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Stationary source emissions — Determination of mass concentration of sulphur oxides — Standard reference method

bsi.

National foreword

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European foreword

This document (EN 14791:2017) has been prepared by Technical Committee CEN/TC 264 “Air quality”, the secretariat of which is held by DIN.

This document supersedes EN 14791:2005.

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of an identical text or by endorsement, at the latest by July 2017, and conflicting national standards shall be withdrawn at the latest by July 2017.

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.

Annex G provides details of significant technical changes between this document and the previous edition.

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

1 Scope

This European Standard specifies the standard reference method (SRM) for the determination of the sulphuric oxide SO_2 in flue gases emitted to the atmosphere from ducts and stacks. It is based on a sampling system and two analytical principles: ion chromatography and the Thorin method.

This European Standard specifies the performance characteristics to be determined and the performance criteria to be fulfilled by measuring systems based on the measurement method. It applies to periodic monitoring and to the calibration or control of automatic measuring systems (AMS) permanently installed on a stack, for regulatory or other purposes.

This European Standard specifies criteria for demonstration of equivalence of an alternative method to the SRM by application of EN 14793:2017.

This European Standard has been validated during field tests on waste incineration, co-incineration and large combustion installations. It has been validated for sampling periods of 30 min in the range of 0,5 mg/m³ to 2 000 mg/m³ of SO_2 for an ion-chromatography variant and 5 mg/m³ to 2 000 mg/m³ of SO_2 for the Thorin method according to emission limit values laid down in the Directive 2010/75/EU.

NOTE 1 Emission limit values for SO_2 laid down in the Directive 2010/75/EU are in the range of 30 mg/m³ to 800 mg/m³.

The emission limit values of EU Directives are expressed in units of mg/m³ of SO_2 on dry basis and at standard conditions of 273 K and 101,3 kPa.

NOTE 2 The characteristics of installations, the conditions during field tests and the values of repeatability and reproducibility in the field are given in Annex A.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

prEN 13284-1:2015, *Stationary source emissions — Determination of low range mass concentration of dust — Part 1: Manual gravimetric method*

EN 14793:2017, *Stationary source emission – Demonstration of equivalence of an alternative method with a reference method*

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

EN ISO 14956:2002, *Air quality - Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty (ISO 14956:2002)*

ISO/IEC Guide 98-3:2008, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

3 Terms and definitions

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

3.1
standard reference method
SRM
reference method prescribed by European or national legislation

[SOURCE: EN 15259:2007]

3.2
reference method
RM
measurement method taken as a reference by convention, which gives the accepted reference value of the measurand

Note 1 to entry: A reference method is fully described.

Note 2 to entry: A reference method can be a manual or an automated method.

Note 3 to entry: Alternative methods can be used if equivalence to the reference method has been demonstrated.

[SOURCE: EN 15259:2007]

3.3
measurement method
method described in a written procedure containing all the means and procedures required to sample and analyse, namely field of application, principle and/or reactions, definitions, equipment, procedures, presentation of results, other requirements and measurement report

[SOURCE: EN 14793:2017]

3.4
alternative method
AM
measurement method which complies with the criteria given by this European Standard with respect to the reference method

Note 1 to entry: An alternative method can consist of a simplification of the reference method.

[SOURCE: EN 14793:2017]

3.5
measuring system
set of one or more measuring instruments and often other devices, including any reagent and supply, assembled and adapted to give information used to generate measured quantity values within specified intervals for quantities of specified kinds

[SOURCE: JCGM 200:2012]

3.6
automated measuring system
AMS
entirety of all measuring instruments and additional devices for obtaining a result of measurement

Note 1 to entry: Apart from the actual measuring device (the analyser), an AMS includes facilities for taking samples (e.g. probe, sample gas lines, flow meters and regulator, delivery pump) and for sample conditioning (e.g. dust filter, pre-separator for interferents, cooler, converter). This definition also includes testing and adjusting devices that are required for functional checks and, if applicable, for commissioning.

Note 2 to entry: The term "automated measuring system" (AMS) is typically used in Europe. The term "continuous emission monitoring system" (CEMS) is also typically used in the UK and USA.

[SOURCE: EN 15267-4:2017]

3.7
calibration
set of operations that establish, under specified conditions, the relationship between values of quantities indicated by a measuring method or measuring system, and the corresponding values given by the applicable reference

Note 1 to entry: In case of automated measuring systems (AMS) permanently installed on a stack the applicable reference is the standard reference method (SRM) used to establish the calibration function of the AMS.

Note 2 to entry: In case of manual methods the applicable reference can be reference materials used as calibration standards to establish the relationship between the output signal of the analytical device and the reference values.

Note 3 to entry: Calibration should not be confused with adjustment of a measuring system.

3.8
measurand
particular quantity subject to measurement

[SOURCE: EN 15259:2007]

Note 1 to entry: The measurand is a quantifiable property of the stack gas under test, for example mass concentration of a measured component, temperature, velocity, mass flow, oxygen content and water vapour content.

3.9
influence quantity
quantity that is not the measurand but that affects the result of the measurement

Note 1 to entry: Influence quantities are e.g. ambient temperature, atmospheric pressure, presence of interfering gases in the flue gas matrix or pressure of the gas sample.

3.10
measurement series
several successive measurements carried out on the same measurement plane and at the same process operating conditions

3.11
measurement site
place on the waste gas duct in the area of the measurement plane(s) consisting of structures and technical equipment, for example working platforms, measurement ports, energy supply

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

[SOURCE: EN 15259:2007]

3.12
measurement plane
plane normal to the centreline of the duct at the sampling position

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

[SOURCE: EN 15259:2007]

3.13
measurement port
opening in the waste gas duct along the measurement line, through which access to the waste gas is gained

Note 1 to entry: Measurement port is also known as sampling port or access port.

[SOURCE: EN 15259:2007]

3.14
measurement line
line in the measurement plane along which the measurement points are located, bounded by the inner duct wall

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

[SOURCE: EN 15259:2007]

3.15
measurement point
position in the measurement plane at which the sample stream is extracted or the measurement data are obtained directly

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

[SOURCE: EN 15259:2007]

3.16
performance characteristic
one of the quantities (described by values, tolerances, range) assigned to equipment in order to define its performance

3.17
quantification limit
lowest amount of an analyte that is quantifiable with a given confidence level

Note 1 to entry: For a manual method the limit of quantification is usually calculated as 10 times the standard deviation of blank measurements provided that the blank value is negligible. This corresponds to a confidence level of 95 %.

3.18
absorption efficiency
ε
ratio of quantity of the analyte q_1 collected in the first absorber divided by the quantity of the analyte collected in the first and the second absorber ($q_1 + q_2$)

$$\varepsilon = q_1 / (q_1 + q_2)$$

3.19
absorber
device in which sulphur oxide is absorbed into an absorption liquid

3.20
repeatability in the laboratory
closeness of the agreement between the results of successive measurements of the same measurand carried out under the same conditions of measurement

Note 1 to entry: These conditions include:

— same measurement method;

— same laboratory;

— same measuring system, used under the same conditions;

— same location;

— repetition over a short period of time.

Note 2 to entry: Repeatability can be expressed quantitatively in terms of the dispersion characteristics of the results.

Note 3 to entry: In this European Standard the repeatability is expressed as a value with a level of confidence of 95 %.

3.21
repeatability in the field
closeness of the agreement between the results of simultaneous measurements of the same measurand carried out with two sets of equipment under the same conditions of measurement

Note 1 to entry: These conditions include:

— same measurement method;

— two sets of equipment, the performances of which are fulfilling the requirements of the measurement method, used under the same conditions;

— same location;

— implemented by the same laboratory;

— typically calculated on short periods of time in order to avoid the effect of changes of influence parameters (e.g. 30 min).

Note 2 to entry: Repeatability can be expressed quantitatively in terms of the dispersion characteristics of the results.

Note 3 to entry: In this European Standard the repeatability under field conditions is expressed as a value with a level of confidence of 95 %.

3.22
reproducibility in the field
closeness of the agreement between the results of simultaneous measurements of the same measurand carried out with several sets of equipment under the same conditions of measurement

Note 1 to entry: These conditions are called field reproducibility conditions and include:

— same measurement method;

— several sets of equipment, the performance of which fulfils the requirements of the measurement method, used under the same conditions;

— same location;

— implemented by several laboratories.

Note 2 to entry: Reproducibility can be expressed quantitatively in terms of the dispersion characteristics of the results.

Note 3 to entry: In this European Standard the reproducibility under field conditions is expressed as a value with a level of confidence of 95 %.

3.23
uncertainty
parameter associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand

3.24
standard uncertainty
u
uncertainty of the result of a measurement expressed as a standard deviation

3.25
combined uncertainty
u_c
standard uncertainty attached to the measurement result calculated by combination of several standard uncertainties according to the principles laid down in ISO/IEC Guide 98-3 (GUM)

3.26
expanded uncertainty
U
quantity defining a level of confidence about the result of a measurement that may be expected to encompass a specific fraction of the distribution of values that could reasonably be attributed to a measurand

$$U = k \times u_c$$

Note 1 to entry: In this European Standard, the expanded uncertainty is calculated with a coverage factor of $k = 2$, and with a level of confidence of 95 %.

Note 2 to entry: The expression overall uncertainty is sometimes used to express the expanded uncertainty.

3.27
uncertainty budget
calculation table combining all the sources of uncertainty according to EN ISO 14956 or ISO/IEC Guide 98-3 in order to calculate the combined uncertainty of the method at a specified value

3.28
emission limit value
ELV
limit value given in regulations such as EU Directives, ordinances, administrative regulations, permits, licences, authorisations or consents

Note 1 to entry: ELV can be stated as concentration limits expressed as half-hourly, hourly and daily averaged values, or mass flow limits expressed as hourly, daily, weekly, monthly or annually aggregated values.

3.29
field blank
test sample obtained according to the field blank procedure

3.30
field blank procedure
procedure used to ensure that no significant contamination has occurred during all the steps of the measurement

Note 1 to entry: This includes for instance the equipment preparation in laboratory, its transport and installation in the field as well as the subsequent analytical work in the laboratory.

3.31
field blank value
result of a measurement performed according to the field blank procedure at the plant site and in the laboratory

3.32
chemical blank value
sulphate ion content of an unexposed sample of the absorption solution, plus reagents that are added to the solution before analysis if necessary

4 Symbols and abbreviations

4.1 Symbols

For the purposes of this document, the following symbols apply.

C_m	mass concentration of sulfur dioxide in the sample gas, in milligrams per cubic metre (of gas)
f_a	equivalent mass of sulfur dioxide of 1 ml of titration solution (barium perchlorate standard volumetric solution) used for titration in Thorin method, in milligrams per millilitre
f_v	ratio of the volume of the pre-treated sample solution (sample absorption solution pre-treated before analyse) to the volume of the aliquot taken for the titration in Thorin method
L_Q	limit of quantification, in milligrams per litre of SO_4^{2-}
m_s	weight of the sample solution (absorption solution used for sampling and rinsing solution), in grams
p_m	absolute pressure at the gas volume meter, in kilopascals
p_{ref}	standard pressure, 101,3 kPa
p_s	saturation vapour pressure of water at gas volume meter temperature, in kilopascals
q_b	mass concentration of sulfate in chemical blank solution, in milligrams per litre (of solution)
q_s	mass concentration of sulfate in sample absorption solution, in milligrams per litre (of solution)
r	repeatability, in milligrams per cubic metre or percentage
R	reproducibility, in milligrams per cubic metre or percentage
R_s	peak resolution
s_r	repeatability standard deviation, in milligrams per cubic metre or percentage
$s_{r,limit}$	maximum allowable repeatability standard deviation, in milligrams per cubic metre
s_R	reproducibility standard deviation, in milligrams per cubic metre or percentage
S_b	volume of titration solution used for titration of chemical blank solution, in millilitre
S_s	volume of titration solution used for the titration of the aliquot of the pre-treated sample solution, in millilitres

t_1	retention time of the first peak, in seconds
t_2	retention time of the second peak, in seconds
T_i	absolute temperature at the gas meter, in Kelvin
T_m	mean absolute temperature at the gas volume meter, in Kelvin
T_{ref}	standard temperature, 273 K
V_1	reading at the gas volume meter at the beginning of the sampling period, in cubic metres
V_2	reading at the gas volume meter at the end of the sampling period, in cubic metres
$V_{m,ref}$	measured dry gas volume, corrected to standard conditions, in cubic metres
V_s	volume of the sample solution (absorption solution used for sampling + rinsing solution), in litres
w_1	peak width, on the time axis, of the first peak, in seconds
w_2	peak width, on the time axis, of the second peak, in seconds
ε	absorption efficiency, in percent
σ	conductivity, in micro-siemens per metre
ρ_{20}^4	density of a liquid at 20 °C compared to water's at 4 °C, in kilograms per litre

4.2 Abbreviated terms

For the purposes of this document, the following abbreviated terms apply.

PE	Polyethylene
PTFE	Polytetrafluoroethene

5 Principle

5.1 General

This European Standard describes the standard reference method (SRM) based on two alternative analytical techniques for determining sulfur dioxide (SO_2) content emitted to atmosphere from ducts and stacks. The specific components and the requirements for the measuring system are described in Clause 6 to Clause 8. A number of performance characteristics with associated performance criteria are specified for the measuring system (see Table 1 and Table 2). The expanded uncertainty of the method shall meet the specifications given in this European Standard. Requirements and recommendations for quality assurance and quality control are given for measurements in the field (see Clause 6 and Clause 8).

5.2 Measuring principle

A sample of gas is extracted via a heated temperature-controlled probe. The sample is filtered and drawn through hydrogen peroxide absorber solutions for a specified time and at a controlled flow rate. The sulfur dioxide in the sampled gas is absorbed and oxidized to sulfate ion. The mass concentration of sulfate in the absorption solutions is subsequently determined using ion chromatography or by titration with a barium perchlorate solution using Thorin as indicator. SO_3 is also absorbed and transformed in sulfate ion and is therefore an interferent.

This European Standard has been validated with a 0,3 % H_2O_2 absorption solution for concentrations lower than 1 000 mg/m³ and with a 3,0 % H_2O_2 absorption solution for higher concentrations but lower than 2 000 mg/m^3. Typical concentration of the absorption solution is 0,3 % H_2O_2. However, for concentrations higher than 1 000 mg/m³ it is recommended, in case of a bad efficiency either to decrease the flow or to increase the H_2O_2 concentration.

6 Description of measuring system

6.1 Reagents

6.1.1 General

During the analysis, use only reagents of recognized analytical grade.

Normal, accepted laboratory safety practices and cleaning procedures for glassware should be followed during reagent preparation.

WARNING — Use the reagents in accordance with the appropriate health and safety regulations.

6.1.2 Hydrogen peroxide

Commercially available solution of H_2O_2; mass content 30 %, $\rho_{20}^4 = 1{,}11\,\mathrm{kg/l}$.

6.1.3 Water

H_2O; ultra pure water with conductivity σ < 10 µS/m.

6.1.4 Absorption solution, H_2O_2

The absorption solution is a hydrogen peroxide solution (6.1.2) diluted to a mass concentration of 0,3 % H_2O_2 in water (6.1.3). For flue-gas concentrations higher than 1 000 mg/m³, it is suggested, in case of a bad efficiency, either to decrease the flow, or to increase the concentration of the absorption solution.

For the preparation of the mass concentration of 0,3 % H_2O_2 in water, thoroughly mix about 10 ml of 30 % of H_2O_2 (6.1.2) with 500 ml of water (6.1.3) and make up with water (6.1.3) to 1 000 ml. Store the solution in a glass or PE bottle in a dark place and for no longer than one week.

WARNING — Decomposition of the solution may occur and may lead to the explosion of the storage bottle. It is recommended that the lid of this bottle is not closed too tightly or to use a security cap.

NOTE Cleanliness of the glassware is important to avoid a possible decomposition of hydrogen peroxide.

6.1.5 Reagents for chromatographic analysis

6.1.5.1 Eluent solution

The choice of eluent depends on the manufacturer's separator column and detector. For the exact composition of the eluent, use a validated solvent for the method and/or refer to the instructions given by the manufacturer.

NOTE For an ion chromatograph using the suppressor technique, a typical eluent is a solution of $1{,}7 \times 10^{-3}$ mol/l of $NaHCO_3$ and $1{,}8 \times 10^{-3}$ mol/l of Na_2CO_3.

6.1.5.2 Standard sulfate stock solution, 10,4 × 10−3 mol/l of SO_4^{2-}

Use a commercially available sulfate stock solution of 1 000 mg/l sulfate ($10{,}4 \times 10^{-3}$ mol/l) with a minimum content of 99,0 %. As an alternative prepare the standard solution as follows:

Dissolve 1,814 g of analytical grade potassium sulfate (K_2SO_4) in water (6.1.3) and dilute to a 1 000 ml volumetric flask. 1 ml of stock solution corresponds to 1 mg of SO_4^{2-}.

NOTE Calibration standards are prepared by diluting the standard stock solution with the absorption solution as specified in 9.2.3.2.

6.1.5.3 Regeneration solution for suppressor

For the exact composition of the suppressor regeneration solution, refer to the instructions given by the manufacturer of the suppressor.

NOTE An example is a solution of $12,5 \times 10^{-3}$ mol/l of H_2SO_4.

6.1.6 Reagent for Thorin analysis

6.1.6.1 2-propanol [$CH_3CH(OH)CH_3$]

Use commercially available 2-propanol [$CH_3CH(OH)CH_3$] in analytical grade (minimum content 99,8 %).

6.1.6.2 Barium perchlorate, standard volumetric solution, c[$Ba(ClO_4)_2$] = 0,005 mol/l

Use a commercially available barium perchlorate solution (80 % 2-propanol/20 % water) with concentration of 0,005 mol/l $Ba(ClO_4)_2$, or prepare the standard solution as follows:

Dissolve 1,7 g of anhydrous barium perchlorate [$Ba(ClO_4)_2$] in about 200 ml of water in a 1 000 ml one-mark volumetric flask. Make up to the mark with 2-propanol (6.1.6.1) and mix well.

Titrate the solution accurately against a 0,005 mol/l standard volumetric sulphuric acid solution.

1 ml of exactly 0,005 mol/l barium perchlorate solution is equivalent to a mass of sulfur dioxide of 0,320 mg; (f_a = 0,320 mg/ml).

6.1.6.3 Potassium hydroxide, standard volumetric solution, c[KOH] = 0,1 mol/l

Use a commercially available solution of 0,1 mol/l KOH in water.

NOTE This reagent is only necessary if the sampling gas contains high concentration of acid components (e.g. SO_2 > 100 mg/m^3 or HCl > 200 mg/m^3 or NO_2 > 400 mg/m^3).

6.1.6.4 Perchloric acid, standard volumetric solution, c[$HClO_4$] = 0,1 mol/l

Prepare an approximate 1 % solution of perchloric acid by mixing 16 ml of a commercially available solution of 60 % perchloric acid in water (6.1.3) and make up with water (6.1.3) to 1 000 ml with water. Store this solution in a glass or PE bottle.

NOTE This reagent is only necessary if the sampling gas contents high concentrations of alkali components (e.g. NH_3 > 50 mg/m^3).

6.1.6.5 Thorin, {4-(2-arsonophenyl-azo)-3-hydroxy-2,7 naphthalene-disulfonic acid disodium salt} 2 g/l solution

Thorin is also known as Thoron or Thoronol, the sodium salt of 4-(2-arsonophenyl-azol)-3-hydroxy-2,7-naphthalene-disulfonic acid.

Dissolve 0,2 g of Thorin in water (6.1.3) in a 100 ml one-mark volumetric flask. Make up to the mark with water and mix well.

Store this solution in a bottle made of glass or polyethylene.

6.2 Sampling equipment

6.2.1 General

A known volume of flue gas is extracted representatively from a duct or a chimney during a certain period of time at a controlled flow rate. A filter removes the dust in the sampled volume, thereafter the gas stream is passed through a series of absorbers containing an absorption solution.

All parts of the sampling equipment upstream of the first absorber shall not react with or adsorb SO_2 (i.e. borosilicate glass, quartz glass, PTFE or titanium are suitable materials).

If an unheated gas connector line is used between the heated filter and the first absorber, it shall be thoroughly rinsed with fresh absorption solution after sampling and the rinsing solutions shall be combined with the sample.

An example of a suitable sampling train is shown in Figure D.1.

6.2.2 Sampling probe

In order to reach the measurement points of the measurement plane, probes of different lengths and inner diameters may be used. The design and configuration of the probe used shall ensure the residence time of the sample gas within the probe is minimised in order to reduce the response time of the measuring system.

NOTE The probe may be marked before sampling in order to demonstrate that the measurement points in the measurement plane have been reached.

When droplets are present in the flue gases, they may contain SO_2 dissolved in it. In that case, the probe is equipped with a nozzle and an isokinetic sampling shall be performed according to prEN 13284-1:2015.

The sampling probe shall be surrounded by a heating jacket capable of producing a controlled temperature of at least 120 °C or 20 °C higher than the (acid) dew point of gases and shall be protected and positioned using an outer tube.

6.2.3 Filter housing

The filter housing may be located either:

— in the duct or chimney, mounted directly behind the entry nozzle (in-stack filtration); or

— outside the duct or chimney, mounted directly behind the suction tube (out-stack filtration).

If condensation is liable to occur in the sampling probe or in the filter housing, then a heated out-stack filter housing shall be used. For out-stack filtration, the filter housing shall be heated at a controlled temperature of at least 120 °C or 20 °C higher than the (acid) dew point of gases. It shall be connected to the probe without any cold path between the two.

Filter housings of different designs may be used, but the residence time of the sample gas shall be minimised.

The filter housing shall have the possibility to be jointed with the probe thereby avoiding leaks.

NOTE A stop valve after the filter housing can be useful to prevent back flush of absorption solution into the probe or into the filter when sampling in flue gases under unfavourable conditions (e.g. high depression in the duct).

In special cases where the sample gas temperature is greater than 200 °C, the heating jacket around the sampling probe, filter housing and connector line may be switched off. However the temperature in the

sampled gas just after the filter housing should not fall below 20 °C above the (acid) dew point temperature.

6.2.4 Particle filter

The filter shall have an 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).

Glass filters cannot be used because glass reacts with SO_3, but ceramic, quartz or PTFE are suitable materials.

6.2.5 Temperature controller

A temperature controller is required for the filter housing. It shall be capable of controlling temperature with an uncertainty of 2,5 K or better.

6.2.6 Absorbers

For efficient absorption two absorbers shall be placed in series.

NOTE 1 Downstream of these absorbers, an extra empty absorber may be used as a liquid trap and as a protection for the downstream equipment.

Some examples of absorbers are given in Annex B.

The absorption efficiency of the first absorber shall be better than 95 % or the concentration of sulfate ion in the second absorber shall be less than the quantification limit. This efficiency shall be checked periodically at the normal flow rate according to the procedure described in 8.9. Except when the absorption efficiency shall be checked, the solutions from the two absorbers can be combined and analysed together.

NOTE 2 Cooling of the absorbers can be useful to avoid excessive evaporation from the first absorption bottle.

6.2.7 Sample gas pump

Leak-free pump capable of drawing sample gas at a set flow-rate is required.

A sampling flow rate between 0,06 m^3/h to about 0,2 m^3/h allows to reach a good absorption with a low pressure of −10 kPa to −30 kPa.

NOTE 1 A small surge tank can be used between the pump and the rotameter to eliminate the pulsation effect of the diaphragm pump on the rotameter.

NOTE 2 A rotameter (optional) facilitates the adjustment of the nominal sampling flow-rate.

NOTE 3 A regulating valve (optional) is useful for adjusting the sample gas flow-rate.

6.2.8 Gas volume meter

Any dry or wet gas volume meter may be used providing the volume is measured with a relative expanded uncertainty not exceeding 5,0 % of the measured volume (at actual conditions).

The gas volume meter shall be equipped with a temperature measuring device with a relative expanded uncertainty not exceeding 2,0 % and shall be associated to an absolute pressure measurement with a relative expanded uncertainty not exceeding 2,0 %. The absolute pressure can be determined from the relative pressure and the ambient pressure.

When using a dry gas volume meter, a condenser and/or a gas drying system shall be used which can lead to a residual water vapour content of less than 10 g/m^3 (equivalent to a dew point of 10,5 °C or a volume content of 1,25 %).

NOTE For example a glass cartridge or absorption bottle packed with silica gel (1 mm to 3 mm particle size), which has been previously dried at least at 110 °C for at least 2 h.

When using a wet gas volume meter, a correction shall be applied for water vapour, to obtain a dry gas sampled volume.

6.3 Analysis equipment

6.3.1 Ion chromatograph

Analysis equipment consists of a complete analytical system with an ion chromatograph and all required accessories including syringes, analytical columns, compressed gases, a detector and a recording device. The essential minimum requirements for an ion chromatograph system for the scope of this European Standard are as follows:

a) sample injection system: constant-volume injection system shall be used;

b) anion separator pre-column (optional): this column is used to protect the measuring device;

c) anion separator column: this column produced the separation of anions in the sample, enabling a clear measurement of the sulfate anion peak area and height. Other anions, which may be present in the sample solution, include F^-, Cl^- and NO_3^-. The resolution power of the separator column shall be sufficient to ensure that the peak resolution R_S shall not fall below 1,3 with

$$R_s = \frac{2 \times (t_2 - t_1)}{w_1 + w_2} \quad (1)$$

where

t_1 retention time of the first peak, in seconds;

t_2 retention time of the second peak, in seconds;

w_1 peak width on the time axis, of the first peak, in seconds;

w_2 peak width on the time axis, of the second peak, in seconds.

In general it is recommended to use a pre-column or an anion guard column to protect the anion separator column. If this is omitted from the system, the retention times shall be shorter. Two different types can be used: those containing the same substrate as the separator column, and those packed with a macro porous polymer.

d) detector: the method of detection should rely on a measurement of the electrical conductivity with or without a suppressor device;

e) recording device: a system using a strip charts recorder and integrator or another computer-based data system is acceptable.

6.3.2 Thorin method

6.3.2.1 General

To determine the titration end point, a photodiode in connection with a titrator or a spectrophotometer can be used.

6.3.2.2 Spectrophotometer (optional)

Use a spectrophotometer with single or double light beam.

When a spectrophotometer with one single light beam is used, it is necessary to be able to tune the incident flux for example, by adjusting a diaphragm or a slot width. The best accuracy is reached when the incident flux can be adjusted to give an absorbance value as close as possible to zero for the highest concentration to be measured. However, the best result is usually obtained when the adjustment of the incident flux gives an absorbance reading of 0,800 for the chemical blank when using an optical cuvette of 20 mm and a value of 0,400 for a cuvette of 10 mm.

6.3.2.3 Glass optical cuvette

Glass optical cuvette of 10 mm or 20 mm optical length. If more than one cuvette is used, then they shall be photometrically matched.

7 Performance characteristics of the SRM

7.1 General

Table 1 and Table 2 give an overview of the performance characteristics and the associated performance criteria of the whole measurement method.

The laboratory implementing the method shall demonstrate that:

— performance characteristics of the method given in Table 1 and Table 2 meet the specified performance criteria;

— quantification limit is lower than 10 % of the daily ELV or the lowest limit value specified for the plant by the local authorities;

— relative expanded uncertainty calculated by combining values of selected performance characteristics by means of an uncertainty budget does not exceed 20,0 % of the daily emission limit value (ELV) or the lowest limit value specified for the plant by the local authorities.

The values of the selected performance characteristics shall be evaluated:

— for the sampling step by means of laboratory tests in order to determine uncertainty of the calibration of the equipment and by means of field tests in order to determine other parameters;

— for analytical step by means of laboratory tests.

7.2 Performance characteristics of the sampling system

Table 1 shows the performance characteristics and performance criteria of the sampling system.

Table 1 — Performance characteristics of the sampling system to be determined in the laboratory (L) and in the field (F) and associated performance criteria

Performance characteristic	L	F	Performance criterion
Sampling			
Determination of the volume of the absorption solution		X	≤ 1,0 % of the volume of solution
Gas volume meter:			
— standard uncertainty of sample volume [b]	X [a]		≤ 2,5 % of the volume of gas sampling [a]
— standard uncertainty of temperature [b]	X [a]		≤ 1,0 % of the absolute temperature [a]
— standard uncertainty of absolute pressure [b]	X [a]		≤ 1,0 % of the absolute pressure [a]
Absorption efficiency [c]		X	≥ 95 %
Leak in the sampling line		X	≤ 2,0 % of the nominal flow rate
Field blank value		X	≤ 10,0 % of ELV

[a] Performance criteria corresponding to the uncertainty of calibration.

[b] The uncertainty of the sampled volume is a combination of uncertainties due to calibration, drift (random drift, drift between two calibrations) and resolution or reading.

The uncertainty of temperature and absolute pressure at the gas volume meter is a combination of uncertainties due to calibration, drift (random drift, drift between two calibrations), resolution or reading, and standard deviation of the mean when several values are used to get the result.

[c] This characteristic is a quality assurance check to quantify the absorption efficiency in the first absorber; but it does not quantify a possible loss of absorption, and therefore it is not included in calculation of expanded uncertainty.

7.3 Performance characteristics of the analysis

7.3.1 Sources of uncertainty

Main possibly sources of uncertainty associated to analysis are:

a) For analysis by ion chromatography:

- performance characteristics of the analysis equipment;
- preparation of calibration standards: purity of stock standard solution, and ratio of dilutions;
- linearity of calibration curve depending on the extend of working range;
- measurement of volume of aliquot solution injected for analyse (ratio of the total absorption solution volume and the volume of the aliquot taken for injection);
- if a dilution of the absorption solution is necessary before analyse: ratio of dilution;
- interferences;

— drift of retention time;

— repeatability.

b) For analyse by titration:

— performance characteristics of analytical equipment;

— preparation of standard volumetric solution (6.1.6.2) used for titration;

— adjustment of pH of absorption solution;

— measurement of volumes of aliquots of titrated solutions (ratio of the volume of the sample solution to be titrated and the volume of the aliquot taken): for the absorption solution and chemical blank;

— detection of the colour change;

— measurement of volume of standard volumetric solution used for titration;

— interferences;

— repeatability.

7.3.2 Performance criterion of analysis

Because all the components of uncertainty attached to the analysis are difficult to identify and to estimate, the laboratory can determine the expanded uncertainty due to analysis by taking the standard deviation of repeatability calculated during an interlaboratory comparison. A maximum performance criterion is given in the following Table 2.

NOTE One example of analytical validation is presented in Annex A. The exercise has been made through a round robin test consisting of sulfate analysed in four solutions by ionic chromatography and by Thorin method. Twenty-two laboratories took part to the test. The round robin test allowed to determine the standard deviation of reproducibility.

Table 2 — Performance characteristics of analytical procedure to be determined in the laboratory (L) and associated performance criterion

Performance characteristic	L	Performance criterion
Repeatability standard deviation of sulfate ions analyse	X	≤ 2,5 % of the measured value (value of quantity of sulfate ions in the solution; in mg of SO_4^{2-} /l of solution)

7.4 Establishment of the uncertainty budget

An uncertainty budget shall be established to evaluate whether or not the method fulfils the requirements for a maximum allowable expanded uncertainty.

The relative expanded uncertainty for this method shall not exceed 20,0 % of the daily emission limit value or of the lowest limit value fixed to the plant by the local authorities. This expanded uncertainty is calculated on dry basis and before correction to the O_2 reference concentration.

The principle of calculation of the combined uncertainty is based on the law on propagation of uncertainty laid down in ISO/IEC Guide 98-3 (GUM):

— determine the standard uncertainties attached to the performance characteristics to be included in the calculation of the uncertainty budget according to ISO/IEC Guide 98-3;

— calculate the uncertainty budget by combining all the standard uncertainties according to ISO/IEC Guide 98-3;

— values of standard uncertainty that are less than 5 % of the maximum standard uncertainty may be neglected;

— calculate the combined uncertainty at the measured value, reported as a dry gas value at actual concentration of oxygen.

NOTE When the concentration of a measured component has to be expressed at an oxygen reference concentration (e.g. 3 % or 11 %), the correction of oxygen can bring an additional uncertainty which could be significant if the difference between the oxygen measured value and the oxygen reference value is too large. Annex F provides information on the contribution of oxygen correction to the uncertainty linked to the concentration.

An example of the calculation of an uncertainty budget is given in Annex C.

8 Field operation

8.1 Measurement planning

Emission measurements at a plant shall be carried out such that the results are representative for the emissions from this plant and comparable with results obtained for other comparable plants. Therefore, measurements shall be planned in accordance with EN 15259.

Before carrying out any measurements, the purpose of the sampling and the sampling procedures shall be discussed with the plant personnel concerned. The nature of the plant process, e.g. steady-state or cyclic, can affect the sampling programme. If the process can be performed in a steady-state, it is important that this is maintained during sampling.

Dates, starting times, duration of survey and sampling periods as well as plant operating conditions during these periods shall be agreed with the plant management.

If no suitable location exists in the plant, and/or that measurements have been carried out during non-steady-state conditions of the plant, which leads to an increase of the uncertainty of the measurements, it shall be stated in the measurement report.

8.2 Sampling strategy

8.2.1 General

Sampling requires a suitable measurement section and measurement plane.

The measurement plane shall be easily reached from convenient measurement ports and a safe working platform (see EN 15259).

8.2.2 Measurement section and measurement plane

The measurement section and measurement plane shall meet the requirements of EN 15259.

8.2.3 Minimum number and location of measurement points

It is necessary to ensure that the gas concentrations measured are representative of the average conditions inside the waste gas duct. Measurements may be performed at one representative measurement point or at any measurement point, if the corresponding requirements on the distribution of SO_2 or any other relevant component specified in 8.3 of EN 15259 are fulfilled. In all other cases the measurements shall be performed as grid measurements. In that case, EN 15259 specifies the minimum number of measurement points to be used and the location in the measurement plane for circular and rectangular ducts.

8.2.4 Measurement ports and working platform

Measurement ports shall be provided for access to the measurement points selected in accordance with EN 15259.

Examples of suitable measurement ports are given in EN 15259.

For safety and practical reasons, the working platform shall comply with the requirements of EN 15259.

8.3 Assembling the equipment

Prepare all the glassware, filters and absorption solutions required for the sampling equipment. Assemble the whole sampling train (an example is given in Annex D). Special care shall be taken during the rinsing of absorbers with fritted gas dividers, as it is difficult to completely recover the absorption liquid used for rinsing these devices. Consequently rinsing needs to be thorough.

The dead volume in the sampling probe, filter housing and tubing up to the first absorber should be minimised.

The two absorbers shall be filled with the appropriate amount of the absorption solution (6.1.4) to guarantee a sufficient gas/liquid contact. An empty absorber may be added behind the second one as a protection for the downstream suction equipment.

8.4 Heating of the sample gas line

Maintain the temperature of the sampling probe and particle filter housing up to include a temperature of at least 120 °C or 20 °C above the (acid) dew-point temperature of the sample gas.

8.5 Leak test

Before starting the measurement, check that there is no significant leakage in the sampling system by use of the following procedure or any other relevant procedure:

— assemble the complete sampling system, including charging the filter housing and absorbers;

— close the nozzle inlet;

— switch on the pump;

— after reaching minimum pressure read or measure the flow rate with an appropriate measuring device;

— the leak flow rate shall not exceed 2,0 % of the expected sample gas flow rate used during measurement.

Perform the leak test at the operating temperature unless this conflicts with safety requirements.

In addition, the integrity of the sampling system can also be also tested during sampling by continuously measuring the concentration of a suitable stack gas component (e.g. O_2) directly in the stack and downstream the sampling system. Any systematic difference between those concentrations indicates a leak in the sampling system.

8.6 Performing sampling

8.6.1 Introduction of the sampling probe in the duct

After the leak test, insert the sampling probe through the measurement port and place the probe at the measurement points in the measurement plane.

Seal the resultant space around the sampling probe and the access hole with an appropriate material such that ambient air is not induced into the duct (nor does any flue gas escape from the duct). In cases where large pressure differences exist between the ambient air and sample gas, care shall be taken that the absorption solution does not leave the absorber.

Control the jacket and filter housing temperatures.

8.6.2 Sampling

Start the sample gas pump and adjust the regulating valve to give the desired sample gas volume flow rate.

NOTE 1 The sampling flow rate can be derived from the information given on the sampled volume of gas given in Table 3 (see 9.3.2), and the chosen sampling period (i.e. 30 min).

Record the reading on the gas volume meter V_1 and the time.

Record the reading of the temperature device T_i and the absolute pressure p_{m} at the gas volume meter at least 5 min after starting sampling and at the end of the sampling period.

NOTE 2 For a sampling system as shown in Figure D.1, with gas volume meter placed downstream the pump, absolute pressure at the gas volume meter is close to atmospheric pressure.

The minimum sampling period is 30 min. However, when the expected mass concentration of sulfur dioxide is low, the sampling period may be extended to have analytical results above the quantification limit of analysis.

At the end of the sampling period, switch off the sampling pump. Care shall be taken that the absorption solution does not leave the absorber. Record the time and the reading on the gas volume meter V_2.

NOTE 3 If the used gas volume meter records volumetric differences, the difference $V_{\mathrm{m}} = (V_2 - V_1)$ can be used directly at the end of sampling instead of V_1 and V_2.

NOTE 4 It is recommended to perform a leak test after sampling when a grid measurement has been performed.

8.6.3 Rinsing of the sampling system and preparation of the samples

Remove the absorber from the sampling system and quantitatively transfer both sample solutions into a bottle of suitable capacity or into two separate bottles if the absorption efficiency shall be checked. The bottles shall be made of an appropriate material.

Rinse thoroughly all the parts of the absorbers, and particularly the fritted glass dividers with absorption solution. Force the solution through the fritted glass dividers, if they exist, using a pressure bulb. If used, the trap shall also be rinsed and the rinsing solution combined with the other rinsing solutions. Add the rinsing solution to the corresponding sample solution in the sample bottle.

The volume of the absorption solution including the rinsing solution is determined with a relative uncertainty less than 1,0 %.

All the unheated parts from the filter housing until the second absorber in the sampling train shall be rinsed.

8.7 Measurement series

To take further flue gas samples, place the appropriate volume of absorption solution into each of the two absorbers, assemble the sampling system and proceed as specified above.

8.8 Field blank

To check the sampling procedure, a field blank shall be performed at least before each measurement series or at least once a day, following the whole measurement procedure specified in this European Standard and including the assembling of the equipment described in 8.3 without the suction step, i.e. without starting and operating the sample gas pump.

The average sample gas volume shall be used for calculation of the field blank value expressed in mg/m^3.

If the equipment in contact with the measured substance is cleaned and reused in the field, a field blank shall also be taken after the measurement series. If several measurements are performed at the same industrial process or on several lines of the same industrial process, then only one single field blank at the beginning and one at the end of the series shall be performed.

The field blank value shall be less than 10 % of the emission limit value (ELV). If the calculated result of measurement is less than the field blank value, the result of measurement shall be reported as less or equal to the field blank value.

The field blank value shall not be subtracted from the result of measurement. However, it is necessary to take into account the field blank value in the calculation of the uncertainty of the measured value (see Annex C).

8.9 Absorption efficiency

8.9.1 General

The absorption efficiency of the first absorber shall be at least 95 % or the concentration of sulfate ion in the second absorber shall be less than the quantification limit. This efficiency shall be checked periodically at the normal flow rate according to the procedure described in 8.9.2. Except when the absorption efficiency shall be checked, the solutions from the two absorbers can be combined and analysed together.

NOTE Cooling of the absorbers may be useful to avoid excessive evaporation from the first absorption bottle.

8.9.2 Test of absorption efficiency

Place a suitable volume of absorption solution into each of the two absorbers, where the first absorber is denoted 1 and the second absorber 2. Assemble the apparatus to obtain a sampling train as illustrated in Figure A.1.

Carry out sampling in normal conditions. At the end of the sampling period, switch off the sampling pump, record the time and volume on the gas meter.

Remove the absorber from the sampling train and transfer the sample solutions from absorber 1 and 2 into two separate sample bottles. If a trap is used behind the absorbers to collect any solution carry-over, its contents shall be combined with the sample of bottle 2. Rinse each absorber with the absorption solution (6.1.4) thoroughly and particularly the fritted glass dividers to recover the absorption solution trapped in it and add the rinsing solutions to the appropriate absorber sample. Rinse all the unheated parts of the sampling system between the filter and the absorber 1 and add the rinsing to the content of bottle 1.

Analyse samples 1 and 2 as described in Clause 9 to determine the sulfate content, q_{S1} and q_{S2}. Calculate the absorption efficiency ε of absorber 1 as follows:

$\varepsilon = (q_{S1} / (q_{S1} + q_{S2})) \times 100\ \%$.

9 Analytical procedure

9.1 General

After sampling, the solutions shall be analysed by one of the following two methods:

— method A: Ion Chromatography Method;

Analytical quantification limit L_Q: equal or above 0,15 mg SO_4^{2-} per litre of absorption solution (corresponding to concentrations equal or above 0,1 mg/m³ SO_2 in flue gas with half an hour sampling in 100 ml absorption solution and 1 l/min flow rate).

— method B: Thorin Method.

Analytical quantification limit L_Q: equal or above 1 mg SO_4^{2-} per litre of absorption solution (corresponding to concentrations equal or above 2,2 mg/m³ SO_2 in flue gas with half an hour sampling in 100 ml solution and 1 l/min flow rate).

The solutions that shall be analysed are:

a) field blanks;

b) samples.

9.2 Ion Chromatography method

9.2.1 General procedure

Start up the ion chromatograph in accordance with the manufacturer's instructions and confirm the readiness for operation (e.g. stable baseline). Check the calibration daily according to 9.2.3.4 and, if necessary, recalibrate as described in 9.2.3.2 and 9.2.3.3.

Before each analysis, the exact total volume of the sample v_S (absorption solution and rinsing solution) is determined using a graduated measuring cylinder (accurate to 1 ml). This may be done gravimetrically taking the density of the solution into account or by transferring the sample into a measuring flask of suitable size and making up to the mark with unused sorption solution by titration.

Load and inject a fixed amount of sample solution. After each analysis, flush the injection loop thoroughly between each sample run using the eluent solution. Use the same size loop for calibration standards and samples. Record the resulting output signal, i.e. sulfate peak size, in units of area or height.

NOTE A filtration of the sample can be necessary.

The width of the retention-time window used to make identifications should be based upon measurements of actual retention-time variations of calibration standards employed over the course of a day. Three times the standard deviation of a retention time or 10 % of the retention time can be used to calculate a suggested window size. However, the experience of the analyst should weigh heavily in the interpretations of the chromatograms.

If the output signal exceeds the calibrated working range of the system, dilute the sample with an appropriate amount of absorption solution and reanalyse. If the resulting chromatogram fails to produce adequate resolution, or the identification of the sulfate peak is questionable, fortify the sample with an appropriate amount of standard solution and reanalyse.

Compute the sample sulfate-concentration q_S in milligrams per litre of solution by comparing sample output signal with the sulfate calibration-curve, taking into account any dilution factor applied.

Similarly, determine the sulfate concentration of the field blank and of the chemical blank. The chemical blank-value shall usually be evaluated each time the absorption solution is prepared.

9.2.2 Interferences

Interference may be caused by contaminants in the reagent, in water and in all the points of the chromatography system such that this leads to high baseline noise or interfering signals.

9.2.3 Calibration

9.2.3.1 Set up of the chromatograph

Establish ion chromatographic operating parameters equivalent to those given in the manufacturer's instructions.

9.2.3.2 Preparation of calibration standards

Prepare calibration standards at a minimum of three concentration-levels over a chosen working range and a zero sample (corresponding to a sample of absorption solution). A calibration standard consists of a sulfate solution prepared in the laboratory from the standard sulfate stock solution (6.1.5.2) and accurately diluted as needed with absorption solution. The standards are used to calibrate the output signal with respect to the sulfate concentration and to establish a corresponding calibration curve.

If the calibrated working range exceeds the linear range of the system, a sufficient number of calibration standards shall be analysed to allow an accurate calibration curve to be established. One of the calibration standards should be at a concentration near, but above, the quantification limit. The other calibration standards should correspond to the range of concentrations expected in the samples or they should define the working range of the detector if the system is operated on a number of attenuation ranges. Each range shall be calibrated individually unless the attenuation range settings are proven to be linear.

NOTE As an example, for sulfur dioxide concentrations in the range 7 mg/m^3 to 333 mg/m^3, with half an hour sampling in 100 ml solution and 1 l/min flow-rate, a working range for sulfate concentrations between 3 mg/l and 150 mg/l is suitable.

9.2.3.3 Calibration of the chromatograph

Inject an appropriate amount of the first calibration standard depending on the injection loop volume. Tabulate the output signal against concentration. Flush the injection loop with eluent solution and repeat for the other calibration standards and zero sample. The results are used to prepare a sulfate calibration curve. Record the retention times during this procedure.

9.2.3.4 Calibrations checks

Verify the calibration curve each working day, whenever the anion eluent is changed or after every 20 samples. Reference material shall be used to check the calibration regularly. In addition, if the retention time varies from the expected values by more than ±10 %, repeat the test using fresh calibration standards. Then, if the results are still more than ±10 %, prepare a new sulfate calibration curve.

9.2.3.5 Measurement range

Nonlinear response within the range of the detector can be noticed when the separator column capacity is exceeded (overloaded). The output signals should be compared for an undiluted sample and for a sample when diluted 1 to 10. If the calculated sulfate concentrations of the two samples are the same, samples with this sulfate concentration do not need to be diluted.

9.3 Thorin Method

9.3.1 Pre-treatment of sample solution before analysis for Thorin method

Measure and monitor the pH of the absorption solution used for sampling using the direct reading pH meter. Adjust the pH of the sample solution to pH 3,5 by adding the appropriate volume of the standard volumetric potassium hydroxide solution (6.1.6.3) or by adding the standard volumetric perchloric acid solution (6.1.6.4) as required. Transfer the resultant solution into a volumetric flask of a suitable nominal capacity. Make up to the mark with water and mix well.

The direct reading pH meter should preferably be equipped with a temperature compensation and shall have a measurement range 0 to 14. The limits of error shall be less than 0,2 units at pH 3,5.

Calibrate the direct reading pH meter using an appropriate buffer solution. The pH of the buffer solution shall be accurately known at a given temperature. After the calibration, rinse the electrodes thoroughly before use.

9.3.2 General procedure

Transfer the aliquot specified in Table 3 of the “pre-treated sample solution” obtained as described below, into a cortical flask of suitable nominal capacity. Add 80 ml of 2-propanol (6.1.6.1) plus four drops of the Thorin solution (6.1.6.5) and mix well. Record the ratio f_V of the volume of the total sample solution to the volume of the aliquot taken.

If the absorption efficiency is checked, treat each absorber solution with its rinsing solution separately.

Table 3 — Example of sampling parameters and analytical solution requirements for typical SO_2 concentrations

Expected mass concentration of sulfur dioxide	Capacity of the absorbers	Volume of the absorption solution to be placed into each absorbers	Volume of the sample gas to pass through the sampling train	Volume of the pre-treated sample solution	Aliquot of the pre-treated sample solution to be titrated	Volume of $Ba(ClO_4)_2$ solution used for the titration the aliquot
mg/m³	ml	ml	m³	ml	ml	ml
30 to 100	100	40	0,100	100	20	1,875 to 6,5
100 to 500	100	40	0,060	100	20	3,75 to 18,75
500 to 1 000	250	80	0,060	250	20	7,5 to 15
1 000 to 2 000	250	80	0,030	250	20	7,5 to 15
2 000 to 5 000	250	80	0,030	250	20	15 to 37,5

Use a burette with a spindle-valve or an automatic titrator. Titrate the solution obtained with the standard volumetric barium perchlorate solution (6.1.6.2) until the end-point is reached (the colour changes from orange-yellow to permanent light pink). Record the titration volume.

NOTE In some types of light, the change in colour from orange-yellow to permanent light pink is very difficult to observe, as for example in fluorescent lighting and direct sunlight. Therefore it is preferable to titrate under a daylight lamp or using a photometer with a glass fibre-optic light guide capable of measuring the transmission of light at a wavelength of 520 nm or 481 nm, and an automatic titrator.

9.3.3 Preparation of a chemical blank solution

Prepare a chemical blank solution by adding 80 ml of 2-propanol (6.1.6.1) and four drops of the Thorin solution (6.1.6.5) to an aliquot of the absorption solution. The volume of the absorption solution used should correspond to the volume of the aliquot of the pre-treated sample solution chosen to be titrated. Analyse the chemical blank solution as specified above. The chemical blank value shall be evaluated each time the absorption solution is prepared.

9.3.4 Interferents

9.3.4.1 Anions

Anions that are absorbed by the absorption solution and that also form sparingly soluble salts with barium ions at pH 3,5 can interfere.

NOTE Interferences by inorganic gaseous chlorine and fluorine compounds and stable oxides are not expected in normal flue gases. In exceptional cases (extremely high flue-gas temperature) interferences by volatile sulphates and volatile salts of polyvalent metal cations can take place.

9.3.4.2 Volatile salts of polyvalent metal cations

Those which respond to the indicator Thorin. The metal cations can be removed from the treated joint sample solution by percolating the latter through a cation exchanger.

10 Expression of results

Calculate the mean value of the of the absolute temperature T_m at the gas volume meter according to Formula (2):

$$T_m = \frac{1}{n}\sum_{i=1}^{n} T_i \quad (2)$$

where

T_i is the *i*th temperature reading taken during sampling, in Kelvin;

n is the number of temperature readings.

Calculate the dry gas volume $V_{m,ref}$ measured at the gas volume meter, at standard conditions, in cubic metre,

— according to Formula (3) if a dry-gas volume meter is used:

$$V_{m,ref} = (V_2 - V_1) \times \frac{T_{ref}}{T_m} \times \frac{p_m}{p_{ref}} \quad (3)$$

— according to Formula (4) if a wet-gas volume meter is used:

$$V_{m,ref} = (V_2 - V_1) \times \frac{T_{ref}}{T_m} \times \frac{p_m - p_s(T_m)}{p_{ref}} \quad (4)$$

where

$V_{m,ref}$ is the measured dry gas volume, corrected to standard conditions, in m^3;

V_1 is the gas volume reading from the gas volume meter at the beginning of the sampling period, at actual conditions of temperature, pressure and humidity, in m^3;

V_2 is the gas volume reading from the gas volume meter at the end of the sampling period, at actual conditions of temperature, pressure and humidity, in m^3;

T_m is the mean absolute temperature of the sampled gas at the gas volume meter, in K;

T_{ref} is the standard temperature, 273 K;

p_m is the absolute pressure at the gas volume meter, in kPa;

$p_s(T_m)$ is the saturation vapour pressure of water at temperature T_m of the gas volume meter, in kPa;

p_{ref} is the standard pressure, 101,3 kPa.

Calculate the mass concentration of sulfur dioxide C_m in mg/m^3 present in the sampled gas at the standard conditions, related to the dry gas, using Formula (5) or Formula (6) depending on the analytical method applied.

For the ion chromatography method, Formula (5) shall be applied:

$$C_{\mathrm{m}} = \frac{\left(q_{\mathrm{s}} - q_{\mathrm{b}}\right) \times v_{\mathrm{s}} \times \frac{64,1}{96,1}}{V_{\mathrm{m,ref}}} \quad (5)$$

where

q_{s} is the mass concentration of sulfate collected in the sample absorption solution, in milligrams per litre;

q_{b} is the mass concentration of sulfate in chemical blank solution, in milligrams per litre (of solution)

v_{s} is the volume of the absorption solution, in litres;

$V_{\mathrm{m,ref}}$ is the volume of dry gas sampled from the gas volume meter, at standard conditions, in cubic metres.

NOTE 1 When the solution from each absorber (1 and 2) and the associated rinsings are analysed individually and the concentrations and volumes of these solutions are denoted as q_{s1}, q_{s2}, v_{s1}, v_{s2} respectively, then the term ($q_{\mathrm{s}} \times v_{\mathrm{s}}$) is replaced by [($q_{\mathrm{s1}} \times v_{\mathrm{s1}}$) + ($q_{\mathrm{s2}} \times v_{\mathrm{s2}}$)].

For the titration method, Formula (6) shall be applied:

$$C_{\mathrm{m}} = \frac{f_{\mathrm{a}} \times f_{\mathrm{v}} \times \left(S_{\mathrm{s}} - S_{\mathrm{b}}\right)}{V_{\mathrm{m,ref}}} \quad (6)$$

where

f_{a} is the equivalent mass of sulfur dioxide of 1 ml of the titration solution (barium perchlorate standard volumetric solution (6.1.6.2)), in milligram per millilitre;

f_{v} is the ratio of the volume of the pre-treated sample solution to the volume of the aliquot taken for the titration;

S_{s} is the volume of titration solution used for the titration of the aliquot of the pre-treated sample solution, in millilitres;

S_{b} is the volume of titration solution used for the titration of the aliquot of the chemical blank solution, in millilitres.

NOTE 2 When the solution from each absorber (1 and 2) and the associated rinsings are analysed individually and the volumes of titration solutions used are denoted as S_{s1}, S_{s2} respectively, then the term ($S_{\mathrm{s}} - S_{\mathrm{b}}$) is replaced by. ($S_{\mathrm{s1}} + S_{\mathrm{s2}} - 2S_{\mathrm{b}}$) if f_{v} is the same for both partial solutions.

Concentrations are generally expressed at a reference concentration of oxygen specified e.g. in European Directives.

The concentration $C_{\mathrm{m,corr}}$ corrected for oxygen is calculated using Formula (7):

$$C_{\mathrm{m,corr}} = \frac{21\% - o_{\mathrm{ref}}}{21\% - o_{\mathrm{m}}} \times C_{\mathrm{m}} \quad (7)$$

where

$C_{\mathrm{m,corr}}$ is the concentration corrected for oxygen;

C_m is the measured concentration at the actual oxygen concentration;

o_m is the measured mean dry oxygen content during the sampling;

o_{ref} is the oxygen reference volume concentration.

11 Equivalence of Thorin and ion chromatography methods

11.1 General

This equivalence between the Thorin and the ion chromatography method has been checked according to EN 14793:2017.

An example of the implementation of the method to check the equivalence of both methods described in this European Standard is given in Annex E.

11.2 Range

The range of equivalence begins at the limit of quantification L_Q of the Thorin method, which is between 3 mg per litre of SO_4^{2-} and approximately 10 mg per litre of SO_4^{2-} (according to the experience of the laboratory).

11.3 Matrix effect

The equivalence has been checked for waste incinerators, co-incinerators and large combustion plants.

11.4 Comparison of repeatability and trueness

The repeatability standard deviation s_r expressed in mg/m³ for the standard reference method is

— for the Ion Chromatography method:

$$s_r(C) = 0,00002C^2 + 0,0096C + 2,471\frac{\text{mg}}{\text{m}^3} \quad (8)$$

— for the Thorin method:

$$s_r(C) = 0,0245C + 1,208\frac{\text{mg}}{\text{m}^3} \quad (9)$$

where C is the measured mass concentration in mg/m³.

The reproducibility standard deviation s_R expressed in mg/m³ for the standard reference method is

— for the Ion Chromatography method:

$$s_R(C) = 0,0678C + 3,47\frac{\text{mg}}{\text{m}^3} \quad (10)$$

— for the Thorin method:

$$s_R(C) = 0,0841C - 0,8086\frac{\text{mg}}{\text{m}^3} \quad (11)$$

where C is the measured mass concentration in mg/m³.

12 Equivalence of an alternative method

In order to show that an alternative method is equivalent to the standard reference method specified in this European Standard, follow the procedures described EN 14793:2017.

The maximum allowable repeatability standard deviation (see Formula (12)) and the reproducibility standard deviation (see Formula (13) and Formula (14)) expressed as a mass concentration in mg/m^3 for the standard reference method are:

$$s_{r,\text{limit}}(C) = 0,051C + 2,3\frac{\text{mg}}{\text{m}^3} \quad (12)$$

— for the Ion Chromatography method:

$$s_R(C) = 0,0678C + 3,47\frac{\text{mg}}{\text{m}^3} \quad (13)$$

— for the Thorin method:

$$s_R(C) = 0,0841C - 0,8086\frac{\text{mg}}{\text{m}^3} \quad (14)$$

where C is the measured mass concentration in mg/m^3.

13 Measurement report

The measurement report shall fulfil the requirements of EN 15259 and shall include the following information:

a) information about the personnel involved in the measurement;

b) description of the location of the measurement points in the measurement plane;

c) changes in the plant operations during sampling, for example burner changes;

d) characteristics of the sampling equipment;

e) for each measurement: sampling date, time and duration as well as identification of samples;

f) measurement results: sampling volume, concentrations;

g) blank values;

h) absorption efficiency.

Annex A
(informative)

Validation of the method in the field

A.1 General

The method has been validated:

— during a round robin test for analytical procedures by inter-laboratory comparison of sulfate analysis of solutions;

— during six field tests, on waste incineration installations, co-incineration installations and large combustion plants for the method (sampling and analysis).

A.2 Round robin test of analytical methods

Twenty-two laboratories took part to the round robin test. The ion chromatography method was carried out by 21 participants and the titration method by six ones.

Four different samples were distributed to the participants and each solution had to be analysed three times:

— blank solution;

— "standard" solution containing (50,1 ± 0,1) mg/l SO_4^{2-};

— "absorption solution" containing approximately 61 mg/l SO_4^{2-};

— "added solution" containing approximately 86 mg/l SO_4^{2-}.

Results of standard deviation of repeatability and reproducibility obtained by the participants are given in Table A.1 and in Table A.2:

Table A.1 — Repeatability standard deviation

Sample	Ion chromatography		Titration method	
	s_r in mg/l SO_4^{2-}	s_r in % of the measured value	s_r in mg/l SO_4^{2-}	s_r in % of the measured value
Standard solution 50,1 mg/l SO_4^{2-}	0,8	1,7	1,0	2,0
Absorption solution approximately 61 mg/l SO_4^{2-}	1,2	2,0	0,8	1,2
Added solution approximately 86 mg/l SO_4^{2-}.	2,1	2,5	1,5	1,7

Table A.2 — Reproducibility standard deviation

Sample	Ion chromatography		Titration method	
	s_R in mg/l SO_4^{2-}	s_R in % of the measured value	s_R in mg/l SO_4^{2-}	s_R in % of the measured value
Standard solution 50,1 mg/l SO_4^{2-}	2,1	4,1	2,7	5,5
Absorption solution approximately 61 mg/l SO_4^{2-}	4,8	8,0	4,7	7,7
Added solution approximately 86 mg/l SO_4^{2-}.	5,6	6,5	6,1	7,0

A.3 Field tests

A.3.1 General

The method has been validated during six field tests, on waste incineration installations, co-incineration installations and large combustion plants. Each test was performed by at least four different European measuring teams originating from 10 countries.

A.3.2 Characteristics of installations

The following field tests were performed:

— 1st field test: INERIS bench-loop at Verneuil en Halatte (France); the bench-loop simulates combustion or waste incineration exhaust gases. Five teams took part in the 1st field test. Double measurements were not performed simultaneously but sequentially. Five different flue gas matrices were generated. Within each matrix, two sequential measurements were performed. Two

additional sequential measurements were performed in flue gas matrices where the flue gas concentrations varied. There was a total of 12 measurements performed by all the teams.

— 2nd field test: waste incinerator in Denmark. Four teams took part to the field test and performed double measurements simultaneously. A total of 16 measurements was performed by all the teams.

— 3rd field test: waste incinerator in Italy. Four teams took part to the field test. Two pairs of two teams performed double measurements simultaneously and the four teams performed single measurements simultaneously. A total of six double measurements was performed by each pair of two teams while a total of 12 single measurements was performed by all teams.

— 4th field test: co-incinerator combined heat and power installation in Sweden. The fluidised bed boilers operate on fuel mixes of wood chips, demolition waste, peat and coal. Two pairs of two teams performed double measurements simultaneously and the four teams performed single measurements simultaneously. A total of six double measurements was performed by each pair of two teams while a total of 12 single measurements was performed by all the teams.

— 5th field test: co-incinerator cement plant in Germany. The fuel could be coal, heavy oil and secondary fuel (e.g. paper, plastics, textiles, and tires). Four teams took part to the field test and performed doubles measurements simultaneously. All the teams performed a total of 16 double measurements.

— 6th field test: coal fired power plant in Germany. Four teams performed their double measurements simultaneously. The total amount of double measurements performed by all teams was 12.

An overview of the flue gas characteristics is given in Table A.3.

Table A.3 — Flue gas characteristics during field tests

Field test	Installation	Fuel	Flue gas characteristics						
			T °C	O_2 %	NO_x mg/m³	SO_2 mg/m³	CO mg/m³	H_2O %	PM mg/m³
1	Power plant [a]	Natural gas	< 150	3 to 13	10 to 1 300	10 to 2 000	20 to 400	10 to 21	< 1
2	Waste incinerator	Municipal waste	90 to 110	8 to 11	180 to 250	25 to 250	5 to 15	13 to 19	1 to 5
3	Waste incinerator	Municipal waste	85 to 105	16 to 18	61 to 78	5 to 50	0 to 2	8 to 12	1 to 5
4	Co-incinerator	Wood, waste, coal	70 to 80	4 to 6	4 to 70	0 to 10	50 to 150	8 to 12	0 to 20
5	Co-incinerator	Coal, oil, waste	140 to 170	4 to 6	440 to 1060	60 to 170	260 to 740	23 to 26	5 to 10
6	Power plant	Coal	130 to 140	8,9 to 9,2	110 to 140	1 000 to 1 130	3 to 6	5,5 to 8	< 50

[a] Bench-loop: flue gas simulation.

A.3.3 Limits of quantification

During the field tests the following quantification limits have been given:

— ion chromatography analyse: 0,15 mg/l SO_4^{2-} to 0,6 mg/l SO_4^{2-}, with an average of 0,3 mg/l SO_4^{2-};

— titration method: 3 mg/l SO_4^{2-} to 30 mg/l SO_4^{2-}. It seems than with a well-trained personal 3 mg/l SO_4^{2-} can be reached.

A.3.4 Repeatability and reproducibility

A.3.4.1 General

Repeatability standard deviation s_r and reproducibility standard deviation s_R are determined from data obtained during inter-laboratory tests at the plants described in A.3.2.

Repeatability standard deviation s_r (see Formula (A.1)) and repeatability in the field r (see Formula (A.2)) are calculated according to ISO 5725-2 and ISO 5725-6 from the results of the double measurements implemented by the same laboratory (see Table A.4 and Table A.5):

$$s_{\mathrm{r}} = \sqrt{\frac{\sum \left(x_i - \overline{x}\right)^2}{n-1}} \tag{A.1}$$

$$r = \sqrt{2}\, t_{0,95;\mathrm{n}-1}\, s_{\mathrm{r}} \tag{A.2}$$

where

s_r is the repeatability standard deviation;

x_i is the i^{th} measured signal;

$\overline{x}$ is the average of the measured signals x_i;

$t_{0,95;n-1}$ is the student factor for a level of confidence of 95 % and a degree of freedom of n–1 with n the number of double measurements;

r is the repeatability in the field.

Reproducibility standard deviation s_R used to estimate the expanded uncertainty U (see Formula (A.3)) and reproducibility in the field R (see Formula (A.4)) are calculated according to ISO 5725-2 from the results of parallel measurements performed simultaneously by several laboratories (see Table A.6 and Table A.7):

$$U = t_{0,95;np-1}\, s_R \tag{A.3}$$

$$R = \sqrt{2}\, t_{0,95;np-1}\, s_R \tag{A.4}$$

where

U is an estimate of the expanded uncertainty;

s_R is the reproducibility standard deviation;

$t_{0,95;np-1}$ is the student factor for a level of confidence of 95 % and a degree of freedom of np–1 with n the number of measurements and p the number of laboratories;

R is the reproducibility in the field.

A.3.4.2 Repeatability

Table A.4 — Repeatability in the field for ion chromatography method

Field test	Concentration		Number of teams	Number of double measurements	Repeatability standard deviation	Repeatability	
					s_r	r	
	Range mg/m³	Average mg/m³			mg/m³	mg/m³	%
1A	16 to 27	21	5	2	2,9	9,3	45
1B	40 to 63	54	5	2	3,1	9,9	18
1C	200 to 241	219	5	2	4,8	15,4	7
1D	884 to 1 038	961	5	2	26	82,4	9
1E	1 889 to 2 174	2 088	5	2	100	319	15
1F	871 to 1 033	930	5	1	24	95,8	10
1G	180 to 221	198	5	1	4,5	17,7	9
2	25 to 210	87	4	16	a	11,6	13
3	6 to 50	27	4	12	b	6,6	25
4	0,4 to 9	3,5	2	5	0,49	2,0	57
5	64 to 169	108	4	12	7,5	22,6	21
6	1 000 to 1 123	1 055	4	12	37	116	11

a $s_r = 0{,}029\ C + 1{,}18$ mg/m³

b $s_r = 0{,}076\ C + 0{,}11$ mg/m³

The following functions expressed as mass concentrations in mg/m³ were determined:

$$s_r(C) = 0,00002\frac{\text{m}^3}{\text{mg}}C^2 + 0,0096\,C + 2,471\frac{\text{mg}}{\text{m}^3} \quad \text{(A.5)}$$

$$s_{r,\text{limit}}(C) = 0,000024\frac{\text{m}^3}{\text{mg}}C^2 + 0,0115\,C + 2,96\frac{\text{mg}}{\text{m}^3} \quad \text{(A.6)}$$

$$r(C) = 0,0000566\frac{\text{m}^3}{\text{mg}}C^2 + 0,0272\,C + 6,99\frac{\text{mg}}{\text{m}^3} \quad \text{(A.7)}$$

where C is the mass concentration expressed in mg/m³.

Table A.5 — Repeatability in the field for Thorin method

Field test	Concentration		Number of teams	Number of double measurements	Repeatability standard deviation	Repeatability	
					s_r	r	
	Range mg/m³	Average mg/m³			mg/m³	mg/m³	%
1A	17 to 27	22	4	2	0,34	1,1	5,1
1B	40 to 63	55	4	2	1,2	3,9	7,1
1C	207 to 241	220	4	2	5,3	17,7	8,0
1D	869 to 1 031	946	4	2	23	78,4	8,3
1E	1 889 to 2 299	2 098	4	2	52	175	8,3
1F	795 to 1 025	926	4	1	23	103	11,1
1G	191 to 221	209	4	1	5	22,5	10,8
2	26 to 204	86	4	16	a	12,3	14,3
3	9 to 51	30	4	12	b	10,6	35,4
4	2,8 to 9,6	5,6	2	11	1,6	5,0	90,9
5	70 to 170	111	3	12	6,8	21,2	19,1
6	973 to 1 089	1 018	4	12	30	93,3	9,2

a $s_r = 0{,}034\ C + 1{,}15$ mg/m³

b $s_r = 0{,}053\ C + 1{,}8$ mg/m³

The following functions expressed as mass concentrations in mg/m³ were determined:

$$s_r(C) = 0,0245\,C + 1,208\,\frac{\text{mg}}{\text{m}^3} \tag{A.8}$$

$$s_{r,\text{limit}}(C) = 0,0294\,C + 1,45\,\frac{\text{mg}}{\text{m}^3} \tag{A.9}$$

$$r(C) = 0,0693\,C + 3,417\,\frac{\text{mg}}{\text{m}^3} \tag{A.10}$$

where C is the mass concentration expressed in mg/m³.

A.3.4.3 Reproducibility

Table A.6 — Reproducibility in the field for ion chromatography method

Field test	Concentration		Number of teams	Number of double measurements	Reproducibility standard deviation	Estimate of expanded uncertainty		Reproducibility	
					s_R	U		R	
	Range mg/m³	Average mg/m³			mg/m³	mg/m³	%	mg/m³	%
1A	16 to 27	21	5	2	4,0	9,0	42,9	13	62
1B	40 to 63	54	5	2	7,0	16	29,7	22	41
1C	200 to 241	219	5	2	15	33	15,1	46	21
1D	884 to 1 038	961	5	2	74	167	17,4	236	25
1E	1 889 to 2 174	2 088	5	2	137	311	14,9	440	21
1F	871 to 1 033	930	5	1	102	282	30,3	398	43
1G	180 to 221	198	5	1	17	47	23,8	66	33
2	25 to 210	87	4	16	a	15,4	17,7	22	25
3	6 to 50	27	4	12	b	5,9	21,8	8,3	31
4	0,4 to 9	3,5	4	12	0,78	1,7	48,6	2,4	69
5	64 to 169	108	3	12	8,9	20	18,5	28	26
6	1 000 to 1 123	1 055	4	12	56	123	11,7	174	16

a $s_R = 0{,}044\ C + 3{,}5$ mg/m³

b $s_R = 0{,}032\ C + 1{,}8$ mg/m³

The following functions expressed as mass concentrations in mg/m³ were determined:

$$s_R(C) = 0{,}0678\,C + 3{,}47\,\frac{\text{mg}}{\text{m}^3} \tag{A.11}$$

$$U(C) = 0{,}135\,C + 6{,}94\,\frac{\text{mg}}{\text{m}^3} \tag{A.12}$$

$$R(C) = 0{,}192\,C + 9{,}81\,\frac{\text{mg}}{\text{m}^3} \tag{A.13}$$

where C is the mass concentration expressed in mg/m³.

Table A.7 — Reproducibility in the field for Thorin method

Field test	Concentration		Number of teams	Number of double measurements	Reproducibility standard deviation	Estimate of expanded uncertainty		Reproducibility	
					s_R	U		R	
	Range mg/m³	Average mg/m³			mg/m³	mg/m³	%	mg/m³	%
1A	17 to 27	22	4	2	4,0	9,4	42,7	13	61
1B	40 to 63	55	4	2	8,1	19	34,5	27	49
1C	207 to 241	220	4	2	15	35	16,0	49	22
1D	869 to 1 031	946	4	2	76	179	18,9	253	27
1E	1 889 to 2 299	2 098	4	2	181	427	20,4	604	29
1F	795 to 1 025	926	4	1	112	357	38,6	504	54
1G	191 to 221	209	4	1	5,0	16	7,7	22	11
2	26 to 204	86	4	16	a	20,8	24,2	30	35
3	9 to 51	30	4	12	b	8	26,7	11	36
4	2,8 to 9,6	5,6	4	8	2,2	5,1	91	7	129
5	70 to 170	111	3	12	8,3	18	16,2	25	23
6	973 to 1 089	1 018	4	12	47	103	10,1	147	14

a $s_R = 0{,}088\,C + 2{,}37$ mg/m³

b $s_R = -0{,}0049\,C + 3{,}6$ mg/m³

The following functions expressed as mass concentrations in mg/m³ were determined:

$$s_R(C) = 0,0841\,C - 0,8086\,\frac{\text{mg}}{\text{m}^3} \tag{A.14}$$

$$U(C) = 0,168\,C - 1,617\,\frac{\text{mg}}{\text{m}^3} \tag{A.15}$$

$$R(C) = 0,2379\,C - 2,287\,\frac{\text{mg}}{\text{m}^3} \tag{A.16}$$

where C is the mass concentration expressed in mg/m³.

A.3.5 Absorption efficiency

Absorption efficiency has been determined for concentrations in the range from 20 mg/m³ to 2000 mg/m³ of SO_2.

Sampling conditions were:

— volume of sampled gas during one half hour: 45 l to 200 l;

— volume of absorption solution in each absorber: 25 ml to 80 ml;

— all results were better than the requirement of 95 %.

Annex B
(informative)

Examples of absorbers

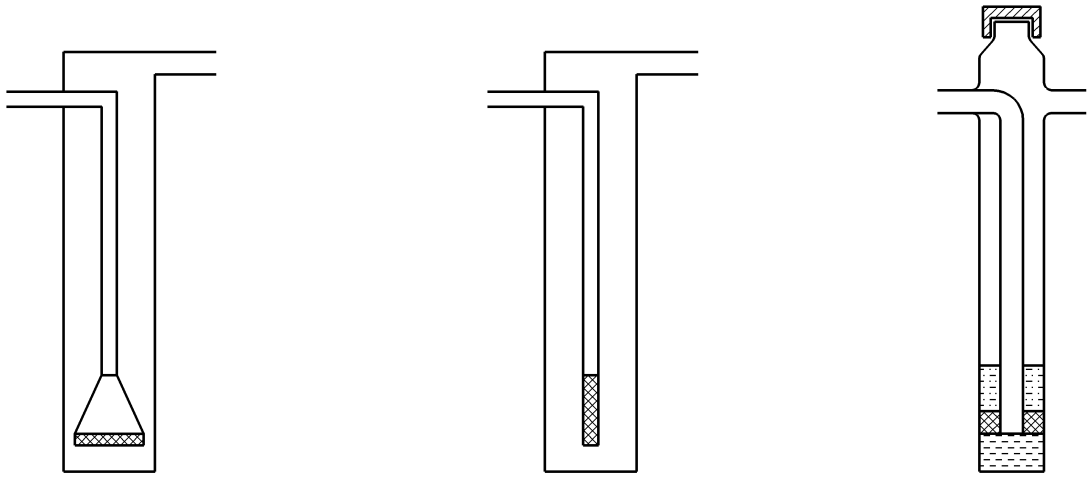


Figure B.1 — Examples of absorbers with fritted gas divider (0,03 m^3/h to 0,18 m^3/h)

NOTE For high absorption efficiency it is advisable to distribute the gas stream in the absorption liquid as homogeneously as possible and have reasonably long contact time between gas and liquid. In practice a sufficient free space should break down any foam, which may be formed while the gas is bubbling through the liquid.

Annex C
(informative)

Example of assessment of compliance of standard reference method for SO_2 with requirements on emission measurements

C.1 Introduction

This informative annex gives an example of the calculation of the uncertainty budget established for configuration 1 to demonstrate compliance with given uncertainty requirements.

The following procedure for calculating the measurement uncertainty is based on the law of propagation of uncertainty as described in EN ISO 14956 or ISO/IEC Guide 98-3 (GUM). The individual standard uncertainties, the combined standard uncertainty and the expanded uncertainty are determined according to the requirements of EN ISO 14956 or ISO/IEC Guide 98-3.

C.2 Elements required for the uncertainty determinations

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

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

The expanded uncertainty U_c is obtained by multiplying a coverage factor k with the combined uncertainty u_c. The value of the coverage factor k is chosen on the basis of the level of confidence required. In most cases, k is taken equal to 2 for a level of confidence of approximately 95 %.

C.3 Example of an uncertainty calculation

C.3.1 Specific conditions in the field

Table C.1 gives one example of the specific conditions of the site, that is to say the values and the variation range of the influence parameters.

The mass flow is homogenous.

Table C.1 — Example of measurement conditions

Specific conditions	Value
Studied concentration of SO_2 (limit value of SO_2 for the site) at standard conditions of temperature (273 K) and pressure (101,325 kPa), and at 11 % oxygen reference concentration	50 mg/m3 corresponding to q_S = 14,56 mg/l SO_4^{2-} of absorption solution
Oxygen reference volume concentration o_{ref}	11 %
Measured oxygen volume concentration o_m	12,3 %
Relative expanded uncertainty of o_m for k = 2	6 %
Volume of solution V_S used for measurement (total volume in two absorbers)	200 ml
Volume of gas sampled	0,049 m³
Mean temperature at the gas volume meter [a]	296,2 K
Mean absolute pressure at the gas meter [b]	100 281 Pa
Analyse	ion chromatography

[a] Mean temperature is calculated from data recording of continuous temperature measurement (one measurement per 30 s leads to 60 measurements in 30 min). The standard deviation of the mean of measurements calculated is equal to 0,231 K.

[b] Mean absolute pressure is calculated from five measurements of relative pressure at the gas volume meter and one measurement of atmospheric pressure during the sampling period.

Table C.2 gives one example of the measured values of relative pressure.

Table C.2 — Measured values of relative pressure

Measurement	Relative pressure p_{rel} at gas volume meter Pa
1	70,5
2	68,7
3	69,0
4	68,6
5	69,8
Mean	69,2
Standard deviation	0,287

Barometric pressure: 100 212 Pa

Mean absolute pressure: 100 281 Pa

C.3.2 Performance characteristics

Table C.3 shows the performance characteristics of the method related to the parameters which can have an influence on the response of the analyser.

Table C.3 — Example of performance characteristics

Performance characteristics	Performance criterion	Results obtained in laboratory or field
Volume of absorption solution: Expanded uncertainty The total volume of solution is determined with a graduated tube: – tolerance of the tube – reading	≤ 2,0 % of the volume of solution	 ±1,4 ml 2 ml
Gas volume sampled: Expanded uncertainty – expanded uncertainty of calibration – drift between two calibrations – reading	≤ 5,0 % of the measured value	 1,5 % of the measured value 1,0 % of the measured value 0,002 m^3
Temperature at the gas volume meter: Expanded uncertainty – expanded uncertainty of calibration – standard deviation (average value) – drift between two adjustments – resolution	≤ 2,0 % of the absolute temperature	 1,0 K 0,231 K 0,2 K 0,1 K
Absolute pressure at gas volume meter: Expanded uncertainty Relative pressure at the gas volume meter; scale of the manometer: 0 Pa to –200 Pa – expanded uncertainty of calibration – resolution – standard deviation (average value) – drift between two calibrations Atmospheric pressure – expanded uncertainty of calibration – drift between two calibrations – resolution	≤ 2,0 % of the measured value	 1,5 Pa 0,1 Pa 0,3 Pa 0,5 Pa 170Pa 60 Pa 10 Pa
Absorption efficiency of the first absorber	> 95,0 %	98 %
Concentration q_S in the absorption solution: — repeatability standard deviation of analysis	≤ 2,5 % of the measured value	2,0 % of the measured value

C.3.3 Model equation and application of rule of uncertainty propagation

C.3.3.1 Concentration of SO_2

The measured SO_2 concentration is calculated by Formula (C.1):

$$C_{\mathrm{m}} = \frac{q_{\mathrm{s}} \times v_{\mathrm{s}} \times \frac{64,1}{96,1}}{V_{\mathrm{m,ref}}} \tag{C.1}$$

where $V_{\mathrm{m,ref}}$ is given by Formula (C.2)

$$V_{\mathrm{m,ref}} = V_{\mathrm{m}} \times \frac{T_{\mathrm{ref}}}{T_{\mathrm{m}}} \times \frac{p_{\mathrm{m}}}{p_{\mathrm{ref}}} = V_{\mathrm{m}} \times \frac{T_{\mathrm{ref}}}{T_{\mathrm{m}}} \times \frac{p_{\mathrm{rel}} + p_{\mathrm{atm}}}{p_{\mathrm{ref}}} \tag{C.2}$$

and

q_{s} is the mass concentration of sulfate collected in the sample absorption solution, in mg/l;

v_{s} is the volume of sample absorption solution, in l;

$V_{\mathrm{m,ref}}$ is the measured dry gas volume, corrected to standard conditions, in m^3;

V_{m} is the sampled gas volume calculated by difference between the gas volume at the end and at the beginning of the sampling period, in m^3 (the value at the beginning of the sampling period corresponds to a reading of an indicator; the value at the end of the sampling period corresponds to the reading of a measured value);

T_{m} is the mean temperature of the sampled gas at the gas volume meter, in K;

T_{ref} is the standard temperature, 273 K;

p_{m} is the absolute pressure at the gas volume meter which is equal to the sum of relative pressure measured at the gas volume meter and the atmospheric pressure, in kPa;

p_{rel} is the relative pressure measured at the gas volume meter, in kPa;

p_{atm} is the atmospheric pressure, in kPa;

p_{ref} is the standard pressure, 101,325 kPa.

Conversion of the concentration of SO_2 at oxygen reference concentration is performed according to Formula (C.3):

$$C_{\mathrm{m,corr}} = \frac{21\% - o_{\mathrm{ref}}}{21\% - o_{\mathrm{m}}} \times C_{\mathrm{m}} \tag{C.3}$$

where

$C_{\mathrm{m,corr}}$ is the SO_2 concentration at oxygen reference concentration, in mg/m³

C_{m} is the SO_2 concentration at measured oxygen concentration in the duct, in mg/m³

o_{ref} is the oxygen reference volume concentration, in %

o_{m} is the measured oxygen volume concentration in the duct, in %

Calculation of the measured volume at standard conditions of temperature and pressure gives:

$$V_{\mathrm{m,ref}} = 0,049\,\mathrm{m}^3 \times \frac{273}{296,2} \times \frac{100,281}{101,325} = 0,045\,\mathrm{m}^3$$

The SO_2 concentration at standard conditions of temperature and pressure, and at the measured oxygen concentration is equal to:

$$C_{\mathrm{m}} = \frac{14,56\frac{\mathrm{mg}}{\mathrm{l}} \times 2001 \times \frac{64,1}{96,1}}{0,045\,\mathrm{m}^3} = 43,4\frac{\mathrm{mg}}{\mathrm{m}^3}$$

The SO_2 concentration at standard conditions of temperature and pressure, and at oxygen reference concentration is equal to:

$$C_{\mathrm{m,corr}} = 43,4\frac{\mathrm{mg}}{\mathrm{m}^3} \times \frac{21\% - 11\%}{21\% - 12,3\%} = 49,9\frac{\mathrm{mg}}{\mathrm{m}^3}$$

C.3.3.2 Calculation of the combined uncertainty of $V_{\mathrm{m,ref}}$ and C_{m}

Based on Formula (C.1) the combined uncertainty of C_{m} can be expressed by Formula (C.4):

$$\frac{u^2(C_{\mathrm{m}})}{(C_{\mathrm{m}})^2} = \frac{u^2(q_{\mathrm{s}})}{(q_{\mathrm{s}})^2} + \frac{u^2(v_{\mathrm{s}})}{(v_{\mathrm{s}})^2} + \frac{u^2(V_{\mathrm{m,ref)}})}{(V_{\mathrm{m,ref}})^2} \tag{C.4}$$

Based on Formula (C.2) and with the assumption that the uncertainties of T_{ref} and p_{ref} are negligible, the combined uncertainty of $V_{\mathrm{m,ref}}$ can be expressed by Formula (C.5):

$$\begin{aligned} u^2(V_{\mathrm{m,ref}}) = &\left(\frac{\partial V_{\mathrm{m,ref}}}{\partial V_{\mathrm{m}}}\right)^2 \times u^2(V_{\mathrm{m}}) + \cdot\left(\frac{\partial V_{\mathrm{m,ref}}}{\partial T_{\mathrm{m}}}\right)^2 \times u^2(T_{\mathrm{m}}) \\ &+ \left(\frac{\partial V_{\mathrm{m,ref}}}{\partial p_{\mathrm{rel}}}\right)^2 \times u^2(p_{\mathrm{rel}}) + \left(\frac{\partial V_{\mathrm{m,ref}}}{\partial p_{\mathrm{atm}}}\right)^2 \times u^2(p_{\mathrm{atm}}) \end{aligned} \tag{C.5}$$

C.3.3.3 Calculation of sensitivity coefficients

The sensitivity coefficients are given by Formula (C.6) to Formula (C.9):

$$\frac{\partial V_{\mathrm{m,ref}}}{\partial V_{\mathrm{m}}} = \frac{T_{\mathrm{ref}}}{T_{\mathrm{m}}} \times \frac{p_{\mathrm{m}}}{p_{\mathrm{ref}}} = \frac{V_{\mathrm{m,ref}}}{V_{\mathrm{m}}} \tag{C.6}$$

$$\frac{\partial V_{\mathrm{m,ref}}}{\partial T_{\mathrm{m}}} = -V_{\mathrm{m}} \quad \times T_{\mathrm{ref}} \times \frac{p_{\mathrm{m}}}{p_{\mathrm{ref}}} \times \frac{1}{T_{\mathrm{m}}^2} = -\frac{V_{\mathrm{m,ref}}}{T_{\mathrm{m}}} \tag{C.7}$$

$$\frac{\partial V_{\mathrm{m,ref}}}{\partial p_{\mathrm{rel}}} = V_{\mathrm{m}} \times \frac{T_{\mathrm{ref}}}{T_{\mathrm{m}}} \times \frac{1}{p_{\mathrm{ref}}} = \frac{V_{\mathrm{m,ref}}}{p_{\mathrm{rel}} + p_{\mathrm{atm}}} = \frac{V_{\mathrm{m,ref}}}{p_{\mathrm{m}}} \tag{C.8}$$

$$\frac{\partial V_{\mathrm{m,ref}}}{\partial p_{\mathrm{atm}}} = V_{\mathrm{m}} \times \frac{T_{\mathrm{ref}}}{T_{\mathrm{m}}} \times \frac{1}{p_{\mathrm{ref}}} = \frac{V_{\mathrm{m,ref}}}{p_{\mathrm{rel}} + p_{\mathrm{atm}}} = \frac{V_{\mathrm{m,ref}}}{p_{\mathrm{m}}} \tag{C.9}$$

Formula (C.5) is equivalent to Formula (C.10):

$$\frac{u^2\left(V_{\mathrm{m,ref}}\right)}{\left(V_{\mathrm{m,ref}}\right)^2} = \frac{u^2\left(V_{\mathrm{m}}\right)}{\left(V_{\mathrm{m}}\right)^2} + \frac{u^2\left(T_{\mathrm{m}}\right)}{\left(T_{\mathrm{m}}\right)^2} + \frac{u^2\left(p_{\mathrm{rel}}\right)}{\left(p_{\mathrm{rel}} + p_{\mathrm{atm}}\right)^2} + \frac{u^2\left(p_{\mathrm{atm}}\right)}{\left(p_{\mathrm{rel}} + p_{\mathrm{atm}}\right)^2} \tag{C.10}$$

Formula (C.4) is equivalent to Formula (C.11):

$$\frac{u^2\left(C_{\mathrm{m}}\right)}{\left(C_{\mathrm{m}}\right)^2} = \frac{u^2\left(q_{\mathrm{s}}\right)}{\left(q_{\mathrm{s}}\right)^2} + \frac{u^2\left(v_{\mathrm{s}}\right)}{\left(v_{\mathrm{s}}\right)^2} + \frac{u^2\left(V_{\mathrm{m}}\right)}{\left(V_{\mathrm{m}}\right)^2} + \frac{u^2\left(T_{\mathrm{m}}\right)}{\left(T_{\mathrm{m}}\right)^2} + \frac{u^2\left(p_{\mathrm{rel}}\right)}{\left(p_{\mathrm{rel}} + p_{\mathrm{atm}}\right)^2} + \frac{u^2\left(p_{\mathrm{atm}}\right)}{\left(p_{\mathrm{rel}} + p_{\mathrm{atm}}\right)^2} \tag{C.11}$$

C.3.3.4 Results of the standard uncertainties calculations

Calculation of standard uncertainties in Table C.4 is based on Formula (C.12) to Formula (C.17):

$$u^2(v_{\mathrm{s}}) = u_{\mathrm{tol}}^2(v_{\mathrm{s}}) + u_{\mathrm{res}}^2(v_{\mathrm{s}}) \tag{C.12}$$

$$u^2(q_{\mathrm{s}}) = u_{\mathrm{rep}}^2(q_{\mathrm{s}}) \tag{C.13}$$

$$u^2\left(V_{\mathrm{m}}\right) = u_{\mathrm{cal}}^2\left(V_{\mathrm{m}}\right) + u_{\mathrm{dr}}^2\left(V_{\mathrm{m}}\right) + 2u_{\mathrm{read}}^2\left(V_{\mathrm{m}}\right) \tag{C.14}$$

$$u^2\left(T_{\mathrm{m}}\right) = u_{\mathrm{cal}}^2\left(T_{\mathrm{m}}\right) + u_{\mathrm{dr}}^2\left(T_{\mathrm{m}}\right) + u_{\mathrm{res}}^2\left(T_{\mathrm{m}}\right) + u_{\mathrm{mean}}^2\left(T_{\mathrm{m}}\right) \tag{C.15}$$

$$u^2\left(p_{\mathrm{rel}}\right) = u_{\mathrm{cal}}^2\left(p_{\mathrm{rel}}\right) + u_{\mathrm{dr}}^2\left(p_{\mathrm{rel}}\right) + u_{\mathrm{res}}^2\left(p_{\mathrm{rel}}\right) + u_{\mathrm{mean}}^2\left(p_{\mathrm{rel}}\right) \tag{C.16}$$

$$u^2\left(p_{\mathrm{atm}}\right) = u_{\mathrm{cal}}^2\left(p_{\mathrm{atm}}\right) + u_{\mathrm{dr}}^2\left(p_{\mathrm{atm}}\right) + u_{\mathrm{res}}^2\left(p_{\mathrm{atm}}\right) \tag{C.17}$$

Table C.4 — Results of the standard uncertainty calculations

Performance characteristic	Formula	Standard uncertainty	Relative standard uncertainty
Volume of the absorption solution	(C.12)	$u(v_S)$	
– tolerance of the tube		$u_{tol}(v_s) = \frac{1{,}4\,\text{ml}}{\sqrt{3}} = 0{,}808\,\text{ml}$	
– resolution		$u_{res}(v_s) = \frac{2\,\text{ml}}{2\sqrt{3}} = 0{,}577\,\text{ml}$	
		$u(v_S)$ = 0,993 ml	$\frac{u(v_s)}{v_s} = 0{,}005$
Concentration in the absorption solution	(C.13)	$u(q_S)$	
– repeatability standard deviation		$u_{rep}(q_s) = \frac{2}{100} \times 14{,}56 \frac{\text{mg}}{\text{l}} = 0{,}291 \frac{\text{mg}}{\text{l}}$	
		$u(q_S)$ = 0,291 mg/l	$\frac{u(q_s)}{q_s} = 0{,}02$
Volume of sampled gas	(C.14)	$u(V_m)$	
– calibration		$u_{cal}(V_m) = \frac{\frac{1{,}5}{100} \times 0{,}049\,\text{m}^3}{2} = 3{,}675 \times 10^{-4}\,\text{m}^3$	
– drift		$u_{dr}(V_m) = \frac{\frac{1}{100} \times 0{,}049\,\text{m}^3}{\sqrt{3}} = 2{,}829 \times 10^{-4}\,\text{m}^3$	
– reading		$u_{res}(V_m) = \frac{0{,}002\,\text{m}^3}{2\sqrt{3}} = 5{,}774 \times 10^{-4}\,\text{m}^3$	
		$u(V_m) = 9{,}39 \times 10^{-4}\,\text{m}^3$	$\frac{u(V_m)}{V_m} = \frac{9{,}39 \times 10^{-4}}{0{,}049} = 0{,}0192$

Temperature at the gas volume meter	(C.15)	$u(T_m)$	
– calibration		$u_{cal}(T_m) = \frac{1\,K}{2} = 0{,}5\,K$	
– drift		$u_{dr}(T_m) = \frac{0{,}2\,K}{\sqrt{3}} = 0{,}115\,K$	
– resolution		$u_{res}(T_m) = \frac{0{,}1\,K}{2\sqrt{3}} = 0{,}03\,K$	
– standard deviation of the mean		$u_{mean}(T_m) = 0{,}231\,K$	
		$u(T_m) = 0{,}566\ K$	$\frac{u(T_m)}{T_m} = 1{,}9 \times 10^{-3}$
Relative pressure at the gas volume meter	(C.16)	$u(p_{rel})$	
– calibration of the manometer		$u_{cal}(p_{rel}) = \frac{1{,}5\,Pa}{2} = 0{,}75\,Pa$	
– drift		$u_{dr}(p_{rel}) = \frac{0{,}5\,Pa}{\sqrt{3}} = 0{,}289\,Pa$	
– resolution of manometer		$u_{res}(p_{rel}) = \frac{0{,}1\,Pa}{2\sqrt{3}} = 2{,}89 \times 10^{-2}\ Pa$	
– standard deviation of the mean		$u_{mean}(p_{rel}) = 0{,}3\,Pa$	
		$u(p_{rel}) = 0{,}858\ Pa$	$\frac{u(p_{rel})}{p_m} = 8{,}55 \times 10^{-6}$

Atmospheric pressure	(C.17)	$u(p_{\mathrm{atm}})$	
– calibration		$u_{\mathrm{cal}}\left(p_{\mathrm{atm}}\right)=\frac{170\,\mathrm{Pa}}{2}=85\,\mathrm{Pa}$	
– drift		$u_{\mathrm{dr}}\left(p_{\mathrm{atm}}\right)=\frac{60\,\mathrm{Pa}}{\sqrt{3}}=34,6\,\mathrm{Pa}$	
– resolution		$u_{\mathrm{res}}\left(p_{\mathrm{atm}}\right)=\frac{10\,\mathrm{Pa}}{2\sqrt{3}}=2,89\,\mathrm{Pa}$	
		$u(p_{\mathrm{atm}})$ = 91,8 Pa	$\frac{u\left(p_{\mathrm{atm}}\right)}{p_{\mathrm{m}}}=9,15\times10^{-4}$

C.3.4 Estimation of the combined uncertainty

The result of the calculation of the combined uncertainty according to the Formula (C.11) is:

– standard uncertainty: $u(C\mathrm{m})$ = 1,48 mg/m³

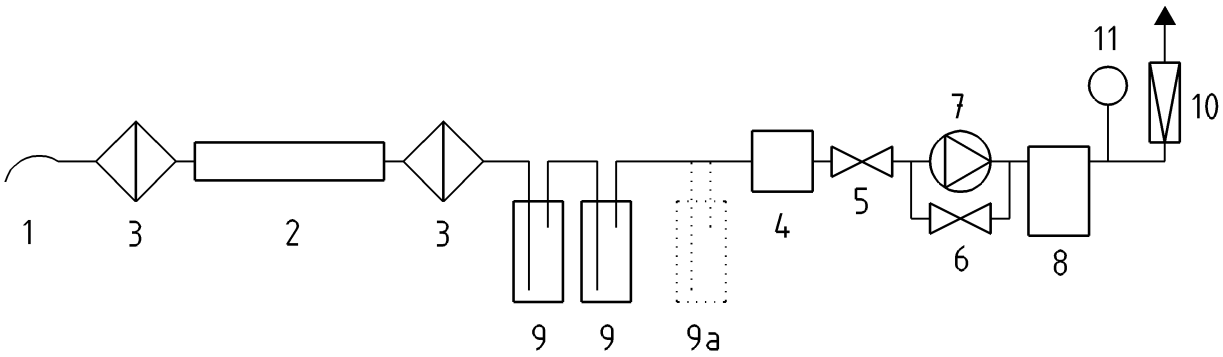
– relative standard uncertainty: $u_{\mathrm{rel}}(C_{\mathrm{m}})$ = 2,97 %

– expanded uncertainty (k = 2): $U(C_{\mathrm{m}})$ = 2,97 mg/m³

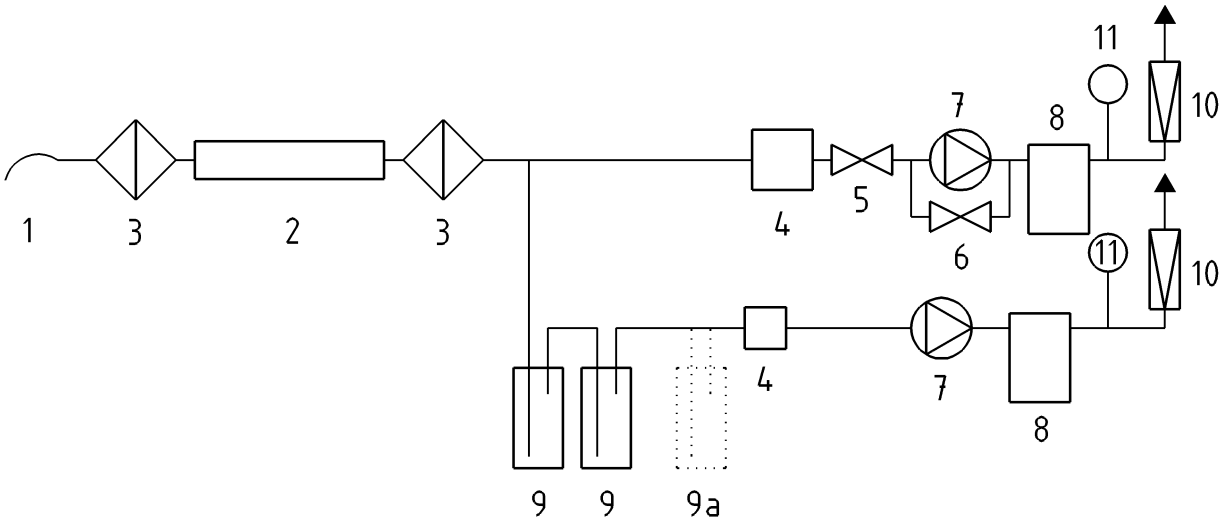
– relative expanded uncertainty (k = 2): $U_{\mathrm{rel}}(C_{\mathrm{m}})$ = 5,94 %

Annex D
(informative)

Type of sampling equipment



a) Main-stream sampling



b) Side-stream sampling

Key

1 Nozzle
2 Probe
3 Filter (either behind or in front of the probe)
4 Dryer cartridge
5 Valve
6 By-pass valve
7 Pump
8 Gas volume meter
9 Absorber
9a Safety bottle (trap)
10 Gas flow meter
11 Temperature and pressure measurement

Figure D.1 — Types of sampling equipment

Annex E
(informative)

Example of comparison of repeatability and trueness of Thorin Method and Ion Chromatography Method

This example provides data to check repeatability and trueness of the Thorin Method compared to those of the Ion Chromatography Method. The calculations according to EN 14793:2017 have been realized considering in one hand that the Ion Chromatography was the RM and in the second hand that the Thorin method was the AM and vice versa. Paired measurements ($n_i = 2$) have been performed simultaneously for the RM and the AM at each test *i*. Table E.1 to Table E.8 were set up according to the rules given in EN 14793:2017. All concentrations in the tables are expressed in mg/m^3.

Table E.1 — Ion Chromatography

Test	Parallel measurements		Number of measure-ments	Mean		Difference	Variance
i	z_{i1}	z_{i2}	n_i	$\bar{z}_i$	$\left(\bar{z}_i - \bar{\bar{z}}\right)^2$	$\left(z_{i1} - z_{i2}\right)$	$s^2\left(\bar{z}_i\right)$
1	43,81	46,32	2	45,07	237,95	–2,510	3,150
2	33,84	36,26	2	35,05	647,22	–2,420	2,928
3	65,68	67,71	2	66,70	38,50	–2,030	2,060
4	97,30	99,32	2	98,31	1430,32	–2,020	2,040
5	203,72	211,26	2	207,49	21608,86	–7,540	28,426
6	130,40	134,95	2	132,68	5210,61	–4,550	10,351
7	57,07	58,64	2	57,86	6,95	–1,570	1,232
8	165,67	176,66	2	171,17	12248,85	–10,990	60,390
9	104,35	110,25	2	107,30	2191,13	–5,900	17,405
10	42,40	43,85	2	43,13	301,56	–1,450	1,051
11	89,26	88,62	2	88,94	809,38	0,640	0,205
12	87,16	86,56	2	86,86	695,35	0,600	0,180
13	51,93	55,01	2	53,47	49,29	–3,080	4,743
14	22,37	22,59	2	22,48	1444,80	–0,220	0,024
15	108,73	108,82	2	108,78	2331,40	–0,090	0,004
16	133,55	139,72	2	136,64	5797,99	–6,170	19,034
17	92,64	97,74	2	95,19	1204,06	–5,100	13,005
18	51,65	55,71	2	53,68	46,38	–4,060	8,242
19	143,31	146,64	2	144,98	7137,64	–3,330	5,544
20	73,75	75,22	2	74,49	195,85	–1,470	1,080

21	38,90	39,56	2	39,23	452,01	–0,660	0,218
22	21,50	21,80	2	21,65	1508,58	–0,300	0,045
23	4,20	3,80	2	4,00	3191,17	0,400	0,080
24	3,50	3,20	2	3,35	3265,03	0,300	0,045
25	2,00	1,80	2	1,90	3432,84	0,200	0,020
26	1,40	1,30	2	1,35	3497,60	0,100	0,005
27	1,30	1,20	2	1,25	3509,43	0,100	0,005
28	5,80	5,30	2	5,55	3018,46	0,500	0,125
29	6,80	6,30	2	6,55	2909,57	0,500	0,125
30	8,70	8,00	2	8,35	2718,63	0,700	0,245
31	10,00	9,30	2	9,65	2584,75	0,700	0,245
32	3,79	1,50	2	2,65	3346,10	2,290	2,622
			N	$\overline{\overline{z}}$	$\mathrm{SSD}\left(\overline{\overline{z}}\right)$	$s^2\left(\overline{\overline{z}}\right)$	$s_r^2\left(\overline{\overline{z}}\right)$
			64	60,49	97068,23	3131,23	5,777

The difference between the two values of the 32nd couple seems to be important. Therefore, an outlier test has been carried out (see Table E.2).

Table E.2 — Ion Chromatography – detection of outliers

Test	**Parallel measurements**		**Outlier test**		
i	z_{i1}	z_{i2}	$\mathrm{d}z_i = \left(z_{i1} - z_{i2}\right)$	$e_i = \frac{\mathrm{d}z_i}{\overline{z}_i}$	G_i
1	43,81	46,32	–2,51	–0,0557	0,51
2	33,84	36,26	–2,42	–0,0690	0,60
3	65,68	67,71	–2,03	–0,0304	0,36
4	97,30	99,32	–2,02	–0,0205	0,30
5	203,72	211,26	–7,54	–0,0363	0,40
6	130,40	134,95	–4,55	–0,0343	0,38
7	57,07	58,64	–1,57	–0,0271	0,34
8	165,67	176,66	–10,99	–0,0642	0,57
9	104,35	110,25	–5,90	–0,0550	0,51
10	42,40	43,85	–1,45	–0,0336	0,38
11	89,26	88,62	0,64	0,0072	0,13
12	87,16	86,56	0,60	0,0069	0,13
13	51,93	55,01	–3,08	–0,0576	0,53
14	22,37	22,59	–0,22	–0,0098	0,23
15	108,73	108,82	–0,09	–0,0008	0,18

16	133,55	139,72	–6,17	–0,0452	0,45
17	92,64	97,74	–5,10	–0,0536	0,50
18	51,65	55,71	–4,06	–0,0756	0,64
19	143,31	146,64	–3,33	–0,0230	0,31
20	73,75	75,22	–1,47	–0,0197	0,29
21	38,90	39,56	–0,66	–0,0168	0,28
22	21,50	21,80	–0,30	–0,0139	0,26
23	4,20	3,80	0,40	0,1000	0,44
24	3,50	3,20	0,30	0,0896	0,37
25	2,00	1,80	0,20	0,1053	0,47
26	1,40	1,30	0,10	0,0741	0,28
27	1,30	1,20	0,10	0,0800	0,32
28	5,80	5,30	0,50	0,0901	0,38
29	6,80	6,30	0,50	0,0763	0,29
30	8,70	8,00	0,70	0,0838	0,34
31	10,00	9,30	0,70	0,0725	0,27
32	3,79	1,50	2,29	0,8658	**5,13**
			$\overline{e}$	0,0284	
			$s(e_i)$	0,1634	

The critical value given by the Grubbs Table for n = 2 is 2,822. All values G_i are lower than the critical value, except for the 32nd couple of points which has to be withdrawn.

Table E.3 — Thorin method

Test	**Parallel measurements**		**Number of measure-ments**	**Mean**		**Difference**	**Variance**
i	x_{i1}	x_{i2}	n_i	$\overline{x}_i$	$\left(\overline{x}_i - \overline{\overline{x}}\right)^2$	$\left(x_{i1} - x_{i2}\right)$	$s^2\left(\overline{x}_i\right)$
1	45,54	49,64	2	47,59	216,12	–4,100	8,405
2	36,08	38,61	2	37,35	622,31	–2,530	3,200
3	67,80	69,90	2	68,85	43,02	–2,100	2,205
4	99,56	101,36	2	100,46	1456,87	–1,800	1,620
5	205,57	213,09	2	209,33	21620,44	–7,520	28,275
6	132,62	136,77	2	134,70	5242,33	–4,150	8,611
7	59,66	60,45	2	60,06	5,00	–0,790	0,312
8	173,04	180,16	2	176,60	13066,53	–7,120	25,347

9	109,41	113,97	2	111,69	2440,25	–4,560	10,397
10	45,77	47,77	2	46,77	240,90	–2,000	2,000
11	93,63	95,25	2	94,44	1033,55	–1,620	1,312
12	88,85	89,09	2	88,97	711,76	–0,240	0,029
13	55,47	58,38	2	56,93	28,79	–2,910	4,234
14	24,70	26,44	2	25,57	1348,44	–1,740	1,514
15	109,29	112,21	2	110,75	2348,27	–2,920	4,263
16	136,94	150,22	2	143,58	6607,89	–13,280	88,179
17	95,89	104,69	2	100,29	1443,92	–8,800	38,720
18	54,84	59,15	2	57,00	28,05	–4,310	9,288
19	114,65	147,19	2	130,92	4709,93	–32,540	529,426
20	60,37	66,65	2	63,51	1,49	–6,280	19,719
21	33,54	36,70	2	35,12	738,27	–3,160	4,993
22	20,12	21,40	2	20,76	1724,83	–1,280	0,819
23	6,70	6,10	2	6,40	3123,81	0,600	0,180
24	5,00	4,60	2	4,80	3305,23	0,400	0,080
25	4,30	3,90	2	4,10	3386,20	0,400	0,080
26	4,20	3,90	2	4,05	3392,03	0,300	0,045
27	4,20	3,90	2	4,05	3392,03	0,300	0,045
28	9,80	9,10	2	9,45	2792,18	0,700	0,245
29	8,70	8,10	2	8,40	2904,25	0,600	0,180
30	11,20	10,40	2	10,80	2651,33	0,800	0,320
31	11,10	10,40	2	10,75	2656,48	0,700	0,245
32	9,60	9,00	2	9,30	2808,06	0,600	0,180
			N	$\overline{\overline{x}}$	$\mathrm{SSD}\left(\overline{\overline{x}}\right)$	$s^2\left(\overline{\overline{x}}\right)$	$s_r^2\left(\overline{\overline{x}}\right)$
			64	62,29	96090,54	3099,69	24,827

The difference between the two values of the 19th couple seems to be important. Therefore, an outlier test has been carried out (see Table E.4).

Table E.4 — Thorin method– detection of outliers

Test	Parallel measurements		Outlier test		
i	z_{i1}	z_{i2}	$\mathrm{d}z_i = (z_{i1} - z_{i2})$	$e_i = \frac{\mathrm{d}z_i}{\overline{z}_i}$	G_i
1	45,54	49,64	–4,10	–0,0862	0,89
2	36,08	38,61	–2,53	–0,0677	0,65
3	67,80	69,90	–2,10	–0,0305	0,17
4	99,56	101,36	–1,80	–0,0179	0,01
5	205,57	213,09	–7,52	–0,0359	0,24
6	132,62	136,77	–4,15	–0,0308	0,17
7	59,66	60,45	–0,79	–0,0132	0,05
8	173,04	180,16	–7,12	–0,0403	0,30
9	109,41	113,97	–4,56	–0,0408	0,30
10	45,77	47,77	–2,00	–0,0428	0,33
11	93,63	95,25	–1,62	–0,0172	0,00
12	88,85	89,09	–0,24	–0,0027	0,19
13	55,47	58,38	–2,91	–0,0511	0,44
14	24,70	26,44	–1,74	–0,0680	0,66
15	109,29	112,21	–2,92	–0,0264	0,12
16	136,94	150,22	–13,28	–0,0925	0,97
17	95,89	104,69	–8,80	–0,0877	0,91
18	54,84	59,15	–4,31	–0,0756	0,75
19	114,65	147,19	–32,54	–0,2485	**2,99**
20	60,37	66,65	–6,28	–0,0989	1,05
21	33,54	36,70	–3,16	–0,0900	0,94
22	20,12	21,40	–1,28	–0,0617	0,57
23	6,70	6,10	0,60	0,0938	1,44
24	5,00	4,60	0,40	0,0833	1,30
25	4,30	3,90	0,40	0,0976	1,48
26	4,20	3,90	0,30	0,0741	1,18
27	4,20	3,90	0,30	0,0741	1,18
28	9,80	9,10	0,70	0,0741	1,18
29	8,70	8,10	0,60	0,0714	1,15

30	11,20	10,40	0,80	0,0741	1,18
31	11,10	10,40	0,70	0,0651	1,07
32	9,60	9,00	0,60	0,0645	1,06
			$\overline{e}$	–0,0173	
			$s(e_i)$	0,0774	

The critical value given by the Grubbs Table for n = 2 is 2,822. All values G_i are lower than the critical value, except for the 19th couple of points which has to be withdrawn.

Table E.5 — Ion Chromatography (19th and 32nd couples skipped)

Test	Parallel measurements		Number of measure-ments	Mean		Difference	Variance
i	z_{i1}	z_{i2}	n_i	$\overline{z}_i$	$\left(\overline{z}_i - \overline{\overline{z}}\right)^2$	$\left(z_{i1} - z_{i2}\right)$	$s^2\left(\overline{z}_i\right)$
1	43,81	46,32	2	45,07	237,95	–2,510	3,150
2	33,84	36,26	2	35,05	647,22	–2,420	2,928
3	65,68	67,71	2	66,70	38,50	–2,030	2,060
4	97,30	99,32	2	98,31	1430,32	–2,020	2,040
5	203,72	211,26	2	207,49	21608,86	–7,540	28,426
6	130,40	134,95	2	132,68	5210,61	–4,550	10,351
7	57,07	58,64	2	57,86	6,95	–1,570	1,232
8	165,67	176,66	2	171,17	12248,85	–10,990	60,390
9	104,35	110,25	2	107,30	2191,13	–5,900	17,405
10	42,40	43,85	2	43,13	301,56	–1,450	1,051
11	89,26	88,62	2	88,94	809,38	0,640	0,205
12	87,16	86,56	2	86,86	695,35	0,600	0,180
13	51,93	55,01	2	53,47	49,29	–3,080	4,743
14	22,37	22,59	2	22,48	1444,80	–0,220	0,024
15	108,73	108,82	2	108,78	2331,40	–0,090	0,004
16	133,55	139,72	2	136,64	5797,99	–6,170	19,034
17	92,64	97,74	2	95,19	1204,06	–5,100	13,005
18	51,65	55,71	2	53,68	46,38	–4,060	8,242
20	73,75	75,22	2	74,49	195,85	–1,470	1,080
21	38,90	39,56	2	39,23	452,01	–0,660	0,218
22	21,50	21,80	2	21,65	1508,58	–0,300	0,045
23	4,20	3,80	2	4,00	3191,17	0,400	0,080

24	3,50	3,20	2	3,35	3265,03	0,300	0,045
25	2,00	1,80	2	1,90	3432,84	0,200	0,020
26	1,40	1,30	2	1,35	3497,60	0,100	0,005
27	1,30	1,20	2	1,25	3509,43	0,100	0,005
28	5,80	5,30	2	5,55	3018,46	0,500	0,125
29	6,80	6,30	2	6,55	2909,57	0,500	0,125
30	8,70	8,00	2	8,35	2718,63	0,700	0,245
31	10,00	9,30	2	9,65	2584,75	0,700	0,245
			N	$\overline{\overline{z}}$	$\mathrm{SSD}\left(\overline{\overline{z}}\right)$	$s^2\left(\overline{\overline{z}}\right)$	$s_r^2\left(\overline{\overline{z}}\right)$
			60	59,60	86560,84	2984,86	5,890

Table E.6 — Thorin method (19th and 32nd couples skipped)

Test	**Parallel measurements**		**Number of measure-ments**	**Mean**		**Difference**	**Variance**
i	x_{i1}	x_{i2}	n_i	$\overline{x}_i$	$\left(\overline{x}_i - \overline{\overline{x}}\right)^2$	$\left(x_{i1} - x_{i2}\right)$	$s^2\left(\overline{x}_i\right)$
1	45,54	49,64	2	47,59	216,12	–4,100	8,405
2	36,08	38,61	2	37,35	622,31	–2,530	3,200
3	67,80	69,90	2	68,85	43,02	–2,100	2,205
4	99,56	101,36	2	100,46	1456,87	–1,800	1,620
5	205,57	213,09	2	209,33	21620,44	–7,520	28,275
6	132,62	136,77	2	134,70	5242,33	–4,150	8,611
7	59,66	60,45	2	60,06	5,00	–0,790	0,312
8	173,04	180,16	2	176,60	13066,53	–7,120	25,347
9	109,41	113,97	2	111,69	2440,25	–4,560	10,397
10	45,77	47,77	2	46,77	240,90	–2,000	2,000
11	93,63	95,25	2	94,44	1033,55	–1,620	1,312
12	88,85	89,09	2	88,97	711,76	–0,240	0,029
13	55,47	58,38	2	56,93	28,79	–2,910	4,234
14	24,70	26,44	2	25,57	1348,44	–1,740	1,514
15	109,29	112,21	2	110,75	2348,27	–2,920	4,263
16	136,94	150,22	2	143,58	6607,89	–13,280	88,179
17	95,89	104,69	2	100,29	1443,92	–8,800	38,720
18	54,84	59,15	2	57,00	28,05	–4,310	9,288
20	60,37	66,65	2	63,51	1,49	–6,280	19,719

21	33,54	36,70	2	35,12	738,27	–3,160	4,993
22	20,12	21,40	2	20,76	1724,83	–1,280	0,819
23	6,70	6,10	2	6,40	3123,81	0,600	0,180
24	5,00	4,60	2	4,80	3305,23	0,400	0,080
25	4,30	3,90	2	4,10	3386,20	0,400	0,080
26	4,20	3,90	2	4,05	3392,03	0,300	0,045
27	4,20	3,90	2	4,05	3392,03	0,300	0,045
28	9,80	9,10	2	9,45	2792,18	0,700	0,245
29	8,70	8,10	2	8,40	2904,25	0,600	0,180
30	11,20	10,40	2	10,80	2651,33	0,800	0,320
31	11,10	10,40	2	10,75	2656,48	0,700	0,245
			N	$\overline{\overline{x}}$	$\mathrm{SSD}\left(\overline{\overline{x}}\right)$	$s^2\left(\overline{\overline{x}}\right)$	$s_r^2\left(\overline{\overline{x}}\right)$
			60	61,77	88564,41	3053,95	8,829

The data presented in Table E.5 and Table E.6 have been evaluated by the procedure described in EN 14793:2017 to demonstrate the equivalence between an Alternative Method with a Reference Method. The statistical results and conclusions are presented in Table E.7 and Table E.8 for the Ion Chromatography Method as the RM and the Thorin Method as the AM and vice versa.

Table E.7 — Presentation of the statistical results of infield demonstration of equivalence

	Thorin Method		**Ion Chromatography Method**	
Systematic deviation				
Grand averages	$\overline{\overline{x}}$	61,77	$\overline{\overline{z}}$	59,60
Repeatability				
Repeatability standard deviation	$s_r\left(\overline{\overline{x}}\right)$	2,971	$s_r\left(\overline{\overline{z}}\right)$	2,427
Variance of repeatability	$s_r^2\left(\overline{\overline{x}}\right)$	8,829	$s_r^2\left(\overline{\overline{z}}\right)$	5,890
Total number of measurements	N	60	N	60
	$s_{r,\text{limit}}\left(x\right)$	0,051 x + 2,3	$s_{r,\text{limit}}\left(z\right)$	0,051 z +2,3
	$s_{r,\text{limit}}\left(\overline{\overline{x}}\right)$	5,45	$s_{r,\text{limit}}\left(\overline{\overline{z}}\right)$	5,34
	$s_R\left(x\right)$	0,0841 x – 0,8086	$s_R\left(z\right)$	0,0678 z + 3,47
	$s_R(\bar{\bar{x}})$	4,39	$s_R\left(\overline{\overline{z}}\right)$	7,51
	$\frac{s_R\left(\overline{\overline{x}}\right)}{\overline{\overline{x}}}$	0,071	$\frac{s_R\left(\overline{\overline{z}}\right)}{\overline{\overline{z}}}$	0,126
	$s\left(\overline{\overline{x}}\right)$	55,26	$s\left(\overline{\overline{z}}\right)$	54,63
	$C_1 = \frac{s\left(\overline{\overline{x}}\right)}{s\left(\overline{\overline{z}}\right)}$	1,0115	$C_1' = \frac{s(\overline{\overline{z}})}{s\left(\overline{\overline{x}}\right)}$	0,9885
	$C_0 = \overline{\overline{x}} - \frac{s\left(\overline{\overline{x}}\right)}{s\left(\overline{\overline{z}}\right)}\overline{\overline{z}}$	1,48	$C_0' = \overline{\overline{z}} - \frac{s\left(\overline{\overline{z}}\right)}{s\left(\overline{\overline{x}}\right)}\overline{\overline{x}}$	–1,46

Table E.8 — Compliance with the criteria

Verification tests	**Value obtained**		**Criterion**	**Conclusion** (results acceptable)
Systematic deviation				
correlation coefficient	r	0,9984	$r \geq 0,97$	yes
slope	C_1	1,0115	$1-\frac{s_R\left(\overline{\overline{z}}\right)}{\overline{\overline{z}}} \leq C_1 \leq 1+\frac{s_R\left(\overline{\overline{z}}\right)}{\overline{\overline{z}}}$ $0,874 \leq C_1 \leq 1,126$	yes
	C_1'	0,9885	$1-\frac{s_R\left(\overline{\overline{x}}\right)}{\overline{\overline{x}}} \leq C_1' \leq 1+\frac{s_R\left(\overline{\overline{x}}\right)}{\overline{\overline{x}}}$ $0,929 \leq C_1 \leq 1,071$	yes
intercept	C_0	1,48	$\lvert C_0 \rvert \leq s_R\left(\overline{\overline{z}}\right)$ $\lvert C_0 \rvert \leq 7,51$	yes
	C_0'	–1,46	$\lvert C_0' \rvert \leq s_R\left(\overline{\overline{x}}\right)$ $\lvert C_0' \rvert \leq 4,39$	yes
Repeatability standard deviation				
	$s_r\left(\overline{\overline{z}}\right)$	2,43 < 5,34	$s_r\left(\overline{\overline{z}}\right) \leq s_{r,\text{limit}}\left(\overline{\overline{z}}\right)$	yes
	$s_r\left(\overline{\overline{x}}\right)$	2,97 < 5,45	$s_r\left(\overline{\overline{x}}\right) \leq s_{r,\text{limit}}\left(\overline{\overline{x}}\right)$	yes

Calculations considering in one hand that the RM was the Ion Chromatography and in the second hand that the Thorin method lead to the same conclusions: both methods are equivalent.

Annex F
(informative)

Calculation of the uncertainty associated with a concentration expressed on dry gas and at an oxygen reference concentration

F.1Uncertainty associated with a concentration expressed on dry gas

The concentration of a measured component expressed for dry gas is calculated according to Formula (F.1):

$$C_{\mathrm{dry}} = C_{\mathrm{wet}} \frac{100\,\%}{100\,\% - h_{\mathrm{m}}} \tag{F.1}$$

where

C_{dry} is the concentration expressed on dry basis;

C_{wet} is the concentration expressed on wet basis;

h_{m} is the volume fraction of water vapour.

The uncertainty associated with a concentration expressed on dry gas is calculated according to Formula (F.2):

$$u^2\left(C_{\mathrm{dry}}\right) = \left(C_{\mathrm{dry}}\right)^2 \times \left(\frac{u^2\left(C_{\mathrm{wet}}\right)}{\left(C_{\mathrm{wet}}\right)^2} + \frac{u^2\left(h_{\mathrm{m}}\right)}{\left(100\,\% - h_{\mathrm{m}}\right)^2} \right) \tag{F.2}$$

where :

$u\left(C_{\mathrm{dry}}\right)$ is the uncertainty associated with a concentration expressed on dry gas;

$u\left(C_{\mathrm{wet}}\right)$ is the uncertainty associated with a concentration expressed on wet gas;

$u\left(h_{\mathrm{m}}\right)$ is the uncertainty associated with the water vapour volume fraction.

Table F.1 — Calculation of the uncertainty on dry gas

Concentration C_{wet} of the measured component:	100 mg/m³ on wet basis
Standard uncertainty of the concentration $u(C_{wet})$:	6 % of measured value
Standard uncertainty of the water vapour content $u(h_m)$:	10 % of measured value

Water vapour content	**Concentration on dry basis**	**Standard uncertainty**	**Relative standard uncertainty**
h_m	C_{dry}	$u(C_{dry})$	$u_{rel}(C_{dry})$
%	mg/m³	mg/m³	%
1	101,01	6,06	**6,00**
2	102,04	6,13	**6,00**
3	103,09	6,19	**6,01**
4	104,17	6,27	**6,01**
5	105,26	6,34	**6,02**
6	106,38	6,42	**6,03**
7	107,53	6,50	**6,05**
8	108,70	6,59	**6,06**
9	109,89	6,68	**6,08**
10	111,11	6,78	**6,10**
11	112,36	6,88	**6,13**
12	113,64	6,99	**6,15**
13	114,94	7,11	**6,18**
14	116,28	7,23	**6,22**
15	117,65	7,36	**6,25**
16	119,05	7,49	**6,30**
17	120,48	7,64	**6,34**
18	121,95	7,79	**6,39**
19	123,46	7,95	**6,44**
20	125,00	8,13	**6,50**
21	126,58	8,31	**6,56**
22	128,21	8,50	**6,63**
23	129,87	8,70	**6,70**
24	131,58	8,92	**6,78**
25	133,33	9,15	**6,86**
26	135,14	9,40	**6,95**
27	136,99	9,66	**7,05**

28	138,89	9,93	**7,15**
29	140,85	10,22	**7,26**
30	142,86	10,53	**7,37**
31	144,93	10,86	**7,50**
32	147,06	11,21	**7,63**
33	149,25	11,59	**7,76**
34	151,52	11,98	**7,91**
35	153,85	12,40	**8,06**

F.2Uncertainty associated with a concentration expressed at a oxygen reference concentration

The concentration of a measured component for oxygen reference conditions is calculated according to Formula (F.3):

$$C_{\mathrm{corr}} = C_{\mathrm{m}} \times \frac{21\% - \left(o_{\mathrm{ref}}\right)_{\mathrm{dry}}}{21\% - \left(o_{\mathrm{m}}\right)_{\mathrm{dry}}} \tag{F.3}$$

where

C_{corr} is the concentration expressed at oxygen reference conditions;

$\left(o_{\mathrm{ref}}\right)_{\mathrm{dry}}$ is the oxygen reference concentration expressed as a volume fraction on dry basis;

C_{m} is the measured concentration at the actual volume fraction of oxygen;

$\left(o_{\mathrm{m}}\right)_{\mathrm{dry}}$ is the actual volume fraction of oxygen in the dry flue gas.

The uncertainty associated with a concentration expressed on dry gas is calculated according to Formula (F.4):

$$u^2\left(C_{\mathrm{corr}}\right) = \left(C_{\mathrm{corr}}\right)^2 \times \left(\frac{u^2\left(C_{\mathrm{m}}\right)}{\left(C_{\mathrm{m}}\right)^2} + \frac{u^2\left(\left(o_{\mathrm{m}}\right)_{\mathrm{dry}}\right)}{\left(21\% - \left(o_{\mathrm{m}}\right)_{\mathrm{dry}}\right)^2} \right) \tag{F.4}$$

where

$u\left(C_{\mathrm{corr}}\right)$ is the uncertainty associated with a concentration expressed at a oxygen reference concentration;

$u\left(C_{\mathrm{m}}\right)$ is the uncertainty associated with a concentration at the actual volume fraction of oxygen;

$u\left(\left(o_{\mathrm{m}}\right)_{\mathrm{dry}}\right)$ is the uncertainty associated with the actual volume fraction of oxygen in the flue gas on dry basis.

The uncertainty associated to the concentration expressed at a reference oxygen volume fraction depends on the uncertainty of the measurement carried out at the actual oxygen volume fraction, and on the uncertainty of measurement of oxygen. It increases with the oxygen volume fraction in the sample gas as shown in Table F.2.

Table F.2 — Calculation of the uncertainty of a concentration expressed at an oxygen reference concentration

Concentration C_m of the measured component:	100 mg/m³ at actual oxygen content
Standard uncertainty of the concentration $u(C_m)$:	4,7 % of the measured value
Relative standard uncertainty of the oxygen content $u_{rel}(o_m)$:	2,5 %
Oxygen reference volume concentration o_{ref}:	11 %

Oxygen volume content	**Concentration at o_{ref} = 11 %** (calculated with o_m)	**Standard uncertainty**	**Relative standard uncertainty**
o_m	C_{corr}	$u(C_{corr})$	$u_{rel}(C_{corr})$
%	mg/m³	mg/m³	%
5	**62,50**	2,98	**4,76**
6	**66,67**	3,20	**4,81**
7	**71,43**	3,47	**4,86**
8	**76,92**	3,80	**4,95**
9	**83,33**	4,22	**5,06**
10	**90,91**	4,75	**5,22**
11	**100,00**	5,45	**5,45**
12	**111,11**	6,40	**5,76**
13	**125,00**	7,77	**6,21**
14	**142,86**	9,80	**6,86**
15	**166,67**	13,03	**7,82**
16	**200,00**	18,56	**9,28**
17	**250,00**	29,05	**11,62**
18	**333,33**	52,40	**15,72**
19	**500,00**	121,05	**24,21**
20	**1000,00**	502,20	**50,22**

Annex G
(informative)

Significant technical changes

Table G.1 — Significant technical changes

Clause	Technical change
1	Directive 2000/76/EC has been replaced by Directive 2010/75/EU.
2	Normative reference to EN 15259 related to requirements for measurement sections and sites and for the measurement objective and plan has been added.
3	Definitions have been reviewed taking into account EN 15259 and new version of VIM (2012). Detection limit is no more considered in the list of definition and in performance characteristics (repeatability at zero or quantification limit are more suitable performance characteristics).
6.2.6 and 8.6	The absorption efficiency of the first absorber shall be better than 95 % or the concentration of sulfate ion in the second absorber shall be less than the quantification limit (instead of detection limit).
8.2	For determination of homogeneity reference to the EN 15259 has been added.
11.4	Equation of s_r has been refined.
12	According to the new rules fixed in the EN 14793:2017, $s_{r,limit}$ has been recalculated.
Annex A	An estimate of the uncertainty calculated through the determination of reproducibility has been added and replace the expression: “reproducibility confidence interval”.
Annex C	The presentation of the calculation of the uncertainty budget has been improved.
Annex E	The presentation of the equivalence of Chromatography method with the Thorin method has been improved to be in line with the EN 14793:2017. Some typing errors have been corrected.
Annex F	New annex on “Calculation of the uncertainty associated with a concentration expressed on dry gas and at a oxygen reference concentration”.

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[4] ISO 5725-6:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 6: Use in practice of accuracy values*

[5] JCGM 200:2012, *International vocabulary of metrology – Basic and general concepts and associated terms (VIM)*

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