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Stationary source emissions — Determination of the mass concentration of sulphur dioxide by instrumental techniques

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National foreword

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Stationary source emissions - Determination of the mass concentration of sulphur dioxide by instrumental techniques

Émissions de sources fixes - Détermination de la concentration massique en dioxyde de soufre par des techniques instrumentales

Emissionen aus stationären Quellen - Ermittlung der Massenkonzentration von Schwefeldioxid mit instrumentellen Verfahren

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European foreword

This document (CEN/TS 17021:2017) has been prepared by Technical Committee CEN/TC 264 "Air quality", the secretariat of which is held by DIN.

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1 Scope

This Technical Specification describes a method for sampling and determining the concentration of gaseous sulphur dioxide (SO_2) emissions from stacks. This method is based on instrumental techniques. It is applicable to both periodic measurements and the calibration of automated measuring systems permanently installed on stacks, for regulatory or other purposes.

2 Normative references

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

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

EN 14793:2016, *Stationary source emission - Demonstration of equivalence of an alternative method with a reference method*

EN 15267-4, *Air quality - Certification of automated measuring systems - Part 4: Performance criteria and test procedures for automated measuring systems for periodic measurements of emissions from stationary sources*

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, *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   A reference method is fully described.

NOTE 2   A reference method can be a manual or an automated method.

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

[SOURCE: EN 15259:2007]

3.3
alternative method
AM
measurement method which complies with the criteria given by this Technical Specification 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]

3.4
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]

3.5
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]

3.6
portable automated measuring system
P-AMS
automated measuring system which is in a condition or application to be moved from one to another measurement site to obtain measurement results for a short measurement period

Note 1 to entry: The measurement period is typically 8 h for a day.

Note 2 to entry: The P-AMS can be configured at the measurement site for the special application but can be also set-up in a van or mobile container. The probe and the sample gas lines are installed often just before the measurement task is started.

[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 system (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: Calibration should not be confused with adjustment of a measuring system.

[SOURCE: EN 15058:2017]

3.8
adjustment
set of operations carried out on a measuring system so that it provides prescribed indications corresponding to given values of a quantity to be measured

Note 1 to entry: The adjustment can be made directly on the instrument or using a suitable calculation procedure.

[SOURCE: EN 15058:2017]

3.9
span gas
test gas used to adjust and check a specific point on the response line of the measuring system

Note 1 to entry: This concentration is often chosen around 80 % of the upper limit of the range

3.10
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.

3.11
interference
negative or positive effect upon the response of the measuring system, due to a component of the sample that is not the measurand

3.12
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. presence of interfering gases, ambient temperature, pressure of the gas sample.

3.13
ambient temperature
temperature of the air around the measuring system

3.14
emission limit value
ELV
limit value given in regulations such as EU Directives, ordinances, administrative regulations, permits, licences, authorizations 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.

3.15
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]

3.16
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]

3.17
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]

3.18
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]

3.19
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]

3.20
performance characteristic
one of the quantities (described by values, tolerances, range) assigned to equipment in order to define its performance

3.21
response time
duration between the instant when an input quantity value of a measuring instrument or measuring system is subjected to an abrupt change between two specified constant quantity values and the instant when a corresponding indication settles within specified limits around its final steady value

Note 1 to entry: By convention time taken for the output signal to pass from 0 % to 90 % of the final variation of indication.

3.22
short-term zero drift
difference between two zero readings at the beginning and at the end of the measurement period

3.23
short-term span drift
difference between two span readings at the beginning and at the end of the measurement period

3.24
lack of fit
systematic deviation within the range of application between the measurement result obtained by applying the calibration function to the observed response of the measuring system measuring test gases and the corresponding accepted value of such test gases

Note 1 to entry: Lack of fit can be a function of the measurement result.

Note 2 to entry: The expression "lack of fit" is often replaced in everyday language by "linearity" or "deviation from linearity".

3.25
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: Repeatability 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 Technical Specification the repeatability is expressed as a value with a level of confidence of 95 %.

3.26
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 Technical Specification, the repeatability under field conditions is expressed as a value with a level of confidence of 95 %.

3.27
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 performances of which are fulfilling 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 Technical Specification, the reproducibility under field conditions is expressed as a value with a level of confidence of 95 %.

3.28
residence time in the measuring system
time period for the sampled gas to be transported from the inlet of the probe to the inlet of the measurement cell

3.29
uncertainty
parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand

3.30
standard uncertainty
u
uncertainty of the result of a measurement expressed as a standard deviation

3.31
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)

3.32
expanded uncertainty
U
quantity defining an interval about the result of a measurement that may be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand

$$U = k \times u_c$$

Note 1 to entry: In this European Technical Specification, the expanded uncertainty is calculated with a level of confidence of 95 %.

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

3.33
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

4   Symbols and abbreviations

4.1 Symbols

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

$A(t_0)$ (result given by the analyser after adjustment at t_0 at span point – result given by the analyser after adjustment at t_0 at zero point) / (calibration gas concentration at span point – calibration gas concentration at zero point)

$B(t_0)$ result given by the analyser after adjustment at t_0 at zero point

C measured concentration

C_{corr} measured concentration corrected for drift

$\text{Drift}(A)$ {[[(result given by the analyser during the drift check at t_{end} at span point – result given by the analyser during the drift check at t_{end} at zero point) / (calibration gas concentration at span point – calibration gas concentration at zero point)] – $A(t_0)$} / ($t_{end} - t_0$)

$\text{Drift}(B)$ (result given by the analyser during the drift check at t_{end} at zero point – result given by the analyser after adjustment at t_0 at zero point) / ($t_{end} - t_0$)

f volume fraction

k	coverage factor
M_{mol}	molar mass
t	time
t_0	time of adjustment
t_{end}	time of check for drift at the end of the measurement period
u	standard uncertainty
u_c	combined uncertainty
U	expanded uncertainty
V_{mol}	molar volume

4.2 Abbreviated terms

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

AM	alternative method
AMS	automated measuring system
P-AMS	portable automated measuring system
PTFE	polytetrafluoroethene
SRM	standard reference method

5 Principle

5.1 General

This Technical Specification describes a method for sampling and determining SO_2 emissions using an instrumental technique. This Technical Specification does not prescribe a specific technique; however, it does prescribe performance criteria in Clause 7 for the analyser and the associated sampling system (the complete measuring system). The performance characteristics of the method shall meet these performance criteria. This Technical Specification also specifies requirements and recommendations for ongoing quality assurance and quality control in Clause 10.

5.2 Measuring principle

The measuring systems used for SO_2 measurements shall be extractive and typically comprise of the following parts:

— a sampling probe;

— a filter;

— a sample gas line;

— a conditioning system;

— an analytical instrument.

There are a number of instrumental techniques available for the analyser, which can measure SO_2 in emissions. Examples include infrared (IR) absorption, ultraviolet (UV) absorption, UV fluorescence and electrochemical cells. The complete sampling system and analytical system is known as a portable automated measuring system (P-AMS).

The concentration of SO_2 is measured as a volume concentration if the analyser is calibrated using a volume concentration standard. The final results for reporting are expressed in milligrams per cubic metre (mg/m^3) and reported at standard conditions (see Clause 11).

6 Description of the measuring system

6.1 General

A sample is extracted from the emission source for the required period of time at a controlled flow rate. A filter removes the dust in the sampled volume before the sample is conditioned (unless configuration 4 is being used) and passed to the analyser.

Different sampling and conditioning configurations are available in order to avoid the water vapour condensation in the measuring system.

Possible configurations are:

— Configuration 1: removal of water vapour by condensation using a cooling system;

— Configuration 2: removal of water vapour through elimination using a permeation drier;

— Configuration 3: dilution with dry, clean ambient air or nitrogen of the gas to be characterized;

— Configuration 4: maintaining a temperature of all parts of the sampling system up to the analyser.

It is important that all parts of the sampling equipment upstream of the analyser are made of materials that do not react with or absorb SO_2.

All components coming into contact with the gas shall be maintained at a temperature of at least 160 °C. For configuration 1 this only applies to components upstream of the conditioning unit. For configuration 3 this only applies to components upstream of the point of dilution. Heating is not required post the dilution point as it is a requirement to decrease the sample acid dew point to below ambient temperature (see 6.2.4.2).

NOTE   For configuration 2 it can be necessary to introduce pre-cooling apparatus before the permeation drier to avoid temperatures of over 120 °C at the permeation tubes as this is likely to cause damage.

If there are droplets present in the stack gas it should be discussed with the local competent authority if this method is appropriate.

The conditions and layout of the sampling equipment contribute to the combined uncertainty of the measurement. In order to minimize this contribution this Technical Specification specifies performance criteria for the sampling system given in Table 1.

Alternative conditioning systems exist and may be acceptable, provided they fulfil the requirements of this Technical Specification. For example, some systems put gas in depression using a simple Sonic nozzle in the collection probe in order to create a partial vacuum (between 50 hPa and 100 hPa absolute) so that the head of collection and the sample gas line does not need to be heated and water vapour condensation is avoided.

Additional analysers for other species shall not be used in series with the described measuring system unless it is known that there are no compatibility issues. For example, chemiluminescence analysers under certain conditions can convert H_2S to SO_2, hence the SO_2 analyser shall not be used downstream of a chemiluminescence analyser.

6.2 Sampling and sample gas conditioning system

6.2.1 Sampling probe

In order to reach the measurement points in 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 minimized in order to reduce the response time of the measuring system.

NOTE 1   The probe can be marked before sampling in order to demonstrate that the measurement points in the measurement plane have been reached.

NOTE 2   A sealable connection can be installed on the probe in order to introduce test gases for adjustment.

6.2.2 Filter

The filter and filter holder shall be made of inert material (e.g. ceramic or sinter metal with an appropriate pore size) and be maintained at a temperature of at least 160 °C. The particle filter shall be changed or cleaned periodically depending on the dust loading at the measurement site.

NOTE   Overloading of the particle filter can increase the pressure drop in the sample gas line.

6.2.3 Sample gas line

The sample gas line shall be heated to a temperature of at least 160 °C between the probe and the conditioning system. It shall be made of a suitable corrosion resistant material (e.g. stainless steel, borosilicate glass, ceramic or titanium; PTFE is only suitable for flue gas temperatures lower than 200 °C).

NOTE 1   The sample gas line does not require heating if a dilution system is used (configuration 3).

NOTE 2   The dew point of sulphuric acid is 120 °C to 150 °C. Some studies have shown that the dew points for some sulphate salts are typically 50 °C to 60 °C.

6.2.4 Sample gas conditioning system

6.2.4.1 Sample cooler (configuration 1) and permeation drier (configuration 2)

The sample gas cooler or the permeation drier are used before the gas enters the analyser in order to separate water vapour from the flue gas. A dew point temperature of 4 °C shall not be exceeded at the outlet of the conditioning system.

Due to ammonium-salt deposition on the tubes, permeation systems cannot be used when NH_3 is present. Annex F provides some information on the chemistry of SO_2 in the presence of NH_3.

Bacterial growth can take place under the moist conditions that occur within sample driers. An appropriate procedure for the inspection and routine cleaning, if required, of the drier shall be in place in order to prevent bacterial growth. Any manufacturer recommendations in this regard shall be followed.

NOTE   The concentrations provided by this sampling configuration are considered to be given on dry basis. However, the results can be corrected for the remaining water vapour (see EN 14790:2017, Annex B).

6.2.4.2 Dilution system (configuration 3)

The dilution technique is an alternative to hot-gas monitoring or sample gas drying. The flue gas is diluted with dry, clean, ambient air or nitrogen free from SO_2. Dilution shall be either in-stack or out-stack. The dilution ratio shall be chosen according to the objectives of the measurement and shall be compatible with the range of the analyser. It shall remain constant throughout the period of the test.

Dilution ratios are dependent upon changes in the flue gas density. Changes in the flue gas temperature, molecular weight and total stack pressure can affect the ratio and resultant concentration measurements.

NOTE 1   If significant changes in the stack temperature are expected an out-stack dilution system or a heated in-stack dilution probe can be used to control the effects of the variation in temperature.

NOTE 2   The pressure effect has been found to be linear, corresponding to approximately a 1 % increase in reading for a 3,5" H_2O increase in absolute pressure [EPA, 1994], so a correction can be applied to control the effects of the variation in pressure.

The dilution shall reduce the dew point temperature to below the ambient level. The dew point temperature at the outlet of the analyser shall be determined in order to correct the results and give them on a dry basis (see Annex B in EN 14790:2017) if the dew-point temperature is greater than 4 °C. The uncertainty associated with this correction shall be included in the uncertainty budget (see Annex B).

6.2.4.3 Heated sample gas line and heated analyser (configuration 4)

The temperature of the components coming into contact with the gas upstream of the heated analyser shall be maintained at a temperature of at least 160 °C.

The concentrations are given on wet basis and shall be corrected so that they are expressed on dry basis. The correction shall be made from the water vapour concentration in the flue gas and the uncertainty associated with this correction shall be included in the uncertainty budget (see Annex B).

6.2.5 Sample gas pump

When a pump is not an integral part of the analyser, an external pump is necessary to draw the flue gas through the apparatus. It shall be capable of operating to the flow and pressure requirements specified by the analyser manufacturer. The pump shall be resistant to corrosion, and compatible with the requirements of the analyser to which it is connected. The whole sampling system associated with the analyser, including the pump, shall meet the criterion in Table 1 related to the influence of gas pressure.

NOTE 1   The quantity of sample gas required can vary between 15 l/h and 500 I/h, depending upon the analyser and the expected response time.

NOTE 2   A sample pump is not be required if a dilution system is used.

6.2.6 Secondary filter

The secondary filter is used to separate fine dust, with a pore size of 1 μm to 2 μm. For example it can be made of glass-fibre, sintered ceramic, stainless steel or PTFE-fibre.

6.2.7 Flow controller and flow meter

This apparatus sets the required flow. A corrosion resistant material shall be used. The sample flow rate into the analyser shall be maintained within the analyser manufacturer's requirements.

NOTE   No additional flow controller or flow meter is necessary when they are part of the analyser itself.

6.3 Analyser equipment

6.3.1 General

The analytical techniques used to measure SO_2 can include, but are not restricted to, the following:

— electrochemical cells;

— non-dispersive infrared (NDIR);

— Fourier transform infrared (FTIR) spectroscopy;

— ultraviolet absorption (UVA);

— ultraviolet fluorescence (UF).

This Technical Specification does not prescribe the technique. Instead, this Technical Specification specifies performance criteria (see Table 1), regardless of the technique used to measure SO_2. Additional requirements described in method specific standards shall be observed.

6.3.2 Pressure and temperature effects

The output signal of the analyser is proportional to the density of SO_2 (number of SO_2 molecules) present in the measurement cell and depends on the absolute pressure and temperature in the measurement cell.

NOTE   The effects of variations of pressure and temperature in the measurement cell can have been taken into account by the manufacturer.

6.3.3 Sampling pump for the analyser

The sampling pump can be separate or part of the analyser. In any case, it shall be capable of operating within the specified flow requirements of the manufacturer of the analyser and pressure conditions required for the measurement cell.

NOTE   A sampling pump is not be required if a dilution system is used.

7 Performance characteristics of the method

Table 1 gives an overview of the performance characteristics of the whole measurement method including the analyser and the sampling and sample gas conditioning system. When this Technical Specification is used as an alternative method (AM) to a standard reference method (SRM), these performance characteristics shall be determined in a general performance test according to the test procedures described in EN 15267-4:2016 (that includes demonstration of equivalence to the SRM in accordance with EN 14793:2016), by an independent test laboratory accredited or recognized by the competent authorities for the implementation of tests procedures of EN 15267-4:2016.

The independent test laboratory shall check the conformity of the P-AMS with the performance criterion attached to each performance characteristics. The maximum allowable deviations as absolute values of the measured values are given as mass concentrations or as percentages of the upper limit of the range.

The applicable range is defined as 1,5 times the ELV for waste incineration processes and 2,5 times the ELV for all other processes.

NOTE   At the time of publication the Industrial Emissions Directives defines the applicable range of 1,5 times the ELV for waste incineration processes and 2,5 times the ELV for all other processes.

Table 1 — Performance characteristics of the method and associated performance criteria for the laboratory test (L) and the field test (F)

Performance characteristic	L	F	Performance criterion	Performance characteristic to be included in the uncertainty budget
Response time	X	X	≤ 200 s	
Detection limit	X		≤ 2,0 %[a]	
Repeatability standard deviation at zero point	X		≤ 2,0 %[a]	X[b]
Repeatability standard deviation at span point	X		≤ 2,0 %[a]	X[b]
Reproducibility standard deviation		X	≤ 3,3 %[a]	X[b]
Lack of fit	X		≤ 2,0 %[a]	X
Short-term zero drift	X		≤ 2,0 %[a]	X
Short-term span drift	X		≤ 2,0 %[a]	X
Influence of ambient temperature change from 5 °C to 25 °C and from 40 °C to 20 °C at zero point	X		≤ 5,0 %[a]	X
Influence of ambient temperature change from 5 °C to 25 °C and from 40 °C to 20 °C at span point	X		≤ 5,0 %[a]	X
Influence of sample gas pressure at span point, for a change Δp of 3 kPa	X		≤ 2,0 %[a]	X
Influence of sample gas flow on extractive P-AMS for a given specification by the manufacturer	X		≤ 2,0 %[a]	X
Influence of voltage, at −15 % below and at +10 % above nominal supply voltage	X		≤ 2,0 %[a]	X
Influence of vibration	X		≤ 2,0 %[a]	X
Cross-sensitivity	X		Total ≤ 4,0 %[c]	X
Losses and leakage in the sample gas line and sample gas conditioning system		X	≤ 2,0 % of the measured value	X[d]

[a]   Percentage value of upper limit of certification range unless specified otherwise.

[b]   The repeatability in the laboratory or the reproducibility in the field shall be used, whichever is greater. If the repeatability in the laboratory is used, only one of both values shall be included in the calculation: the first possibility is to choose the repeatability standard deviation got from laboratory tests corresponding to the closest concentration to the actual concentration in stack, or the higher (relative) standard deviation of repeatability independently of the concentration measured in stack.

[c]   Interferents that shall be tested are at least those given in EN 15267–4:2016, Annex B. The sums of contributions to uncertainty producing positive and negative effects are calculated separately. The maximum of their absolute value shall be compared with the performance criterion.

[d]   If the leak test is performed under severe conditions of depression, then the leak can be considered as negligible in normal conditions.

8 Suitability of the measuring system for the measurement task

An uncertainty budget shall be established by the user to determine for which measurement range the measuring system fulfils the uncertainty requirement.

If this method is used as an alternative to a standard reference method, the relative expanded uncertainty, calculated on a dry basis and before correction to oxygen reference concentration, shall not exceed 15 % of the daily emission limit value (ELV) or at the lowest limit value fixed to the plant by the local authority.

The measurement range that could be covered by the measuring system can be extended if the user demonstrates that the uncertainty with the actual variation range of influence quantities and values of interferents at a particular plant is lower than the maximum allowable expanded uncertainty.

Table 1 indicates which performance characteristics shall be included in the uncertainty budget.

The principle of calculation of the combined standard uncertainty is based on the law of 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, including the uncertainty of the calibration gas;

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

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

NOTE   When the concentration of a measured component is expressed at an O_2 reference concentration (e.g. 3 % or 11 %), the correction affects the uncertainty and can be significant, particularly if there is a significant difference between the actual and reference O_2 concentrations. Annex B provides guidance on how to account for this additional uncertainty.

Table 2 — Default influence quantities to be applied for the determination of the uncertainty budget

Influence quantity	Default variations range on site
Ambient temperature	±15 °C
Electric voltage at span level	230 V ± 20 V

Table 2 provides default values that can be used in the absence of on-site information. An example of the evaluation of an uncertainty budget is given in Annex A.

9 Field operation

9.1 Measurement section and measurement plane

Emission measurements at a plant shall be carried out such that the results are representative for the emissions from the 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 sampling 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.

9.2 Sampling strategy

9.2.1 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).

9.2.2 Measurement section and measurement plane

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

9.2.3 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 the SO_2 concentration or any other relevant component specified in 8.3 of EN 15259:2007 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.

9.2.4 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.

9.3 Choice of the measuring system

To choose an appropriate analyser, sample gas line and conditioning unit, the following characteristics of the flue gases shall be considered before a field campaign:

— flue gas moisture content and dew point;

— temperature of exhaust gases;

— dust loading;

— expected concentration range of SO_2 and emission limit values;

— expected concentration of potentially interfering substances, including at least the components listed in EN 15267-4:2016, Annex B.

Methane is a known interferent for SO_2 and emissions for gas engines are sometimes above the level tested for cross-sensitivity under EN 15267-4, hence consideration should be given to this in selecting a measuring system suitable for the measurement task.

The measurement range shall be adapted to the measuring objective. Generally, this means that the measurement range is high enough to cover the peak emission and at least 150 % of the half hourly ELV.

To avoid long response times, the sample gas line should be as short as possible. If necessary, a bypass pump should be used. A heated filter appropriate to the dust loading shall be used.

9.4 Setting of the measuring system on site

9.4.1 General

The complete measuring system, including the sampling systems, the sample gas conditioning system and the analyser, shall be connected according to the manufacturer's instructions and the nozzle of the probe placed at the measurement points in the duct (see 9.2).

The sample gas conditioning system, sampling probe, filter, connection tube and analyser shall be stabilized at the required temperature. At the same time, a constant pressure shall be achieved in the measuring chamber of the analyser.

After pre-heating, the flow passing through the sampling system and the analyser shall be adjusted to the chosen flow rate to be used during measurement.

When both the analyser and sampling system have been set-up, and before zero and span adjustments, the proper functioning of analyser and sampling system shall be checked. Any data recording and data processing system used shall be adapted to the measurement objective and to the response time of the measuring system.

9.4.2 Preliminary zero and span check, and adjustments

9.4.2.1 Test gases

The zero gas shall be a gas containing no significant amount of sulphur dioxide (For example, nitrogen or purified air).

NOTE   Some analysers can require purified air rather than nitrogen, for example UV fluorescence, as otherwise a satisfactory zero of the analyser cannot be achieved.

The span gases used to adjust the analyser shall have concentrations traceable to SI units. The expanded uncertainty on the analytical certificate of the span gas shall not exceed 2,0 % for SO_2.

When the analyser is used for regulatory purposes the span gas shall have a known concentration of approximately the half hourly ELV or 50 % to 90 % of the selected range of the analyser.

9.4.2.2 Adjustment of the analyser

At the beginning of the measuring period, zero and span gases are supplied to the analyser directly, without passing through the sampling system. Adjustments are made until the correct zero and span gas values are given by the data sampling system:

— check and adjust the zero value;

— check and adjust the span value;

— in case of adjustments, check again zero to see if there is no significant change.

NOTE   It may be necessary to use a t-piece at the interface of the test gas cylinder in order to avoid over pressurizing the analyser.

9.4.3 Check of the sampling system including the leak test

Before starting the measurement, check that there is no significant leakage in the sampling system by use of one of the two following procedures or any other relevant procedure validated during the general performance test (see Clause 7):

— zero and span gas are supplied to the analyser through the sampling system, as close as possible to the nozzle (in front of the filter if possible); differences between the readings at zero and at span point shall not exceed 2,0 % of the span value;

— assemble the complete sampling system; close the nozzle and 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.

NOTE   The leak test can be carried out before the adjustment of the analyser.

9.4.4 Zero and span checks after measurement

At the end of the measuring period and at least once a day, zero and span checks shall be performed at the inlet of the analyser by supplying test gases.

The results of these checks shall be documented. In case of deviation between checks after measurement and preliminary adjustments, values of deviation shall be indicated in the measurement report.

If the span or zero drifts are greater than 2,0 % of the span value, it is necessary to correct both for zero and span drifts (Annex E shows a procedure for correction of data for drift effect).

The drift of zero and span shall be lower than 5,0 % of the span value; otherwise, the results shall be rejected.

The concentration C_{corr} corrected according to time t for the concentration C given by the analyser shall be calculated according to Formula (1):

$$C_{corr} = \frac{C - \left(B(t_0) + \text{Drift}(B) \times t \right)}{\left(A(t_0) + \text{Drift}(A) \times t \right)} \tag{1}$$

where

$A(t_0)$ is (result given by the analyser after adjustment at t_0 at span point – result given by the analyser after adjustment at t_0 at zero point) / (calibration gas concentration at span point – calibration gas concentration at zero point);

$B(t_0)$ is the result given by the analyser after adjustment at t_0 at zero point;

$\text{Drift}(A)$ is {[[result given by the analyser during the drift check at t_{end} at span point – result given by the analyser during the drift check at t_{end} at zero point) / (calibration gas concentration at span point – calibration gas concentration at zero point)] – $A(t_0)$} / ($t_{end} - t_0$);

$\text{Drift}(B)$ is (result given by the analyser during the drift check at t_{end} at zero point – result given by the analyser after adjustment at t_0 at zero point) / ($t_{end} - t_0$);

$t_{end} - t_0$ is the duration of the measurement period in minutes (duration between adjustment and check for drift at the end of the measurement period).

An example of drift check and of drift correction is given in Annex E.

10 Ongoing quality control

10.1 Introduction

Quality control is critically important in order to ensure that the uncertainty of the measured values for sulphur dioxide is kept within the stated limits during extended automatic monitoring periods in the field. This means that maintenance, as well as zero and span adjustment procedures shall be followed, as they are essential for obtaining accurate and traceable data.

10.2 Frequency of checks

Table 3 shows the minimum required frequency of checks. The test laboratory shall implement the relevant European Standards for the determination of performance characteristics.

Table 3 — Frequency of checks

Checks	Frequency	Action criteria
Cleaning or changing of particulate filters at the sampling inlet and at the monitor inlet	Every campaign, if needed[a]	
Leak test	Every campaign	
Zero and span adjustment	Every campaign	
Drift	Every campaign	
Regular maintenance of several parts of the measuring system	As required by manufacturer	As required to maintain the performance of the analyser
Lack of fit	At least every year and after repair of the analyser	As required and when lack of fit exceeds 2,0 % of the range
Check of conditioning system (optional)[b]	Recommended annually, but the user should consider the amount of use of the system and adjust the frequency accordingly	
[a] The particle filter shall be changed periodically depending on the dust loading at the measurement site. During this filter change the filter housing shall be cleaned. Overloading of the particle filter can increase the pressure drop in the sampling system.		
[b] This test is not mandatory. Annex D provides procedure for carrying out this check.		

11 Expression of results

The measurement results shall be expressed as mass concentrations.

A volume fraction f (e.g. in 10^{-6} which is often expressed as ppm) is converted to a mass concentration C (e.g. in mg/m^3) by Formula (2):

$$C = f \frac{M_{mol}}{V_{mol}} \qquad (2)$$

where

M_{mol} is the relative molecular mass of SO_2 assuming natural isotopic abundance (64,06 g/mol);

V_{mol} is the volume occupied by one mole of gas at 273,13 K and 101,3 kPa assuming ideal gas behaviour (22,4 l/mol).

If the measurement result has to be corrected to reference conditions the corresponding equations in Annex C of EN 15259 shall be used.

12 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 point(s) in the measurement plane;

c)   information about the analyser and description of the sampling and conditioning line;

d)   operating range;

e)   details of the quality and the concentrations of the calibration gases used;

f)   details on the adjustments performed before and after actual sampling;

g)   measurement results with sampling date, time and duration;

h)   information on flue gas characteristics (temperature, velocity, moisture, pressure).

Annex A
(informative)

Example of uncertainty estimation for the method and compliance with required emissions measurement uncertainty

A.1 General

The following procedure is based on the law of propagation of uncertainty as described in EN ISO 14956 and ISO/IEC Guide 98-3. The individual standard uncertainties, the combined standard uncertainty and the expanded uncertainty are determined in accordance with the requirements of EN ISO 14956 and ISO/IEC Guide 98-3.

An example uncertainty budget is provided based on synthetic data and assuming the measuring system performance characteristics were determined by an independent laboratory in accordance with EN 15267-3 (i.e. assuming a scenario where the P-AMS has been tested prior to the publication of EN 15267-4).

A.2 Elements required for the uncertainty determinations

A.2.1 Model function

The Model function describes the relationship between the output value y and input quantities x_i :

$$y = f\left(x_1, x_2, \ldots, x_N\right) \tag{A.1}$$

The input quantities are a combination of variables and constants, where in the idealized situation physical parameters such as ambient pressure and temperature remain constant between calibration and measurement, whilst variables such as the response of an analyser are 'calibrated out' using reference materials. However, this is rarely the case as, for example, the calibration gas (an input quantity) has some uncertainty (an influence quantity). Consequently, it is necessary to determine the uncertainty (influence quantity) of each input quantity (uncertainty source) and then combine these in order to estimate the uncertainty of the output value.

A.2.2 Determination of uncertainty

The uncertainty of each source is acquired from calibration certificates, repeated measurements, measurements to determine the magnitude of influence across a given range, or a combination of all of these.

The standard uncertainty determined from a series of repeat measurements is given by:

$$u_i = \sqrt{\frac{1}{n-1} \sum_{j=1}^{n} \left(q_j - \bar{q}\right)^2} \tag{A.2}$$

where

u_i is the standard uncertainty of the ith uncertainty source;

q_j is the jth repeat reading of the output quantity;

$\bar{q}$ is the mean of all q_j ;

n is the number of repeat measurements.

For uncertainty sources where the upper and lower bounds of deviation are known, the standard uncertainty is given by:

$$u_i = \frac{\sqrt{\left(x_{i,max} - x_{i,adj}\right)^2 + \left(x_{i,min} - x_{i,adj}\right)\left(x_{i,max} - x_{i,adj}\right) + \left(x_{i,.min} - x_{i,adj}\right)^2}}{\sqrt{3}}$$ (A.3)

where

$x_{i,max}$ is the maximum quantity of the ith uncertainty source;

$x_{i,min}$ is the minimum quantity of the ith uncertainty source;

$x_{i,adj}$ is the nominal value of the ith uncertainty source (usually the value at calibration).

The formula uses a divisor of $\sqrt{3}$, hence a rectangular probability distribution is assumed, i.e. an equal probability of the input quantity taking a value across the interval between these limits. If the deviations from the upper and lower bounds are equal $\left(\left|x_{i,max} - x_{i,adj}\right| = \left|x_{i,min} - x_{i,adj}\right| = \Delta x_i\right)$ then Formula (A.3) simplifies to:

$$u_i = \frac{\Delta x_i}{\sqrt{3}}$$ (A.4)

or if either $x_{i,max} = x_{i,adj}$ or $x_{i,min} = x_{i,adj}$ then Formula (A.3) simplifies to:

$$u_i = \frac{x_{i,max} - x_{i,min}}{\sqrt{3}}$$ (A.5)

The divisor in Formulae (A.3), (A.4) and (A.5) is exchanged for other values for alternative probability distributions as laid out in EN ISO 14956 and ISO/IEC Guide 98-3.

If uncertainties are used from certificates the standard uncertainty is found by dividing the uncertainty value by the quoted coverage factor k.

A.2.3 Combined standard uncertainty

In accordance with the law of propagation of uncertainty set out in EN ISO 14956 and ISO/IEC Guide 98-3 the combined uncertainty as a function of output value y is determined by combining uncertainties as a function of x by:

$$u_c(y) = \sqrt{\sum_{i=1}^{N} c_i^2 u^2(x_i)}$$ (A.6)

where

u_c is the combined standard uncertainty;

c_i is the sensitivity coefficient of the ith uncertainty;

N is the total number of uncertainty sources.

The sensitivity coefficient c_i relates the uncertainty u(xi) to the output y. Often, particularly when the uncertainty source and output are of the same unit, the coefficient takes the value of unity. Conversely, when the units are not identical the coefficient in effect becomes a factor to convert between one set of units and the other. Otherwise, either the coefficient can be a known value (possibly determined via experiment, e.g. effect of ambient temperature on concentration output) or is determined from the partial differential of the model function with respect to the input quantity:

$$\frac{\partial f}{\partial x_i} \tag{A.7}$$

A.2.4 Expanded uncertainty

The combined standard uncertainty is multiplied by the coverage factor k to give a confidence interval of approximately 95 %. The value of the coverage factor is $k_{95} = 2$ unless there is more than one random uncertainty source. Where this is the case the effective degrees of freedom v_{eff} are determined using the Welch-Satterthwaite formula and the student t table to determine a modified coverage factor $k_{95} = t_{95}$:

$$v_{eff} = \frac{u_c^4}{\sum_{i=1}^{N} \frac{u_i^4}{v_i}} \tag{A.8}$$

where

v_i is the degrees of freedom of the ith uncertainty source.

The degrees of freedom of each systematic uncertainty source is considered as infinity whilst those for each random source are determined by:

$$v = n - 1 \tag{A.9}$$

Where n is the number of repeat measurements carried out in determining the uncertainty via standard deviation.

Having determined v_{eff} the modified coverage factor t_{95} is found in the student t table (Table A.1).

Table A.1 — Student t table

v_{eff}	t_{95}	v_{eff}	t_{95}	v_{eff}	t_{95}	v_{eff}	t_{95}
1	13,97	7	2,43	18	2,15	45	2,06
2	4,53	8	2,37	20	2,13	50	2,05
3	3,31	10	2,28	25	2,11	60	2,04
4	2,87	12	2,23	30	2,09	80	2,03
5	2,65	14	2,20	35	2,07	100	2,02
6	2,52	16	2,17	40	2,06	∞	2,00

A.2.5 Uncertainty budget template

It is recommended that the uncertainty budget is presented in tabular format including information with respect to uncertainty sources, probability distributions, sensitivity coefficients, combined standard and expanded uncertainties (Table A.2):

Table A.2 — Recommended uncertainty budget template

Symbol	Source of uncertainty	Value	Probability distribution	Divisor	c_i	$c_i u(x_i)$	v_i or v_{eff}
u_c	Combined standard uncertainty		normal			$\sqrt{\sum_{i=1}^{N} c_i^2 u_i^2(x_i)}$	$\dfrac{u_c^4}{\sum_{i=1}^{N} \dfrac{u_c^4}{v_i}}$
U_{95}	Expanded uncertainty		t-distribution			$k_{95} u_c$	

A.3 Example uncertainty budget

A.3.1 Identification of uncertainty sources

A.3.1.1 General

A list of uncertainty sources that are expected to affect the output quantity is compiled (Table A.3). Generally, uncertainty sources are expected to correlate with performance characteristics (Clause 6, Table 1). Consequently, for systems type approved in accordance with EN 15267-3 or EN 15267-4 the issued certificate will contain information that can be used in compiling the uncertainty budget.

Table A.3 — Identified uncertainty sources

Number	Source of uncertainty	Assigned symbol
1	Concentration indicated by the analyser	u_{read}
2	Repeatability standard deviation at span point[a]	u_r
3	Lack of fit	u_{lof}
4	Short-term zero drift	$u_{d,z}$
5	Short-term span drift	$u_{d,s}$
6	Influence of ambient temperature	u_{at}
7	Influence of electrical voltage	u_v
8	Influence of vibration	u_{vib}
9	Influence of sample gas pressure	u_p
10	Influence of sample gas flow	u_f
11	Cross-sensitivity	u_{int}
12	Losses and leakage in the sampling system	u_{loss}
13	Calibration gas	u_{CRM}
[a] As described previously (see Table 1) either the repeatability determined at zero or span level is used in the uncertainty calculation.		

A.3.1.2 Concentration indicated by the analyser

The uncertainty due to the resolution of the analyser u_{read} is considered as negligible and is excluded from the budget. Any uncertainty less than 5 % of the greatest uncertainty may be excluded.

A.3.1.3 Uncertainty sources with rectangular probability distributions

Using lack of fit as an example, there is an equal probability that a value is taken within the interval $[-x_{i,\max}; +x_{i,\max}]$. Furthermore, as the deviation from the upper and lower bounds is equal Formula (A.4) is applied:

$$u_{\text{lof}} = \frac{x_{\text{lof,max}} - x_{\text{lof,adj}}}{\sqrt{3}}$$

Other uncertainty sources with a rectangular probability distribution are listed below:

— Short-term zero drift $u_{d,z}$;

— Short-term span drift $u_{d,s}$;

— Lack of fit u_{lof};

— Influence of ambient temperature u_t;

— Influence of electrical voltage u_{v};

— Influence of vibration u_{vib};

— Influence of sample gas pressure u_{p};

— Influence of sample gas flow u_{f};

— Losses and leakage in the sampling system u_{loss}.

The applicability of Formulae (A.3), (A.4) and (A.5) to the above uncertainty sources depends on whether there is an equal probability of the input quantity taking a value across the uncertainty interval. For example, for losses and leakage in the sampling system the chances of sample being either gained or lost are not equal. Indeed, it would be reasonable to assume that sample can only be lost, in which case Formula (A.5) is applicable as with this assumption $x_{i,\max} = x_{i,\text{adj}}$.

For some performance characteristics the range across which the influence is determined is not necessarily the same in EN 15267-3 as in EN 15267-4. However, as the influence value is quoted for a defined range it is usually possible to determine the sensitivity to the input quantity and from this estimate the contribution to the uncertainty budget. For example, the influence of ambient temperature is quoted across a given temperature range, hence normalization to the range gives the sensitivity per temperature unit. As shown in Table A.5 the product of this with the ambient temperature variation across the monitoring period estimates the uncertainty contribution from this input quantity.

A.3.1.4 Cross-Sensitivity

In cross-sensitivity testing all positive and negative deviations from the measurand zero point and span point due to each potential interferent listed in Annex B of EN 15267-4:2017 are summed giving four values. The maximum absolute value of the four is taken as the value for the cross-sensitivity

performance characteristic. Hence, the simplest approach to this uncertainty source is to use this value and assume a rectangular probability distribution (i.e. Formula (A.4) is applicable).

Alternatively, if sufficient information is available (e.g. from the certificate) the uncertainty can be determined by combining knowledge of the individual sensitivity to each interferent with the maximum concentration reached by each interferent during the monitoring period. With this approach again all positive and negative deviations in excess of 0,5 % of the span point are summed at zero point and span point and the greatest absolute value of the four taken as the uncertainty for use in the uncertainty budget.

The former approach is used in the following example.

A.3.1.5 Uncertainty sources with normal probability distributions

The repeatability standard deviation at span point is determined by repeat measurements, hence the probability distribution is normal resulting in a divisor of unity.

The calibration gas uncertainty is of a normal probability distribution quoted at 95 % confidence, $k = 2$ (i.e. an expanded uncertainty). The standard uncertainty is returned by dividing the expanded uncertainty by the quoted coverage factor.

A.3.2 Site specific conditions

A.3.2.1 General

Table A.4 — Site specific conditions

Specific conditions	Value/range
Range of analyser	0 to 75 mg/m^3 (0 to 26 × 10^{-6})
Studied concentration of SO$_2$: limit value of SO$_2$ for the site at an oxygen reference volume concentration	50 mg/m^3
Conditions on the field Sample flow during adjustment Sample flow variation during monitoring Sample pressure during adjustment Sample pressure variation during monitoring Ambient temperature during adjustment Ambient temperature variation during monitoring Voltage during adjustment[a] Voltage variation during monitoring	60 l/h 55 l/h to 65 l/h 100 kPa 97,5 kPa to 102,5 kPa 285 K 283 K to 308 K 110 V 107 V to 115,5 V
Oxygen reference volume concentration: O$_{2,ref}$	11 %
Calibration gas Reading of calibration gas during checking of sampling system SO$_2$ in N$_2$, without interferent	26 × 10^{-6} × (1 ± 2 %), $k = 2$ 25,7 × 10^{-6}

> [a]   110V is used as the example as this is a typical supply voltage for many oil refineries across Europe. Other installations can have a different supply voltage.

A.3.2.2   Result of example uncertainty calculation

Partial differentials are not required to determine the sensitivity coefficients c_i as the data are taken from the type approval certificate (although as these data are synthetic no actual certificate exists), which provides the direct impact of each uncertainty source on the output. Consequently, as the sensitivity is embedded within the value (e.g. for ambient temperature 0,2 % / 10 K) the sensitivity coefficients serve for most uncertainty sources to convert the relative value (i.e. values expressed as a % of certified range) to an absolute uncertainty (ppm).

Table A.5 — Uncertainty budget calculation

Symbol	Source of uncertainty	Value	Probability distribution	Divisor d	c_i	$c_i u(x_i)$	V_i or V_{eff}
u_r	Repeatability standard deviation at span point	0,35 %	normal	1	$\dfrac{R}{100}$	$c_r \dfrac{0,35}{d_r}$	$n-1$
u_{lof}	Lack of fit	0,4 %	rectangular	$\sqrt{3}$	$\dfrac{R}{100}$	$c_{lof} \dfrac{0,4}{d_{lof}}$	∞
$u_{d,z}$	Zero drift	0,01 %	rectangular	$\sqrt{3}$	$\dfrac{R}{100}$	$c_{d,z} \dfrac{0,01}{d_{d,z}}$	∞
$u_{d,s}$	Span drift	0,5 %	rectangular	$\sqrt{3}$	$\dfrac{R}{100}$	$c_{d,s} \dfrac{0,5}{d_{d,s}}$	∞
u_{at}	Influence of ambient temperature	0,2 % / 10 K	rectangular	$\sqrt{3}$	$\dfrac{1}{10}\dfrac{R}{100}$	$c_{at} \dfrac{0,2\sqrt{\left(t_{max}-t_{adj}\right)^2 + \left(t_{min}-t_{adj}\right)\left(t_{max}-t_{adj}\right) + \left(t_{min}-t_{adj}\right)^2}}{d_{at}}$	∞
u_v	Influence of electrical voltage	0,12 % / 10 V	rectangular	$\sqrt{3}$	$\dfrac{1}{10}\dfrac{R}{100}$	$c_v \dfrac{0,12\sqrt{\left(v_{max}-v_{adj}\right)^2 + \left(v_{min}-v_{adj}\right)\left(v_{max}-v_{adj}\right) + \left(v_{min}-v_{adj}\right)^2}}{d_v}$	∞
u_{vib}	Influence of vibration	0,4 %	rectangular	$\sqrt{3}$	$\dfrac{R}{100}$	$c_{vib} \dfrac{0,4}{d_{vib}}$	∞
u_p	Influence of sample gas pressure	1,0 % / 3 kPa	rectangular	$\sqrt{3}$	$\dfrac{1}{3}\dfrac{R}{100}$	$c_p \dfrac{1,0\left(p_{max}-p_{adj}\right)}{d_p}$	∞
u_f	Influence of sample gas flow	0,2 % / 10 l.h^{-1}	rectangular	$\sqrt{3}$	$\dfrac{1}{10}\dfrac{R}{100}$	$c_f \dfrac{0,2\left(f_{max}-f_{adj}\right)}{d_f}$	∞

Symbol	Source of uncertainty	Value	Probability distribution	Divisor d	c_i	$c_i u(x_i)$	V_i or V_{eff}
u_{int}	Cross-sensitivity	1,4 %	rectangular	$\sqrt{3}$	$\dfrac{R}{100}$	$c_{int}\dfrac{1,4}{d_{int}}$	∞
u_{loss}	Losses and leakage in the sampling system	0,3 ppm	rectangular	$\sqrt{3}$	1	$c_{loss}\dfrac{l_{max}-l_{min}}{d_{loss}}$	∞
u_{CRM}	Calibration gas	0,5 ppm, $k=2$	normal	2	1	$c_{CRM}\dfrac{0,5}{d_{CRM}}$	∞
u_c	**Combined standard uncertainty**		**normal**			$\sqrt{\sum_{i=1}^{N}c_i^2 u_i^2(x_i)}$	$\dfrac{u_c^4}{\sum_{i=1}^{N}\dfrac{u_c^4}{V_i}}$
U_{95}	**Expanded uncertainty**		**t-distribution**			$k_{95}u_c$	

Table A.6 — Populated uncertainty budget

Symbol	Source of uncertainty	Value	Probability distribution	Divisor d	c_i	$c_i u(x_i)$	$_i$ or $_{eff}$
u_r	Repeatability standard deviation at span point	0,35 %	normal	1	$\dfrac{26}{100}=0,260$	$0,260\dfrac{0,35}{1}=0,091$	19
u_{lof}	Lack of fit	0,4 %	rectangular	$\sqrt{3}$	$\dfrac{26}{100}=0,260$	$0,260\dfrac{0,4}{\sqrt{3}}=0,060$	∞
$u_{d,z}$	Zero drift	0,01 %	rectangular	$\sqrt{3}$	$\dfrac{26}{100}=0,260$	$0,260\dfrac{0,01}{\sqrt{3}}=0,002$	∞
$u_{d,s}$	Span drift	0,5 %	rectangular	$\sqrt{3}$	$\dfrac{26}{100}=0,260$	$0,260\dfrac{0,5}{\sqrt{3}}=0,075$	∞
u_{at}	Influence of ambient temperature	0,2 % / 10 K	rectangular	$\sqrt{3}$	$\dfrac{1}{10}\dfrac{26}{100}=0,026$	$0,026\dfrac{0,2\sqrt{(308-285)^2+(283-285)(308-285)+(283-285)^2}}{\sqrt{3}}=0,066$	∞
u_v	Influence of electrical voltage	0,12 % / 10 V	rectangular	$\sqrt{3}$	$\dfrac{1}{10}\dfrac{26}{100}=0,026$	$0,026\dfrac{\sqrt{(115,5-110)^2+(107-110)(115,5-110)+(107-110)^2}}{\sqrt{3}}=0,009$	∞
u_{vib}	Influence of vibration	0,4 %	rectangular	$\sqrt{3}$	$\dfrac{26}{100}=0,260$	$0,260\dfrac{0,4}{\sqrt{3}}=0,060$	∞

Symbol	Source of uncertainty	Value	Probability distribution	Divisor d	c_i	$c_i u(x_i)$	ν_i or ν_{eff}
u_p	Influence of sample gas pressure	1,0 % / 3 kPa	rectangular	$\sqrt{3}$	$\dfrac{1}{3}\dfrac{26}{100}=0,087$	$0,087\dfrac{1,0(102,5-100)}{\sqrt{3}}=0,125$	∞
u_f	Influence of sample gas flow	0,2 % / 10 l/h	rectangular	$\sqrt{3}$	$\dfrac{1}{10}\dfrac{26}{100}=0,026$	$0,026\dfrac{0,2(65-60)}{\sqrt{3}}=0,015$	∞
u_{int}	Cross-sensitivity	1,4 %	rectangular	$\sqrt{3}$	$\dfrac{26}{100}=0,260$	$0,260\dfrac{1,4}{\sqrt{3}}=0,210$	∞
u_{loss}	Losses and leakage in the sampling system	$0,3 \times 10^{-6}$	rectangular	$\sqrt{3}$	1	$1\dfrac{0,3}{\sqrt{3}}=0,173$	∞
u_{CRM}	Calibration gas	$0,5 \times 10^{-6}$ $k=2$	normal	2	1	$1\dfrac{0,5}{2}=0,250$	∞
u_c	**Combined standard uncertainty** (10^{-6})		**normal**			**0,419**	**n/a**
U_{95}	**Expanded uncertainty** (10^{-6})		$k=2$			**0,838**	

A.4 Evaluation of compliance with a required measurement uncertainty

Using Formula (2) the expanded uncertainty is converted into mass concentration, giving:

$$U_{95} = 2,394 \text{ mg/m}^3$$

NOTE 1   The uncertainties associated with M_{mol} and V_{mol} are negligible compared to other sources described in the uncertainty budget and hence are neglected.

Using waste incinerators as the example; the Industrial Emissions Directive requires that the expanded uncertainty at 95 % confidence for a single measured result on a dry basis shall not exceed 20 % of the daily emission limit value. Also, assuming the method is being used as an alternative to the SRM, there is a requirement to demonstrate that the uncertainty of the AM does not exceed that of the SRM. EN 14791 specifies an expanded uncertainty 20 % of the daily ELV, i.e. identical to the directive requirement. However, this Technical Specification requires demonstration of an expanded uncertainty of 15 % of the daily ELV, the most stringent of the three requirements. Consequently, conformance to the uncertainty requirement of this Technical Specification demonstrates conformance with all requirements.

NOTE 2   All uncertainty values are under dry conditions and before conversion to O_2 reference concentration.

The daily emission limit value for SO_2 from a waste incineration processes is 50 mg/m³, hence:

$$U_{\text{req}} = 50 \times \frac{15}{100} \text{ mg/m}^3 = 7{,}5 \text{ mg/m}^3$$

$$U_{95} = 2{,}394 \text{ mg/m}^3$$

$$U_{95} \le U_{\text{req}}$$

The expanded uncertainty conforms to the required uncertainty requirements.

Where the instrumental technique measures wet sample there is additional uncertainty to take into account, as the determined expanded uncertainty associated with the measurement shall be compared to the relevant requirement on a dry basis and before correction to oxygen reference conditions. Annex C provides method for estimating the uncertainty associated with a measurement where it is necessary to convert the measurement result to dry conditions.

Annex B
(informative)

Calculation of the uncertainty associated with a concentration expressed under dry conditions and at an oxygen reference concentration

B.1 Uncertainty associated with a concentration expressed under dry conditions

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

$$C_{dry} = C_{wet} \frac{100\%}{100\% - h_m}$$

(B.1)

where

$\quad C_{dry}$ is the concentration expressed on dry basis;

$\quad C_{wet}$ is the concentration expressed on wet basis;

$\quad h_m$ is the volume fraction of water vapour.

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

$$u^2\left(C_{dry}\right) = \left(C_{dry}\right)^2 \times \left(\frac{u^2\left(C_{wet}\right)}{\left(C_{wet}\right)^2} + \frac{u^2\left(h_m\right)}{\left(100\% - h_m\right)^2} \right)$$

(B.2)

where

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

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

$\quad u\left(h_m\right)$ is the uncertainty associated with the water vapour volume fraction.

Table B.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 $u(h_m)$ .... 9 % of measured value	

Water vapour content h_m %	Concentration on dry basis C_{dry} mg/m³	Standard uncertainty $u(C_{dry})$ mg/m³	Relative standard uncertainty $u_{rel}(C_{dry})$ %
1	101,01	6,06	6,00
2	102,04	6,13	6,00
3	103,09	6,19	6,01
4	104,17	6,26	6,01
5	105,26	6,34	6,02
6	106,38	6,41	6,03
7	107,53	6,49	6,04
8	108,70	6,58	6,05
9	109,89	6,67	6,07
10	111,11	6,76	6,08
11	112,36	6,86	6,10
12	113,64	6,96	6,12
13	114,94	7,07	6,15
14	116,28	7,18	6,18
15	117,65	7,30	6,21
16	119,05	7,43	6,24
17	120,48	7,56	6,28
18	121,95	7,70	6,32
19	123,46	7,85	6,36
20	125,00	8,01	6,41
21	126,58	8,18	6,46
22	128,21	8,35	6,51
23	129,87	8,54	6,57
24	131,58	8,74	6,64
25	133,33	8,94	6,71
26	135,14	9,17	6,78
27	136,99	9,40	6,86
28	138,89	9,65	6,95
29	140,85	9,91	7,04
30	142,86	10,19	7,13
31	144,93	10,49	7,24
32	147,06	10,80	7,34
33	149,25	11,13	7,46
34	151,52	11,49	7,58
35	153,85	11,87	7,71

B.2 Uncertainty associated with a concentration expressed at a O₂ reference concentration

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

$$C_{\text{corr}} = C_{\text{m}} \times \frac{21\% - \left(o_{\text{ref}}\right)_{\text{dry}}}{21\% - \left(o_{\text{m}}\right)_{\text{dry}}}$$

(B.3)

where

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

$\left(o_{\text{ref}}\right)_{\text{dry}}$ 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;

$\left(o_{\text{m}}\right)_{\text{dry}}$ 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 (B.4):

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

(B.4)

where

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

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

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

The uncertainty associated with the measured concentration expressed at a reference oxygen volume fraction depends on the uncertainty of the measured under dry conditions and the uncertainty of the oxygen measurement. It increases with the oxygen volume fraction in the sample gas as shown in Table B.2.

Table B.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**

<div align="center">

Annex C
(normative)

Annual lack of fit test

</div>

C.1 Description of test procedure

In this test procedure a regression line is established between the analyser readings and the reference values. Then the mean of the analyser readings at each reference material level is calculated. Then the deviation (residual) of this average to the regression line is determined.

C.2 Establishment of the regression line

A linear regression for the function in Formula (C.1) is established:

$$x_i = a + B(c_i - \overline{c})$$

(C.1)

For the calculation, all measurement points are taken into account. The total number of measurement points (n) is equal to the product of the number of reference material levels (including zero) and the number of repetitions at each reference level.

a is found from:

$$a = \frac{1}{n}\sum_{i=1}^{n} x_i$$

(C.2)

where

a is the mean of all x_i;

x_i is the ith analyser reading;

n is the total number of analyser readings.

B is found from:

$$B = \frac{\sum_{i=1}^{n} x_i (c_i - \overline{c})}{\sum_{i=1}^{n} (c_i - \overline{c})^2}$$

(C.3)

where

$\overline{c}$ is the mean of all c_i;

c_i is the ith reference material value.

Secondly the function $x_i = a + B(c_i - \overline{c})$ is converted into $x_i = A + Bc_i$ through calculation of A according to Formula (C.4):

$$A = a - B\overline{c}$$

(C.4)

C.3 Calculation of the residuals

The mean analyser reading at each reference concentration level is found from:

$$\overline{x_c} = \frac{1}{m_c} \sum_{i=1}^{m_c} x_{c,i} \tag{C.5}$$

where

$\overline{x_c}$ is the mean of all x_i at reference concentration level c (i.e. all $x_{c,i}$);

$x_{c,i}$ is the ith analyser reading at reference concentration level c;

m_c is the number of readings taken at reference concentration level c.

The residual d_c at each reference concentration level is found from:

$$d_c = \overline{x_c} - (A + Bc) \tag{C.6}$$

d_c is expressed with respect to the upper limit of the certification range from:

$$d_{c,\text{rel}} = \frac{d_c}{x_u} \cdot 100\ \% \tag{C.7}$$

C.4 Test requirements

Following the procedure described above, the annual lack of fit test shall meet the below minimum requirements:

— the certified range of the analyser shall be covered by a minimum of five equally distributed reference concentration levels including zero;

— any supplementary range shall be covered by a minimum of five approximately equally distributed reference concentration levels including zero;

— the analyser mean at each reference concentration level shall be determined from three consecutive analyser readings.

Whether using a single gas cylinder with a dilution system or a series of cylinders the concentration at each reference level shall be known to an uncertainty of not more than 2,0 % of either certification or supplementary range, as applicable.

Annex D
(informative)

Annual check of conditioning system

D.1 General

An annual test can be carried out to check that the conditioning system is successfully removing water vapour from sampled gas avoiding significant losses of SO_2 via either demonstration through participation in a suitable proficiency testing scheme or through user testing.

D.2 Demonstration via proficiency testing scheme participation

An appropriate scheme is a scheme based either on a real stack or a stack simulation facility (often referred to as a 'test bench') operated by a competent organization, where one possible method to demonstrate competence is accreditation under EN ISO/IEC 17043.

If the user has measured during participation in a scheme a wet gas stream of SO_2 containing a minimum of 10 % water vapour by volume and the provider has awarded a *satisfactory* score then it is considered that the user has demonstrated that the conditioning unit is operating successfully.

Generally, when a *satisfactory* score is awarded to a participant in a proficiency testing scheme this means that the measurand has been quantified to less than or equal to twofold the allowable deviation (deviation from the reference value). The allowable deviation is usually linked to uncertainty requirements in applicable directives. Therefore, for monitoring of SO_2, scheme providers will often set the allowable deviation to be not more than 20 % of the ELV of the industrial process plant visited or simulated.

D.3 Demonstration via direct user testing of conditioning system

The user can demonstrate successful operation of the conditioning system by carrying out direct testing as outlined below.

For this method a gas blender including liquid injection system is required calibrated by a competent organization, where one method to demonstrate competence is by EN ISO/IEC 17025 accreditation. It is expected that a wet SO_2 gas mixture is created either by injection and vaporization of liquid water into a heated stream of gaseous SO_2 in carrier gas or injection of a liquid sample including a known amount of dissolved SO_2 into heated carrier gas.

The gas blender is used to generate an amount of SO_2 either representative of the type of processes that are typically measured or approximating the analyser certification range (assuming the analyser has been certified under either EN 15267-3 or EN 15267-4). The water content by volume is at least 10 %.

The uncertainty of the reference concentration of SO_2 is calculated by combining the standard uncertainties associated with the flow rate of the carrier gas, flow rate of SO_2 gas and rate of liquid water injection. Or if a liquid sample containing dissolved SO_2 is used the standard uncertainties that are combined include the flow rate of the carrier gas, rate of liquid injection and amount of dissolved SO_2. Standard uncertainties are combined via the root sum of squares and the result multiplied by a coverage factor of $k = 2$ to give an expanded uncertainty.

The measuring system is calibrated using zero and span gases injected directly into the analyser (see 9.4.2.2). The measuring system is then used to sample the wet SO_2 generated via the gas blender.

NOTE   It can be necessary to use a t-piece between the gas blender and the measuring system inlet to avoid over-pressurizing the measuring system.

Three consecutive readings are taken and the mean determined. If the measured mean is ≤ 2,0 % of the reference concentration of SO_2 successful operation of the conditioning unit has been demonstrated.

The test criterion of 2,0 % can be adjusted if the uncertainty associated with the reference concentration is a significant proportion of the test criterion. If the uncertainty associated with the reference concentration is greater than 0,3 times the test criterion then the test criterion is adjusted as below:

$$a' = \sqrt{a^2 + u_{cr}^2}$$ (D.1)

where

u_{cr} is the expanded uncertainty associated with the reference concentration;

a is the test criterion;

a' is the adjusted test criterion.

In this situation, if the measured mean resides within the limit described by a' then it is considered that successful operation of the conditioning unit has been demonstrated.

Annex E
(informative)

Procedure for correction of data from drift effect

Table E.1 shows a spreadsheet example based on the correction procedure given in 9.4.4.

Table E.1 — Spreadsheet example for correction of data from drift effect

	B	C	D	E	F	G	H	I
				Input data				
3		concentration unit		10^{-6}				
4				concentration given by the analyser				
5			calibration gas concentration	adjustment at t_0 (before measurement)	check at t_f (end of measurement)			
6		span point	900	898	900			:to be filled
7		zero point	0	3	1			: list choice
8		time		10:00:00	15:00:00			
9		duration (h)		5:00:00 (F8-E8)				
10		duration (min)		300 (HOUR(E9)*60+ MINUTE(E9)				
11								
12								
13				Calculation of zero and span drift				
14				adjustment	check	deviation		
15		A: span point		0,99444 (E6-E7)/(D6-D7)	0,99889 (F6-F7)/(D6-D7)	0,00444 (F15-E15)		
16		B_{corr}: zero point corrected of span		3,017 (E7/E15)	1,001 (F7/F15)	−2,016 (F16-E16)		
17								
18		drift at zero point	−0,22 % ((G16)/D6)					
19		drift at span point	0,44 % ((D6*G15)/D6)					
20								
21		*If the drift at zero or at the span point is greater than 2 % of the selected span point*						
22								
23	Equation to calculate the concentration C_{corr} corrected according to time t for the concentration C given by the analyser							
24								

25				value at t_0	drift per min			
26		A (span point)		0,994444 (E15)	0,00001481 (G15/E10)			43
27		B (zero point not corrected of span)		3,000000 (E7)	–0,006667 ((F7-E7)/E10)			
28								
29	$C_{\text{corr}} = [C - (B(t_0) + \text{Drift}(B) \times t)] / [A(t_0) + \text{Drift}(A) \times t]$							
30	$C_{\text{corr}} = [C - (E27 + F27 \times t)] / [E26 + F26 \times t]$							
31	:							
32	$\rightarrow$ $C_{\text{corr}} =$	$(C-(3{,}000000-0{,}006667*t))/(0{,}994444+0{,}00001481*t)$						
33	*To apply the formula in a calculation file:*							
34	*– copy cell C32 above;* *– in the calculation file click on "edition – special paste – values" in the first cell dedicated to a corrected value;* *– insert before formula "=" then the concentration value measured and replace "t" by its value in min.*							
35								

Annex F
(informative)

Chemistry of SO$_2$ aqueous solubility

Generally, the reactivity and solubility of SO$_2$ in aqueous media is strongly influenced by pH and temperature. For example, when the solute in water, SO$_2$ can be completely evolved by an increase in temperature.

In water, SO$_2$ is partly physically dissolved and partly chemically bound as sulphite (H$_2$SO$_3$), which is a relatively weak acid. Consequently, with addition of a stronger acid (e.g. sulphuric acid, H$_2$SO$_4$) the solubility of SO$_2$ can be reduced to negligible levels.

When alkaline components such as NH$_3$ are present, a rapid reaction of the sulphite will shift the solubility equilibrium resulting in an increase in the amount of SO$_2$ dissolved. Under oxidizing conditions, SO$_2$ reacts slowly with oxygen (air) to form SO$_3$, which reacts with water to form sulphuric acid irreversibly. These effects are well known at plants with DeNO$_x$-Units when sulphur containing fuels are combusted, as corrosion of the exhaust system can occur in areas where the surface temperature is below the acid dew point. Hence, in the presence of NH$_3$ measuring systems using conditioning units are at risk of under-reading the amount of emitted SO$_2$.

Again, SO$_2$ losses can be prevented by addition of a strong acid (e.g. 10 % H$_3$PO$_4$ or 10 % H$_2$SO$_4$) at the inlet of the conditioning unit. If the pH of the condensate is sufficiently lowered the reaction of SO$_2$ in the presence of NH3 no longer takes place and losses are reduced to negligible levels (such conditioning systems are commercially available). Evidence available to date has shown that maintaining of pH of ~4 is sufficiently acidic to avoid significant losses of SO$_2$ in some applications.

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