCDD	0,01	31,23	0,36
OctaCDD	0,001	44,28	0,045
2,3,7,8-TCDF	0,1	14,58	1,44
1,2,3,7,8-PentaCDF	0,05	26,73	1,35
2,3,4,7,8- PentaCDF	0,5	27,18	13,5
1,2,3,4,7,8- HexaCDF	0,1	37,8	3,78
1,2,3,7,8,9-HexaCDF	0,1	2,25	0,225
1,2,3,6,7,8-HexaCDF	0,1	37,98	3,78
2,3,4,6,7,8-HexaCDF	0,1	38,88	3,87
1,2,3,4,6,7,8-HeptaCDF	0,01	78,3	0,81
1,2,3,4,7,8,9-HeptaCDF	0,01	13,23	0,18
OctaCDF	0,001	30,33	0,027

G.6.2 Performance characteristics of the method

Table G.6 — Performance characteristics of the method

Parameter	Performance characteristics of the method used
Sampled gas volume V_d : Uncertainty of calibration of the meter Drift between 2 calibration Reading	±2 % of the measured value 1 % of the measured value 0,002 m^3
Temperature at the gas meter $\overline{T_d}$: Uncertainty of calibration of the Pt100 + display Resolution of the display Drift	±1,0 K 0,1 K 0,2 K
Atmospheric pressure P_{atm} : Maximal error permitted Reading	±300 Pa 20 Pa
Relative pressure at the gas meter $\overline{P_{rel}}$: (range 0–200 Pa) Uncertainty of calibration of the sensor Resolution Lack of fit Drift between two calibration	±0,6 Pa 0,01 Pa 1,4 % PE 1,0 % PE
Absoption efficiency of the adsorber material	96 %
Analysis : standard deviation of reproducibility of the analysis	30 % of the measured value

G.6.3 Calculation of the concentration

Volume of air sampled at standard conditions of temperature and pressure according to Formula (G.4) is:

$$V_{0d} = V_d \times \frac{273}{\overline{T_d}} \times \frac{P_d}{101325} = 732 \times \frac{273}{296{,}2} \times \frac{100281}{101325} = 667{,}26\ \mathrm{m}^3$$

Concentration of PCDD/PCDF:

Table G.7 — Concentrations of each congener and total concentration

Isomer	Concentration at actual oxygen concentration		Concentration at reference oxygen concentration	
	ng/m^3	ng I-TEQ /m^3	ng/m^3	ng I-TEQ /m^3
2,3,7,8-TCDD	0,01213	0,00607	0,00422705	0,00422705
1,2,3,7,8-PentaCDD	0,00809	0,00081	0,01188857	0,00594429
1,2,3,4,7,8-HexaCDD	0,01051	0,00108	0,00792572	0,00079257
1,2,3,4,7,8-HexaCDD	0,00809	0,00081	0,01030343	0,00105676
1,2,3,7,8,9-HexaCDD	0,04677	0,00054	0,00792572	0,00079257
1,2,3,4,6,7,8-HeptaCDD	0,06632	0,00007	0,04583705	0,00052838
OctaCDD	0,02184	0,00216	0,06499086	6,6048E-05
2,3,7,8-TCDF	0,04003	0,00202	0,02139943	0,00211352
1,2,3,7,8-PentaCDF	0,04071	0,02022	0,03923229	0,00198143
2,3,4,7,8- PentaCDF	0,05661	0,00566	0,03989277	0,01981429
1,2,3,4,7,8- HexaCDF	0,00337	0,00034	0,05548001	0,005548
1,2,3,7,8,9-HexaCDF	0,05688	0,00566	0,00330238	0,00033024
1,2,3,6,7,8-HexaCDF	0,05823	0,00580	0,0557442	0,005548
2,3,4,6,7,8-HexaCDF	0,11727	0,00121	0,05706515	0,0056801
1,2,3,4,6,7,8-HeptaCDF	0,01981	0,00027	0,11492287	0,00118886
1,2,3,4,7,8,9-HeptaCDF	0,04542	0,00004	0,019418	0,00026419
OctaCDF	0,01213	0,00607	0,0445161	3,9629E-05
total concentration C_{0d}	**0,6168 ng/m^3**		**0,6046 ng/m^3**	
total concentration	C_{0d}	**0,057 ng I-TEQ /m$_0^3$**	$C_{0dO2ref}$	**0,056 ng I-TEQ /m$_0^3$**

G.6.4 Calculation of standard uncertainties

Table G.8 — Calculation of standard uncertainties $u(V_d)$, $u(\overline{T_d})$, $u(P_{atm})$, $u(P_{rel})$

Performance characteristics	Standard uncertainty	Relative Standard uncertainty
Sampled gas volume V_d (see Formula (G.9)	$u(V_d) = \sqrt{\left(\frac{2\times 732}{2\times 100}\right)^2 + \left(\frac{1/100\times 732}{\sqrt{3}}\right)^2 + 2\left(\frac{0{,}002}{2\sqrt{3}}\right)^2 + } = 8{,}45\ \mathrm{m}^3$ (see Formula (G.9))	$\frac{u(V_d)}{V_d} = 0{,}0115$
Temperature at the gas meter $\overline{T_d}$	$u(\overline{T_d}) = \sqrt{3{,}23^2 + \left(\frac{1}{2}\right)^2 + \left(\frac{0{,}1}{2\sqrt{3}}\right)^2 + \left(\frac{0{,}2}{\sqrt{3}}\right)^2} = 3{,}27\ \mathrm{K}$ (see Formula (G.10))	$\frac{u(\overline{T_d})}{\overline{T_d}} = 0{,}0110$
Atmospheric pressure P_{atm}	$u(P_{atm}) = \sqrt{\left(\frac{300}{\sqrt{3}}\right)^2 + \left(\frac{20}{2\sqrt{3}}\right)^2} = 173{,}30$ Pa	$\frac{u(P_{atm})}{P_d} = 1{,}73.10^{-3}$
relative pressure at the gas meter $\overline{P_{rel}}$	$u(\overline{P_{rel}}) = \sqrt{0{,}269^2 + \left(\frac{0{,}6}{2}\right)^2 + \left(\frac{0{,}01}{2\sqrt{3}}\right)^2 + \left(\frac{1{,}0/100\times 200}{\sqrt{3}}\right)^2 + \left(\frac{1{,}4/100\times 200}{\sqrt{3}}\right)^2} = 2{,}027$ Pa (see Formula (G.17))	$\frac{u(\overline{P_{rel}})}{P_d} = 2{,}02.10^{-5}$

According to Formula (G.9), the standard uncertainty associated with the volume of sampled gas at standard conditions of temperature and pressure:

$$\frac{u(V_{0,d})}{V_{0,d}} = \sqrt{\left(\frac{u(V_d)}{V_d}\right)^2 + \left(\frac{u(\overline{T_d})}{\overline{T_d}}\right)^2 + \left(\frac{u(P_{atm})}{P_d}\right)^2 + \left(\frac{u(P_{rel})}{P_d}\right)^2} = 0{,}0115$$

For each congener:

$$u(m_{Xi}) = \frac{30}{100} \times m_{Xi}$$

see also Table G.5.

G.6.5 Calculation of the expanded uncertainty associated with concentration

Combined standard uncertainty referred to Formula (G.15):

$$\frac{u^2(C_{t,0d})}{C_{t,0d}{}^2} = 0{,}0109 + 0{,}0115 = 0{,}0224$$

$$u(C_{0d}) = 0{,}0085 \text{ ng I-TEQ /m}^3$$

Referred to Formula (G.23) the expanded uncertainty with k = 2:

$$U_c(C_{0d}) = 0{,}017 \text{ ng I-TEQ /m}^3$$

$$U_{c,rel}(C_{0d}) = 30{,}0 \text{ \%}$$

Additional uncertainty due to losses in the sampling line (2 %), breakthrough: 2 %, leak: 1 %:

$$U_c(C_{0d}) = 0{,}0198 \text{ ng I-TEQ /m}^3$$

$$U_{c,rel}(C_{0d}) = 35{,}0 \text{ \%}$$

Annex H
(informative)

Example for calculation of measurement results for standard conditions

H.1 General

The calculation of stack gas velocity from the differential pressure measurements made with a Pitot tube requires knowledge of the stack gas density, which is determined from the temperature, static pressure and gas molar mass.

In order to refer the measured flow to standard conditions measurements of the following parameters of the stack gas are required:

— temperature,

— water vapour content,

— where necessary measurements may be required of the oxygen or CO_2 content.

These data may be obtained from calibrated automated monitoring instruments installed on the stack.

H.2 Dry volumetric flow rate in standard conditions

The dry volumetric flow rate in standard conditions is calculated according to Formula (H.1):

$$Q_{\upsilon,0d} = Q_{\upsilon,w} \cdot \frac{P_c}{101325} \cdot \frac{273{,}15}{T_c} \cdot \frac{100 - [H_2O]w}{100} \tag{H.1}$$

where

$Q_{\upsilon,0d}$ is the dry volume flow rate, in the standard conditions of temperature and pressure, in metre cubic per second;

$Q_{\upsilon,w}$ is the volume flow rate on wet gas in the actual conditions of temperature T and pressure P_c in metre cubic per second ;

P_c is the absolute pressure in the duct, on the measurement section, in Pascal;

T_c is the temperature of gas, on the measurement section, in Kelvin;

$[H_2O]_w$ is the water vapour content of gas in the duct, in % volume on wet gas.

Requirements on temperature and pressure sensors calibration described in 8.3 should be taken into account.

The H_2O monitor should be calibrated during QAL2 operations.

Calculate the conversion of the volumetric flow rate to a reference oxygen concentration according to Formula (H.2).

$$Q_{\upsilon,Od,02ref} = Q_{\upsilon,Od} \cdot \frac{21 - [O_2]_d}{21 - [O_2]_{ref}} \tag{H.2}$$

where

$Q_{\upsilon,Od,O2ref}$ is the dry volumetric flow rate, in the standard conditions of temperature and pressure, and on reference oxygen concentration, in metre cubic per second ;

$Q_{\upsilon,Od}$ is the dry volumetric flow rate, in the standard conditions of temperature and pressure and on actual oxygen concentration, in metre cubic per second ;

$[O_2]_{ref}$ is the reference oxygen concentration, in % volume;

$[O_2]_d$ is the oxygen concentration measured in the duct during the exploration of the duct in % volume.

The O_2 monitor should be calibrated according to QAL2 (see Reference [2]) operations.

The flue gas data may be obtained from calibrated automated monitoring instruments installed on the stack or directly measured by the sampling system. All flue gas parameters measured by the sampling system directly needs to be calibrated and drift controlled (see EN 14181 [2]).

Annex I
(normative)

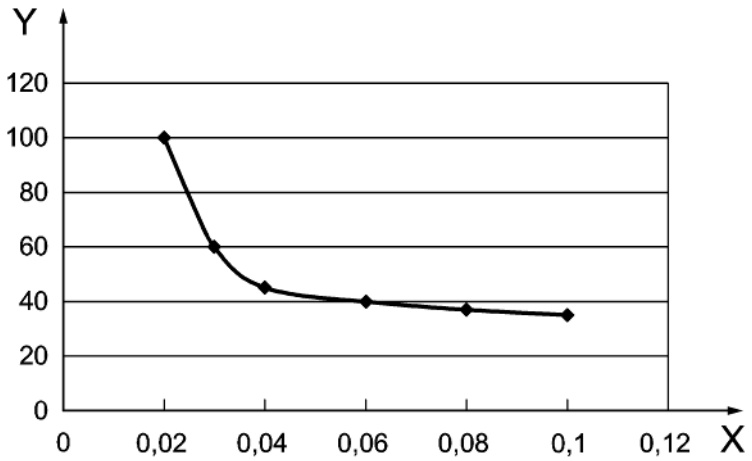
Adaption of the maximum deviation in relation to the PCDD/PCDF/PCB concentration

For measurement results in the range of 0,1 ng I-TEQ/m^3 (at standard conditions, dry) the difference between the I-TEQ values determined by the long term sampling shall be within + 35 % (see EN 1948-3:2006, Annex B) of the value determined by the SRM. If the measurement results of the SRMs are much lower than 0,1 ng I-TEQ/m^3 the difference between the SRM results and the long-term sampling system results can be greater according to Table I.1 (see also 7.1, i),7)).

The comparison has to be made at the level of 0,1 ng I-TEQ/m^3 (at standard conditions) on an appropriate site. If the test shall be realized on all the sites, give an a curve of acceptable differences according to the level of concentration

Table I.1 — Maximum deviation of the long term sampling system results depending on the absolute concentration determined by the SRM

Concentration ng I-TEQ/m^3 (at standard conditions, dry)	Maxim. deviation %
0,02	100
0,03	60
0,04	45
0,06	40
0,08	37
0,1	35



Key

X concentration in ng I-TEQ/m^3(at standard conditions)

Y maximum deviation in %

Figure I.1 — Graphic presentation of the maximum deviation versus concentration

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