

**DIN EN 1948-1****DIN**

ICS 13.040.40

Supersedes  
DIN EN 1948-1:1997-05

**Stationary source emissions –  
Determination of the mass concentration of PCDDs/PCDFs and  
dioxin-like PCBs –  
Part 1: Sampling of PCDDs/PCDFs  
English version of DIN EN 1948-1:2006-06**

Emissionen aus stationären Quellen –  
Bestimmung der Massenkonzentration von PCDD/PCDF und dioxin-ähnlichen PCB –  
Teil 1: Probenahme von PCDD/PCDF  
Englische Fassung DIN EN 1948-1:2006-06

Document comprises 67 pages

## National foreword

This standard has been prepared by CEN/TC 264 'Air quality' (Secretariat: Germany), Working Group WG 1 'Dioxins – Emissions' (Secretariat and Convenorship: Germany).

The responsible German body involved in its preparation was the *Kommission Reinhaltung der Luft (KRdL) im VDI und DIN* (VDI/DIN Air Quality Commission).

This European Standard has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association to support Essential Requirements of EU Directive 94/67/EC of 16 December 1994 on the incineration of hazardous waste. This directive is now replaced by EU Directive 2000/76/EC of 4 December 2000 on the incineration of waste, and this European Standard also supports the Essential Requirements of the new EU Directive 2000/76/EC. In Annex III of EU-Directive 2000/76/EC it is specified that 'Sampling and analysis of all pollutants including dioxins and furans as well as reference measurement methods to calibrate automated measurement systems shall be carried out as given by CEN Standards...'.  
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The revision of this EN between 2001 and 2004 only refers to the normative part. The information given in the informative annexes as examples of operation are kept unchanged, as they represent the state of the art at the time of validation measurements of EN 1948:1996 between 1992 and 1995. The precision and the performance characteristics were determined between 1992 and 1995 in four comparative and validation trials at waste incinerators sponsored by the European Commission, the European Free Trade Association and the German Federal Environment Agency.

## Amendments

This standard differs from DIN EN 1948-1:1997-05 as follows:

a) Extension of the scope:

DIN EN 1948 can now also be applied for wide concentration ranges and various emission sources and the described measurement methods are also suitable for the determination of other low-volatile substances, e.g. of dioxine-like PCBs.

b) Inclusion of new terms and definitions, and corrections:

The following terms are concerned: 'field blank', 'analytical blank', 'sampling standard', 'recovery standard', 'dioxin-like PCBs', 'flue gas sample volume', 'measurement series/sampling campaign', 'isokinetic sampling', 'limit of detection', 'limit of quantification', 'WHO-TEF/WHO-TEQ'.

c) Harmonization of the specifications with European Standards EN 13284-1, EN 14790 and EN 14789.

d) Addition and correction of requirements for:

- sampling devices and materials;
- cleaning of the sampling devices;
- sampling;
- method validation;
- field blank determination;
- sample recovery from the sampling train

- sample storage;
- sampling report.

e) Revision and update of the informative Annex A relating to the toxicity of PCDD/PCDF/PCB according to the requirements of the WHO.

A detailed list of all amendments is given in the foreword to EN 1948-1:2006.

### Previous editions

DIN EN 1948-1: 1997-05

## National Annex NA (informative)

### Bibliography

VDI 2464-1, *Ambient air measurement — Indoor air measurement — Measurement of polychlorinated biphenyls (PCBs) — GC/MS method for PCB 28, 52, 101, 138, 153, 180*

VDI 2464-2, *Ambient air measurement — Indoor air measurement — Measurement of polychlorinated biphenyls (PCBs) — HR-GC/HR-MS method for coplanar PCBs*

VDI 3498-1, *Ambient air measurement — Indoor air measurement — Measurement of polychlorinated dibenzo-p-dioxins and dibenzofurans — Method using large filters*

VDI 3498-2, *Ambient air measurement — Indoor air measurement — Measurement of polychlorinated dibenzo-p-dioxins and dibenzofurans — Method using small filters*

VDI 3499-1, *Emission measurement — Determination of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) — Dilution method — Example of application of DIN EN 1948 for the concentration range < 0,1 ng I-TEQ/m<sup>3</sup> and supplement to DIN EN 1948 for the concentration range > 0,1 ng I-TEQ/m<sup>3</sup>; Determination in filter dust, ash and slag*

VDI 3499-2, *Emission measurement — Determination of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) — Filter/condenser method — Example of application of DIN EN 1948 for the concentration range < 0,1 ng I-TEQ/m<sup>3</sup> and supplement to DIN EN 1948 for the concentration range > 0,1 ng I-TEQ/m<sup>3</sup>*

VDI 3499-3, *Emission measurement — Determination of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) — Cooled probe method — Example of application of DIN EN 1948 for the concentration range < 0,1 ng I-TEQ/m<sup>3</sup> and supplement to DIN EN 1948 for the concentration range > 0,1 ng I-TEQ/m<sup>3</sup>*

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English Version

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

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

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

This European Standard was approved by CEN on 23 January 2006.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

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

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## Foreword

This European Standard (EN 1948-1:2006) has been prepared by Technical Committee CEN/TC 264 "Air quality", the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by September 2006, and conflicting national standards shall be withdrawn at the latest by September 2006.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

This European Standard supersedes EN 1948-1:1996.

This European Standard has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association to support Essential Requirements of EU Directive 94/67/EC of 16 December 1994 [i] on the incineration of hazardous waste. This directive is now replaced by EU Directive 2000/76/EC of 4 December 2000 on the incineration of waste [ii] and this European Standard also supports the Essential Requirements of the new EU Directive 2000/76/EC (see also Annex E).

The precision and the performance characteristics were determined between 1992 and 1995 in four comparative and validation trials at waste incinerators sponsored by the European Commission, the European Free Trade Association and the German Federal Environment Agency.

The revision of this EN between 2001 and 2004 only refers to the normative part. The information given in the informative annexes as examples of operation are kept unchanged, as they represent the state of the art at time of the validation measurements of EN 1948:1996 between 1992 and 1995.

This European Standard EN 1948:2006 consists of three parts dealing with the determination of the mass concentration of PCDDs and PCDFs in stationary source emissions:

Part 1: Sampling of PCDDs/PCDFs;

Part 2: Extraction and clean-up of PCDDs/PCDFs;

Part 3: Identification and quantification of PCDDs/PCDFs.

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

In addition for the sampling, extraction and analyses of dioxin-like PCBs the Technical Specification CEN/TS 1948-4<sup>1</sup> is developed and will be transferred to a European Standard after corresponding validation measurements or after an approval time of three years respectively.

Important changes made in the revision of EN 1948-1:

1. **Title:** Broadening of the title with regard to the future EN 1948-4 for the determination of dioxin-like PCBs
2. **Foreword:**

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<sup>1</sup>) To be published.

- Deletion of all precursor documents which were basis for elaboration of EN 1948 as well as the names of the standardisation bodies involved in the elaboration of EN 1948
  - Update of the hint regarding mandate of the standardisation project and regarding fulfilment of the Essential Requirements of EU Directives 94/67/EC and 2000/76/EC
  - Addition of a hint, that the revision only refers to the normative parts of the standard. The Informative Annex B "Examples of operation" is kept unchanged and represents the state of the art at time of the validation measurements of EN 1948:1996 between 1992 and 1995
  - Addition of hint with regard to the future document EN 1948-4 dealing with the analyses of dioxin-like PCBs
3. **Introduction:** New hint that only skilled operators who are trained in handling highly toxic compounds should apply the method described in this European Standard (identical to EN 1948-2 and EN 1948-3)
4. **Scope:**
- Addition of a hint, that EN 1948 can be applied for wide concentration ranges and various emission sources
  - Addition of a hint, that the described measurement methods are suitable for determination of other low-volatile substances, e.g. of dioxin-like PCBs
5. **Normative references:**
- Update of the references to EN 1948-2:2006, EN 1948-3:2006
  - Reference to EN 13284-1:2001 regarding determination of low range mass concentration of dust instead of ISO 9096, therefore deletion of all references to ISO 9096 and replacement by EN 13284-1:2001
  - Additional normative reference to EN ISO/IEC 17025:2005
  - Deletion of reference to ISO 4793:1980
6. **Clause 3 Terms and definitions:**
- Distinction between Clause 3 "Terms and definitions" and Clause 4 "Symbols and abbreviations" resulting in a different numbering of the following chapters
  - Corrected definition of "field blank" for clarification
  - Corrected definition of "analytical blank" for clarification
  - Corrected definition of "sampling standard": only furans
  - "Syringe standard" renamed to read "recovery standard"
  - Corrected definition of "recovery standard": only dioxins
  - Additional definition of "dioxin-like PCBs"
  - Additional definition of "flue gas sample volume"
  - Additional definition of "measurement series" resp. "sampling campaign"



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

14. **Clauses 7.4, 7.5, 7.6 Additional sampling minimum requirements for the 3 different methods:**

- Addition of a footnote, that a temperature limit of 125 °C is required for the filter of the filter/condenser method to avoid chemical reactions on activated surfaces.
- Deletion of the requirement to connect the sampling device according to figures in Annex B
- Deletion of the requirement to cool des sample gas temperature with a maximum of 20 °C resp. 40 °C

15. **Clause 9.3.4.2 Changing sampling line:** Additional requirement of leak check when changing sampling

16. **Clause 9.3.5.1 Sample recovery from the sampling train:** Additional requirements with regard to rinsing the equipment, the rinsing solution becomes part of the sample

17. **Clause 9.3.5.2 Sample storage:** Deletion of the requirement to store the samples below 4 °C. Additional requirement to use screw-caps with aluminium-lined seals for storing

18. **Clause 9.4 Calculation of flue gas volume:** Correction of the formula for conversion to standard conditions

19. **Clause 9.5 Sampling report:**

- Addition of the content and the relevance of the sampling report
  - e) Addition of requirement regarding the identification of the used parts of the sampling equipment
  - g) Harmonisation of the requirement regarding isokinetic sampling according to EN 13284-1:2001

20. **Annex A:** Revision/update of the Toxicity of PCDD/PCDF according to the requirements of the WHO

21. **Annex B:** Addition of bibliography references

22. **Annex B 1.5b:** Correction of filter position

23. **Annex E / F:** Deletion of annexes dealing with humidity and oxygen content determination

24. **Annex E:** Update of the hint regarding mandate of the standardisation project and regarding fulfilment of basic requirements of EU Directives 94/67/EC and 2000/76/EC

25. **Bibliography:** Update

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and the United Kingdom.

## Introduction

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

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

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

## 1 Scope

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

This European Standard has been developed to measure PCDD/PCDF concentrations at about 0,1 ng I-TEQ/m<sup>3</sup> in stationary source emissions.

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

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

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

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

During comparison measurements of the three sampling methods on municipal waste incinerators at the level of about 0,1 ng I-TEQ/m<sup>3</sup> these methods have been deemed comparable within the expected range of uncertainty. Validation trials were performed on the flue gas of municipal waste incinerators at the level of about 0,1 ng I-TEQ/m<sup>3</sup> and a dust loading of from 1 mg/m<sup>3</sup> to 15 mg/m<sup>3</sup>. Although this European Standard is primarily developed and validated for gaseous streams emitted by waste incinerators, the practical experience shows that it can be applied for wide concentration ranges and various emission sources.

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

Besides the determination of PCDDs/PCDFs the described measurement methods are suitable for determination of other low-volatile substances, e.g. of dioxin-like PCBs (details for sampling and analyses see CEN/TS 1948-4), although no validated performance characteristics are available yet.

## 2 Normative references

The following referenced documents are indispensable for the application of this European Standard. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 1948-2:2006, *Stationary source emissions — Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs — Part 2: Extraction and clean-up of PCDDs/PCDFs*

EN 1948-3:2006, *Stationary source emissions — Determination of the mass concentration of PCDDs/PCDFs and dioxin-like PCBs — Part 3: Identification and quantification of PCDDs/PCDFs*

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

EN 14789, *Stationary source emissions — Determination of volume concentration of oxygen (O<sub>2</sub>) — Reference method — Paramagnetism*

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

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

### 3 Terms and definitions

For the purposes of this European Standard, the terms and definitions given in EN 1948-2:2006, EN 1948-3:2006 and the following apply.

#### 3.1

##### **analytical blank value**

value determined by a blank sample covering the complete analytical procedure including extraction, clean-up, identification and quantification including all the relevant reagents and materials

#### 3.2

##### **congener**

any one of the 210 individual PCDDs/PCDFs

#### 3.3

##### **dioxin-like PCBs**

any PCB showing similar toxicity as the 2,3,7,8-substituted PCDDs/PCDFs according to WHO [iii]

#### 3.4

##### **extraction standard**

<sup>13</sup>C<sub>12</sub>-labelled 2,3,7,8-chlorine substituted PCDDs/PCDFs, added before extraction. These standards are also used for calculation of results

#### 3.5

##### **field blank value**

value determined by a blank sample covering a specific procedure to ensure that no significant contamination has occurred during all steps of the measurement and to check that the operator can achieve a quantification level adapted to the task

#### 3.6

##### **flue gas sample volume**

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

#### 3.7

##### **isokinetic sampling**

sampling at a flow rate such that the velocity and direction of the gas entering the sampling nozzle are the same as the velocity and direction of the gas in the duct at the sampling point

[EN 13284-1:2001, definition 3.5 ]

#### 3.8

##### **keeper**

high boiling point solvent added to the sampling standard solution

#### 3.9

##### **limit of detection (LOD)**

minimum value of the measurand for which the measuring system is not in the basic state, with a stated probability

NOTE 1 The limit of detection, also referred to as capability of detection, is defined by reference to the applicable basic state. But it may be different from "zero", for instance for oxygen measurement as well as when gas chromatographs are used.

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

NOTE 2 The measurement value can be distinguished from the analytical blank value with a confidence of 99 %. The limit of detection is expressed as the mean analytical blank value ( $b_{ave}$ ) plus three times the standard deviation of the analytical blank ( $s_b$ ).

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

where

$LOD$  is the detection limit;

$b_{ave}$  is the mean analytical blank value;

$s_b$  is standard deviation of the analytical blank.

NOTE 3 In this European Standard the limit of detection should preferably be calculated from the analytical blank  $b_{ave}$ . If this is not possible, the limit of detection can be calculated from the signal to noise ratio according to EN 1948-3:2006, 8.1.

### 3.10 limit of quantification (LOQ)

limit above which a quantification of the measurand is possible, expressed as the mean analytical blank value plus, either, five to ten times the standard deviation of the analytical blank. The factor  $F$  depends to the accepted measurement uncertainty.

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

where

$LOQ$  is the quantification limit;

$b_{ave}$  is the mean analytical blank value;

$s_b$  is standard deviation of the analytical blank

NOTE In this European Standard the limit of quantification should preferably be calculated from the analytical blank  $b_{ave}$ . If this is not possible, the limit of quantification can be calculated from the signal to noise ratio according to EN 1948-3:2006, 8.1 using the requirement of EN 1948-3:2006, 8.3e.

### 3.11 measurement series sampling campaign

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

### 3.12 pattern

chromatographic print of any series of PCDD/PCDF isomers

### 3.13 PCDD/PCDF isomers

PCDDs or PCDFs with identical chemical composition but different structure

### 3.14 profile

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

**3.15****recovery standard**<sup>13</sup>C<sub>12</sub>-labelled 2,3,7,8-chlorine substituted PCDDs, added before GC injection**3.16****sampling standard**<sup>13</sup>C<sub>12</sub>-labelled 2,3,7,8-chlorine substituted PCDFs, added before sampling**3.17****spiking**addition of <sup>13</sup>C<sub>12</sub>-labelled PCDDs and PCDFs standards**3.18****standard pressure**

101,3 kPa

**3.19****standard temperature**

273,15 K

**3.16****WHO-TEF**

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

**3.17****WHO-TEQ**

toxic equivalent obtained by multiplying the mass determined with the corresponding WHO-TEF including PCDDs, PCDFs and PCBs (for detailed description see Annex A)

NOTE WHO-TEQ<sub>PCB</sub>, WHO-TEQ<sub>PCDD/PCDF</sub> should be used to distinguish different compound classes.**4 Symbols and abbreviations****4.1 General****HRGC**

high resolution gas chromatography

**HRMS**

high resolution mass spectrometry

**I-TEF**

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

**I-TEQ**

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

**LOD**

limit of detection

**LOQ**

limit of quantification

**PCB**

polychlorinated biphenyl

**PCDD/PCDF**

polychlorinated dibenzo-p-dioxin/dibenzofuran

**PTFE**

polytetrafluoroethylene

**PU foam**

polyurethane foam

**WHO-TEF**

toxic equivalent factor of the World Health Organisation

**WHO-TEQ**

toxic equivalent of the World Health Organisation

**4.2 Congeners of PCDD/PCDF**

**TCDD**

Tetrachlorodibenzo-p-dioxin

**PeCDD**

Pentachlorodibenzo-p-dioxin

**HxCDD**

Hexachlorodibenzo-p-dioxin

**HpCDD**

Heptachlorodibenzo-p-dioxin

**OCDD**

Octachlorodibenzo-p-dioxin

**TCDF**

Tetrachlorodibenzofuran

**PeCDF**

Pentachlorodibenzofuran

**HxCDF**

Hexachlorodibenzofuran

**HpCDF**

Heptachlorodibenzofuran

**OCDF**

Octachlorodibenzofuran

**5 Principle of the complete PCDD/PCDF measurement procedure**

**5.1 Sampling**

**5.1.1 General**

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



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

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

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

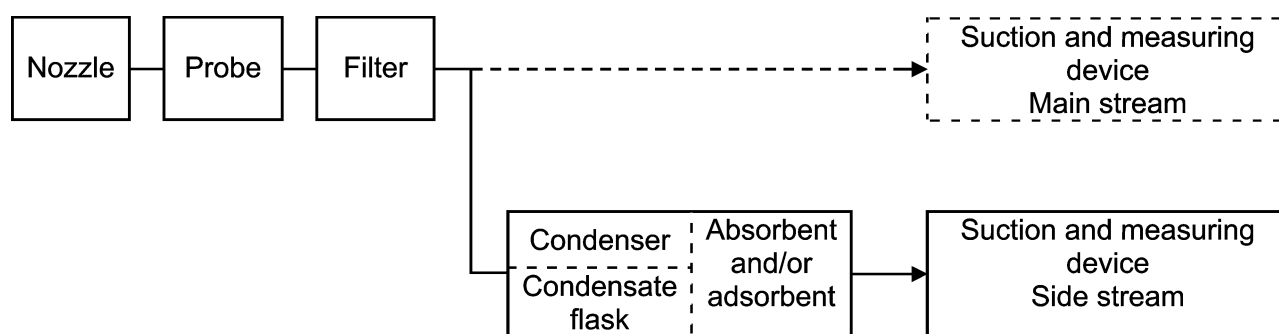
The main collecting parts are spiked with  $^{13}\text{C}_{12}$ -labelled PCDDs/PCDFs before sampling to determine the sampling recovery rate of the congeners. The sample gas is brought to a temperature specific to the sampling system and the gaseous and particulate PCDDs/PCDFs are trapped.

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

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

### 5.1.2 Filter/condenser method

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



- - - optional

**Figure 1 — Schematic representation of the filter/condenser method**

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

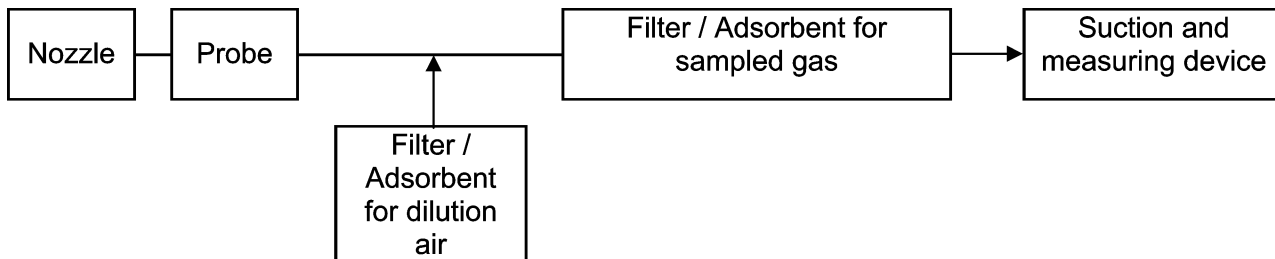
In a variant of this sampling system the solid adsorber unit can be linked between condenser and condensate flask (see Figure B.5).

<sup>2)</sup> In order to avoid chemical reactions on activated surfaces the temperature limit of  $125\text{ °C}$  is required.

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).

**5.1.3 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).



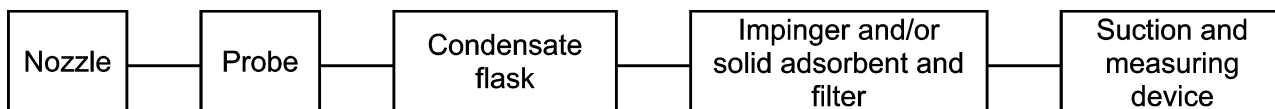
**Figure 2 — Schematic representation of the dilution method**

The sample gas is collected via a heated probe. The waste gas is cooled very rapidly in a mixing channel below 40 °C using dried, filtered and, if appropriate, cooled air. An upper temperature can be used if it is demonstrated that the results obtained are equivalent. The dilution avoids the relative humidity of the sampling gas rising to 100 %.

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.

**5.1.4 Cooled probe method**

The principle of the method is shown in Figure 3.



**Figure 3 — Schematic representation of the cooled probe method**

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, in which it is cooled below 20 °C. An upper temperature can be used if it is demonstrated that the results obtained are equivalent.

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.

**5.2 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 the performance of the identification and quantification method. 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 verification of the method performance for each single sample shall be part of a validated quality assurance protocol.

In EN 1948-2 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 1948-2:2006.

### 5.3 Identification and quantification

This European 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 information which enables the identification of isomers (position of Cl substituents) whereas the mass spectrometric parameters enable the differentiation between congeners with different numbers of chlorine substituents and between dibenzo-p-dioxins and furans.

In EN 1948-3 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 1948-3:2006.

## 6 Sampling device and materials

### 6.1 General sampling device

See Annex B for detailed description of examples of sampling devices which can meet the minimum requirements. However, this can depend on the experimental conditions and each user still shall prove that the minimum requirements for sampling are met during sampling.

#### 6.1.1 General

The requirements of the sampling devices follow EN 13284-1.

#### 6.1.2 Sampling system

All parts of the system in contact with the flue gas: nozzle, probe, glass tubes, filter holder, filter casing, condenser, bubbler, solid adsorber cartridge etc.

#### 6.1.3 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 pressure gauge/flow velocity).

#### 6.1.4 Moisture measuring device

To determine the moisture in the waste gas in accordance with EN 14790.

#### 6.1.5 Micromanometer

To measure the flue gas pressure in the duct.

#### 6.1.6 Oxygen measurement system

To determine the oxygen content in accordance with EN 14789.

NOTE If the oxygen concentration exceeds 19 %, the uncertainty of the oxygen-related measurement result is greater than given in EN 1948-3:2006, Clause 14 Performance characteristics.

#### **6.1.7 Syringe or micro-pipettes**

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

#### **6.1.8 Volume measurement device**

To determine the sample gas volume, the accuracy of the volume measurement device shall be  $\pm 2 \%$ .

#### **6.1.9 Flow rate measurement device**

To measure the volume flow rate to allow isokinetic conditions to be maintained.

#### **6.1.10 Barometer and pressure gauge**

To determine the pressure, the absolute measurement uncertainty shall be  $\pm 1 \%$  [EN 13284-1].

#### **6.1.11 Thermometer**

To determine the temperature, absolute measurement uncertainty shall be  $\pm 1 \%$ , Temperature in Kelvin [EN 13284-1].

### **6.2 Materials**

#### **6.2.1 General**

For detailed description of adsorbents and filter and their purification, see Annex C and Annex A of EN 1948-2:2006. The reagents shall be of high purity to meet the criteria of blank analysis to have a low PCDD/PCDF background concentration.

#### **6.2.2 Sampling system**

All parts of the sampling system coming in contact with the flue gas which constitutes the sample including the last adsorption stage, shall be made from glass, quartz or titanium.

#### **6.2.3 Sealings (in contact with flue gas)**

Made of PTFE.

#### **6.2.4 Filter**

Made of quartz or glass fibre, meeting the minimum requirements (see Clause 7).

#### **6.2.5 Quartz wool (if used)**

May be used as a pre-filter in high dust concentrations.

### 6.2.6 Solid adsorbent

XAD-2<sup>3)</sup>, polyurethane foam (PU foam), other solid adsorbents (e.g. Porapak PS<sup>2)</sup>) meeting the minimum requirements (see Clause 7). See Annex A of EN 1948-2:2006, for examples on material specification.

### 6.2.7 Cooling fluid

To cool the condenser or the cooled probe.

### 6.2.8 Ice bath (if used)

To cool the impingers and condensate flasks.

### 6.2.9 Silica gel

For the drying towers.

### 6.2.10 Reagents

acetone;  
methyl alcohol (methanol);  
toluene;  
methylene chloride (dichloromethane);  
2-methoxyethanol, 2-ethoxyethanol or 2,2'-oxydiethanol (diethylene glycol);  
distilled water.

## 6.3 Cleaning the sampling device

The cleaning procedure shall be suitable to meet the requirement of the blanks. Several methods for cleaning the sampling devices, which is coming, or have been, in contact with the flue gas, is described in Annex B and in Annex A of EN 1948-2:2006.

Three procedures for cleaning the sampling devices are given as examples:

- 1) Cleaning of the sampling equipment in the laboratory. Normally rinsing with water and detergent, followed by rinsing with solvent and/or treatment in a muffle oven preferably at 400 °C to 450 °C (not higher than 380 °C for titanium) for several hours, to remove any traces of organics.
- 2) Rinsing with solvent prior to sampling (can be done either in the laboratory if parts are carefully wrapped in aluminium foil, or at sampling site when connecting the sampling train).
- 3) Rinsing the equipment being in contact with the flue gas with solvents after the sampling. This rinsing solution is an important part of the sample.

Rinsing with solvents normally include two different solvents, where one of them is miscible with water (e.g. acetone and/or methanol followed by toluene). When rinsing equipment wetted by condensate, it is very important to use the water miscible solvent first, to remove the water.

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<sup>3)</sup> 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 Standard and does not mean any approval of the named products by CEN.

## 7 Minimum requirements for sampling

### 7.1 Method validation criteria

- a) Plane filter efficiency better 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 [EN 13284-1:2001, 6.2.7]. The filter is upstream of the sampling train in case of the filter/condenser method and the dilution method, or before the last adsorption stage in case of the cooled probe method.
- b) An adsorption stage e.g. solid adsorbents or impingers for collecting gaseous PCDDs/PCDFs is part of the sampling train. A minimum absorption/adsorption efficiency of 90 % for the gaseous PCDDs/PCDFs (that are filter passing PCDDs/PCDFs) of this adsorbent/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 absorption/adsorption stage shall be duplicated by placing an additional absorption/adsorption stage in series.
  - Sufficient sample volume shall be collected during the validation trial so that the quantification limit is less than 5 % of the total amount collected (expressed in I-TEQ).
  - The original sampling train and the additional absorption/adsorption stage shall be analysed separately. More than 90 % of the total I-TEQ shall be found in the original sampling train.
  - The average adsorber temperature during validation of the method shall not be exceeded during the sampling campaign. Otherwise, an additional validation for an accordingly higher temperature shall be performed.

### 7.2 Minimum requirements for sampling

- a) The isokinetic sampling shall be carried out according to EN 13284-1.
- b) Sampling shall be carried out at representative positions in the duct according to EN 13284-1.
- c) A leak check shall 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.
- d) A field blank shall be taken before each sampling campaign (see 7.3 for details).
- e) The permissible limits of quantification (LOQs) for the individual congener *i* shall be as follows:

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

LOQ      limit of quantification;  
 I-TEF    international toxic equivalency factor.

NOTE 1    A flue gas sample volume of at least 4 m<sup>3</sup> is recommended to reach the quantification limit of the analytical laboratories.

NOTE 2    According to the EU Council Directive 2000/76/EC on incineration of waste [ii] the minimum sampling time is 6 h, the maximum sampling time is 8 h. The validation of this standard was performed for a sampling time of 6 h.

- f) The sampling train is spiked with  $^{13}\text{C}_{12}$ -labelled PCDDs/PCDFs as follows:

Method	Spiked part of the equipment
Filter/condenser method:	Filter and/or adsorbents;
Dilution method:	Filter;
Cooled-probe method:	Condensate flask and/or filter and/or adsorbents.

- g) 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 (e.g. toluene): Minimum volume 100 µl with 4 % tetradecane as keeper)
$^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDF	400
$^{13}\text{C}_{12}$ -1,2,3,7,8,9-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<sup>3</sup> flue gas sample volume (dry gas) and to measure the concentration of 0,1 ng I-TEQ/m<sup>3</sup>. 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.

- h) The sampling standard solution contains 4 % tetradecane as keeper.
- i) If during sampling a change of the spiked part becomes necessary, the new part shall be spiked with the same sampling standard solution. This shall be taken into account for the calculation of the sampling standard recovery.
- j) The sampling flow rate shall be in the range the method is validated for.
- k) 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).

### 7.3 Field blank requirements

The field blank is taken at the operator's site according to the following procedure:

- the sampling train is mounted at the same location as the flue gas samples of the measurement series;
- the probe is not inserted into the stack;
- no gas is drawn through the sampling train;
- a leak check is performed;
- the sampling train is dismantled.

A field blank procedure shall be performed at least before each measurement series.

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 emission limit value.

If several measurements are performed during the same sampling campaign and according to the same procedure, and if the measurements are performed on the same industrial process or on several lines of the same industrial process, then a single field blank shall be performed.

The field blank shall not be deducted from the measured value.

The value of this field blank shall not exceed 10 % of the emission limit value assuming the same volume as for sampling. If the calculated value measured is less than the preceding field blank value, the reported result is defined as less or equal to the blank.

**NOTE** In case of monitoring dioxin emissions significantly lower than 0,1 ng I-TEQ/m<sup>3</sup>, the field blank may be in the same range as the measured concentration.

All field blanks shall be reported with the corresponding measured values.

#### **7.4 Additional sampling minimum requirements for the filter/condenser method**

For schematic representation, see Figure 1.

- a) The filter is run below 125 °C inside or outside the stack <sup>4)</sup>. The sample gas temperature in the filter holder, however, shall be above its dew point.
- b) Impingers or solid adsorbents are used as absorbents/adsorbents.
- c) If a variant with flow division is chosen, the ratio of the main and side streams shall be kept constant ( $\pm 10\%$ ).

#### **7.5 Additional sampling minimum requirements for the dilution method**

For schematic representation, see Figure 2.

- a) Condensation on the filter shall be avoided.
- b) A solid adsorber stage is downstream from the filter.
- c) The sampling device shall contain a dilution air verification adsorption stage (i.e. a filter and adsorbent) which shall be replaced and stored after each measurement. It shall be analysed if the measurement result exceeds the emission limit value. In other cases it can be discarded.
- d) The field blank shall include the verification adsorption stage for the dilution air.

#### **7.6 Additional minimum requirements for the cooled probe method**

For schematic representation, see Figure 3.

The filter is incorporated before the last absorption/adsorption stage.

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



## 8 Safety measures and transport

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

## 9 Preparations and sampling

### 9.1 Advance preparations at the sampling site

#### 9.1.1 Selection of suitable sampling location

The sampling location should be chosen so as to meet the requirements given in EN 13284-1.

The duct dimensions shall be determined before the sampling visit either by measurement in accordance with EN 13284-1, or, if access to the duct is not feasible, from plans of the plant. This allows the required number of sampling points to be assessed (see EN 13284-1) and hence the number and orientation of the sampling lines can be determined and hence the position of the sampling ports required can be decided (see EN 13284-1) and, if not already present, fitted to the duct.

The sampling ports should be positioned to allow access to all the required sampling positions within the duct with the equipment available. The port design should also allow easy movement of the sampling train along the sampling line.

The working platform should be designed to enable the sampling train to be used without any flexible hoses between the probe and the sample collection devices. This may not always be possible but if the requirements are not met then this should be noted in the sampling report. If a suitable permanent platform is not present the scaffolding should meet the requirements of EN 13284-1.

### 9.2 Advance preparations at the laboratory

#### 9.2.1 Preparation of equipment

The following measuring devices shall possess valid calibration and operate correctly:

- a) gas meters;
- b) velocity measurement device (e.g. pitot tubes);
- c) flow measurement device (e.g. orifice plates);
- d) pressure measurement devices (e.g. manometers);
- e) temperature measurement device (e.g. thermocouples);
- f) balances;
- g) nozzles.

The operation of the pumps, flow control valves and manometers shall also be checked.

### **9.2.2 Preparation of parts of the sampling train in contact with the sample**

Examples of proven adsorbents cleaning procedures are given in Annex C and in Annex A of EN 1948-2:2006. The purity of reagents should be checked on a batch by batch basis. The purity of reagents shall meet the requirement of the blank analysis.

The integrity of the glassware shall be checked and any visible contamination removed. Further cleaning shall take place to guarantee the required level of cleanliness.

The main sampling compartment shall have the sampling standard solution shown in Table 1 added to it either at the laboratory or at site.

The cleaned glassware and probes shall be securely sealed against contamination and placed in clean containers for transport.

## **9.3 Sampling at the plant**

### **9.3.1 Initial checks**

Check that the platform is safe to use and allows the correct use of the sampling train.

Check that the power supply has a suitable socket, is of the correct voltage and is able to supply adequate current.

Check that the sampling ports are in the correct positions and that the plugs may be removed. Examine the inside of the port to ensure there is not an excessive deposit of ash and that nothing will prevent free movement of the probe.

### **9.3.2 Preliminary survey**

Measure the stack dimensions following EN 13284-1.

The flue gas velocity and temperature profiles shall be determined before sampling to ensure that the sampling position is suitable and to provide information for nozzle selection. The flue gas oxygen and moisture contents, atmospheric pressure and temperature shall be determined and recorded in order to allow calculation of the flue gas density and hence to aid nozzle selection.

### **9.3.3 Assembly of apparatus**

The nozzle size used shall allow isokinetic sampling at all the required sampling points.

The equipment is then assembled taking care to ensure no significant contamination is introduced into the sampling train. No grease for the connections shall be used.

The leak rate of the sampling train is then measured and recorded according to EN 13284-1.

If a cooling device is used to reduce the adsorbent temperature such as ice baths or water recirculation this shall be turned on and then any heater before the probe enters the duct. The sampling port plug is removed and the probe introduced into the duct. The gas meter initial reading and the duct static pressure shall be recorded. The alignment of the pitot tube and the nozzle in duct shall be checked to ensure they are facing the gas flow.

### 9.3.4 Sampling

#### 9.3.4.1 Record keeping

The following parameters are required to be periodically recorded (at least every 15 min) to enable the validation of the sampling: velocity in duct, temperature in duct, flow rate through sampling train, filter temperature, adsorbent temperature.

The oxygen content shall be measured during sampling and recorded.

#### 9.3.4.2 Changing sampling line

Sampling shall be carried out according to EN 13284-1, on at least two sampling lines. If this is not possible for some existing installations, sampling shall be undertaken at multipoints along a single sample line, but this may not be to the stated precision. Such deviations from the standard shall be fully reported.

The sampling train shall be leak checked when changing the sampling line. If it is necessary to change part of the apparatus this should be recorded in the sampling log book. A potential leak may be detected by measuring the oxygen concentration in the exhaust of the sampling train.

### 9.3.5 After sampling

#### 9.3.5.1 Sample recovery from the sampling train

The sampling train is removed from the duct, taking care not to introduce contamination from the sampling port walls. If necessary it should be left to cool and leak check is performed. The final leak rate is recorded.

The apparatus is then disassembled. Special care shall be taken in recovering the probe in case of the cooled probe method. Inner surfaces of sample train components which are not transferred to the laboratory shall be rinsed with solvents (this normally includes two different solvents, where one of them is miscible with water e.g. acetone and/or methanol followed by toluene). The rinsing solution becomes part of the sample. Each part of the sample is either securely sealed or placed into pre-cleaned containers as necessary. The sample parts are labelled in such a way as to ensure they can be identified.

#### 9.3.5.2 Sample storage

The samples shall be stored in the dark not higher than room temperature (approximately 25 °C). A chain of custody shall be taken of all vessels containing the sample.

For sample storage the use of screw-caps with aluminium-lined seals is recommended to avoid contamination.

## 9.4 Calculation of flue gas sample volume

The flue gas volume sampled under gas meter conditions should be calculated from Equation (4):

$$V_{\text{meter}} = U_{\text{end}} - U_{\text{start}} \quad (4)$$

where

$V_{\text{meter}}$  is the measured volume of the sample;

$U_{\text{end}}$  is the instrument reading of the volume after sampling;

$U_{\text{start}}$  is the instrument reading of the volume before sampling.

The flue gas sample volume should then be corrected to standard conditions of temperature, pressure, and reference conditions of humidity and oxygen content according to Equation (5):

$$V_{nr} = V_{meter} \times \frac{T_n (p_{atmos} + p_{st} - p_{H_2O})}{p_n T_{meter}} \times \frac{21 - O_m}{21 - O_{ref}} \quad (5)$$

where

- $V_{nr}$  is the measured volume under standard and reference conditions;
- $V_{meter}$  is the measured volume of the sample;
- $T_n$  is the standard temperature (273,15 K);
- $T_{meter}$  is the sample temperature in the gas meter, in K;
- $p_{atmos}$  is the atmospheric pressure, in kPa;
- $p_{st}$  is the difference between static pressure in the gas meter and the atmospheric pressure, in kPa;
- $p_{H_2O}$  is the water vapour partial pressure in the gas meter, in kPa;
- $p_n$  is the standard pressure (101,3 kPa);
- $O_m$  is the oxygen content in the duct, in %;
- $O_{ref}$  is the oxygen reference content, in %.

## 9.5 Sampling report

The following parameters shall be recorded in order to demonstrate compliance with this European Standard. The parameters of the sampling report shall be agreed with the client in accordance with EN ISO/IEC 17025.

a) Basic information:

- 1) flue gas sample volume;
- 2) expected concentration in the sample;
- 3) basic information of the plant.

a) Measurement information:

- 1) institution, personnel;
- 2) site, sampling location within the site;
- 3) date, time.

b) Statement:

- 1) the sampling was performed in accordance with EN 1948-1:2006;
- 2) in case of departure(s) here from, justification(s) shall be given.

c) Precision:

indications of the reproducibility and repeatability which may be expected under similar conditions to the validation measurements are given in EN 1948-3.

- d) Gas parameters in the duct:
- 1) duct data (dimensions etc.);
  - 2) measurement positions in the duct;
  - 3) O<sub>2</sub> content (measured how, when);
  - 4) moisture content (measured how, when);
  - 5) CO<sub>2</sub> content (measured how, when);
  - 6) calculation of the gas density;
  - 7) velocity profile;
  - 8) temperature profile;
  - 9) pressure data (static, atmospheric).
- e) Sampling train:
- 1) name of method;
  - 2) identification of the used parts of the sampling equipment.
- f) Scheme of sampling train:
- 1) filter data (dimensions, efficiency data from manufacturer);
  - 2) absorbant/adsorbent data (quality, quantity/dimensions);
  - 3) verification adsorption stage used if required;
  - 4) pre-rinsing (before sampling) carried out if required.
- g) Sampling data:
- 1) diameter of nozzle and probe;
  - 2) temperature in duct during sampling;
  - 3) flow rate through filter, through absorber/adsorber unit;
  - 4) maximum temperature at filter during sampling;
  - 5) maximum temperature at condenser or absorber/adsorber unit;
  - 6) mean gas meter temperature;
  - 7) moisture of sampled gas (measured how, when);
  - 8) pressure at gas meter;
  - 9) volume sampled at gas meter conditions;
  - 10) reference O<sub>2</sub>/CO<sub>2</sub> content;

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- 11) moisture content used in the reported PCDD/PCDF concentrations;
  - 12) volume sampled in m<sup>3</sup> at standard conditions of temperature and pressure, reference O<sub>2</sub>/CO<sub>2</sub>, wet and/or dry gas;
  - 13) isokinetic ratio (calculated in accordance with EN 13284-1);
  - 14) leak checks results before and after sampling;
  - 15) sampling duration, start, end, stoppages, date;
  - 16) for the measurement with division of flow: side stream:
    - i) volume sampled at gas meter;
    - ii) volume sampled in m<sup>3</sup> at standard conditions of temperature and pressure, reference O<sub>2</sub>/CO<sub>2</sub>, wet and/or dry gas.
- h) Spiking:
- 1) compartment spiked;
  - 2) quantity and quality of sampling standard solution;
  - 3) recovery of <sup>13</sup>C<sub>12</sub>-1,2,3,7,8-PeCDF, <sup>13</sup>C<sub>12</sub>-1,2,3,7,8,9-HxCDF, <sup>13</sup>C<sub>12</sub>-1,2,3,4,7,8,9-HpCDF to be filled in later according to the results obtained applying EN 1948-2 and EN 1948-3.
- i) Field blank and rinsing solution of reused equipment (if required).  
When the analytical results have been examined the sampling report shall state whether:
- 1) the field blank was less than 10 % of the emission limit value;
  - 2) the calculated value was greater than the field blank value;
  - 3) the concentration in the following sample did not exceed the emission limit value.
- j) Calculation according to EN 1948-3:2006, Clause 12.

In Annex D a typical sampling record to be filled in at the sampling site is given for information.

## Annex A (informative)

### Toxicity and toxic equivalency

#### A.1 General

The dioxins and furans with chlorine atoms at the 2, 3, 7, and 8 positions are considered the most toxic. Of these, 2,3,7,8-chlorodibenzo-p-dioxin (TCDD) has by far the highest toxicity, is the most studied and best known. Animal studies have shown that 2,3,7,8-TCDD can be lethal in very small concentrations. In the row of known toxins it is one of the most toxic substances [v]. Different PCDD/PCDF congeners have many of the same biological effects but with different strength.

#### A.2 Effect mechanism

The present model for some of the effects of dioxins is the initial binding to cytosolic receptors of aromatic hydrocarbons (Ah receptor). The resulting complex associates with dioxin responsive DNA elements which leads to the expression of certain genes and as a further result to increased protein biosyntheses and the induction of cytochrome P450 dependent monooxygenases. These in turn can affect the metabolism of other substances and thus lead to disturbances in biological functions. To a large extent the effects of dioxins are seen as a consequence of this mechanism. However, this cannot explain all toxic effects of dioxins especially the extremely high toxicity [vi].

The effect mechanisms causing immune system suppression, carcinogenicity or hormone disruption are not yet well understood.

#### A.3 The TEQ system

In the environment PCDDs/PCDFs practically never appear as single compounds but always as a complex mixture associated with other structurally related (“dioxin-like”) compounds such as PCBs.

The TEQ system uses 2,3,7,8-TCDD as the standard to which the toxicity of the other compounds is weighted as toxic equivalents (TEQs). This normalisation is based on the assumption that PCDDs/PCDFs and dioxin-like compounds act through the same mechanism of action. The toxic effects are assessed through subchronic toxicity studies and from certain biochemical properties such as Ah receptor binding capacity.

The toxic potential of a single congener is indicated through its toxic equivalence factor (TEF) describing the individual toxicity relative to the toxic effect of 2,3,7,8-TCDD. For the TEQ calculation the amount or concentration of each relevant congener is multiplied with the corresponding TEF. When all congeners are given as “equivalents of 2,3,7,8-TCDD” they can simply be added up and the resulting TEQ represent the total toxicity of the mixture.

Even if there still remain uncertainties concerning the toxicity of PCDDs/PCDFs [iii; vii] there have been established international toxic equivalency factors (I-TEF) by the NATO [viii] (see Table A.1) and recently by the WHO [iii] standardising the toxicity of 2,3,7,8-Cl substituted dioxins and furans and recently certain dioxin-like PCBs. For all other congeners which may be present in a sample, a TEQ value of zero is assigned.

**Table A.1 — International toxic equivalency factors (I-TEF) of 17 dibenzodioxins and dibenzofurans [viii]**

Dibenzodioxins		Dibenzofurans	
Congener	I-TEF	Congener	I-TEF
2,3,7,8-TCDD	1	2,3,7,8-TCDF	0,1
1,2,3,7,8-PeCDD	0,5	2,3,4,7,8-PeCDF	0,5
1,2,3,4,7,8-HxCDD	0,1	1,2,3,7,8-PeCDF	0,05
1,2,3,7,8,9-HxCDD	0,1	1,2,3,4,7,8-HxCDF	0,1
1,2,3,6,7,8-HxCDD	0,1	1,2,3,7,8,9-HxCDF	0,1
1,2,3,4,6,7,8-HpCDD	0,01	1,2,3,6,7,8-HxCDF	0,1
OCDD	0,001	2,3,4,6,7,8-HxCDF	0,1
		1,2,3,4,6,7,8-HpCDF	0,01
		1,2,3,4,7,8,9-HpCDF	0,01
		OCDF	0,001

The NATO scheme has been adopted internationally as a basis for the TEQ determination and is e.g. also adopted in Annex I of Council Directive 2000/76/EC of 4 December 2000 on the incineration of waste [ii]. During recent years the toxicity of PCDDs/PCDFs has been reported mainly in I-TEQ <sup>5)</sup>.

The most recent TEQ scheme, developed by the World Health Organisation (WHO) and the International Programme on Chemical Safety (IPCS) standardises the toxicity of 17 dioxin and furan congeners and includes for the first time 12 dioxin-like PCBs. It reflects the present knowledge about toxic effects of PCDDs/PCDFs and dioxin-like PCBs. Another aspect is that the WHO-TEQ system is not only applicable to humans but also to mammals, fish and birds (see Table A.2).

The WHO-TEQ approach is linked to a WHO recommendation concerning a Tolerable Daily Intake (TDI) for humans of 1 pg to 4 pg WHO-TEQ/kg body weight (including PCBs) which should not be exceeded. The TDI was recommended on the basis of critical effects (including developmental, reproductive, hormonal, immune system and neuro-behavioural effects), dose-response relationships and quantitative risk extrapolation.

In the sense of an international harmonised risk assessment, which should be based on the most current knowledge, it appears to be reasonable to accept the WHO-TEQ system and to discuss the WHO-TDI as an assessment scale for future risk assessment at international level.

There are certain limits giving rise to criticism to the TEQ systems: they are restricted mainly to effects mediated by the Ah receptor and they do not include aspects related to transport, uptake and accumulation of the single congeners which are important with regard to toxic effects. These aspects depend on congener specific physicochemical properties such as persistence, bio-concentration factor, vapour pressure etc. For the assessment of environmental effects it might therefore be necessary to investigate the fate of the single congeners after their emission from the sources. A high emission value of a certain congener does not necessarily correspond to high environmental exposure.

However, the TEQ approach has been developed as a pragmatic tool allowing the assessment and indication of the toxicity of complex PCDD/PCDF mixtures in a single TEQ value and it is broadly accepted.

---

5) Other TEQ systems such as the Nordic system "NTEQ" or "Eadon-TEQ" or "BGA/UBA-TEQ" or "EPA-TEQ" have been developed using slightly different TEFs for single congeners. In the case of "BGA/UBA-TEQ" and "EPA-TEQ" TEFs have been assigned also to the sum of non 2,3,7,8-substituted homologue groups. To sum up one can say that the related assessment of the toxicity is generally comparable to the I-TEQ values according to the NATO TEQ system.



Table A.2 — WHO Toxic Equivalency Factors (WHO-TEFs) for mammals, fish and birds [iii]

Congener	Humans/Mammals	Birds	Fish
2,3,7,8-TCDD	1	1	1
1,2,3,7,8-PeCDD	1	1	1
1,2,3,4,7,8-HxCDD	0,1	0,05	0,5
1,2,3,6,7,8-HxCDD	0,1	0,01	0,01
1,2,3,7,8,9-HxCDD	0,1	0,1	0,01
1,2,3,4,6,7,8-HpCDD	0,01	<0,001	0,001
OCDD	0,000 1	0,000 1	<0,000 1
2,3,7,8-TCDF	0,1	1	0,05
1,2,3,7,8-PeCDF	0,05	0,1	0,05
2,3,4,7,8-PeCDF	0,5	1	0,5
1,2,3,4,7,8-HxCDF	0,1	0,1	0,1
1,2,3,6,7,8-HxCDF	0,1	0,1	0,1
1,2,3,7,8,9-HxCDF	0,1	0,1	0,1
2,3,4,6,7,8-HxCDF	0,1	0,1	0,1
1,2,3,4,6,7,8-HpCDF	0,01	0,01	0,01
1,2,3,4,7,8,9-HpCDF	0,01	0,01	0,01
OCDF	0,000 1	0,000 1	<0,000 1
3,4,4',5-TCB (81)	0,000 1	0,1	0,000 5
3,3',4,4'-TCB(77)	0,000 1	0,05	0,000 1
3,3',4,4',5-PeCB (126)	0,1	0,1	0,005
3,3',4,4',5,5'-HxCB (169)	0,01	0,001	0,000 05
2,3,3',4,4'-PeCB (105)	0,000 1	0,000 1	<0,000 005
2,3,4,4',5-PeCB (114)	0,000 5	0,000 1	<0,000 005
2,3',4,4',5-PeCB (118)	0,000 1	0,000 01	<0,000 005
2',3,4,4',5-PeCB (123)	0,000 1	0,000 01	<0,000 005
2,3,3',4,4',5-HxCB (156)	0,000 5	0,000 1	<0,000 005
2,3,3',4,4',5'-HxCB (157)	0,000 5	0,000 1	<0,000 005
2,3',4,4',5,5'-HxCB (167)	0,000 01	0,000 01	<0,000 005
2,3,3',4,4',5,5'-HpCB (189)	0,000 1	0,000 01	<0,000 005

## Annex B (informative)

### Examples of operation

#### B.1 General

The revision of this EN between 2001 and 2004 only refers to the normative part. The information given in this informative Annex as examples of operation are kept unchanged, as they represent the state of the art at time of the validation measurements of EN 1948:1996 between 1992 and 1995.

Examples of operation of the three different sampling systems

- a) Filter/condenser method (for details see also [ix; x; xi]);
- b) Dilution method (for details see also [xii]);
- c) Cooled probe method (for details see also [xiii; xiv; xv; xvi]).

which were used to perform the validation measurements (6 h sampling duration) are described in this annex. These systems meet the minimum requirements, but the procedures differ in some details.

#### B.2 Filter/condenser method

##### B.2.1 Summary of apparatus design

The sampling train is shown in Figure B.1 (details see also [iix]). The sample gas is sucked through the nozzle, probe and filter (< 125 °C). Then the gas passes the condenser and the condensate flask. Downstream there are two bubblers filled with diethylene glycol/water (1:2 v/v). At the end there is the pump and the volume measurement and regulation device.

- a) Filter casing (in stack filter) made out of glass, outside diameter 50 mm, length 160 mm;
- b) Thimble type glass fibre filter 30 mm x 100 mm; high efficiency;
- c) Probe made out of glass, inside diameter 10 mm;
- d) Condenser, coiled type with 8 coils, inside diameter of passage 10 mm, condenser height 290 mm;
- e) Bubbler without frit with a volume of 0,5 l filled with 150 ml diethylene glycol/water (1:2 v/v), inside diameter 80 mm, height 320 mm;
- f) Cooling aggregate.

The sampling train is validated for volume flow rates of around 2 m<sup>3</sup>/h.

##### B.2.2 Adsorbent and cleaning procedure

The reagents used as adsorbents are of HPLC grade. Before use 1 l of the glycol/water (1:2, v/v) mixture is extracted three times with 150 ml of pesticide grade dichloromethane.

### B.2.3 Glassware cleaning procedure before sampling

The glassware is cleaned in the laboratory. At the sampling site the equipment is rinsed again with dichloromethane before use.

### B.2.4 Spiking position

The filter is spiked by distribution of the sampling standard solution on the filter before sampling. If a new filter is required during sampling the replacement is also spiked and a record is kept to enable the calculated sampling standard recoveries to be corrected. Additionally the condensate flask may be spiked, too/or instead of.

### B.2.5 Equipment assembly procedure

The equipment is assembled according to Figure B.1 taking care not to contaminate any of the surfaces in contact with the sample.

- a) Connect the condenser with the cooling aggregate or with the water pipe;
- b) Connect the filter unit (out stack filter) with the nozzle, the probe, and the condenser (if the temperature of the sample gas is  $< 125\text{ }^{\circ}\text{C}$  in stack filtering is possible);
- c) Connect the condensate flask and downstream the bubblers;
- d) Connect the pump and volume measurement and regulation system;
- e) If necessary start the heating of the probe and filter casing.

### B.2.6 Leak check procedure

The sampling train is leak checked by plugging the nozzle and turning the automatic flow control unit on. The pump will evacuate the system and then cut out if the flow is sufficiently low as to indicate the absence of a leak.

### B.2.7 Sample gas flow rate control

The sample gas flow rate is adjusted continuously by a microprocessor controlled solenoid valve. This ensures that, if the correct nozzle size is chosen, isokinetic conditions are maintained within 2 % using the assuming moisture content of the flue gases.

### B.2.8 Sampling

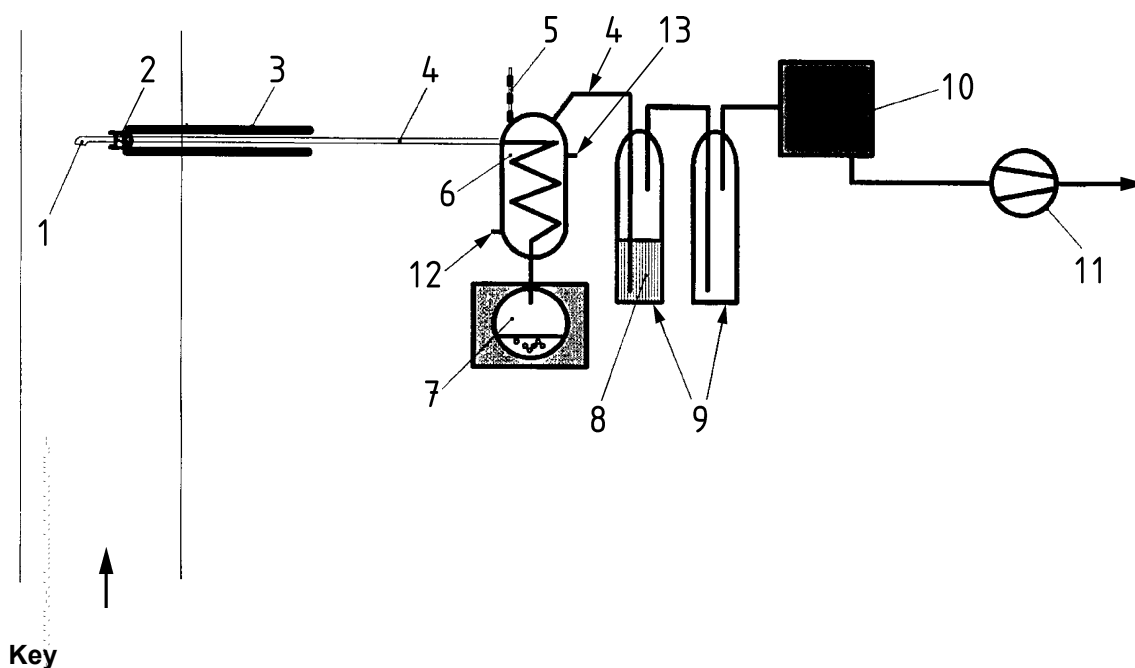
- a) Insert the probe in the duct, the nozzle turned away from the gas flow;
- b) Adjust the heating/cooling of the probe and/or filter casing to ensure a temperature of less than  $125\text{ }^{\circ}\text{C}$  but at least  $10\text{ }^{\circ}\text{C}$  above the dew point in the filter holder;
- c) Switch on the cooling device and adjust to obtain the desired temperature in the condenser itself and the adsorber unit, and in any case less than  $20\text{ }^{\circ}\text{C}$  but avoiding icing;
- d) Position the nozzle at the measuring point and secure it in that position. Turn the nozzle in the direction of gas flow;
- e) Switch on the pump and adjust the flow rates to ensure isokinetic sampling at the nozzle.

### B.2.9 Equipment disassembly procedure

At the end of sampling the pump and heaters are turned off and the probe is withdrawn from the duct and allowed to cool. The sampled gas volume is then recorded. The condenser is turned off and the sampling train leak checked. After this the sampling train is disconnected with care:

- a) The glassware and connections are rinsed with 100 ml each of acetone and dichloromethane;
- b) The rinsing solutions are combined with the condensate;
- c) The bubbler solutions are transferred to a clean glass bottle and the bubblers are rinsed with water, then acetone and then dichloromethane;
- d) The filter casing is capped.

All the parts are properly labelled.



#### Key

- |   |                     |    |   |
|---|---------------------|----|---|
| 1 | nozzle              | 8  | Diethylene glycol                       |
| 2 | thimble filter      | 9  | bubbler                                 |
| 3 | heated probe        | 10 | drying tower                            |
| 4 | connections (glass) | 11 | suction device (pump, valve, gas meter) |
| 5 | temperature control | 12 | cooling water inlet                     |
| 6 | condenser           | 13 | cooling water outlet                    |
| 7 | condensate flask    |    |   |

Figure B.1 — Schematic representation of the filter/condenser method; variant without flow division

## B.3 Filter/condenser method - Variant with flow division

### B.3.1 Summary of apparatus design

A diagram of the apparatus is given in Figure B.2. All the gas sampled passes through a glass nozzle and a glass probe to a filter. A portion of the gas passing through the filter and a flow divider is sub-sampled through a condenser, and a condensate flask to an adsorber unit. Details of the design of the filter casing are given in Figure B.3 and of the adsorber cartridge and condenser in Figure B.4.

In order to ensure good isokinetic conditions and to avoid as far as possible particulate deposition on the walls, inside diameter of nozzle and probe should be 8 mm at the minimum.

Depending on the waste gas temperature the probe is equipped with a heating or cooling device in order to bring the temperature of the gas sampled at less than 125 °C. The temperature in the filter casing should be at least 10 °C above dew point.

The sampling train uses a flat filter of 125 mm diameter and at least 30 g of XAD-2, packed according to the laboratory's Quality Manual.

The sampling system is validated for volume flow rates in the range of 0,5 m<sup>3</sup>/h to 0,7 m<sup>3</sup>/h (side stream) and 3 m<sup>3</sup>/h to 5 m<sup>3</sup>/h (main stream).

### B.3.2 Adsorbent and cleaning procedure

The adsorbent used is XAD-2 (20 mesh to 50 mesh). The adsorbent is cleaned following the description in Annex C.

### B.3.3 Glassware cleaning procedure before sampling

A new probe and nozzle made out of glass each are preferably used for each test.

### B.3.4 Spiking position

The filter is spiked by distributing 20 µl to 30 µl portions of the sampling standard solution at different places on the filter. The filter is left in a vertical position for a short time until the solvent has evaporated. The filter is used for sampling not earlier than 2 h after the sampling standards has been applied. The spiked filter may be stored for several days. Additionally, the XAD-2 adsorbent may be spiked, too/or instead of.

If during sampling a change of the spiked filter is necessary, the new one has to be spiked in the same way. This has to be taken into account for calculation.

### B.3.5 Equipment assembly procedure

The equipment is taken in its packing boxes to the sampling position. The boxes are opened and the equipment assembled according to Figure B.2. The use of greases or flexible tubes is prohibited for parts of the sampling train that come into contact with the sampled gas.

- a) Connect the condenser with the cooling aggregate or with the water pipe;
- b) Insert the solid adsorber cartridge filled with XAD-2;
- c) Connect the drying tower and downstream the pump and the gas meter of the side stream;
- d) Connect the condenser with the filter unit by means of the flow divider
- e) Connect the main pump and gas meter (mean stream) with the filter unit via the flow divider;

- f) Connect the probe to the filter unit;
- g) Insert the thermoelements
- h) Darken the gas leading parts up to the drying tower with aluminium foil;
- i) If necessary start the heating of the probe and filter box.

### **B.3.6 Leak check procedure**

The sampling train is leak checked by evacuating with plugged nozzle and measuring the volume flow to the minimum vacuum used during sampling. The measured volume flow should be < 5 % of the normal flow rate.

### **B.3.7 Sample gas flow rate control**

The main sample gas flow rate is adjusted to be isokinetic. The side stream is adjusted to keep the ratio between side and main stream constant ( $\pm 10\%$ ), ensuring that the velocity in the XAD-2 cartridge does not exceed 34 cm/s.

### **B.3.8 Sampling**

- a) Insert the probe in the duct, the nozzle turned away from the gas flow;
- b) Adjust the heating/cooling of the probe and/or filter casing to ensure a temperature of less than 125 °C but at least 10 °C above the dew point in the filter holder;
- c) Switch on the condenser cooling device and adjust to obtain the desired temperature in the condenser itself and the adsorber unit, and in any case less than 20 °C but avoiding icing;
- d) Position the nozzle at the measuring point and secure it in that position. Turn the nozzle in the direction of gas flow;
- e) Switch on the pumps and adjust the flow rates to ensure isokinetic sampling at the nozzle;
- f) Adjust the flow rate to keep the ratio of flow rates constant  $\pm 10\%$ .

### **B.3.9 Equipment disassembly procedure**

At the end of sampling the pumps and heaters are turned off and the valves are closed. The probe is withdrawn from the duct and allowed to cool. The sampled gas volumes of the main and side streams are recorded. The condenser is then turned off. The sampling train is leak checked. (If there is very low pressure in the stack, it is recommended to insert a valve behind the filter to avoid particle losses by ventilation.)

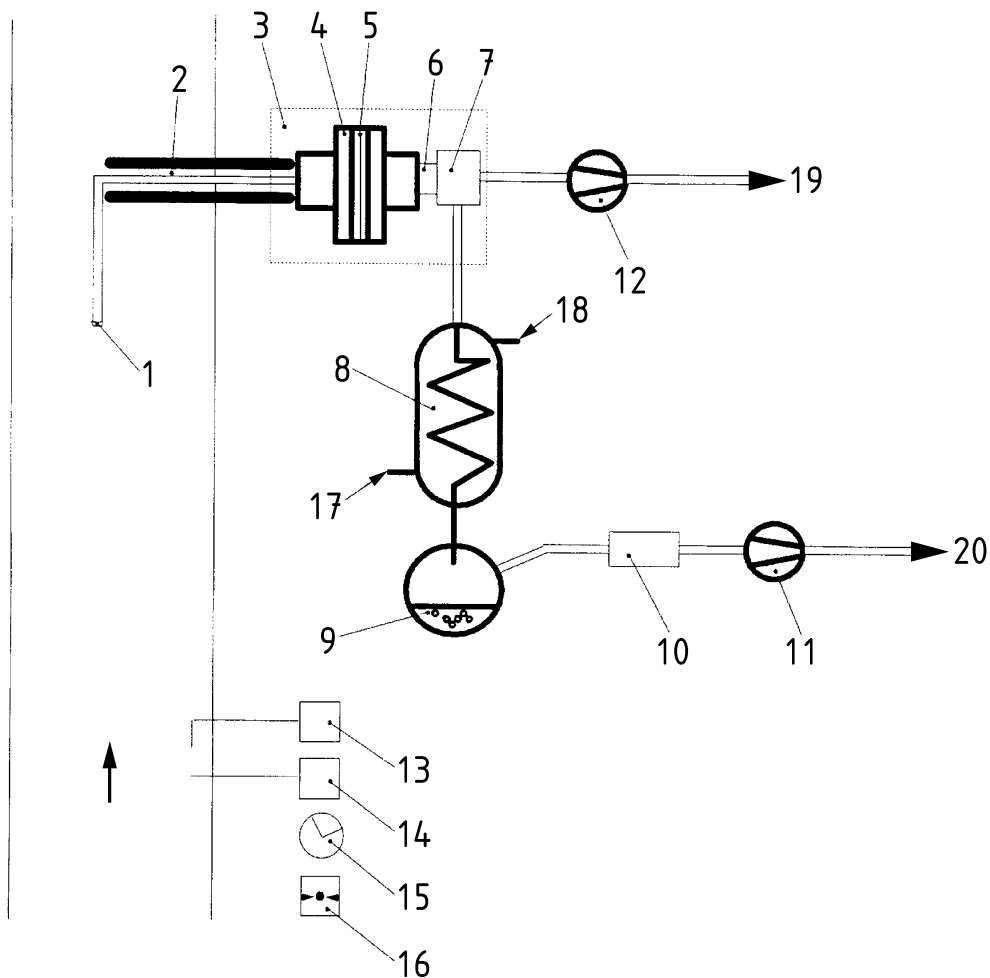
After this, disassemble with care:

- a) Collect the nozzle and probe taking off eventual deposits on the external parts with a glass wool swab dipped in acetone, plug the orifices with caps or aluminium foil and put all these parts in their transport boxes;
- b) Isolate the filter eventually in its filter casing with capped orifices and transport it in a clean glass box, protected from light;
- c) Collect the condensate in a brown flask if the device is reused for another sampling;
- d) Collect the condenser, close it with non greased glass stoppers and put it in a transport box;
- e) Isolate the solid adsorber cartridge and close it with socket glass stoppers and put it in its transport box.

All the parts are properly labelled.

The following is done normally at the laboratory.

- f) Rinse the inner part of nozzle and probe vigorously first with acetone, then toluene, repeat the operation. If some deposits are visible, use a quartz wool swab dipped in acetone. This swab is later added to the filter. If this does not remove the deposits it is necessary to cut up the probe and boil it in toluene. This process is repeated twice;
- g) The filter holder is rinsed with around 20 ml of toluene twice, this solution is added to the extraction solvent of the Soxhlet apparatus. The condenser is rinsed with acetone or refluxed boiled with toluene. This rinsing solution is added to the condensate;
- h) The XAD-2 is taken out of the cartridge for extraction and the cartridge is rinsed with toluene. The rinsing is added to the condensate.



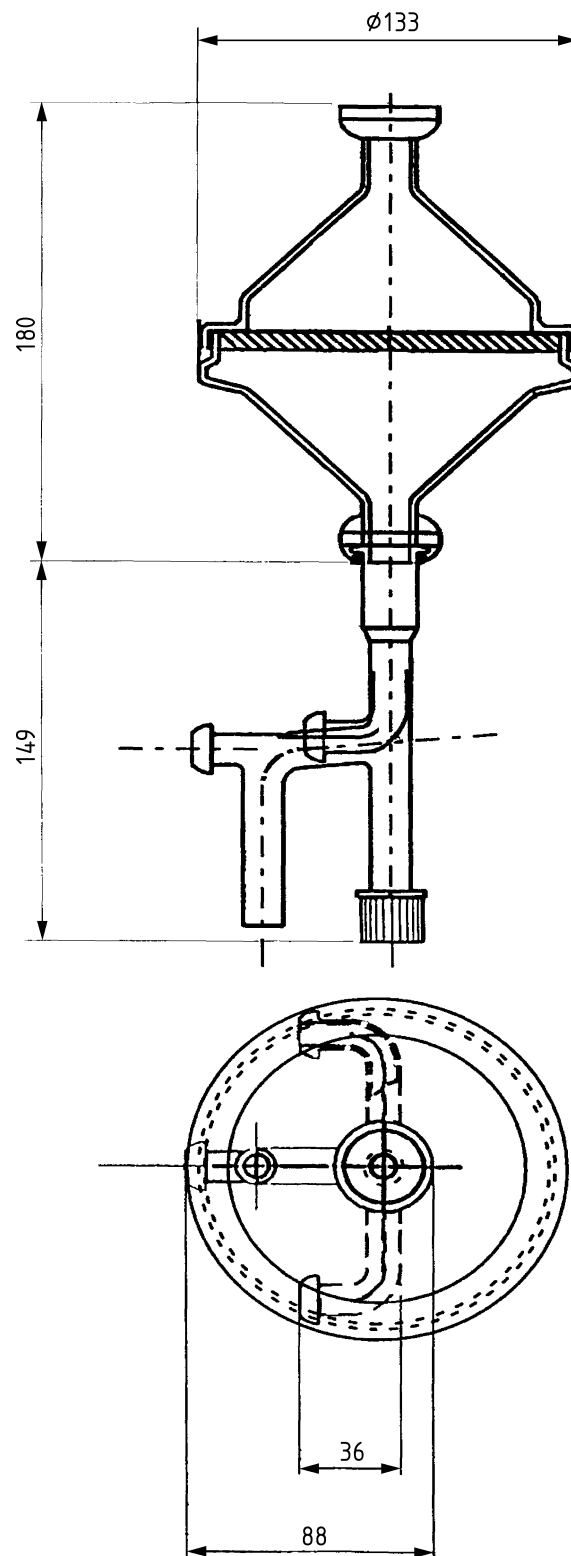
**Key**

- |    |  |    |  |
|----|--|----|--|
| 1  | sampling nozzle                                  | 11 | suction device main stream<br>15 l/min max.  |
| 2  | probe (eventually heated; 790 mm to<br>1 190 mm) | 12 | suction device main stream<br>120 l/min max. |
| 3  | temperature related casing (box;<br>T < 125 °C)  | 13 | gas velocity and pressure device             |
| 4  | filter holder                                    | 14 | gas thermometer                              |
| 5  | filter (diameter = 125 mm)                       | 15 | clock  |
| 6  | Thermometer                                      | 16 | atmospheric pressure device                  |
| 7  | flow divider                                     | 17 | cooling water inlet                          |
| 8  | condenser  | 18 | cooling water outlet                         |
| 9  | condensate bottle (1 l)                          | 19 | main stream outlet                           |
| 10 | solid adsorber and/or impinger unit              | 20 | side stream outlet                           |

**Figure B.2 — Schematic representation of the sampling train  
Variant of the filter/condenser method with flow division**



Dimensions in millimetres



**Figure B.3 — Detailed representation of the filter casing  
(Filter/condenser method with flow division)**

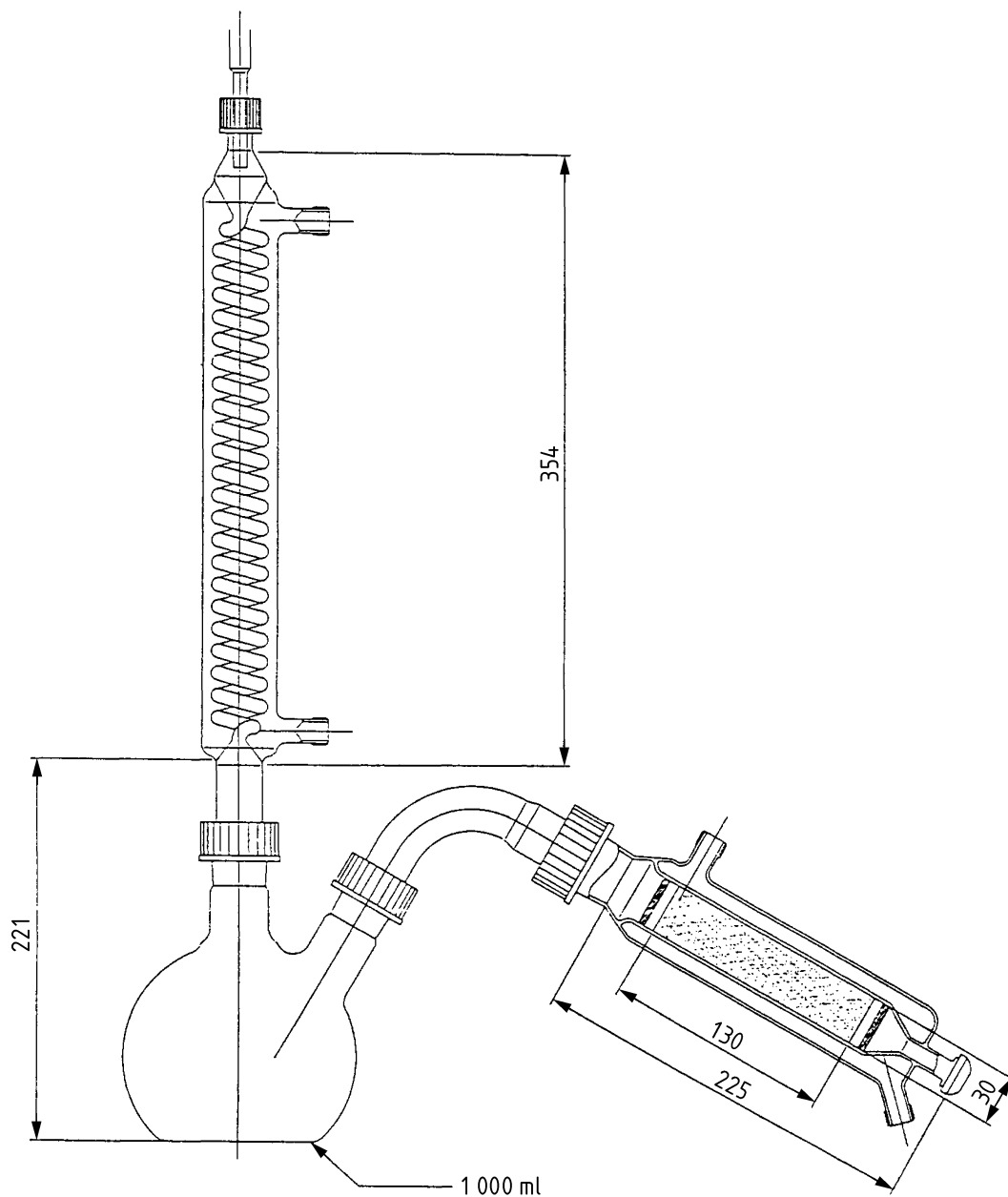


Figure B.4 — Detailed representation of the condenser and adsorber cartridge  
(Filter/condenser method with flow division)

## B.4 Filter/condenser method - Variant with solid adsorbent upstream of the condensate flask

### B.4.1 Summary of apparatus design

The sampling train is shown in Figure B.5 (details see also [x]).

The flue gas enters the sampling train through an electrically heated glass lined probe. This is connected to a glass filter casing in which a quartz filter is supported on a PTFE filter holder. The filter casing is inside an electrically heated box. It is followed by a water cooled coil condenser and a water cooled XAD-2 resin filled cartridge. The condensate and the gas passes through the resin to a round bottomed flask in which the condensate is collected. The temperature of the gas in the probe and the filter are regulated to between the dew point of the flue gas and 120 °C. Alongside the probe are strapped a K-type thermocouple to monitor the flue gas temperature and a S-type pitot tube to measure the flue gas flow rate.

After the condensate flask the gas is drawn through a silica gel filled drying train to a pump, a gas meter and an orifice plate flow measurement device.

The sampling system is constructed on the basis of a flow rate of around 5 l/min to 25 l/min. All parts of the sampling train not in contact with the sample are connected together with flexible hoses.

### B.4.2 Adsorbent and cleaning procedure

The adsorbent used is supplied pre-cleaned.

The reagents used are glass distilled grade.

### B.4.3 Sampling train cleaning procedure before sampling

The sampling train is thoroughly cleaned in the laboratory by removing all visible contamination by scrubbing with detergent and water followed by a rinse with deionised water, drying and a toluene rinse. The glassware with the exception of the probe is then treated in an oven at 450 °C overnight and then carefully sealed either with glass stoppers, aluminium foil or by enclosing it in a plastic bag.

### B.4.4 Spiking position

The filter is spiked by distribution of the sampling standard solution on the filter before sampling. If a new filter is required during sampling the replacement is also spiked and a record is kept to enable the calculated sampling standard recoveries to be corrected.

### B.4.5 Equipment assembly procedure

The equipment is assembled as shown in Figure B.5. No part is unsealed until the last moment and great care is taken not to contaminate any of the surfaces in contact with the sample.

- a) Connect the condenser with the cooling aggregate or with the water pipe;
- b) Connect the condenser with the filter unit and the solid adsorber cartridge;
- c) Connect the condensate flask with the solid adsorber cartridge;
- d) Connect drying tower, pump and volume measurement device with the condensate flask;
- e) Connect the probe and nozzle with filter casing;

- f) Insert the thermoelements;
- g) If necessary start heating of the probe and filter casing.

#### **B.4.6 Leak check procedure**

The sampling train is leak checked by plugging the probe's nozzle and evacuating the sampling train to 50 kPa below atmospheric pressure. The volume flow rate through the sampling train should be less than 0,03 m<sup>3</sup>/h for the system to be used. Otherwise the leak has to be located and cured.

#### **B.4.7 Sample gas flow rate control**

The sample gas flow rate is adjusted manually. Readings are taken every 10 min of the flue gas data, and gas meter inlet and outlet temperatures, the gas meter and atmospheric pressures and the flue gas velocity and sample gas flow rates. These are used to calculate the desired sample gas flow rate required to maintain isokinetic conditions.

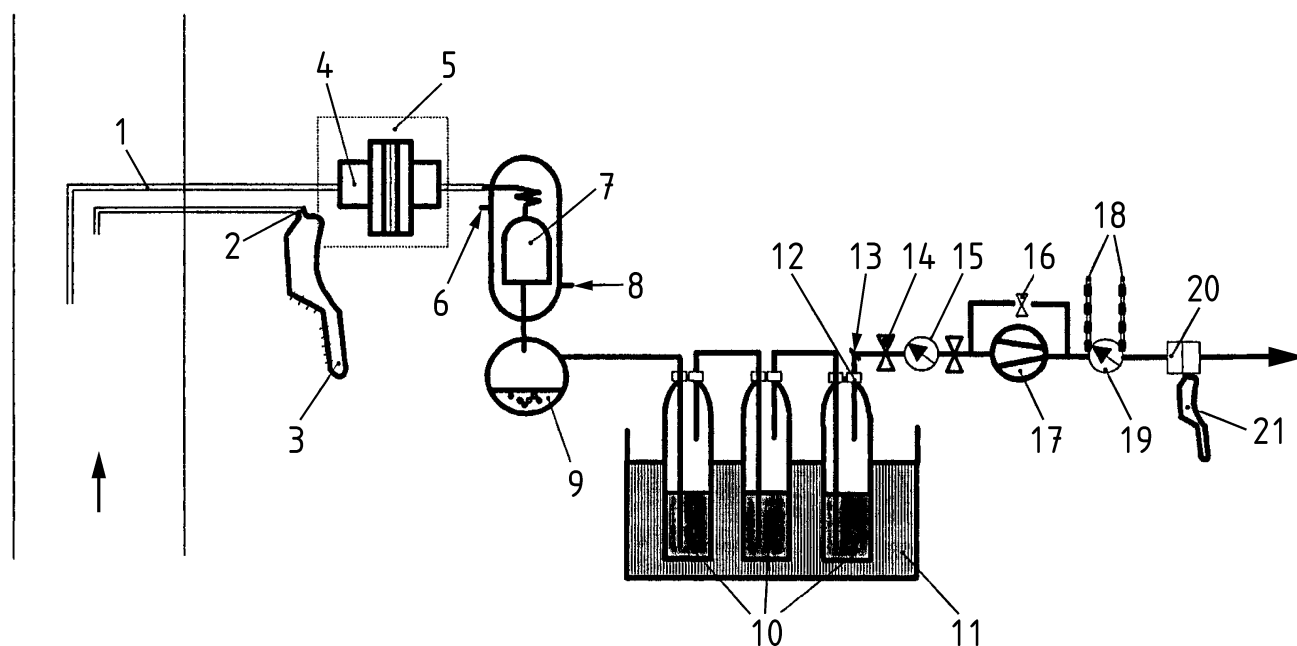
#### **B.4.8 Sampling**

- a) Insert the probe in the duct, the nozzle turned away from the gas flow;
- b) Switch on the cooling device and adjust to obtain the desired temperature in the condenser itself and the adsorber unit, and in any case less than 20 °C but avoiding icing;
- c) Adjust the heating/cooling of the probe and/or filter casing to ensure a temperature of less than 125 °C but at least 10 °C above the dew point in the filter holder;
- d) Position the nozzle at the measuring point and secure it in that position. Turn the nozzle in the direction of gas flow;
- e) Switch on the pump and adjust the flow rate to ensure isokinetic sampling at the nozzle.

#### **B.4.9 Equipment disassembly procedure**

The system is closed down by shutting the flow control valves and turning off the pump. The heaters are turned off and the filter box oven door is opened. The probe is removed from the duct, allowed to cool and the sampling train leak checked.

- a) The cooling water is turned off once the filter temperature has reduced to ambient conditions;
- b) The probe is disconnected from the filter and washed with toluene;
- c) The probe washings are collected in a toluene washed bottle;
- d) The filter and resin cartridges are disconnected and are then sealed with glass fittings;
- e) The condensate collection flask is sealed or if an excess is collected during sampling poured into a pre-cleaned glass bottle;
- f) The remaining parts of glassware are washed with toluene which is combined with the probe washings.



### Key

- |    |                   |    |                         |
|----|-------------------|----|-------------------------|
| 1  | glass lined probe | 12 | thermocouple            |
| 2  | Pitot tube        | 13 | flexible umbilical link |
| 3  | manometer         | 14 | check valve             |
| 4  | filter holder     | 15 | vacuum gauge            |
| 5  | heated box        | 16 | by pass valve           |
| 6  | water out         | 17 | pump                    |
| 7  | XAD-2 resin       | 18 | thermocouples           |
| 8  | ice water in      | 19 | dry gas meter           |
| 9  | condensate        | 20 | orifice                 |
| 10 | Silica gel        | 21 | manometer               |
| 11 | ice bath          |    |                         |

**Figure B.5 — Representation of the sampling train of the filter/condenser method  
Variant adsorbent upstream the condensate flask**

## B.5 Dilution method - Automated variant

### B.5.1 Summary of apparatus design

Figure B.6 represents the schematic procedure of the sampling system (details see also [xii]). The key device is the mixing channel. In Figure B.7 the filter casing is depicted in detail for two different flue gas sample volume flow rates.

The sample gas is sucked through the nozzle and the probe (3). In the mixing channel (4) the waste gas is mixed turbulently with dry dilution air. The air entering at right angles to the direction of the stream is first deflected; the waste gas then enters the air stream at about the middle of the mixing channel through a heat-insulated tube reaching therein.

The sampling filter (5) is located at the exit from the mixing channel (4) and the dilution air filter (6) is located at the entry to the mixing channel.

The filter area loading should not exceed  $0,5 \text{ m}^3/\text{m}^2\text{s}$ . The gas temperature at the sampling filter (5) is measured during sampling and then registered or recorded. It should not exceed  $40 \text{ }^\circ\text{C}$ .

The shut-off or control valves for the total gas stream or the dilution air (10, 12) are controlled by means of a servomotor via an evaluation and control unit or a PC (9).

Measuring devices for the characteristics of the waste gas, i.e. pressure, temperature, waste gas velocity and waste gas composition, are additionally required in the waste gas channel for the sampling procedure. These waste gas data being likewise obtained from the evaluation and control unit or a PC (9). A vacuum pump (13), a Roots blower or a compressed air-driven ejector is used for the suction. The air conducted to the mixing channel is dried in a drying tower (14) and cooled, if appropriate.

- a) mixing channel:
- |                    |               |
|--------------------|---------------|
| length             | 250 mm        |
| diameter           | 50 mm         |
| internal diameter  | 8 mm to 10 mm |
| actual mixing zone | 150 mm        |

- b) sampling filter casing (see Figure B.7)

The sampling system is validated for flue gas sample volume flow rates of  $1,5 \text{ m}^3/\text{h}$  to  $4 \text{ m}^3/\text{h}$ .

### B.5.2 Adsorbent and cleaning procedure

The PU foam (solid adsorbent) is cleaned in accordance with the description in Annex C.

### B.5.3 Device cleaning procedure before sampling

The nozzle, probe (made of titanium) and the filter casings are cleaned with acetone and toluene.

### B.5.4 Spiking position

The sample gas filter is spiked by distributing  $20 \mu\text{l}$  to  $30 \mu\text{l}$  portions of the sampling standard solution at different places at the filter. The filter is used for sampling not earlier than 2 h after the sampling standards have been applied. The PU foam can be spiked, too.

### B.5.5 Equipment assembly procedure

The sample apparatus including any secondary aggregates should be entirely assembled according to Figure B.6

- a) Adjust the 2 filters and the adsorbents in the 2 filter casings (for sampling and dilution air);
- b) The nozzle, probe, and filter casings are linked together. (The filter and the solid adsorber unit for cleaning the ambient air (dilution air) are handled according to 7.5).

### B.5.6 Leak check procedure

The sampling train is leak checked by evacuating with plugged nozzle and measuring the volume flow to the minimum pressure used during sampling. The measured volume flow should be < 5 % of the normal flow rate of the total gas stream (sample and dilution air).

### B.5.7 Sample gas flow rate control

The sample gas flow rate is adjusted automatically.

### B.5.8 Sampling

The probe is fitted in the waste gas channel, the shut-off valve (11) remaining closed at first. In addition, the probe is preheated to the temperature of the waste gas.

The isokinetic partial stream sampling of PCDDs/PCDFs is regulated by the evaluation and control unit (9) or a PC. At the start of the sampling process the control valves (10) and (12) are opened first. The pump is switched on and the shut-off valve (11) is opened subsequently and sampling commences.

By means of the control valves (11) (12), the relevant waste gas air streams can be regulated. Care has to be taken that a temperature of 40 °C at the sampling filter (5) is not exceeded.

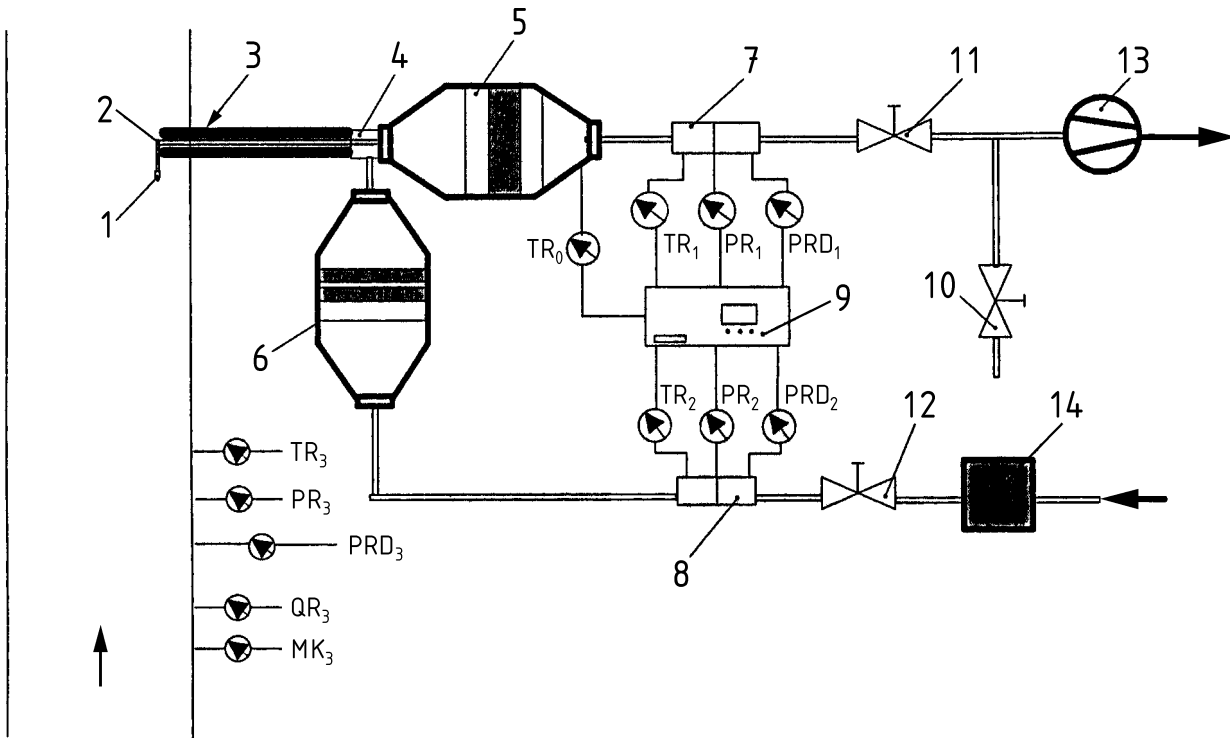
Sampling may be interrupted at any time (by closing the shut-off valve (11)), e.g. for measurements in the cross section of the duct to incorporate the nozzle in another measurement axis, and then continued with unchanged settings. During sampling, the flue gas sample volume flow rate (or difference between dilution air and total gas stream), the gas temperature at the sampling filter and the waste gas condition are recorded or automatically recorded.

Sampling is terminated by closing the shut-off valve (11) and the control valves (12) and by switching off the suction aggregate (13).

### B.5.9 Equipment disassembly procedure

The probe is taken out of the duct

- a) Disassemble the nozzle, probe and the filter casings with care;
- b) Isolate the sampling filter and PU plug as well as the filter and PU plugs of the dilution air system and transport these in clean boxes;
- c) Rinse the nozzle, probe and filter casings with acetone and toluene (if particles or residues are present on the inner surface of the device take them off with a glass wool swab dipped in acetone. The glass wool has to be extracted together with the filter later). The rinsing solutions are stored in the dark and below ambient temperature before extraction.



**Key**

- |  |                                     |
|--|-------------------------------------|
| 1 nozzle   | 11 shut-off valve, total gas stream |
| 2 elbow joint  | 12 control valve, dilution air      |
| 3 probe (controllably heated)  | 13 pump                             |
| 4 mixing channel   | 14 drying tower                     |
| 5 sampling filter (plan glass fibre filter + PU foam plug)                                   |                                     |
| 6 dilution air filter (plan glass fibre filter + PU foam plug and verification PU foam plug) |                                     |
| 7 flow measurement, total gas stream (waste gas and dilution air)                            |                                     |
| 8 flow measurement, dilution air   |                                     |
| 9 optional control unit or PC  |                                     |
| 10 regulation valve (total gas stream)   |                                     |

**Abbreviations**

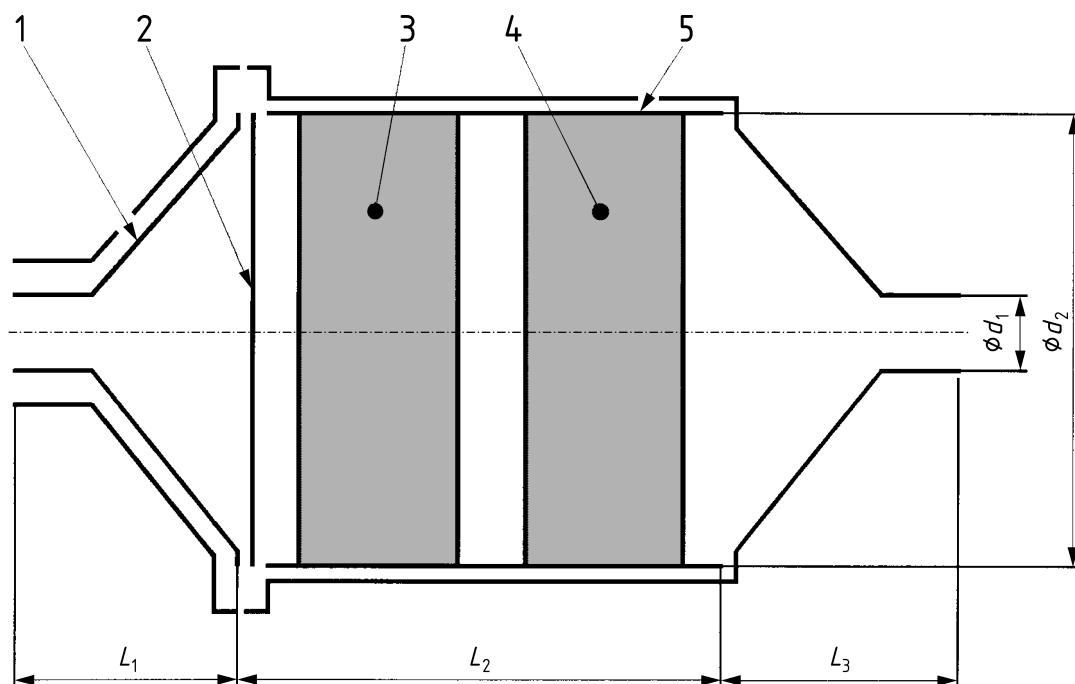
- |     |   |
|-----|---|
| TR  | temperature sensor                                    |
| PR  | pressure gauge  |
| PDR | differential pressure gauge                           |
| QR  | gas stream volume meter                               |
| MK  | O <sub>2</sub> or CO <sub>2</sub> concentration meter |

The indices used for the temperature and pressure gauges represent the following gas streams:

- |   |  |
|---|--|
| 0 | total gas stream from filter                 |
| 1 | total gas stream in the duct                 |
| 2 | dilution air in the flow measurement channel |
| 3 | waste gas stream                             |

**Figure B.6 — Schematic representation of the automated dilution method**





		Total diluted waste gas stream <sup>a)</sup>	
		30 m <sup>3</sup> /h to 40 m <sup>3</sup> /h	15 m <sup>3</sup> /h to 20 m <sup>3</sup> /h
Filter casing	length	390 mm	330 mm
	diameter	250 mm	180 mm
1 Glass inside funnel	length $L_1$	120 mm	100 mm
	internal diameter $d_1$	50 mm	40 mm
	internal diameter $d_2$	180 mm	130 mm
2 Plan fibre filter	diameter $d_2$	180 mm	130 mm
3 PU foam plug	length	50 mm	50 mm
	diameter	180 mm	130 mm
4 Verification PU foam plug	length	50 mm	50 mm
	diameter	180 mm	130 mm
5 Glass inside cylinder	length $L_2$	150 mm	120 mm
	internal diameter $d_2$	180 mm	130 mm
Dilution air filter		the same like sampling filter	

<sup>a)</sup> Filter area loading should not exceed 0,5 m<sup>3</sup>/m<sup>2</sup>s

**Figure B.7 — Detailed representation of the sampling filter casing**

## B.6 Dilution method - Manual variant

### B.6.1 General

Since this variant is nearly identical to the automated version only the differences are described in this subclause.

### B.6.2 Summary of apparatus design

The sampling train is shown in Figure B.8. This system is similar to the automated version apart from the automated volume flow regulation and using a folded filter WB 50<sup>6)</sup> instead of a plan filter.

- a) Nozzle, elbow joint, probe, made out of titanium;
- b) Mixing channel out of titanium, length 250 mm, outside diameter 50 mm, internal diameter 9 mm, actual mixing zone 150 mm;
- c) Filter casing, stainless steel, length 220 mm, diameter 230 mm (for sampling filter);
- d) PU foam (polyurethane foam) length 50 mm, diameter 250 mm;
- e) Filter casing out of stainless steel, length 220 mm, diameter 230 mm (for dilution air filter);
- f) Thimble filter: micronfilter type WB 50<sup>6)</sup>, glass fibre, diameter 185 mm, area approx. 1 m<sup>2</sup>;
- g) Polyurethane foam, length 50 mm. Specifications: thickness 5 cm, density (EN ISO 845:1988 [xvii]) 35 kg/m<sup>3</sup>.

This dilution system is validated for flue gas sample volume flow rates of 1,5 m<sup>3</sup>/h to 4 m<sup>3</sup>/h.

### B.6.3 Leak check procedure

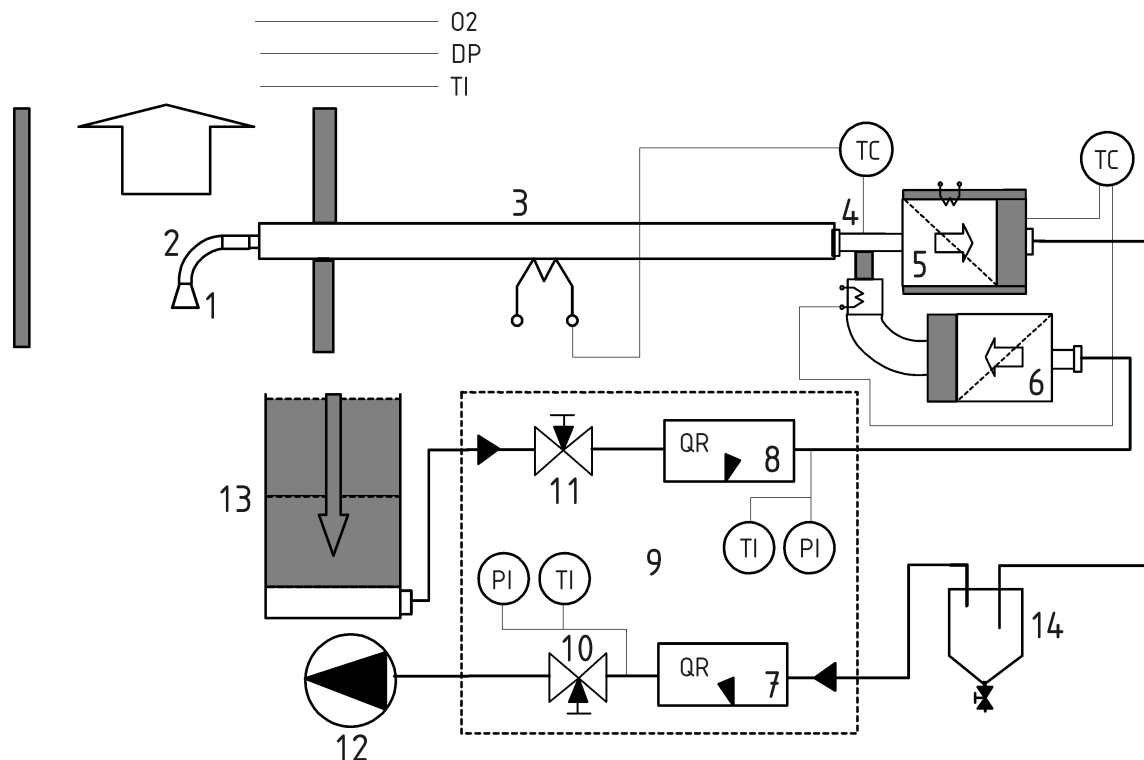
The sampling train is leak checked by plugging the nozzles of both the probe and the drying tower and turning on the pump. The system is evacuated to 75 kPa and the valve to the pump closed. If the rate of increase of pressure in the system is less than 0,2 kPa/min the system is used.

### B.6.4 Sample gas flow rate control

The sample gas flow rate is adjusted manually by calculating the desired flow rate from measurements of the stack gas conditions.

---

<sup>6)</sup> Folded filter WB 50 is the trade-name of a product supplied by Dräger, Germany and is an examples of a suitable commercially available product. This indication is only made for information of the user of this European Standard and does not mean any approval of the named products by CEN.

**Key**

- |    |   |    |                             |
|----|---|----|-----------------------------|
| 1  | nozzle  | 11 | control valve, dilution air |
| 2  | elbow joint   | 12 | pump                        |
| 3  | probe   | 13 | silica gel bed              |
| 4  | mixing channel  | 14 | dehumidifier                |
| 5  | sampling filter and PU foam                           |    |                             |
| 6  | dilution air filter, PU foam and verification PU foam |    |                             |
| 7  | flow measurement, diluted flue gas stream             |    |                             |
| 8  | flow measurement, dilution air                        |    |                             |
| 9  | control unit  |    |                             |
| 10 | control valve, diluted flue gas stream                |    |                             |

**Abbreviations**

- |    |                             |
|----|-----------------------------|
| TI | temperature sensor          |
| PI | differential pressure gauge |
| QR | gas stream volume meter     |
| TC | temperature controller      |
| DP | differential pressure       |

**Figure B.8 — Schematic representation of the sampling train of the manual dilution system**

## B.7 Cooled probe method - Variant 1

### B.7.1 Summary of apparatus design

The sampling train is shown in Figure B.9 (details see also [xiii; xiv]). A sample is withdrawn from the gas stream and collected via a water condenser in a condensate flask, in the bubbler system, on the adsorption material and on a glass fibre filter. The sampling gas is cooled below 20 °C. The condensate and most of the particle are caught in a condensate flask. Downstream, bubbler and solid adsorbents are linked in order to collect the gaseous PCDDs/PCDFs. A filter is placed in front of the last adsorbent to increase the sampling efficiency of small particles.

- a) The nozzle is made of titanium, quartz or borosilicate glass;
- b) Condensate flask with ground glass joint 60, 2 l volume;
- c) Bubbler for 200 ml ethylene glycol;
- d) Adsorbent-filter module. Glass container (internal diameter 55 mm) to hold two solid adsorbents (PU, diameter 60 mm, length 50 mm) with the plan filter between. The filter holder is made of PTFE.

The water cooled probe is represented in Figure B.10. The probe consists of two tubes. The inside tube (not included in Figure B.10) that carries off the flue gases has an internal diameter of 8 mm and is made of titanium, quartz or borosilicate glass. The outside tube (with inside and outside mantle) that supports the cooling of the inside tube is made of stainless steel or similar material. The inside tube is fitted into the outside tube with PTFE gaskets and quick connect fittings.

No grease for the connections should be used. The sampling train together with a pitot tube are mounted on a trolley that runs on a rail in order to change the sampling position inside the duct easily during the measurement period. The sampling train is validated for flue gas sample volume flow rates in the range of 0,5 m<sup>3</sup>/h to 2,5 m<sup>3</sup>/h.

### B.7.2 Adsorbent and cleaning procedure

The reagents used are pesticide grade. The PU foam is cleaned by soxhlet extraction 8 h with toluene and acetone sequentially.

### B.7.3 Glassware cleaning procedure before sampling

A new probe is used for each sample period. The glassware is cleaned in the laboratory with detergent and water, rinsed with distilled water, acetone and then toluene and allowed to dry. The glassware is then baked at 500 °C for 24 h. On removal from the oven it is carefully wrapped in aluminium foil and put into the transport boxes.

### B.7.4 Spiking position

The content of the first bubbler is spiked with the sampling standard solution prior to sampling. If the condensate flask becomes full during sampling it is replaced with another containing the labelled standards. (This has to be taken into account by calculation.)

### B.7.5 Equipment assembly procedure

The equipment is assembled as shown in Figure B.9 taking care not to contaminate any of the surfaces in contact with the sample.

- a) The adsorbent module consists of a PU foam, a glass fibre filter and an additional PU foam. It is loaded in a clean area to avoid contamination, wrapped with aluminium foil and stored in a clean environment until sampling;
- b) Condensate: Add 200 ml of distilled water into the condensate flask in the laboratory before sampling;
- c) Bubbler: Add 200 ml of ethylene glycol into the bubbler in the laboratory before sampling;
- d) During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin;
- e) Add the sampling standards to the condensate flask;
- f) Place crushed ice around the condensate flask and around the bubbler;
- g) Exchange the silica gel in the drying tower;
- h) Turn on the cooling water in the probe.

### B.7.6 Leak check procedure

The sampling train is leak checked by plugging the nozzle and turning on the pump. If a flow is detectable a leak is present and shall be cured.

### B.7.7 Sample gas flow rate control

The flue gas conditions are checked at regular intervals of either 5 min or 10 min depending on the variability in the flue gas velocity. The sample gas flow rate is then adjusted to maintain isokinetic conditions.

### B.7.8 Sampling

- a) Insert the probe in the duct, the nozzle turned away from the gas flow;
- b) Adjust the cooling of the probe to ensure a temperature of less than 20 °C downstream the cooled probe but avoiding icing;
- c) Position the nozzle at the measuring point and secure it in that position. Turn the nozzle in the direction of gas flow;
- d) Switch on the pump and adjust the flow rates to ensure isokinetic sampling at the nozzle.

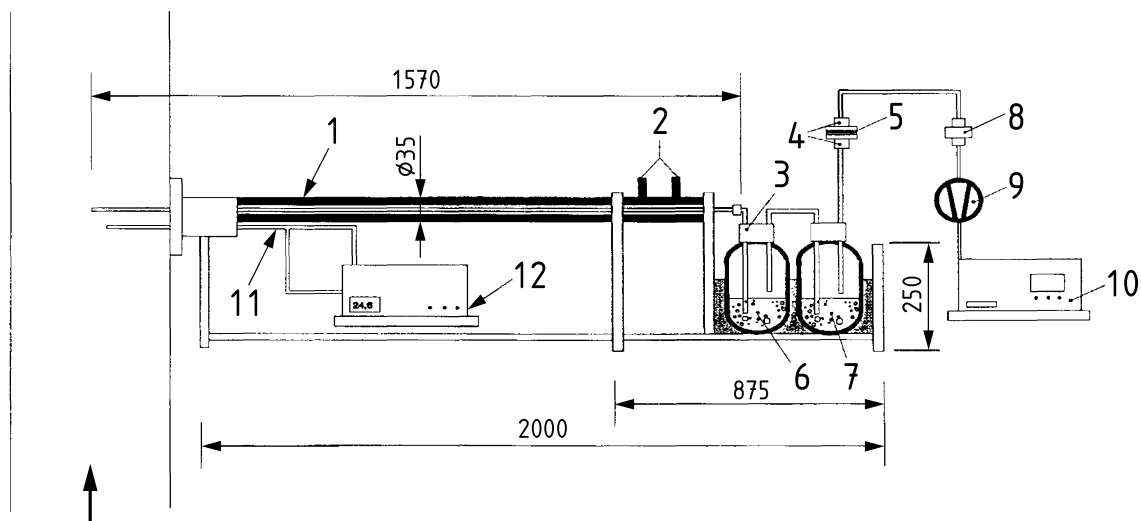
### B.7.9 Equipment disassembly procedure

At the end of sampling the valve is shut, the pump turned off and the probe is withdrawn from the duct. Cooling liquid is maintained until the probe is cold. The sampled gas volume is then recorded and the sampling train leak checked.

- a) The probe is washed by drawing about 400 ml of acetone and the 400 ml of toluene through the sampling train into the condensate flask;
- b) The probe is then disconnected from the condensate flask, and the insert is removed from the mantle;
- c) The ends of the probe insert are sealed with aluminium foil;
- d) The remaining parts of the sampling train in contact with the sample are taken to a clean area;
- e) The adsorbent module is disconnected from the bubbler and wrapped in foil

- f) The glass fittings for the condensate flask and of the bubbler are rinsed with acetone and then toluene, wrapped in foil and taken back to the laboratory. The flasks are then stoppered.

Dimensions in millimetres

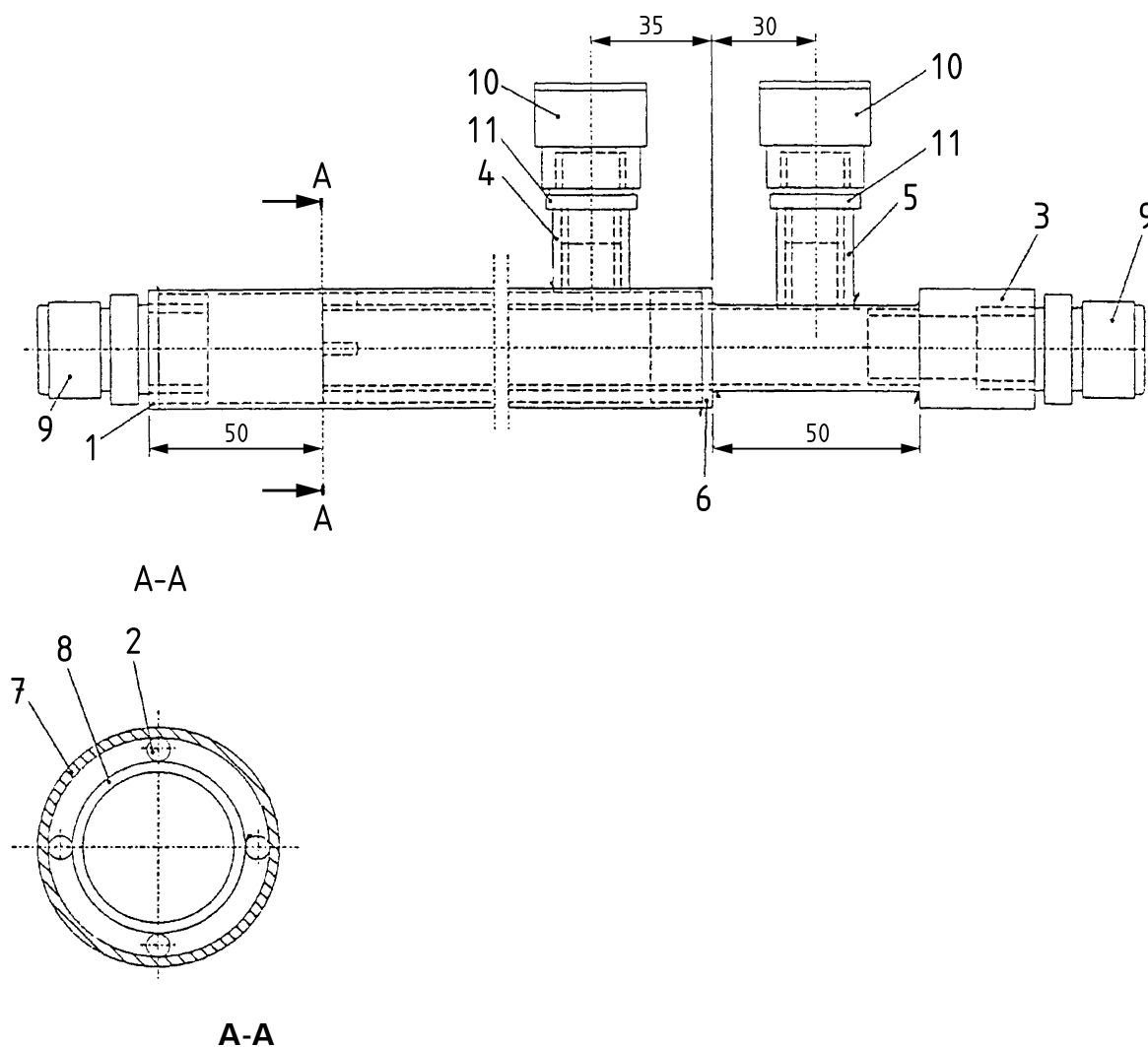


**Key**

- 1 water cooled probe
- 2 cooling water
- 3 bubbler
- 4 PU foam
- 5 filter
- 6 condensate flask
- 7 organic solvent
- 8 drying agent
- 9 pump
- 10 volume regulation unit
- 11 Pitot tube
- 12 pressure measurement unit

**Figure B.9 — Schematic representation of the cooled probe method - Variant 1**

Dimensions in millimetres

**Key**

- 1 distance ring
- 2 distance piece
- 3 distance ring
- 4 distance ring
- 5 distance ring
- 6 distance ring
- 7 outside tube (outside mantle)
- 8 outside tube (inside mantle)
- 9 screw coupling
- 10 screw coupling
- 11 nipple

**Figure B.10 — Detailed representation of the water cooled probe of variant 1**

## B.8 Cooled probe method - Variant 2

### B.8.1 Summary of apparatus design

The sampling train is shown in Figure B.11 (details see also [xv]). Compared to the other cooled probe method this variant allows to collect greater sample gas volumes during the same time intervals. The sampled flue gas flows through a water jacketed glass probe to a multi-tube condenser (see Figure B.12). The condenser consists of a bundle of 20 to 50 glass tubes (300 mm to 400 mm length, 10 mm to 20 mm diameter). The combination of water cooled probe and condenser reduce the flue gas temperature by the required amount. Two PU foams (in an adsorber unit, see Figure B.14), two multi jet impingers (see Figure B.13) filled with ethoxyethanol, and a filter between two PU foams are connected in series. The sampling system is validated for volume flow rates of 5 m<sup>3</sup>/h to 10 m<sup>3</sup>/h.

### B.8.2 Adsorbent and cleaning procedure

The adsorbent used is a toluene diisocyanate (TDI) polyether foam with a density of about 33 g/l. The foam is used in 100 mm by 100 mm cylinders.

The polyurethane foam plugs are cleaned by sequential 2 h to 3 h soxhlet extractions with ultrapure grade methanol, dichloromethane, toluene and acetone. Then they are dried in a vacuum oven at 40 °C overnight.

The methoxyethanol used is also ultrapure grade.

### B.8.3 Glassware cleaning procedure before sampling

The glassware is cleaned in the laboratory by consecutive rinsing with dichloromethane, toluene, methanol and acetone, followed by either overnight heating in an oven at 350 °C or by prolonged exposure to ultraviolet radiation.

### B.8.4 Spiking position

The sampling standard solution is added to the first PU foam plug prior to sampling. Fractions of the amount used are uniformly distributed over its surface at least 12 h prior to sampling.

### B.8.5 Equipment assembly procedure

The equipment is assembled as shown in Figure B.11 taking care not to contaminate any of the surfaces in contact with the sample.

- a) Fix the PU foams in the adsorber cartridge and the plan filter between the last two plugs and fill the impingers with methoxyethanol;
- b) Connect the nozzle, water cooled probe, condenser and condensate flask;
- c) Connect the two sets of impinger and PU foam (with the filter between the PU foams);
- d) Connect the pump and volume measurement and regulation device;
- e) Connect the water cooled probe and the condenser to the cooling aggregate or with the water pipe;
- f) Prepare the ice bath for cooling the condensate flask.



### B.8.6 Leak check procedure

The sampling train is leak checked by plugging the nozzle and turning on the pump. If a gas flow is detectable, a leak is present and shall be cured.

### B.8.7 Sample gas flow rate control

A pitot tube is positioned in the duct to measure the flue gas velocity near the sampling point. The flue gas conditions are checked at 10 min intervals or more frequently depending on the variability in the flue gas velocity. The sample gas flow rate is then adjusted manually to maintain isokinetic conditions.

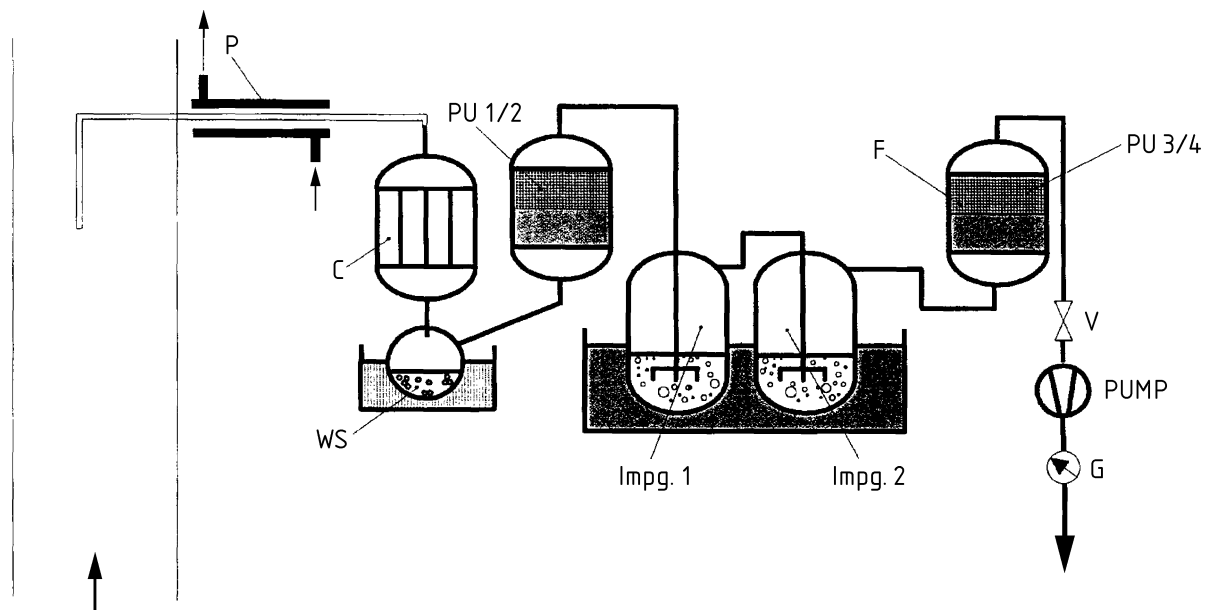
### B.8.8 Sampling

- a) Insert the probe in the duct, the nozzle turned away from the gas flow;
- b) Adjust the cooling of the probe to ensure a temperature of less than 20 °C but avoiding icing;
- c) Position the nozzle at the measuring point and secure it in that position. Turn the nozzle in the direction of gas flow;
- d) Switch on the pump and adjust the flow rates to ensure isokinetic sampling at the nozzle.

### B.8.9 Equipment disassembly procedure

At the end of sampling the valve is shut, the pump turned off and the probe is withdrawn from the duct. Water flow is maintained until the probe is cold. The sampled gas volume is then recorded and the sampling train leak checked.

- a) The probe is washed by drawing about 400 ml of acetone and 400 ml of toluene into the condensate flask;
- b) The probe is then disconnected from the condensate flask, and the insert is removed from the probe mantle. The ends of the probe are sealed with aluminium foil;
- c) The remaining parts of the sampling train in contact with the sample are taken to a clean area;
- d) The adsorbent module and the PU foam filter module are disconnected from the impinger and wrapped in foil;
- e) The glass fittings for the condensate flask and the impinger are rinsed with acetone and then toluene, wrapped in foil and taken back to the laboratory. The flasks are then sealed.

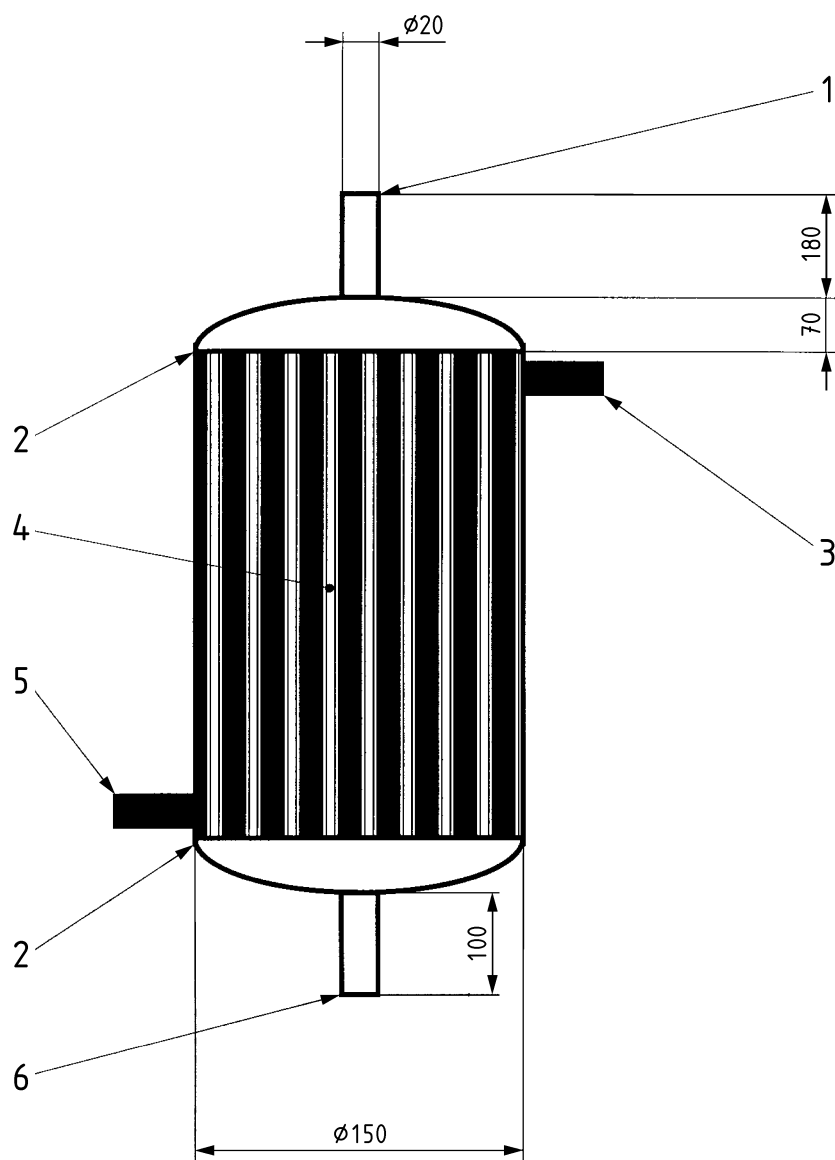


**Key**

- P cooled probe
- C condenser
- PU 1/2 Polyurethane foam 1 and 2
- PU 3/4 Polyurethane foam 3 and 4
- Impg. 1 impinger 1
- Impg. 2 impinger 2
- F filter
- WS condensate flask
- V valve
- PUMP pump
- G gasmeter

**Figure B.11 Schematic representation of the cooled probe method – Variant 2**

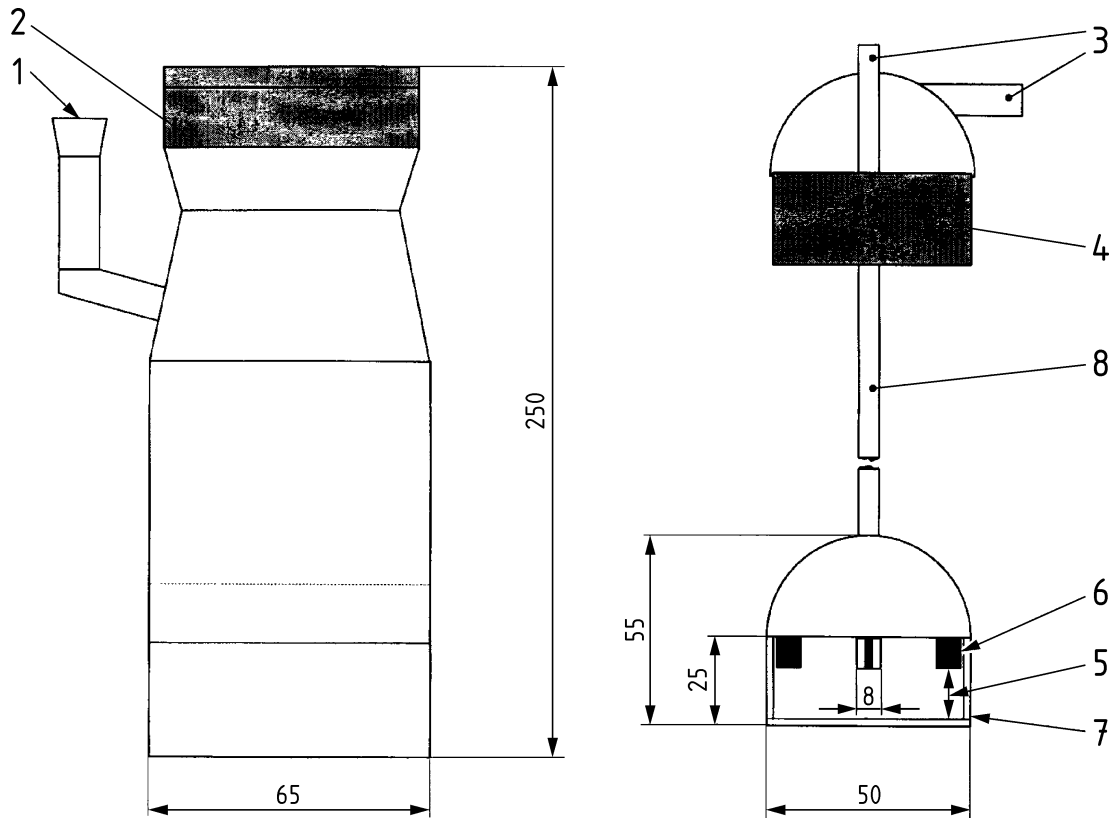
Dimensions in millimetres

**Key**

- 1 gas inlet
- 2 ground joint 180 mm plus lock ring and seal
- 3 water outlet, length 80 mm, diameter 20 mm
- 4 tubes: length 290 mm, internal diameter 10 mm, total number 55, diameter 150 mm
- 5 cooled water inlet
- 6 gas outlet

NOTE All parts are made out of glass.

**Figure B.12 — Detailed representation of the multi-tube cooler  
Cooled probe method for the variant 2**

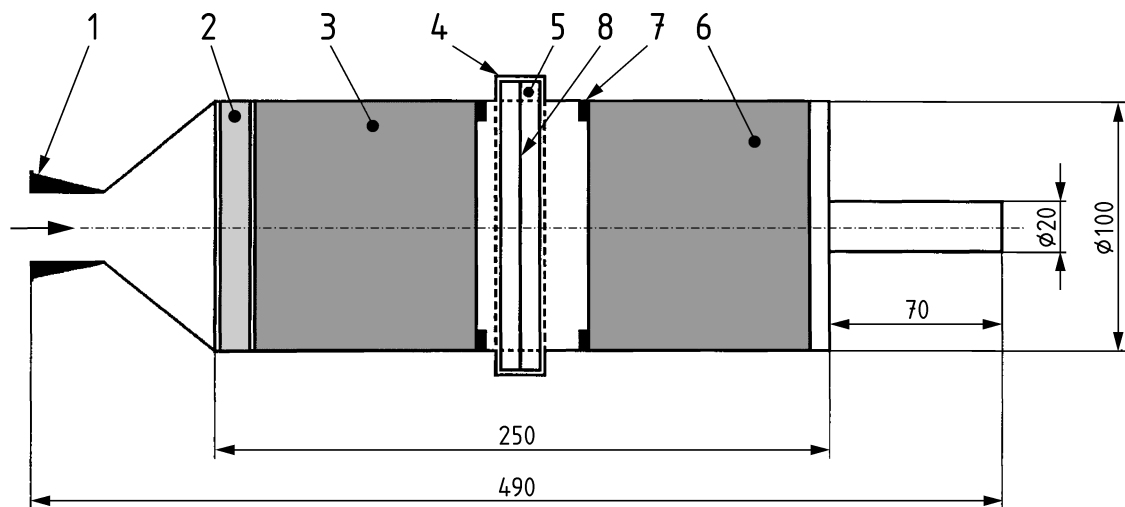


**Key**

- 1 refilling inlet joint 14/23
- 2 joint 60/46
- 3 special joint 15 mm inner diameter
- 4 joint 60/45
- 5 distance jet/plate 3 mm to 4 mm
- 6 jet bore 2 mm
- 7 plate 3 mm thickness
- 8 tube, diameter 12 mm to 15 mm

**Figure B.13 — Representation of the impinger of a variant of the cooled probe method**

Dimensions in millimetres

**Key**

- 1 ground glass joint 45
- 2 perforated glass plate
- 3 PU foam 1
- 4 locking ring
- 5 ground glass joint
- 6 PU foam 2
- 7 glass ring; against this ring the filter is positioned
- 8 plan filter

**Figure B.14 — Representation of the solid adsorber unit**

## Annex C (informative)

### Examples of adsorbents and their preparations and cleaning

#### C.1 General

Solid adsorbent (if used):

XAD-2, Poropak PS, polyurethane (PU) (TDI polyether flexible foam)

For additional examples see Annex A of EN 1948-2:2006.

#### C.2 XAD-2

The amount of XAD-2 should be 30 g minimum in a glass cartridge of internal diameter smaller than 32 mm and the linear velocity smaller than 34 cm/s.

Cleaning of the XAD-2: the resin is purified by being first successively washed several times with water, methanol and dichloromethane until the filtrates are no longer turbid. The XAD-2 is then extracted in a Soxhlet apparatus with toluene for at least 48 h, the extract being renewed several times. The XAD-2 is then washed with dichloromethane and the residual dichloromethane is removed in a rotary evaporator under controlled vacuum (50 kPa, bath temperature 40 °C). The cleanliness of the resin is checked through extraction with toluene and GC/MS analysis. Even if the commercial resin is already cleaned, this shall be checked, too. The purified XAD-2 is stored in a glass bottle with a gastight screw cap.

#### C.3 PU foam

With a density of about 33 g/l.

The thickness of the PU foams should be 5 cm in case of a velocity of 300 mm/s of sample gas through the PU foam.

Preparation of the PU foams: The PU foam plugs are cut out from foam disks to form a cylinder of appropriate size and are purified as follows:

- a) Boil for 2 h to 3 h successively in the following solvents: methanol, dichloromethane, toluene, acetone;
- b) Squeeze out the acetone, spread out on an aluminium sheet and allow to dry, best overnight in a vacuum drying oven at 40 °C.

The purified PU foam plugs are stored in brown glass bottles without being pressed down. A representative number of the cleaned PU foam plugs are re-extracted and the extract analysed for PCDDs/PCDFs.

#### C.4 Poropak PS

Cleaning of the Poropak PS: Poropak PS (50 mesh to 80 mesh) is extracted in a Soxhlet apparatus first with acetonitrile for 8 h, then with toluene for 4 h and finally with dichloromethane for 4 h. It is then dried for 3 h at 80 °C. The dried material is stored in glass bottles with ground-joint stoppers. The solvents used for the extraction are each distilled twice before use.

## Annex D (informative)

### Sampling measurement record

Issued by:  
Reference:

Date:  
Page 1/3

DATES OF MEASUREMENT CAMPAIGN:		DATE OF MEASUREMENT:	
SAMPLING SITE		SAMPLING PERSONNEL	
WASTE GAS CONDITIONS			
SAMPLING LOCATION			
STACK CROSS SECTION		m <sup>2</sup>	
TEMPERATURE		°C	
PRESSURE, Static		kPa	
PRESSURE, Differential		kPa	
PRESSURE, Atmospheric		kPa	
O <sub>2</sub> (on dry gas)		% - (v/v)	
HUMIDITY (on wet gas)		% - (v/v)	
CO <sub>2</sub> (on dry gas)		% - (v/v)	
DUST CONCENTRATION at standard conditions		mg/m <sup>3</sup>	
VOLUME FLOW at standard conditions		m <sup>3</sup> /h dry	
SAMPLING CONDITIONS			
		TRAIN 1	TRAIN 2
RESULT of the LEAK CHECK			
START OF SAMPLING		h : min	
END OF SAMPLING		h : min	
INTERRUPTION PERIOD		h : min	
INTERRUPTION PERIOD		h : min	
SAMPLING DURATION		h : min	
FLUE GAS SAMPLE VOLUME at the gas meter temperature pressure at standard reference conditions 101,325 kPa, 273,15 K, dry, reference O <sub>2</sub> /CO <sub>2</sub>		m <sup>3</sup> °C kPa m <sup>3</sup>	
FLUE GAS SAMPLE VOLUME "GASEOUS" at the gas meter temperature pressure at 101,325 kPa, 273,15 K, dry, reference O <sub>2</sub> /CO <sub>2</sub>		m <sup>3</sup> °C kPa m <sup>3</sup>	
THEORETICAL ISOKINETIC FLUE GAS SAMPLE VOLUME		m <sup>3</sup>	
ISOKINETIC RATIO			

Issued by:  
Reference:

Date:  
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<b>SAMPLING TRAIN CONDITION</b>			
<b>METHOD</b>			
<b>LABORATORY</b>			
TRAIN IDENTIFICATION			
NOZZLE MATERIAL			
SAMPLING NOZZLE Depth to wall	m		
DISTANCE NOZZLE 1 / NOZZLE 2 (optional)	m		
NOZZLE DIAMETER	mm		
PROBE MATERIAL			
PROBE DIAMETER	mm		
PROBE LENGTH	m		
PROBE HEATED	°C		
DISTANCE NOZZLE - FILTER	m		
DISTANCE NOZZLE - COOLER	m		
<b>FILTER</b>			
IDENTIFICATION			
TYPE			
MATERIAL			
QUALITY			
AREA	m <sup>2</sup>		
TEMPERATURE	°C		
<b>CONDENSER</b>			
IDENTIFICATION			
TYPE			
MATERIAL			
QUALITY			
DIAMETER	mm		
TEMPERATURE	°C		
<b>ADSORBENT STAGE</b>			
IDENTIFICATION			
TYPE			
MATERIAL			
QUANTITY	g		
DIAMETER	mm		
LENGTH	mm		
TEMPERATURE	°C		
VELOCITY	m/s		
<b>COMPARTMENT SPIKED</b>			



Issued by:  
Reference:

Date:  
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SCHEMATIC REPRESENTATION OF THE SAMPLING TRAIN
PRE-MEASUREMENT
VELOCITY PROFILE
OTHER PARAMETERS - REMARKS

## **Annex E** (informative)

### **Relations to EU Directives**

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 94/67/EC of 16 December 1994 on the incineration of hazardous waste and of EU Council Directive 2000/76/EC of 4 December 2000 on the incineration of waste.

**WARNING:** Other requirements and other EU Directives may be applicable to the product(s) falling within the scope of this standard.

This standard is likely to support requirements of EU Directive 94/67/EC on the incineration of hazardous waste and of EU Council Directive 2000/76/EC on the incineration of waste.

Compliance with this standard provides one means of conforming with the specific essential requirements of the Directive concerned and associated EFTA regulations.

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- 
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