



SLOVENSKI STANDARD

SIST EN 1948-1:1999

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Stationary source emissions - Determination of the mass concentration of
PCDDs/PCDFs - Part 1: Sampling

Emissionen aus stationären Quellen - Bestimmung der Massenkonzentrationen von
PCDDs/PCDFs - Teil 1: Probenahme

Emissions de sources fixes - Détermination de la concentration massique en
PCDDs/PCDFs - Partie 1: Prélèvement

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Ta slovenski standard je istoveten z: EN 1948-1:1996

ICS:

13.040.40 Stationary source emissions

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EUROPEAN STANDARD

EN 1948-1

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EUROPÄISCHE NORM

December 1996

ICS 13.040.40

Descriptors: Air, quality, air pollution, gaseous effluents, emission, incinerators, determination, concentration, PCDD, PCDF, sampling, extraction

English version

Stationary source emissions — Determination of the mass concentration of PCDDs/PCDFs — Part 1: Sampling

Emissions de sources fixes — Détermination de la concentration massique en PCDDs/PCDFs —
Partie 1: Prélèvement

Emissionen aus stationären Quellen — Bestimmung der Massenkonzentrationen von PCDDs/PCDFs —
Teil 1: Probenahme

iTeh STANDARD PREVIEW

This European Standard was approved by CEN on 1996-12-27. CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration.

Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.

CEN

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

Central Secretariat: rue de Stassart 36, B-1050 Brussels

Foreword

This European Standard has been prepared by Technical Committee CEN/TC 264, Air quality, the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by June 1997, and conflicting national standards shall be withdrawn at the latest by June 1997.

This European Standard has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association, and supports essential requirements of EU Directive(s).

For relationship with EU Directive(s), see informative annex H, which is an integral part of this Standard.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

This European Standard was elaborated by AENOR (Spain)

AFNOR (France)

BSI (United Kingdom)

DIN (Germany)

DS (Denmark)

NNI (Netherlands)

NSF (Norway)

ON (Austria)

SFS (Finland)

SIS (Sweden)

SNV (Switzerland)

UNI (Italy)

The precision and the performance characteristics were determined in four comparative and validation trials at waste incinerators sponsored by the European Commission, the European Free Trade Association and the German Federal Environment Agency.

This European Standard EN 1948 : 1996 consists of three parts dealing with the determination of the mass concentration of PCDDs and PCDFs in stationary source emissions:

Part 1: *Sampling*

Part 2: *Extraction and clean-up*

Part 3: *Identification and quantification*

All three parts are necessary for the performance of the dioxin measurements.

The European Standard was developed on the basis of the following national standards or guidelines:

NF X 43-313 : 1991 *Air quality — Stationary source emissions — Determination of PCDD/PCDF*

Nordic : 1987 *Recommended method for dioxin measurements in flue gases from waste incineration, Swedish Environmental Protection Agency*

Unichim Method N° 825 : 1989 *Stationary source emission measurements — Conveyed gas flows — Sampling and determination of organic micropollutants*

— *Sampling*

— *PAH determination*

— *PCDD and PCDF determination*

— *PCB determination*

VDI 3499 Part 1 : 1990 (draft) *Emission measurement — Measurement of residual materials — Determination of polychlorinated dibenzodioxins and dibenzofurans in flue and stack gas of incineration and firing plants — Dilution method — Determination in filter dust, potash and slag*

VDI 3499 Part 2 : 1993 (draft) *Emission measurement — Determination of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) — Filter/condenser method*

VDI 3499 Part 3 : 1996 (draft) *Emission measurement — Determination of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) — Cooled probe method*

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Introduction

Two groups of related chlorinated aromatic ethers are known as polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs); they consist of a total of 210 individual substances (congeners): 75 PCDDs and 135 PCDFs.

PCDDs and PCDFs can form in the combustion of organic materials; they also occur as undesirable by-products in the manufacture or further processing of chlorinated organic chemicals. PCDDs/PCDFs enter the environment via these emission paths and through the use of contaminated materials. In fact, they are universally present in very small concentrations. The 2,3,7,8-chlorine substituted congeners are toxicologically significant. Toxicologically much less significant than tetrachlorinated to octachlorinated dibenzodioxins/ dibenzofurans are the 74 monochlorinated to trichlorinated dibenzodioxins/dibenzofurans (for toxicity equivalent factors, see annex A).

1 Scope

This part of the Standard specifies the sampling of PCDDs/PCDFs. It is an integral part of the complete measurement procedure. The use of the other two parts EN 1948-2 : 1996 and EN 1948-3 : 1996 describing extraction and clean-up and identification and quantification, respectively, is necessary for the determination of the PCDDs/PCDFs.

This Standard has been developed to measure concentrations at about 0,1 ng I-TEQ/m³ in stationary source emissions.

This Standard specifies both method validation and a framework of quality control requirements which have to be fulfilled by any PCDD/PCDF sampling.

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

'Filter/Condenser Method'

'Dilution Method'

'Cooled Probe Method'

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

During comparison measurements on municipal waste incinerators at the level of about 0,1 ng I-TEQ/m³, these three methods have been deemed comparable within the expected range of uncertainty.

Validation trials were performed on the flue gas of municipal waste incinerators at the level of about 0,1 ng I-TEQ/m³ and a dust loading of from 1 mg/m³ to 15 mg/m³.

In principle it is not possible to evaluate the accuracy (trueness and precision) of emission measurements. Following the validation trials, the internal and external variabilities were calculated for the process considered and are given in clause 13 of EN 1948-3 : 1996. These variabilities give an indication of the variabilities which have been observed when using this standard and need to be taken into account when expressing results.

The procedure described in the three parts of EN 1948 : 1996 specifies requirements which shall be met in order to measure the 17 congeners necessary to calculate the total I-TEQ (see table A.1).

2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

EN 1948-2 : 1996	Stationary source emissions — Determination of the mass concentration of PCDDs/PCDFs — Part 2: Extraction and clean-up
EN 1948-3 : 1996	Stationary source emissions — Determination of the mass concentration of PCDDs/PCDFs — Part 3: Identification and quantification
ISO 4793 : 1980	Laboratory sintered (fritted) filters — Porosity grading, classification and designation
ISO 845 : 1988	Cellular plastics and rubbers — Determination of apparent (bulk) density
ISO 9096 : 1992	Stationary source emissions — Determination of concentration and mass flow rate of particulate material in gas-carrying ducts — Manual gravimetric method

A bibliography is shown in annex C (informative).

3 Definitions and abbreviations

3.1 Definitions

For the purposes of this standard, the following definitions apply:

3.1.1 spiking

Addition of $^{13}\text{C}_{12}$ -labelled PCDDs and PCDFs standards.

3.1.2 isokinetic sampling

Sampling at a rate such that the velocity of the gas entering the sampling nozzle is the same as that of the gas in the duct at the sampling point [ISO 9096 : 1992].

3.1.3 operational performance characteristics

Measures which deal with the influence of the physical and chemical environment and maintenance problems, for example mains voltage, temperature, supply of certain substances, set-up time, period of unattended operation.

3.1.4 statistical performance characteristics

Measures which quantify, for measured values, possible deviations resulting from the random part of the measuring process; these are, for example, repeatability or instability.

3.1.5 control blank

A sample taken at the plant site in an identical manner to the normal samples including the spiking, without introducing the probe into the flue and without introducing air into the sampling train. All the compartments up to and including the last collecting stage shall be rinsed or extracted in the normal manner.

3.1.6 extraction blank

A blank sample covering the complete analytical procedure including extraction, clean-up, identification and quantification including all the relevant reagents and materials.

3.1.7 sampling standard

$^{13}\text{C}_{12}$ -labelled 2,3,7,8-chlorine substituted PCDDs/PCDFs, added before sampling.

3.1.8 extraction standard

$^{13}\text{C}_{12}$ -labelled 2,3,7,8-chlorine substituted PCDDs/PCDFs, added before extraction. These standards are also used for calculation of results.

3.1.9 syringe standard

$^{13}\text{C}_{12}$ -labelled 2,3,7,8-chlorine substituted PCDDs/PCDFs, added before GC injection.

3.1.10 keeper

High boiling point solvent added to the sampling standard solution.

3.1.11 congener

Any one of the 210 individual PCDDs/PCDFs.

3.1.12 PCDD/PCDF isomers

PCDDs or PCDFs with identical chemical composition but different structure.

3.1.13 pattern

Chromatographic print of any series of PCDD/PCDF isomers.

3.1.14 profile

Graphic representation of the sums of the isomer concentrations of the PCDDs and the PCDFs.

3.1.15 standard pressure

101,325 kPa.

3.1.16 standard temperature

273,15 K.

3.2 Abbreviations

3.2.1 I-TEQ

International toxic equivalent (for a detailed description, see table A.1).

3.2.2 I-TEF

International toxic equivalent factor (for a detailed description, see table A.1).

3.2.3 GC/MS

Gas chromatography / Mass spectrometry.

3.2.4 HRGC

High resolution gas chromatography.

3.2.5 HRMS

High resolution mass spectrometry.

3.2.6 TCDD

Tetrachlorodibenzo-p-dioxin.

3.2.7 PeCDD

Pentachlorodibenzo-p-dioxin.

3.2.8 HxCDD

Hexachlorodibenzo-p-dioxin.

3.2.9 HpCDD

Heptachlorodibenzo-p-dioxin.

3.2.10 OCDD

Octachlorodibenzo-p-dioxin.

3.2.11 TCDF

Tetrachlorodibenzofuran.

3.2.12 PeCDF

Pentachlorodibenzofuran.

3.2.13 HxCDF

Hexachlorodibenzofuran.

3.2.14 HpCDF

Heptachlorodibenzofuran.

3.2.15 OCDF

Octachlorodibenzofuran.

3.2.16 PCDD/PCDF

Polychlorinated dibenzo-p-dioxin/dibenzofuran.

3.2.17 PTFE

Polytetrafluoroethylene.

4 Principle of the complete PCDD/PCDF measurement procedure

4.1 Sampling

4.1.1 General

Gas is sampled isokinetically in the duct. The PCDDs/PCDFs, both adsorbed on particles and in the gas phase, are collected in the sampling train. The collecting parts can be a filter, a condensate flask and a solid or liquid adsorbent appropriate to the sampling system chosen. There is the choice between three different sampling systems:

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

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

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

Sampling shall be carried out according to 8.3.4.2 of ISO 9096 : 1992 until a European Standard for dust sampling is available. Exceptions with their justification shall be reported.

The minimum requirements of the sampling procedure to be met are described in this Standard. Examples of operation are listed in annex B. The described systems meet the minimum requirements of clause 6, but differ in their approach.

4.1.2 Filter/condenser method

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

The filter is placed downstream of the nozzle (in the stack) or after the probe (out of the stack). The filter has to be kept below 125 °C, but above the flue gas dew point. When a high dust loading is expected, a quartz wool filter or a cyclone may be incorporated into the sampling train before the filter to prevent the filter from being overloaded. Downstream, a condenser is attached. The sample gas is cooled to below 20 °C. The gaseous and aerosol parts of the PCDDs and PCDFs are captured by impingers and/or solid adsorbents.

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

The system with division of flow differs in the way that after filtering there is a flow divider. The main stream with a high volume flow to handle the isokinetic conditions passes the filter. The side stream after flow division is identical to the device with condenser and adsorber unit described above (see figure B.2).

4.1.3 Dilution method

The principle of the method is shown in figure 2. Differences in the details of this system are possible (see figures B.6 and B.8).

The sample gas is collected via a heated probe. The waste gas is cooled very rapidly to temperatures below 40 °C in a mixing channel using dried, filtered and, if appropriate, cooled air. The dilution avoids the temperature of the sampling gas falling below the flue gas dew point.

After dilution a filter is used to collect the particulate PCDDs/PCDFs contained in the waste gas stream. For the separation of the gaseous PCDDs/PCDFs a solid adsorbent is linked downstream.

4.1.4 Cooled probe method

The principle of the method is shown in figure 3.

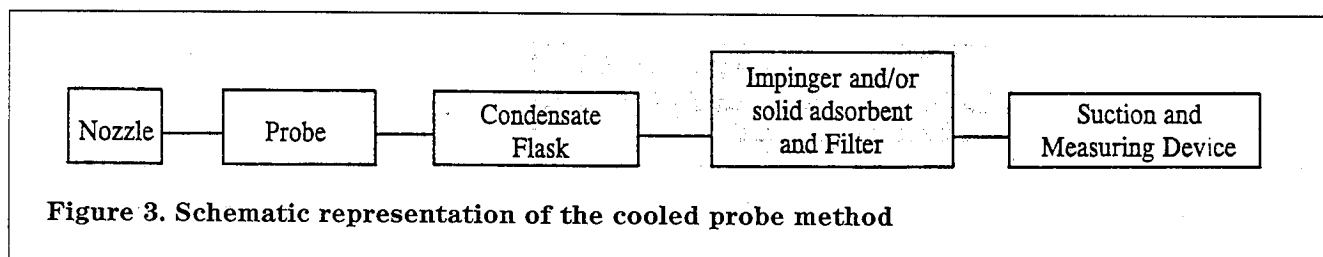
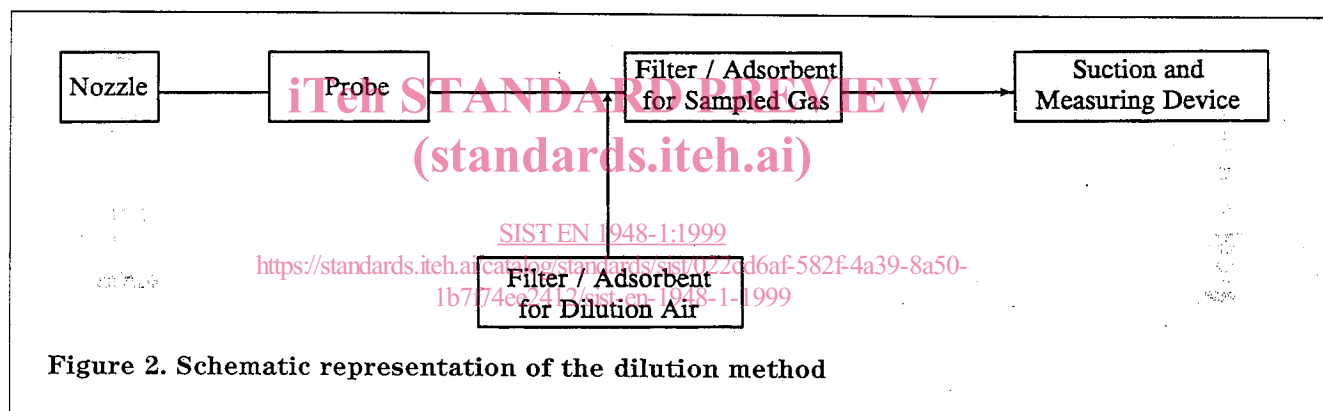
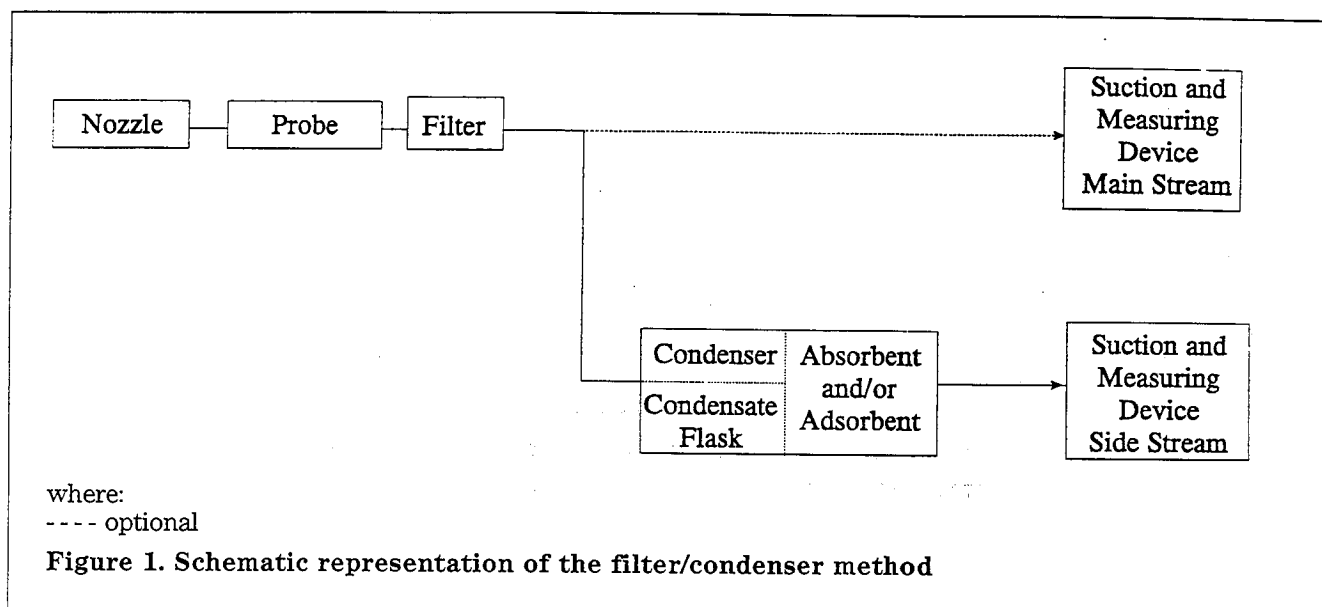
Different systems of this variant are possible (see figures B.9 and B.11). The sample gas passes the nozzle and a water-cooled probe.

The sample gas is cooled below 20 °C. The condensate is caught in a condensate flask. Downstream, impingers/bubblers and/or solid adsorber units are linked in order to collect the gaseous PCDDs/PCDFs. Before the last impinger/bubbler or solid adsorbent, there is a filter to separate small particles and to break aerosols.

4.2 Extraction and clean-up

Extraction is necessary to isolate the PCDDs/PCDFs from the sample and to collect them in an appropriate solvent volume. Extraction procedures are normally based on soxhlet extraction of filters and adsorbents, and liquid extraction of condensates. Sample clean-up is usually carried out by multi-column chromatographic techniques using a range of adsorbents. The main purpose of cleaning the raw sample extracts is to remove sample matrix components, which may overload the separation method, disturb the quantification or otherwise severely impact on the performance of the identification and quantification method. Furthermore, it results in an enrichment of analytes in the final sample extract. In principle any clean-up method can be used which recovers the analytes in sufficient quantities. Furthermore, the final sample extract should not affect adversely the performance of the analytical system or the quantification step. Methods shall have been tested thoroughly and comply with a set of method validation criteria before being employed. In addition, the control of the method performance for each single sample has to be part of a validated quality assurance protocol.

In EN 1948-2 : 1996 the minimum requirements for extraction and clean-up to be met are described as well as examples of operation. Examples of operation are given in annex A of EN 1948-2 : 1996.



4.3 Identification and quantification

This standard is based on the use of high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) for separation and detection, combined with isotope dilution of samples at different stages for quantification of PCDDs/PCDFs in emission samples. At present, this technique is the only analytical technique that can provide sufficient sensitivity, selectivity and specificity for the determination of minute amounts of PCDDs/PCDFs in emission samples. The gas chromatographic parameters offer the information for identification of isomers (position of Cl substituents) whereas the mass spectrometric parameters enable the differentiation between the homologue congeners of polychlorinated dibenzo-p-dioxins and dibenzofurans with a different number of Cl substituents.

In EN 1948-3 : 1996 the minimum requirements for identification and quantification to be met are described as well as examples of operation. Examples of operation are given in annex A of EN 1948-3 : 1996.

5 Sampling device and materials

5.1 Sampling device

5.1.1 General device

Pitot tube with a differential pressure gauge (alternatively a micromanometer) for measuring the static and dynamic pressure in the waste gas channel (for calculating the gas flow velocity)

moisture measuring device to determine the moisture in the waste gas; $\pm 1\%$ (V/V), absolute

micromanometer to measure the flue gas pressure in the duct

oxygen measurement system to determine the oxygen content; $\pm 0,5\%$ (V/V), absolute

syringe to add the $^{13}\text{C}_{12}$ -labelled standard solution (sampling standards)

pressure gauge ± 1 kPa, absolute

volume measurement device accuracy of the sampled gas volume $\pm 5\%$ of the value measured

flow rate measurement device to measure the volume flow rate to allow isokinetic conditions to be maintained

5.1.2 Sampling device for the filter/condenser method

5.1.2.1 Without division of sample gas

Dimensions of proved sampling devices for different sample volumes are listed in figure B.1.

nozzle made of titanium, quartz or glass, inside diameter according to the measurement task

elbow joint made of titanium, quartz or glass

probe made of titanium, quartz or glass, heatable, temperature electronically controlled

filter holder made of titanium, glass or quartz

filter casing heatable, temperature controlled

quartz wool cartridge (if used) made of quartz or glass

glass tubes to connect filter casing and condenser, e.g. supported with spherical joints and with clamps

condenser to cool the sample gas down to below 20°C

condensate flask made of glass

bubbler used as absorbent for gaseous PCDD/PCDF

solid adsorbent cartridge to house the solid adsorbent

drying tower filled with moisture-adsorbing material (e.g. silica gel)

temperature measurement device to measure the temperature of the sample gas at the filter and the condenser outlet ($\pm 2,5^\circ\text{C}$)

suction device consists of pump and valve to regulate the volume flow keeping isokinetic conditions

connections made of glass, quartz or titanium; behind the last ab/adsorbent stage plastic tubes are allowed

5.1.2.2 With division of sample gas

See figure 1.

Dimensions of proved sampling devices are listed in figures B.2, B.3 and B.4.

sampling device	listed in 5.1.2.1 and additionally:	mixing channel	with an axial waste gas inlet and a coaxial dilution air feed
flow divider	to keep a certain ratio between main and side stream, inside the filter casing	two measurement devices	for measuring the dilution air flow and the total gas flow (waste gas plus dilution air)
suction device	with a separate pump, flow regulation and gas meter to keep a proportion ($\pm 10\%$) to the main flow rate	two thermocouples (or other suitable thermometric devices)	for measuring the temperature – in the probe – of the filter
connections	made of glass, quartz or titanium (or corrosion resistant stainless steel after the last adsorber stage)	two thermocouples (or other suitable thermometric devices)	for measuring the temperature – at the nozzles
		two pressure gauges	for measuring – the effective pressure at the nozzles – the pressure in the waste gas channel

5.1.3 Sampling device for the dilution method

See figure 2.

Dimensions of proved sampling devices are listed in annex B, figures B.6, B.7 and B.8.

The sampling apparatus consists of:

nozzle	internal diameter depending on the suction output; made of corrosion-resistant material, e.g. glass, quartz, titanium	two differential pressure gauges	for measuring the differential pressure at the nozzles
elbow joint	made of corrosion-resistant material, e.g. glass, quartz, titanium	two control valves (or automatically operated valves)	with suitable control characteristics (alternatively motor-driven)
probe	internal tube made of corrosion-resistant material, e.g. glass, quartz or titanium, having been found satisfactory. Heating is controllable	suction device	consists of pump and valve
two filter casings	for mounting the glass fibre filter and the PU foam plugs, one casing for the sampling filter and one for the dilution air filter; made of corrosion-resistant materials, e.g. stainless steel or glass funnel and cylinder.	heat exchanger (required at ambient air temperatures $> 25^\circ\text{C}$)	for cooling the dilution air
		drying tower	packed with desiccant, e.g. blue gel; for drying the dilution air
		optionally a control and evaluation unit or a PC	if automatic control of the gas stream is desired

5.1.4 Sampling device for the cooled probe method

See figure 3.

Dimensions of proved sampling devices for different sample volumes are listed in figures B.9 to B.14.

nozzle	made of titanium, quartz, glass or PTFE (PTFE for waste gas temperatures below 180 °C)
elbow joint	made of titanium, quartz or glass
water cooled probe	water cooled double casing tube. The inside tube is made of titanium, glass or quartz (see figure B.10)
thermoelement	to measure the temperature of the sample gas behind the probe
condensate flask	made of glass
impinger (if used)	made of glass
solid adsorber cartridge (if used)	made of glass
filter holder	to hold the filter
drying tower	filled with moisture-adsorbing material, e.g. silica gel
suction device	consists of a pump and a gas regulation system

5.2 Materials

For detailed description of adsorbents and filter and their purification, see annex D and annex A of EN 1948-2 : 1996.

filter	quartz or glass fibre, meeting the minimum requirements (see clause 6)
quartz wool (if used)	
solid adsorbent	XAD-2 PU foam Porapak PS Florisil or other solid adsorbents meeting the minimum requirements (see clause 6)
cooling fluid	to cool the condenser or the cooled probe
ice bath	to cool the impingers and condensate flasks
silica gel	for the drying towers
acetone	
methanol	
toluene	
dichloromethane	
methoxyethanol, ethoxyethanol or diethylene glycol	
distilled water	

The reagents shall be of high purity to meet the criteria to have a low PCDD/PCDF background concentration.

6 Minimum requirements for sampling

6.1 Method validation criteria

- a) The sampling train shall use a filter with a minimum retention efficiency of 99,5 % for a test aerosol with a maximum abundance at a particle diameter of 0,3 μm . The filter is upstream of the sampling train in the case of the filter/condenser method and the dilution method, or before the last adsorption stage in the case of the cooled probe method. (Test data from the supplier's quality control programme are sufficient for this purpose).
- b) An adsorption stage, e.g. solid adsorbents (PU, XAD-2, Porapak PS) or impingers (e.g. methoxyethanol or ethoxyethanol) for collecting gaseous PCDDs/PCDFs is part of the sampling train. A minimum ab/adsorption efficiency of 90 % for the gaseous PCDDs/PCDFs (that are filter passing PCDDs/PCDFs) of this ab/adsorbent shall be shown in a separate test.
- c) A validation trial shall be carried out at least once with each design of sampling equipment. In this validation trial the last ab/adsorption stage shall be duplicated.
 - Sufficient sample shall be collected during the validation trial so that the detection limit for the total I-TEQ is less than 5 % of the total amount collected (expressed in I-TEQ).
 - The original sampling train and the additional ab/adsorption stage be analyzed separately. More than 90 % of the total I-TEQ shall be found in the original sampling train.

6.2 Minimum requirements for sampling

- a) A control blank including a leak check shall be taken before each sampling campaign. The value of this control blank shall not exceed 10 % of the limiting value (in I-TEQ) assuming the same volume as for sampling. If the calculated value measured is less than the preceding blank value, the reported result is defined as less than or equal to the blank.
- b) If parts of the sampling train are cleaned at site before being reused, a final rinse of all surfaces reused which are in contact with the sample shall be performed. The rinsing solution shall be stored. It shall be analysed when the concentration of the following sample exceeds the limiting value.
- c) The maximum sampling time is 8 h.
- d) The sampling train is spiked with $^{13}\text{C}_{12}$ -labelled PCDDs/PCDFs where the PCDDs/PCDFs are collected.
- e) The $^{13}\text{C}_{12}$ -labelled standards are used as follows (see table 1).

Table 1. Mass of labelled sampling standards to be added

Congeners added	Total amount in pg added (Solution: Total volume 100 μl : (toluene, 4 % tetradecane))
$^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDF	400
$^{13}\text{C}_{12}$ -1,2,3,7,8-HxCDF	400
$^{13}\text{C}_{12}$ -1,2,3,4,7,8,9-HpCDF	800

The masses of the labelled standards to be added are 400 pg for PeCDF and HxCDF and 800 pg for HpCDF each on the basis of 10 m^3 sampling volume (dry gas) and a concentration of 0,1 ng I-TEQ/ m^3 . The sampling standard solution shall be at least 100 μl . If a considerably higher or lower mass of native PCDDs/PCDFs is expected in the sample, the masses of the $^{13}\text{C}_{12}$ -labelled standards to be added should be adapted accordingly.

- f) The sampling standard solution contains 4 % tetradecane as keeper.
- g) If during sampling a change of the spiked part becomes necessary, the new part has to be spiked with the same sampling standard solution. This has to be taken into account for the calculation of the sampling standard recovery.
- h) A leak check has to be carried out before and after every sampling procedure. The sampling train with plugged nozzle is evacuated to the minimum pressure used during sampling and the volume flow rate shall be less than 5 % of the normal flow rate.
- i) The isokinetic sampling shall be carried out according to ISO 9096 : 1992, until a European Standard for dust sampling is available.
- j) Sampling shall be carried out at representative positions in the duct according to ISO 9096 : 1992, until a European Standard for dust sampling is available.
- k) The sampling flow rate shall be in the range the method is validated for.
- l) 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 : 1996).