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Incorporating corrigendum April 2014

BSI Standards Publication

Ambient air — Standard method for the measurement of the concentration of sulphur dioxide by ultraviolet fluorescence

National foreword

This British Standard is the UK implementation of EN 14212:2012, incorporating corrigendum April 2014. It supersedes BS EN 14212:2005 which is withdrawn.

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English Version

Ambient air - Standard method for the measurement of the concentration of sulphur dioxide by ultraviolet fluorescence

Qualité de l'air ambiant - Méthode normalisée pour le mesurage de la concentration en dioxyde de soufre par fluorescence U.V.

Luftqualität - Messverfahren zur Bestimmung der Konzentration von Schwefeldioxid mit Ultraviolett-Fluoreszenz

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Contents

Foreword 4
1 Scope 5
2 Normative references 5
3 Terms and definitions 6
4 Abbreviated terms 11
5 Principle 11
5.1 General 11
5.2 Measuring principle 11
5.3 Type approval test 12
5.4 Field operation and quality control 12
6 Sampling 13
6.1 General 13
6.2 Sampling location 13
6.3 Sampling system 13
6.4 Control and regulation of sample flow rate 14
6.5 Sampling pump for the manifold 14
7 Analyser equipment 15
7.1 General 15
7.2 Selective traps for interfering agents 15
7.3 Optical assembly 15
7.4 Pressure measurement 15
7.5 Flow rate indicator 15
7.6 Sampling pump for the analyser 16
7.7 Internal sulphur dioxide span source 16
7.8 Particle filter 16
8 Type approval of ultraviolet fluorescence sulphur dioxide analysers 16
8.1 General 16
8.2 Relevant performance characteristics and performance criteria 17
8.3 Design change 18
8.4 Procedures for determination of the performance characteristics during the laboratory test 19
8.5 Determination of the performance characteristics during the field test 29
8.6 Type approval and uncertainty calculation 33
9 Field operation and ongoing quality control 34
9.1 General 34
9.2 Suitability evaluation 34

9.3 Initial installation **36**
9.4 Ongoing quality assurance/quality control **37**
9.5 Calibration of the analyser **39**
9.6 Checks **40**
9.7 Maintenance **44**
9.8 Data handling and data reports **45**
9.9 Measurement uncertainty **45**
10 Expression of results **46**
11 Test reports and documentation **46**
11.1 Type approval test **46**
11.2 Field operation **47**
Annex A (normative) **Test of lack of fit** **49**
Annex B (informative) **Sampling equipment** **51**
Annex C (informative) **Ultraviolet fluorescence analyser** **53**
Annex D (informative) **Manifold testing** **54**
Annex E (normative) **Type approval** **56**
Annex F (informative) **Calculation of uncertainty in field operation at the hourly limit value** **75**
Annex G (informative) **Calculation of uncertainty in field operation at the daily limit value** **83**
Annex H (informative) **Calculation of uncertainty in field operation at the annual critical level** **93**
Annex I (informative) **Significant technical changes** **103**
Bibliography **104**

Foreword

This document (EN 14212:2012) has been prepared by Technical Committee CEN/TC 264 “Air quality”, the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by February 2013, and conflicting national standards shall be withdrawn at the latest by February 2013.

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

This document supersedes EN 14212:2005.

The technical changes made since EN 14212:2005 are listed in Annex I of this European Standard.

According to the CEN/CENELEC Internal Regulations, the national standards organisations 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, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

1 Scope

This European Standard specifies a continuous measurement method for the determination of the concentration of sulphur dioxide present in ambient air based on the ultraviolet fluorescence measuring principle. This standard describes the performance characteristics and sets the relevant minimum criteria required to select an appropriate ultraviolet fluorescence analyser by means of type approval tests. It also includes the evaluation of the suitability of an analyser for use in a specific fixed site so as to meet the data quality requirements as specified in Annex I of Directive 2008/50/EC [1] and requirements during sampling, calibration and quality assurance for use.

The method is applicable to the determination of the mass concentration of sulphur dioxide present in ambient air up to 1000 $\mu g/m^3$. This concentration range represents the certification range for SO_2 for the type approval test.

NOTE 1 Other ranges may be used depending on the levels present in ambient air.

NOTE 2 When the standard is used for other purposes than for measurements required by Directive 2008/50/EC, the ranges and uncertainty requirements may not apply.

The method covers the determination of ambient air concentrations of sulphur dioxide in zones classified as rural areas, urban-background areas and traffic-orientated locations and locations influenced by industrial sources.

The results are expressed in $\mu g/m^3$ (at 20 °C and 101,3 kPa).

NOTE 3 1 000 $\mu g/m^3$ of SO_2 corresponds to 376 nmol/mol of SO_2.

This standard contains information for different groups of users.

Clauses 5 to 7 and Annexes C and D contain general information about the principles of sulphur dioxide measurement by ultraviolet fluorescence analyser and sampling equipment.

Clause 8 and Annex E are specifically directed towards test houses and laboratories that perform type-approval testing of sulphur dioxide analysers. These sections contain information about:

— Type-approval test conditions, test procedures and test requirements;

— Analyser performance requirements;

— Evaluation of the type-approval test results;

— Evaluation of the uncertainty of the measurement results of the sulphur dioxide analyser based on the type-approval test results.

Clauses 9 to 11 and Annexes F and G are directed towards monitoring networks performing the practical measurements of sulphur dioxide in ambient air. These sections contain information about:

— Initial installation of the analyser in the monitoring network and acceptance testing;

— Ongoing quality assurance/quality control;

— Calculation and reporting of measurement results;

— Evaluation of the uncertainty of measurement results under practical monitoring conditions.

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 15267-1, *Air quality — Certification of automated measuring systems — Part 1: General principles*

EN 15267-2, *Air quality — Certification of automated measuring systems — Part 2: Initial assessment of the AMS manufacturer's quality management system and post certification surveillance for the manufacturing process*

EN ISO 6142, *Gas analysis — Preparation of calibration gas mixtures — Gravimetric method (ISO 6142)*

EN ISO 6143, *Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures (ISO 6143)*

EN ISO 6144, *Gas analysis — Preparation of calibration gas mixtures — Static volumetric methods (ISO 6144)*

EN ISO 6145-6, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 6: Critical orifices (ISO 6145-6)*

EN ISO 6145-7, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 7: Thermal mass-flow controllers (ISO 6145-7)*

EN ISO 6145-10, *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 10: Permeation method (ISO 6145-10)*

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

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

ENV 13005:1999, *Guide to the expression of uncertainty in measurement*

3 Terms and definitions

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

3.1
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: Types of adjustment of a measuring system include zero adjustment of a measuring system, offset adjustment, and span adjustment (sometimes called gain adjustment).

Note 2 to entry: Adjustment of a measuring system should not be confused with calibration, which is a prerequisite for adjustment.

[SOURCE: JCGM 200:2012 (VIM) [2]]

Note 3 to entry: In the context of this standard, adjustment is performed on measurement data rather than on the analyser.

3.2
ambient air
outdoor air in the troposphere, excluding workplaces as defined by Directive 89/654/EEC, where provisions concerning health and safety at work apply and to which members of the public do not have regular access

[SOURCE: 2008/50/EC [1]]

3.3
analyser
measuring system that provides an output signal which is a function of the concentration, partial pressure, flow or temperature of one or more components of a gas mixture

3.4
availability of the analyser
fraction of the time period for which valid measuring data of the ambient air concentration is available from an analyser

3.5
calibration
operation that, under specified conditions, in a first step, establishes a relation between the quantity values with measurement uncertainties provided by measurement standards and corresponding indications with associated measurement uncertainties and, in a second step, uses this information to establish a relation for obtaining a measurement result from an indication

Note 1 to entry: A calibration may be expressed by a statement, calibration function, calibration diagram, calibration curve, or calibration table. In some cases, it may consist of an additive or multiplicative correction of the indication with associated measurement uncertainty.

Note 2 to entry: Calibration should not be confused with adjustment of a measuring system, often mistakenly called “self-calibration”, nor with verification of a calibration.

Note 3 to entry: Often, the first step alone in the above definition is perceived as being calibration.

[SOURCE: JCGM 200:2012 (VIM) [2]]

Note 4 to entry In the context of this standard, calibration is a comparison of the analyser response to a known gas concentration with a known uncertainty when the information obtained from the comparison is used for the successive adjustment (if needed) of the analyser.

3.6
certification range
concentration range for which the analyser is type-approved

3.7
check
verification that the analyser is still operating within specified performance limits

3.8
combined standard uncertainty
standard uncertainty of the result of a measurement when that result is obtained from the values of a number of other quantities, equal to the positive square root of a sum of terms, the terms being the variances or co-variances of these other quantities weighted according to how the measurement result varies with changes in these quantities

[SOURCE: ENV 13005:1999]

3.9
coverage factor
numerical factor used as a multiplier of the combined standard uncertainty in order to obtain an expanded uncertainty

[SOURCE: ENV 13005:1999]

3.10
designated body
body which has been designated for a specific task (type approval tests and/or QA/QC activities in the field) by the competent authority in the Member States

3.11
detection limit
smallest concentration of a measurand that can be reliably detected by a specific measurement process

Note 1 to entry: The detection limit is calculated as $3{,}3x(s_z/B)$ where s_z is the standard deviation of analyser response at zero measurand concentration (see 8.4.5) and B is the slope of the calibration function [3].

3.12
expanded uncertainty
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

Note 1 to entry: The fraction may be viewed as the coverage probability or level of confidence of the interval.

Note 2 to entry: To associate a specific level of confidence with the interval defined by the expanded uncertainty requires explicit or implicit assumptions regarding the probability distribution characterised by the measurement result and its combined standard uncertainty. The level of confidence that may be attributed to this interval can be known only to the extent to which such assumptions may be justified.

[SOURCE: ENV 13005:1999]

Note 3 to entry: For the purpose of this European Standard, the expanded uncertainty is the combined standard uncertainty multiplied by a coverage factor k=2 resulting in an interval with a level of confidence of 95 %.

3.13
fall time
difference between the response time (fall) and the lag time (fall)

3.14
independent measurement
individual measurement that is not influenced by a previous individual measurement by separating two individual measurements by at least four response times

Note 1 to entry: The largest value of response time (rise) and response time (fall) are intended.

3.15
individual measurement
measurement averaged over a time period equal to the response time of the analyser

Note 1 to entry: The largest value of response time (rise) and response time (fall) are intended.

Note 2 to entry: This definition differs from the meaning of the concept “individual measurement” in Directive 2008/50/EC [1].

3.16
influence quantity
quantity that is not the measurand but that affects the result of the measurement

[SOURCE: ENV 13005:1999]

3.17
interferent
component of the air sample, excluding the measured constituent, that affects the output signal

3.18
lack of fit
maximum deviation from the linear regression line of the average of a series of measurement results at the same concentration

3.19
lag time
time interval from the moment at which a step change of sample concentration occurs at the inlet of the analyser to the moment at which the output reading reaches a level corresponding to a predefined change of the stable output reading

3.20
limit value
level fixed on the basis of scientific knowledge, with the aim of avoiding, preventing or reducing harmful effects on human health and/or the environment as a whole, to be attained within a given period and not to be exceeded once attained

[SOURCE: 2008/50/EC [1]]

3.21
long term drift
difference between zero or span readings over a determined period of time (e.g. period of unattended operation)

3.22
monitoring station
enclosure located in the field in which an analyser has been installed to monitor concentrations of one or more ambient air pollutants

3.23
parallel measurements
measurements from different analysers, sampling from one and the same sampling manifold starting at the same time and ending at the same time

3.24
performance characteristic
one of the parameters assigned to equipment in order to define its performance

3.25
performance criterion
limiting quantitative numerical value assigned to a performance characteristic, to which conformance is tested

3.26
period of unattended operation
time period over which the drift complies with the performance criterion for long term drift

3.27
repeatability (of results of measurement)
closeness of the agreement between the results of successive individual measurements of sulphur dioxide carried out under the same conditions of measurement

Note 1 to entry: These conditions include:
a) the same measurement procedure;
b) the same observer;
c) the same analyser, used under the same conditions;
d) at the same location;
e) repetition over a short period of time.

3.28
reproducibility under field conditions
closeness of the agreement between the results of simultaneous measurements with two analysers in ambient air carried out under the same conditions of measurement

Note 1 to entry: These conditions are called field reproducibility conditions and include:
a) the same measurement procedure;
b) two identical analysers, used under the same conditions;

c) at the same monitoring station;
d) the period of unattended operation.

3.29
residence time inside the analyser
time period for the sampled air to be transported from the inlet of the analyser to the reaction chamber

3.30
residence time in the sampling system
time period for the sampled air to be transferred to the inlet of the analyser

3.31
response time
time interval from the instant at which a step change of sample concentration occurs at the inlet of the analyser to the instant at which the output reading reaches a level corresponding to a predefined change of the output reading

3.32
sampled air
part of ambient air that is transferred through the sampling inlet and sampling system for subsequent measurement

3.33
sample gas temperature
temperature of the sampled gas at the sample inlet

Note 1 to entry: The term "gas" may refer to a test gas used in type-approval testing or to ambient air transferred to the analyser.

3.34
sampling system
assembly of components needed to transfer ambient air to the analyser

3.35
short-term drift
difference between zero or span readings at the beginning and end of a 12 h period

3.36
standard uncertainty
uncertainty of the result of a measurement expressed as a standard deviation

[SOURCE: ENV 13005:1999]

3.37
surrounding temperature
temperature of the air directly surrounding the analyser

3.38
total residence time
sum of the residence time in the sampling system and the residence time inside the analyser

3.39
type approval
decision taken by a designated body that the pattern of an analyser conforms to specified requirements

3.40
type approval test
examination of two or more analysers of the same pattern which are submitted by a manufacturer to a designated body including the tests necessary for approval of the pattern

3.41
uncertainty (of measurement)
parameter associated with the result of a measurement that characterises the dispersion of the values that could reasonably be attributed to the measurand

[SOURCE: ENV 13005:1999]

4 Abbreviated terms

FEP perfluoro-ethylene-propylene;

MFC mass flow controller;

PTFE polytetrafluoroethylene.

5 Principle

5.1 General

This standard describes the method for measurement of the concentration of sulphur dioxide in ambient air by means of ultraviolet fluorescence. The requirements, the specific components of the ultraviolet fluorescence analyser and its sampling system are described. A number of performance characteristics with associated minimum performance criteria are given for the analyser. The actual values of these performance characteristics for a specific type of analyser shall be determined in a so-called type approval test for which procedures have been described. The type approval test comprises a laboratory test and a field test. The selection of a type-approved analyser for a specific measuring task in the field is based on the calculation of the expanded uncertainty of the measurement method. In this expanded uncertainty calculation, the actual values of various performance characteristics of a type-approved analyser and the site-specific conditions at the monitoring station are taken into account (see 9.6). The expanded uncertainty of the method shall not exceed 15% for fixed measurements or 25 % for indicative measurements, as specified in Annex I of Directive 2008/50/EC [1]. Requirements and recommendations for quality assurance and quality control are given for the measurements in the field (see 9.4).

5.2 Measuring principle

UV (ultraviolet) fluorescence is based on the emission of light by SO_2 molecules excited by UV radiation when they return to their ground state:

The first reaction step is:

$$SO_2 + h\nu \rightarrow SO_2^* \quad (1)$$

In the second step the excited SO_2^* molecule returns to its ground state, emitting an energy $h\nu'$ according to the reaction:

$$SO_2^* \rightarrow SO_2 + h\nu' \text{ (UV)} \quad (2)$$

The intensity of the fluorescence radiation is proportional to the number of SO_2 molecules in the detection volume and is therefore proportional to the concentration of SO_2.

Therefore:

$$F = k \times c_{SO_2} \quad (3)$$

where

F is the intensity of fluorescence radiation;

k is the factor of proportionality;

c_{SO_2} is the concentration of SO_2.

Before entering the fluorescence analyser, the air sample is passed through a filter in order to exclude interferences caused by contamination with particles.

The sampled air is scrubbed to remove any interference by aromatic hydrocarbons that may be present. A hydrocarbon scrubber device is used to achieve this.

The sampled air is then introduced into a reaction chamber, where it is irradiated by UV light in the wavelength range between 200 nm and 220 nm. The UV fluorescent light emitted in the wavelength range of 240 nm to 420 nm, is optically filtered and then converted to an electrical signal by a UV detector, for example, a photomultiplier tube.

The response of the analyser is proportional to the number of SO_2 molecules in the reaction chamber. Therefore, temperature and pressure either need to be kept constant, or, if variation of these parameters occurs, the measured values need to be corrected.

The concentration of sulphur dioxide is directly measured in volume/volume units (if the analyser is calibrated using a volume/volume standard). The final results for reporting are expressed in $\mu g/m^3$ using standard conversion factors (see Clause 10).

5.3 Type approval test

The type approval test is based on the evaluation of performance characteristics determined under a prescribed series of tests. In this European Standard, test procedures are described for the determination of the actual values of the performance characteristics for at least two analysers in a laboratory and the same analysers in the field, operated in parallel in both cases. The type approval laboratory tests shall not include the sampling system and external data acquisition system, but shall include analyser sampling line and filter. The type approval field test may include a sampling inlet and a sampling system. However, the influence of these components on the test results shall be minimised by proper maintenance.

A designated body shall perform these tests. The evaluation for type approval of an analyser is based on the calculation of the expanded uncertainty in the measuring result based on the numerical values of the tested performance characteristics and compared with a prescribed maximum uncertainty.

The type approval of an analyser and subsequent QA and QC procedures provide evidence that the defined requirements concerning data quality laid out in Annex I of Directive 2008/50/EC [1] can be satisfied.

Appropriate experimental evidence shall be provided by

— type approval tests performed under conditions of intended use of the specified method of measurement, and

— calculation of expanded uncertainty of results of measurement by reference to ENV 13005.

5.4 Field operation and quality control

Prior to the installation and operation of a type-approved analyser at a monitoring station, an expanded uncertainty calculation shall be performed with the actual values of the performance, obtained during the type approval tests, and the site-specific conditions at that monitoring station. This calculation shall be used to demonstrate that the type-approved analyser meets the requirements for all applicable limit values under the actual conditions present at that specific monitoring station.

After the installation of the approved analyser at the monitoring station, its correct functioning shall be tested.

Requirements for quality assurance and quality control are given for the operation and maintenance of the sampling system, as well as for the analyser, to ensure that the uncertainty of subsequent measurement results obtained in the field is not compromised.

6 Sampling

6.1 General

Depending on the installation of the ultraviolet fluorescence analyser at a monitoring station, a single sampling line for the analyser may be chosen. Alternatively, sampling can take place from a sampling system consisting of a common sampling inlet with a sampling manifold to which other analysers and equipment may be attached. Conditions and layout of the sampling system will contribute to the uncertainty of the measurement; to minimise this contribution to the expanded uncertainty, requirements for the sampling equipment are given in the following sub-clauses.

NOTE In Annex B, different arrangements of the sampling equipment are schematically presented.

The following factors may, through decrease in the concentration of sulphur dioxide, contribute to the uncertainty of the measurement when considering the sampling as an integral part of the measurement:

— loss of sulphur dioxide in the sampling system;

— loss of sulphur dioxide in the particle filter.

These factors are recognised to be relevant, but currently cannot be quantified for lack of appropriate assessment methods. As a consequence, the contributions of these factors are not considered in the uncertainty assessment applied in this standard. The effect of these factors is minimised through minimum requirements (see 6.3) and application of appropriate QA/QC measures (see 9.4 to 9.6) and maintenance (see 9.7).

6.2 Sampling location

The location where the ambient air shall be sampled and analysed is not specified as this depends strongly on the category of a monitoring station (such as measurements taken in e.g. a rural area or background area). Guidance and criteria on sampling points on a micro scale are given in Annex III of Directive 2008/50/EC [1].

6.3 Sampling system

6.3.1 Construction

The sampling system shall include a sampling inlet and may include the following components:

— a sampling line or manifold;

— a particle filter placed between the sampling line or manifold and the inlet of the analyser;

— a sampling pump in case a sampling manifold is used.

The sample inlet shall be constructed in such a way that ingress of rainwater into the sampling line or manifold is prevented. The sampling line or manifold shall be as short as practical to minimise the residence time.

In the case where a sampling manifold is used, an additional pump is necessary with sufficient capacity to fulfil the sampling requirements stated in the previous sub-clauses (see also 6.5 and Annex B).

The material of the sample inlet as well as the sampling line or manifold can influence the composition of the sample. In practice, the best materials, such as polytetrafluoroethylene (PTFE), perfluoro-ethylene-propylene (FEP), borosilicate glass or stainless steel, shall be used. The influence of the material of the sampling inlet and line or manifold on the measured concentrations of sulphur dioxide due to losses shall be < 2,0 %.

NOTE This value can be achieved when the quality assurance and quality control requirements (see Clause 9) are followed.

The sampling line or manifold may be moderately heated to avoid condensation. Condensation may occur in the case of high ambient temperature and/or humidity.

The influence of the pressure drop along the sampling inlet and line or manifold and the particle filter on the measured concentrations shall be ≤ 1,0 %.

6.3.2 Particle filter

A particle filter shall be placed between the sampling line or manifold and the inlet of the analyser. The filter shall retain all particles likely to alter the performance of the analyser. It shall be made of PTFE. The material of the filter housing shall be chemically inert to sulphur dioxide.

NOTE 1 The filter may be internal to the analyser (see 7.8) or external. In case the analyser contains a built-in filter, an external filter is not necessary.

NOTE 2 A pore size of the filter of 5 µm usually fulfils this requirement.

NOTE 3 Suitable materials for the filter housing are for example PTFE, stainless steel, or borosilicate glass.

The particle filter shall be conditioned before used in measurements. The filter shall be changed periodically depending on the dust loading at the sampling site (as indicated in 9.7). The filter housing shall be cleaned at least every six months. Overloading of the filter may cause loss of sulphur dioxide by adsorption on the particle matter and may increase the pressure drop in the sampling line.

6.3.3 Loss of sulphur dioxide

Depending on the location of the particle filter, the sampling system can be contaminated by deposition of dust. This can induce losses of sulphur dioxide. The sampling system shall be cleaned (as stated in 9.4.2) with a frequency which is dependent on the site-specific conditions.

6.3.4 Conditioning

The sampling system and the particle filter shall be conditioned (at initial installation and after each cleaning) to avoid temporary decreases in the measured sulphur dioxide concentrations by sampling ambient air for a period of at least 30 min at the nominal sample flow rate. Conditioning may also be done in the laboratory before installation.

These conditioning periods shall not be included in the calculation of the availability of the analyser during the type approval test (8.5.7).

NOTE Conditioning during field operation is considered a part of normal maintenance. Consequently, the concentrations measured during conditioning need not be included in the calculation of data capture, and hourly, daily and annual averages.

6.4 Control and regulation of sample flow rate

The sample flow rate into the analyser shall be maintained within the specifications of the manufacturer of the analyser.

NOTE The flow rate into the ultraviolet fluorescence analyser is usually controlled by means of restrictors.

6.5 Sampling pump for the manifold

When a sampling manifold is used, a pump (or similar device, e.g. a blower) is necessary for sampling ambient air and suction of the sampled air through the sampling manifold. The inlet of the sampling pump for the sampling manifold shall be located at the end of the sampling manifold (see Annex B). The sampling pump shall have sufficient rating to ensure that all analysers connected to the manifold are supplied with the required amount of air and to ensure that the residence time is ≤ 5 s. To verify functioning of this pump, it is recommended to install a flow alarm system. An example of a sampling manifold is given in Annex B.

The influence of the pressure drop induced by the manifold sampling pump on the measured concentration shall be ≤ 1,0 %.

7 Analyser equipment

7.1 General

A schematic diagram of a UV fluorescence analyser is given in Annex C.

A UV fluorescence analyser consists of the principal components which are described in 7.2 to 7.6.

7.2 Selective traps for interfering agents

One or more selective traps shall be used before the fluorescence cell to remove interfering gases such as aromatic hydrocarbons.

These selective traps shall not retain any SO_2, and shall be replaced regularly in accordance with the manufacturer's instructions.

If high concentrations of H_2S are expected in the ambient air, a selective scrubber should be used.

7.3 Optical assembly

The optical assembly consists of a UV lamp, a fluorescence cell, a reference sensor and a UV detector.

The UV lamp emission may be pulsed electronically or mechanically in order to enable synchronous detection and amplification of the signal. The lamp shall have a stabilised power supply to ensure a stable emission of light. An optical filter is used to restrict the wavelengths to a range which allows excitation of the sulphur dioxide molecule and minimises the interferences due to water vapour, aromatic hydrocarbons or nitrogen monoxide. This filter shall remove radiation at wavelengths longer than 600 nm, to minimise any interference produced by the UV fluorescence of unsaturated hydrocarbons, which radiate at these wavelengths.

The reference sensor in the extension of the beam path behind the reaction chamber checks the constancy of the UV lamp and is used to correct the fluorescence signal or to control the UV lamp.

The fluorescence cell shall be made of material inert to SO_2 and UV radiation. The cell shall be heated to a constant temperature above the water vapour dew point to avoid water condensation and to minimise temperature changes. An optical trap in the fluorescence cell shall be used to prevent reflection of the UV radiation.

The UV detector, for example a photomultiplier tube, detects the fluorescence light emitted by the SO_2 molecules in the fluorescence cell. A selective optical filter placed in front of the photomultiplier tube reduces the signal due to scattering of incident light.

The optical assembly shall be placed in a heated temperature-controlled enclosure.

7.4 Pressure measurement

The output signal of the analyser is proportional to the density of SO_2 (number of SO_2 molecules) present in the reaction chamber and depends on the pressure in the chamber. Variations of internal pressure shall be measured and the signal corrected.

The signal shall be corrected also for external pressure and temperature fluctuations. Significant pressure variations are due to synoptic meteorological changes (up to $\pm$ 3 %) or by the altitude of the measurement site (e.g. approximately 10 % decrease in pressure for a 800 m rise in altitude).

NOTE One of the main causes of a reduced pressure in the reaction chamber is a pressure drop in the sample line.

7.5 Flow rate indicator

A flow rate indicator shall be included in the analyser.

It is recommended that the flow rate be kept constant by means of a flow controller.

7.6 Sampling pump for the analyser

The sampling pump is situated at the outlet of the analyser, and draws the sample through the analyser. It 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 reaction chamber.

If the use of the UV lamp produces ozone, it is recommended to vent this ozone outside the monitoring station and away from the sampling inlet. A suitable charcoal filter may be used for trapping ozone.

7.7 Internal sulphur dioxide span source

Some analysers are equipped with an internal span source. This span source shall not be used for calibration purposes. The concentrations generated by this internal span source may be used for functional tests only.

7.8 Particle filter

An analyser will generally contain an internal particle filter (see 6.3.2). This filter shall be considered an integral part of the analyser for type-approval testing.

8 Type approval of ultraviolet fluorescence sulphur dioxide analysers

8.1 General

The determination of the concentration of sulphur dioxide in ambient air shall fulfil the requirement of a maximum uncertainty in the measured values, which is prescribed by Annex I of Directive 2008/50/EC (15% for fixed measurements or 25 % for indicative measurements). In order to achieve an uncertainty less than (or equal to) this required uncertainty, the ultraviolet fluorescence analyser shall fulfil all the criteria for a number of performance characteristics which are given in this standard. The values of the selected performance characteristics shall be evaluated by means of laboratory tests and field tests. By combining the values of the selected performance characteristics in the expanded uncertainty calculation, a judgement shall be made whether or not the ultraviolet fluorescence analyser meets the criterion of maximum uncertainty prescribed by Annex I of Directive 2008/50/EC (15% for fixed measurements or 25 % for indicative measurements).

This process of assessment (type approval test) of the values of the performance characteristics comprises laboratory tests and field tests and the calculation of the expanded uncertainty. At least two analysers of the same type shall be tested in the laboratory. Two of these analysers shall be tested during the field test. All analysers tested are required to pass all tests.

The type approval procedure shall fulfil the certification requirements laid down in EN 15267-1 and EN 15267-2. A designated body shall perform the type approval tests. The designated body for the type approval test shall be accredited for these activities according to EN ISO/IEC 17025. The type approval shall be awarded by or on behalf of the competent authority.

EN 15267-1 specifies the general principles of the product certification of automated measuring systems (AMS) for monitoring emissions from stationary sources and ambient air quality. This product certification consists of the following sequential stages:

a) performance testing of an AMS;

b) initial assessment of the AMS manufacturer’s quality management system;

c) certification;

d) post-certification product-surveillance.

EN 15267-2 covers the supplementary requirements for an AMS manufacturer's management system to EN ISO 9001 [5] for the control of design and manufacturing of AMS. This European Standard also serves as a reference document for auditing the AMS manufacturer's management system.

8.2 Relevant performance characteristics and performance criteria

The performance characteristics which shall be determined during a laboratory and field test, and their related performance criteria, are given in Table 1. Table 1 applies to those ranges that are specified as normative in the scope of this standard. When type-approval tests are performed on analysers with other certification ranges, the performance criteria stated in absolute units such as nmol/mol/K may need to be modified in order to meet the uncertainty criteria in Annex I from Directive 2008/50/EC.

The determination of the value of the performance characteristics stated in Table 1 shall be performed by a designated body during the laboratory test and field test according to the procedures described in 8.4, 8.5 and Annex A.

Table 1 — Relevant performance characteristics and criteria

No.	Performance characteristic	Symbol	Section	Lab. test	Field test	Performance criterion for SO_2
1	Repeatability standard deviation at zero	s_{rz}	8.4.5	x		≤ 1,0 nmol/mol
2	Repeatability standard deviation at concentration c_t (at a level of the hourly limit)	$s_{r,ct}$	8.4.5	x		≤ 3,0 nmol/mol
3	Lack of fit (residual from the linear regression function)		8.4.6			
3a	Largest residual from the linear regression function at concentrations higher than zero	r_{max}		x		≤ 4,0 % of the measured value
3b	Residual at zero	r_z		x		≤ 5,0 nmol/mol
4	Sensitivity coefficient of sample gas pressure	b_{gp}	8.4.7	x		≤ 2,0 nmol/mol/kPa
5	Sensitivity coefficient of sample gas temperature	b_{gt}	8.4.8	x		≤ 1,0 nmol/mol/°C
6	Sensitivity coefficient of surrounding temperature	b_{st}	8.4.9	x		≤ 1,0 nmol/mol/°C
7	Sensitivity coefficient of electrical voltage	b_V	8.4.10	x		≤ 0,3 nmol/mol/V
8	Interferents at zero and at concentration c_t (at a level of the hourly limit) [b]		8.4.11			
8a	H_2O with concentration 19 mmol/mol [c]	$X_{H2O,z,ct}$		x		≤ 10 nmol/mol
8b	H_2S with concentration 200 nmol/mol	$X_{H2S,z,ct}$		x		≤ 5,0 nmol/mol

No.	Performance characteristic	Symbol	Section	Lab. test	Field test	Performance criterion for SO_2
8c	NH_3 with concentration 200 nmol/mol	$X_{NH3,z,ct}$		x		≤ 5,0 nmol/mol
8d	NO with concentration 500 nmol/mol	$X_{NO,z,ct}$		x		≤ 5,0 nmol/mol
8e	NO_2 with concentration 200 nmol/mol	$X_{NO2,z,ct}$		x		≤ 5,0 nmol/mol
8f	m-xylene with concentration 1 µmol/mol	$X_{yl,z,ct}$		x		≤ 10,0 nmol/mol
9	Averaging effect	E_{av}	8.4.12	x		≤ 7,0 % of the measured value
10	Reproducibility standard deviation under field conditions	$s_{r,f}$	8.5.5		x	≤ 5,0 % of the average of a three month period
11	Long-term drift at zero level	$D_{l,z}$	8.5.4		x	≤ 4,0 nmol/mol
12	Long-term drift at span level [a]	$D_{l,s}$	8.5.4		x	≤ 5,0 % of maximum of certification range
13	Short-term drift at zero level	$D_{s,z}$	8.4.4	x		≤ 2,0 nmol/mol over 12 h
14	Short-term drift at span level [a]	$D_{s,s}$	8.4.4	x		≤ 6,0 nmol/mol over 12 h
15	Response time (rise)	t_r	8.4.3	x		≤ 180 s
16	Response time (fall)	t_f	8.4.3	x		≤ 180 s
17	Difference rise time and fall time	t_d	8.4.3	x		≤ 10 s
18	Difference sample/calibration port [d]	ΔX_{sc}	8.4.13	x		≤ 1,0 %
19	Period of unattended operation		8.5.6		x	3,0 months or less if manufacturer indicates a shorter period, but not less than 2 weeks
20	Availability of the analyser	A_a	8.5.7		x	> 90 %

[a] Span level is 70 % to 80 % of the certification range.
[b] Performance criterion is set both at zero and test gas concentration level.
[c] A H_2O-concentration of 19 mmol/mol equals 80 % RH at 20 °C and 101,3 kPa.
[d] If relevant.

NOTE µmol/mol = ppm; nmol/mol = ppb

8.3 Design change

When the manufacturer makes design changes, the manufacturer shall notify the test laboratory and relevant body, unless the manufacturer has evidence to show that the analyser still meets the performance stated in the original analyser certificate. The following three classes of changes to type-approved analyser are defined as follows:

— Type 0: changes that have no measurable influence to the performance of the analyser;

— Type 1: changes that can have an influence on the performance of the analyser, but where subsequent tests prove that such changes do not have a significant influence;

— Type 2: changes that have a significant influence on the performance of the analyser.

A significant influence reduces the performance of the analyser compared to that recorded in the certificate for the stipulated performance characteristics. The manufacturer shall evaluate all changes to a type-approved analyser. Where Type 2 changes are identified, further evaluation shall be carried out by a test laboratory in liaison with the relevant body. It is essential that the manufacturer documents all changes and evaluations in accordance with the requirements of EN ISO 9001 and EN 15267-2 in such a way that they can be audited.

When the manufacturer makes Type 2 changes to the analyser, the test laboratory in consultation with the Competent Authority shall determine whether supplementary or complete retesting is required to maintain type approval.

8.4 Procedures for determination of the performance characteristics during the laboratory test

8.4.1 General

A designated body shall perform the determination of the performance characteristics in the laboratory as a part of the type approval test. The quality of the materials and equipment used in the described test procedures shall be in accordance with the requirements given in this standard. The tests shall be performed on at least two analysers of the same type in the laboratory test.

8.4.2 Test conditions

8.4.2.1 General

Before operating the analyser, the operating instructions of the manufacturer shall be followed particularly with regard to the set-up of equipment and the quality and quantity of the consumable products necessary.

The analyser should be allowed to warm up during the time specified by the manufacturer before undertaking any tests. If the warm-up time is not specified, a minimum of 4 h is recommended.

If auto rescaling and self-correction for drift are optional to the analyser, then these functions shall be disabled during the laboratory tests.

If an auto-rescaling function or self-correction function are not optional and considered a “normal operational condition”, then the times and magnitudes of any self-correction shall be available to the test laboratory. The magnitude of the auto zero and the auto span drift corrections both have the same restrictions as laid down in the performance characteristics.

When applying test gases to the analyser, the test gas system shall be operated sufficiently long before starting the tests in order to stabilise the concentrations applied to the analyser. The analyser shall be tested with the particle filter installed.

Most analyser systems are able to give an output signal as a moving average over an adjustable period of time and some systems automatically change this integration time as a function of the frequency of the fluctuations in concentration of the detected pollutant. These options are typically used in order to smooth output data. It needs no demonstration that the set value for the averaging time or the use of an active filter will influence the result of the averaging test and response time test. During laboratory and field tests for the type approval, the settings of the monitor shall be as the manufacturer requires. Auto zeroing and auto-scaling capabilities shall be disabled during the lab tests; during field tests the monitor shall be in the configuration as used. All settings shall be noted in the test report.

8.4.2.2 Parameters

During the test for each individual performance characteristic, the values of the following parameters shall be stable within the specified range given in Table 2.

Table 2 — Set points and stability of test parameters

Parameter	Set points	Stability
Sample gas pressure	Manufacturer's specification (except for the sample gas pressure test, see 8.4.7)	± 0,2 kPa
Sample gas temperature	20 °C to 23 °C (except for the sample gas temperature test, see 8.4.8)	± 2 °C
Surrounding temperature	20 °C to 23 °C (except for the temperature of the surrounding air test, see 8.4.9)	± 2 °C
Electrical voltage[a]	At nominal line voltage and within manufacturer's specifications (except for the voltage dependence test, see 8.4.10)	± 1 %
Sample flow to the analyser	Manufacturer's specification	± 1 %
[a] For an analyser operating on direct current the type approval test of voltage variation shall be carried out over the range of ± 10 % of the nominal voltage.		

8.4.2.3 Test gases

For the determination of the various performance characteristics, test gases traceable to (inter)nationally accepted standards shall be used unless otherwise stated in this European Standard. Methods for the generation of test gases are given in Table 3.

Table 3 — Methods for preparation of test gases

Method	Description	Traceability/ Standard to be used
Cylinder	Gas cylinder of SO_2 gas mixture in (synthetic) air	EN ISO 6142 EN ISO 6143
Dynamic dilution	Dynamic dilution of sulphur dioxide-air mixtures	EN ISO 6145-6 or EN ISO 6145-7
Permeation	Determination of the mass loss of a permeable tube containing SO_2	EN ISO 6145-10
Static dilution	Preparation by means of injecting known amounts of SO_2 into a known volume of air	EN ISO 6144

The maximum permitted expanded uncertainty (95 % confidence) in the concentration of gases used for laboratory tests is 3 %.

Possible contamination of zero and span gas shall not significantly influence the results of the laboratory tests. Therefore, the span gases and zero gas shall meet the following specifications given in Tables 4a to 4d:

Table 4a — Specification for purity of span gas

Pollutant	Concentration
H_2S	≤ 0,1 µmol/mol
NH_3	≤ 2,0 nmol/mol
NO	≤ 1,0 nmol/mol
NO_2	≤ 1,0 nmol/mol
m-xylene	≤ 1,0 nmol/mol
Water	≤ 150 µmol/mol

Table 4b — Specification for purity of zero gas for interferents testing

Pollutant	Concentration
H_2S	≤ 0,1 µmol/mol
NH_3	≤ 2,0 nmol/mol
NO	≤ 1,0 nmol/mol
NO_2	≤ 1,0 nmol/mol
m-xylene	≤ 1,0 nmol/mol
Water vapour	≤ 150 µmol/mol
SO_2	≤ 1,0 nmol/mol

Table 4c — Specification for purity of zero gas for other tests

Pollutant	Concentration
H_2S	≤ 0,1 µmol/mol
NH_3	≤ 10 nmol/mol
NO	≤ 1,0 nmol/mol
NO_2	≤ 1,0 nmol/mol
m-xylene	≤ 1,0 nmol/mol
Water vapour	≤ 150 µmol/mol
SO_2	≤ 1,0 nmol/mol

It is advisable to perform the field tests with the same set of cylinders and zero air generators, exclusively reserved for the tests. The stability of both the zero air and the span gas should be guaranteed over a period longer than the test period.

8.4.3 Response time

8.4.3.1 General requirements

The response time of the analyser shall be determined at the nominal sample flow rate specified by the manufacturer.

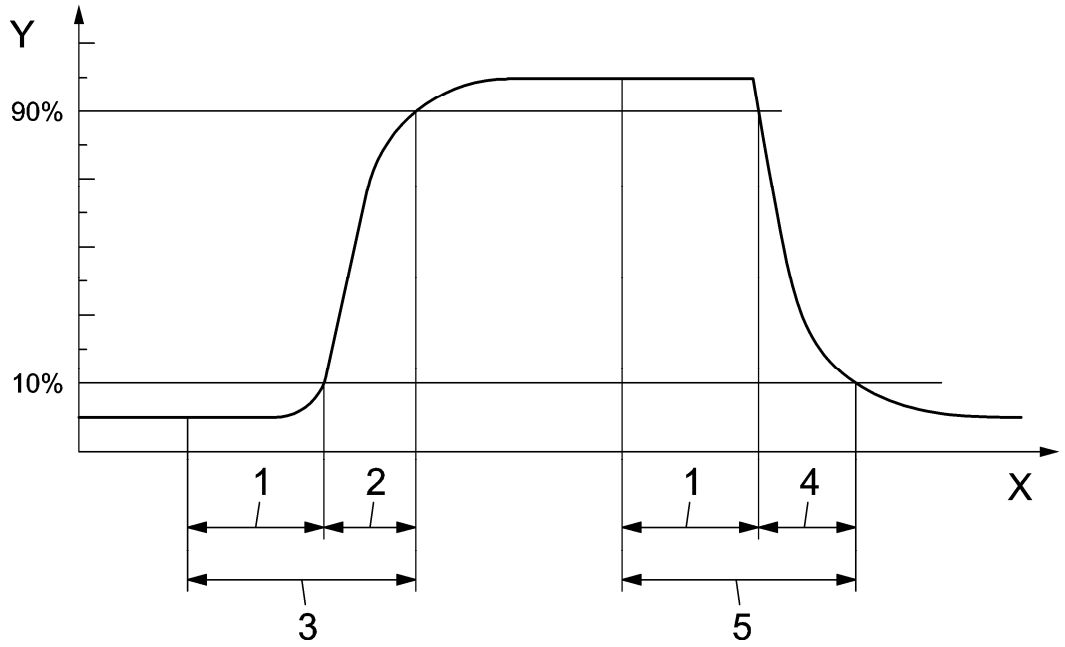
The sample flow rate shall be kept constant within the requirements as given in 8.4.2 (± 1 %) during the test.

8.4.3.2 Test procedure

The determination of the response time shall be carried out by applying to the analyser a step function in the concentration from less than 20 % to about 80 % of the maximum of the certification range of sulphur dioxide and vice versa (see Figure 1).

NOTE Usually zero gas and span gas are used for this test.

The change from zero gas to span gas and vice versa needs to be made almost instantaneously, with the use of a suitable valve. The valve outlet shall be mounted direct to the inlet of the analyser, and both zero gas and span gas shall have the same amount of gas in excess, which is vented by the use of a tee. The gas flows of both zero gas and span gas shall be chosen in such a way that the dead time in the valve and tee can be neglected compared to the lag time of the analyser system. The step change is made by switching the valve from zero gas to span gas. This event needs to be timed and is the start (t = 0) of the (rise) lag time according to Figure 1. When the reading over 5 min is constant to within ± 2 % of the test gas (span) concentration, the span gas can be changed to zero gas again; this event is the start (t = 0) of the (fall) lag time. When the reading over 5 min is stable to within 3 nmol/mol of the zero gas concentration the whole cycle as shown in Figure 1 is complete.



Key

Y analyser response
X time
1 lag time
2 rise time
3 response time (rise)
4 fall time
5 response time (fall)

Figure 1 — Diagram illustrating the response time

The elapsed time (response time) between the start of the step change and reaching 90 % of the analyser final stable reading of the applied concentration shall be measured. The whole cycle shall be repeated four times. The average of the four response times (rise) and the average of the four response times (fall) shall be calculated.

The difference in response times shall be calculated according to:

$$t_d = \bar{t}_r - \bar{t}_f \quad (4)$$

where

t_d is the difference between response time (rise) and response time (fall), in s;

$\bar{t}_r$ is the response time (rise) (average of the four response times - rise), in s;

$\bar{t}_f$ is the response time (fall) (average of the four response times - fall), in s.

t_d, $\bar{t}_r$ and $\bar{t}_f$ shall comply with the performance criteria in Table 1.

8.4.4 Short-term drift

After the required stabilisation period (8.4.2.1), the analyser shall be adjusted at zero and span level (around 70 % to 80 % of the maximum of the certification range of sulphur dioxide). Wait the time equivalent to one independent reading and then record 20 individual measurements, first at zero and then at span concentration. From these 20 measurements, the average is calculated for zero and span level.

The analyser shall be kept running under the laboratory conditions (8.4.2.2) while analysing ambient air. After a period of 12 h, zero gas and subsequently span gas is fed to the analyser. Wait the time equivalent to one independent reading and then record 20 individual measurements, first at zero and then at span concentration. The averages for zero and span level shall be calculated.

NOTE Compliance with this test shows that drift is not the dominant factor in any of the test results.

The short-term drift at zero and span level shall be calculated as follows:

$$D_{s,z} = (C_{z,2} - C_{z,1}) \quad (5)$$

where

$D_{s,z}$ is the 12-hour drift at zero, in nmol/mol;

$C_{z,1}$ is the average concentration of the measurements at zero at the beginning of the drift period, in nmol/mol;

$C_{z,2}$ is the average concentration of the measurements at zero at the end of the drift period, in nmol/mol.

$D_{s,z}$ shall comply with the performance criterion in Table 1.

$$D_{s,s} = (C_{s,2} - C_{s,1}) - D_{s,z} \quad (6)$$

where

$D_{s,s}$ is the 12-hour drift at span, in nmol/mol;

$C_{s,1}$ is the average concentration of the measurements at span level at the beginning of the drift period, in nmol/mol;

$C_{s,2}$ is the average concentration of the measurements at span level at the end of the drift period, in nmol/mol.

$D_{s,s}$ shall comply with the performance criterion in Table 1.

8.4.5 Repeatability standard deviation

After waiting the time equivalent of one independent reading, 20 individual measurements both at zero concentration and at a test concentration (c_t) similar to the hourly limit value shall be performed.

From these measurements, the repeatability standard deviation (s_r) at zero concentration and at concentration c_t (hourly limit value) shall be calculated according to:

$$s_r = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}} \quad (7)$$

where

s_r is the repeatability standard deviation, in nmol/mol;

x_i is the ith measurement, in nmol/mol;

$\bar{x}$ is the average of the 20 measurements, in nmol/mol;

n is the number of measurements, n = 20.

The repeatability standard deviation shall be calculated separately for both series of measurements (zero gas and concentration c_t).

s_r shall comply with the performance criterion in Table 1, both at zero and at the test concentration c_t (hourly limit value).

The repeatability standard deviation at zero is used in combination with the slope of the calibration function determined in 8.4.6 to calculate the detection limit of the analyser as [3]:

$$l_{det} = 3{,}3 \times \frac{s_{r,z}}{B} \quad (8)$$

where

l_{det} is the detection limit or the analyser, in nmol/mol;

$s_{r,z}$ is the repeatability standard deviation at zero, in nmol/mol;

B is the slope of the calibration function determined according to Annex A using the data from 8.4.6.

8.4.6 Lack of fit of linearity of the calibration function

The lack of fit of linearity of the calibration function of the analyser shall be tested over the range of 0 % to 95 % of the maximum of the certification range of sulphur dioxide, using at least six concentrations (including the zero point). The analyser shall be adjusted at a concentration of about 80 % of the maximum of the certification range. At each concentration (including zero) at least five individual measurements shall be performed.

The concentrations shall be applied in the following sequence: 80 %, 40 %, 0 %, 60 %, 20 % and 95 %. After each change in concentration, at least four response times shall be taken into account before the next measurement is performed.

The uncertainty in the dilution ratios for the applied concentrations shall be less than 1,5 % with respect to each other.

NOTE The design of the test (number of concentrations and number of repetitions) is such that the deviation from a linear function can be determined with sufficient accuracy. The test is also sufficiently robust to detect the case of non-linearity in the range from zero to some concentration at the lower end of the range as well as non-linearity from that lower end of the range to the higher end of the range.

Calculation of the linear regression function and residuals shall be performed according to Annex A. All the (relative) residuals from the linear regression function shall fulfil the criteria as stated in Table 1.

The largest value of the relative residuals is reported as r_{max} and shall be taken into account in demonstrating compliance with type approval requirements.

8.4.7 Sensitivity coefficient to sample gas pressure

Measurements are taken at a concentration of about 70 % to 80 % of the maximum of the certification range of sulphur dioxide at an absolute pressure of about 80 kPa ± 0,2 kPa and at an absolute pressure of about

110 kPa ± 0,2 kPa. At each pressure after waiting the time equivalent to one independent reading, three individual measurements are recorded. From these three measurements, the averages at each pressure are calculated.

Measurements at different pressures shall be separated by at least four response times.

The sample gas pressure influence is calculated by:

$$b_{gp} = \left| \frac{(C_{P2} - C_{P1})}{(P_2 - P_1)} \right| \quad (9)$$

where

b_{gp} is the sample gas pressure sensitivity coefficient, in nmol/mol/kPa;

C_{P1} is the average concentration of the measurements at sampling gas pressure P_1, in nmol/mol;

C_{P2} is the average concentration of the measurements at sampling gas pressure P_2, in nmol/mol;

P_1 is the minimum sampling gas pressure, in kPa;

P_2 is the maximum sampling gas pressure, in kPa.

b_{gp} shall comply with the performance criterion in Table 1.

8.4.8 Sensitivity coefficient to sample gas temperature

Measurements shall be performed at sample gas temperatures of $T_{G,1}$ = 0 °C and $T_{G,2}$ = 30 °C. A concentration around 70 % to 80 % of the maximum of the certification range of sulphur dioxide shall be applied. Wait the time equivalent to one independent and record three individual measurements at each temperature. The sample gas temperature, measured at the inlet of the analyser, shall be held constant for at least 30 min.

The influence of sample gas temperature is calculated from:

$$b_{gt} = \left| \frac{(C_{GT,2} - C_{GT,1})}{(T_{G,2} - T_{G,1})} \right| \quad (10)$$

where

b_{gt} is the sample gas temperature sensitivity coefficient, in nmol/mol/K ;

$C_{GT,1}$ is the average concentration of the measurements at sample gas temperature $T_{G,1}$, in nmol/mol;

$C_{GT,2}$ is the average concentration of the measurements at sample gas temperature $T_{G,2}$, in nmol/mol;

$T_{G,1}$ is the minimum sample gas temperature, in °C;

$T_{G,2}$ is the maximum sample gas temperature, in °C.

b_{gt} shall comply with the performance criterion in Table 1.

8.4.9 Sensitivity coefficient to the surrounding temperature

The sensitivity of the analyser readings to the surrounding temperature shall be determined by performing measurements at the following temperatures (within the specifications of the manufacturer):

a) at the minimum temperature $T_{S,1}$ = 0 °C;

b) at the temperature $T_{S,0}$: see Table 2;

c) at the maximum temperature $T_{S,2}$ = 30 °C.

For these tests, a climate chamber is necessary.

A concentration around 70 % to 80 % of the maximum of the certification range of sulphur dioxide shall be applied. At each temperature setting after waiting the time equivalent to one independent reading three individual measurements at zero and at span shall be recorded.

At each temperature setting, the criteria for warm-up or stabilisation time are to be met according to 8.4.2.1.

At the first temperature ($T_{S,0}$) the analyser shall be adjusted at zero and at span level (70 % to 80 % of the maximum of the certification range). Then three individual measurements are recorded after waiting the time equivalent to one independent reading at $T_{S,0}$, at $T_{S,1}$ and again at $T_{S,0}$. This procedure shall be repeated at the temperature sequence of $T_{S,0}$, $T_{S,2}$, and at $T_{S,0}$.

In order to exclude any possible drift due to factors other than temperature, the measurements at $T_{S,0}$ are averaged, which is taken into account in the following formula for calculation of the sensitivity coefficient for temperature dependence:

$$b_{st} = \left| \frac{x_T - \frac{x_1 + x_2}{2}}{T_S - \overline{T_{S,0}}} \right| \tag{11}$$

where

b_{st} is the surrounding temperature sensitivity coefficient at zero or span and at $T_{S,1}$ or $T_{S,2}$, in nmol/mol/K;

x_T is the average of the measurements at $T_{S,1}$ or $T_{S,2}$, in nmol/mol;

x_1 x_1 is the first average of the measurements at $T_{S,0}$, in nmol/mol;

x_2 is the second average of the measurements at $T_{S,0}$, in nmol/mol;

T_S is the extreme surrounding temperature at which the test is performed, in °C;

$\overline{T_{S,0}}$ is the average of the surrounding temperatures at set point (see Table 2), in °C;

$T_{S,1}$ is the minimum surrounding temperature, in °C;

$T_{S,2}$ is the maximum surrounding temperature, in °C.

For reporting the surrounding temperature dependence the higher value is taken of the two calculations of the temperature dependence at $T_{S,1}$ and $T_{S,2}$.

b_{st} shall comply with the performance criterion in Table 1.

8.4.10 Sensitivity coefficient to electrical voltage

The sensitivity coefficient of electrical voltage shall be determined at both ends of the specified voltage range, V_1 and V_2 at zero concentration and at a concentration around 70 % to 80 % of the maximum of the certification range of sulphur dioxide. After waiting the time equivalent to one independent measurement, three individual measurements at each voltage and concentration level shall be recorded.

The voltage dependence is calculated from:

$$b_v = \left| \frac{\left(C_{V_2} - C_{V_1}\right)}{\left(V_2 - V_1\right)} \right| \quad (12)$$

where

b_v is the voltage sensitivity coefficient, in nmol/mol/V;

C_{V_1} is the average concentration reading of the measurements at voltage V_1, in nmol/mol;

C_{V_2} is the average concentration reading of the measurements at voltage V_2, in nmol/mol;

V_1 is the minimum voltage (V) specified by the manufacturer;

V_2 is the maximum voltage (V) specified by the manufacturer.

For reporting the dependence on voltage, the highest value of the result at zero and span level shall be taken.

b_v shall comply with the performance criterion in Table 1.

For an analyser operating on direct current, the type approval test of voltage variation shall be carried out over the range of ± 10 % of the nominal voltage.

8.4.11 Interferents

The analyser response to certain interferents, which are to be expected to be present in ambient air, shall be tested. The interferents can give a positive or negative response. The test shall be performed at zero and at a test concentration (c_t) of sulphur dioxide similar to the hourly limit value.

The concentration of the mixtures of the test gases with the interferent shall have an expanded uncertainty of ≤ 5 % and shall be traceable to (inter)nationally accepted standards. The interferents to be tested and their respective concentrations are given in Table 1. The influence of each interferent shall be determined separately. A correction on the concentration of the measurand shall be made for the dilution effect due to addition of an interferent (e.g. water vapour).

After adjustment of the analyser at zero and span level, the analyser shall be fed with a mixture of zero gas and the interferent to be investigated with the concentration as given in Table 1. With this mixture, one independent measurement followed by two individual measurements shall be carried out. This procedure shall be repeated with a mixture of the measurand at concentration c_t and the interferent to be investigated. The influence quantity at zero and concentration c_t are calculated from:

$$X_{int,z} = x_z \quad (13)$$

$$X_{int,c_t} = x_{c_t} - c_t \quad (14)$$

where

$X_{int,z}$ is the influence quantity of the interferent at zero, in nmol/mol;

x_z is the average of the measurements at zero, in nmol/mol.

X_{int,c_t} is the influence quantity of the interferent at concentration c_t, in nmol/mol;

x_{c_t} is the average of the measurements at concentration c_t, in nmol/mol;

c_t is the sulphur dioxide test gas concentration at the level of the hourly limit value, in nmol/mol.

The influence quantities of the interferents shall comply with the performance criteria in Table 1, both at zero and at concentration c_t.

8.4.12 Averaging test

The averaging test gives a measure of the uncertainty in the averaged values caused by short-term concentration variations in the sampled air shorter than the time scale of the measurement process in the analyser. In general, the output of an analyser is a result of the determination of a reference concentration (normally zero) and the actual concentration which takes a certain time.

For the determination of the uncertainty due to the averaging, the following concentrations are applied to the analyser and readings are taken at each concentration (see Figure 2): a stepwise varied concentration of SO_2 between zero and a concentration c_t of sulphur dioxide similar to the hourly limit value.

The time period (t_c) of the constant SO_2 concentration shall be at least equal to a period necessary to obtain four independent readings (which equals at least 16 response times). The time period (t_v) of the varying SO_2 concentration shall be at least equal to a period to obtain four independent readings. The time period (t_{SO2}) for the SO_2 concentration shall be 45 s followed by a period (t_{zero}) of 45 s of zero concentration.

Further:

c_t is the test gas concentration, in nmol/mol;

t_V is a whole number of t_{SO2} and t_{zero} pairs, and contains a minimum of three such pairs.

The change from t_{SO2} to t_{zero} shall be within 0,5 s. The change from t_C to t_V shall be within one response time of the analyser under test.

The averaging effect (E_{av}) is calculated according to:

$$E_{av} = \frac{C_{av,c} - 2C_{av,v}}{C_{av,c}} \times 100 \quad (15)$$

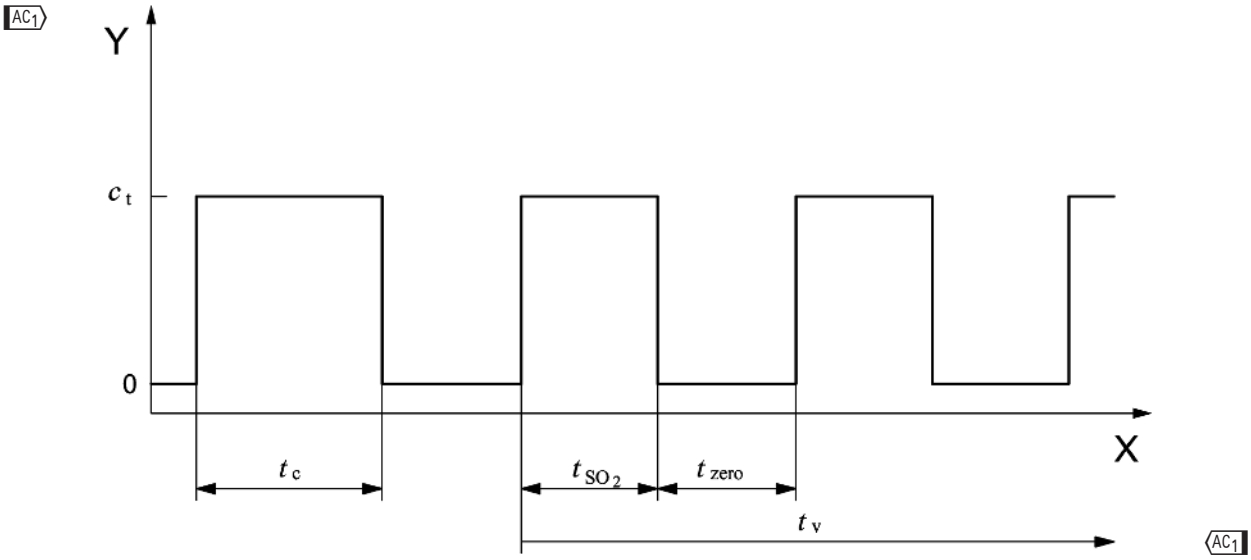
where

E_{av} is the averaging effect, in %;

$C_{av,c}$ is the average of the at least four independent measurements during the constant concentration period (t_c), in nmol/mol;

$C_{av,v}$ is the average of the at least four independent measurements during the variable concentration period (t_v), in nmol/mol.

The test sequence shall be repeated at least three times. The average of the results for E_{av} shall be reported.



Key

Y concentration (nmol/mol)
X time

Figure 2 — Concentration variations for the averaging effect test

8.4.13 Difference sample/calibration port

If the analyser has different ports for feeding sample gas and calibration gas, the difference in response of the analyser to feeding through the sample or calibration port shall be tested. The test shall be carried out by feeding the analyser with a test gas with a concentration of 70 % to 80 % of the maximum of the certification range of sulphur dioxide through the sample port. The test shall consist of one independent followed by two individual measurements. After a period of at least four response times, the test shall be repeated using the calibration port. The difference shall be calculated according to:

$$\Delta x_{sc} = \frac{x_{sam} - x_{cal}}{c_t} \times 100 \quad (16)$$

where

Δx_{sc} is the difference sample/calibration port, in %;

x_{sam} is the average of the measured concentration using the sample port, in nmol/mol;

x_{cal} is the average of the measured concentration using the calibration port, in nmol/mol;

c_t is the concentration of the test gas, in nmol/mol.

Δx_{sc} shall comply with the performance criterion in Table 1.

8.5 Determination of the performance characteristics during the field test

8.5.1 General

The determination of the performance characteristics in the field as a part of the type approval test shall be performed by a designated body. The quality of the materials and equipment used in the described test procedures shall be in accordance with the requirements given in this standard.

In the field test during a period of three months, two analysers are tested for availability (period of unattended operation), reproducibility in the field and long-term drift. The analysers are run in parallel at one and the same sampling point at a selected monitoring station with specific ambient air conditions (8.5.2). Operational requirements are given for the correct determination of the long-term drift and the reproducibility under field conditions (8.5.3).

8.5.2 Selection of a monitoring station for the field test

The selection of a monitoring station is based on the following criteria:

a) Location:

   1) traffic orientated station (≤ 10 m from kerb-side).

b) Monitoring station facilities:

   1) sufficient capacity of the sampling manifold;

   2) enough room to place two analysers with calibration gases and/or calibration facilities;

   3) surrounding temperature control for the analysers, climate controlled at (20 ± 4) °C with temperature registration;

   4) stable electrical voltage.

c) Other items that could be considered:

   1) presence of telemetry/telephone facilities for remote surveillance of the functioning of the equipment;

   2) accessibility.

8.5.3 Operational requirements

After installation of the analysers at the monitoring station, the proper functioning of the analysers shall be tested. This is comprised of (among other things) the proper connections to the sampling manifold, sample gas flows, correct temperatures of e.g. reaction chambers, response to zero and span gases, data transmission and other items which shall be judged necessary by the designated body

After verification of the proper functioning, the analysers shall be zeroed and adjusted at a value of about 70 % to 80 % of the maximum of the certification range of sulphur dioxide.

During the three-month period the maintenance requirements, by the manufacturer of the analyser shall be followed.

Measurements with zero and span gases shall be performed every two weeks. The concentration c_t of the span gas shall be around 70 % to 80 % of the maximum of the certification range. One independent measurement followed by four individual measurements shall be performed at both zero and at concentration c_t. The measurement results shall be recorded.

To exclude the effect of contamination of the filter when determining the drift of the analyser, the zero and span gases shall be fed to the analyser without passing through the filter.

To avoid the possibility that the filter loading affects the results of the comparison of the two analysers and to ensure that the filter loading will not compromise the quality of the air pollution data collected, the filter shall be changed just before each bi-weekly calibration. Filters that have been pre-conditioned in the laboratory using sulphur dioxide gas mixtures shall be used.

During the three-month period, no manual zero and span adjustments shall be made to the analyser, as this will influence the determination of the long-term drift. The measurement data from the analyser shall only be corrected in a mathematical way, assuming a linear drift since the last zero and span check.

If an auto-rescaling function or self-correction function is included and considered a “normal operational condition”, it shall be enabled during the field tests. The magnitude of any self-correction shall be available to the test laboratory. The magnitude of the auto zero and the auto span drift corrections over the period of unattended operation (long-term drift) both have the same restrictions as laid down in the performance characteristics.

For the determination of the various performance characteristics, test gases (air containing a certain sulphur dioxide concentration) shall be used, traceable to (inter)nationally accepted standards, unless otherwise stated in this European Standard. Various methods for the generation of test gases are given in Table 3 (see 8.4.2.3).

The uncertainties in zero and span gases used for the field tests shall be proven to be insignificant. Possible contamination of zero and span gas shall not significantly influence the results of the laboratory and field tests. Therefore, the test gases and zero gas shall meet the following specifications:

— maximum permitted expanded uncertainties in the concentration of gases used for field tests: 5 %;

— specification of the purity of test-gases and zero gas (expressed as absolute values) as given in Table 4.

It is advised to perform the field tests with the same set of cylinders and zero air generators exclusively reserved for the tests. The stability of both the zero air and the span gas should be guaranteed over a period longer than the test period.

8.5.4 Long term drift

After each bi-weekly zero and span check, the drift of the analysers under test shall be calculated at zero and at span following the procedures as given underneath. If the drift compared to the initial calibration exceeds one of the performance criteria for drift at zero or span level, the “period of unattended operation” equals the number of weeks till the observation of the infringement, minus two weeks. For further (uncertainty) calculations, the values for “long term drift” are the values for zero and span drift over the period of unattended operation.

At the beginning of the drift period, five individual measurements are recorded (after waiting the time equivalent to one independent measurement just after the calibration) at zero and at span level.

The long-term drift is calculated as follows:

$$D_{l,z} = (C_{z,1} - C_{z,0}) \quad (17)$$

where

$D_{l,z}$ is the drift at zero, in nmol/mol;

$C_{z,0}$ is the average concentration of the measurements at zero at the beginning of the drift period (just after the initial calibration), in nmol/mol;

$C_{z,1}$ is the average concentration of the measurements at zero at the end of the drift period, in nmol/mol.

$D_{l,z}$ shall comply with the performance criterion in Table 1.

$$D_{l,s} = \frac{\left(C_{s,1} - C_{s,0}\right) - D_{l,z}}{C_{s,1}} \times 100 \quad (18)$$

where

$D_{l,,s}$ is the drift at span concentration c_t, in %;

$C_{s,0}$ is the average concentration of the measurements at span level at the beginning of the drift period just after the initial calibration, in nmol/mol;

$C_{s,1}$ is the average concentration of the measurements at span level at the end of the drift period, in nmol/mol;

$D_{L,z}$ is the drift at zero, in nmol/mol.

$D_{l,s}$ shall comply with the performance criterion in Table 1.

NOTE For the determination of a systematic or random drift, a graph with the zero and span gas readings can be useful.

8.5.5 Reproducibility standard deviation under field conditions

The reproducibility standard deviation under field conditions is calculated from the measured hourly averaged data during the three-month period.

The difference $\Delta x_{f,i}$ for each (ith) parallel measurement is calculated from:

$$\Delta x_{f,i} = x_{f,1,i} - x_{f,2,i} \quad (19)$$

where

$\Delta x_{f,i}$ is the ith difference in a parallel measurement, in nmol/mol;

$x_{f,1,i}$ is the ith measurement result of analyser 1, in nmol/mol;

$x_{f,2,i}$ is the ith measurement result of analyser 2, in nmol/mol.

The reproducibility standard deviation under field conditions ($s_{r,f}$) is calculated according to:

$$s_{r,f} = \frac{\left(\sqrt{\frac{\sum_{i=1}^{n} \Delta x_{f,i}^2}{2n}} \right)}{c_f} \times 100 \quad (20)$$

where

$s_{r,f}$ is the reproducibility standard deviation under field conditions, in %;

n is the number of parallel measurements;

c_f is the average concentration of sulphur dioxide measured during the field test, in nmol/mol.

The reproducibility standard deviation for sulphur dioxide under field conditions, $s_{r,f}$, shall comply with the performance criterion in Table 1.

8.5.6 Period of unattended operation

The period of unattended operation is the time period within which the drift is within the performance criterion for long-term drift. If the manufacturer specifies a shorter period for maintenance, then this will be taken as the period of unattended operation. If one of the analysers malfunctions during the field test, then the field test shall be restarted to show whether the malfunction was coincidental or the result of poor design.

NOTE A minimum period of unattended operation is normally recommended to be at least two weeks.

8.5.7 Period of availability of the analyser

The correct operation of the analysers shall be checked at least every 14 days. It is recommended to perform this check every day during the first 14 days. These checks consists of plausibility checks on the measured values, as well as on status signals and other relevant parameters, when available. Time, duration and nature of any malfunctioning shall be logged.

The total time period with useable measuring data is the period during the field test during which valid measuring data of the ambient air concentrations are obtained. In this time period, the time needed for calibrations, conditioning of sample system and filters (6.3) and maintenance shall not be included.

The availability of the analyser is calculated as:

$$A_a = \frac{t_u}{t_t} \times 100 \quad (21)$$

where

A_a is the availability of the analyser, in %;

t_u is the total time period with validated measuring data;

t_t is the time period of the field test minus the time for calibration, conditioning and maintenance.

t_u and t_t shall be expressed in the same units (e.g. hours).

The availability of each analyser shall comply with the criterion in Table 1.

8.6 Type approval and uncertainty calculation

The type approval of the analyser consists of the following steps:

a) The value of each individual performance characteristic tested in the laboratory shall fulfil the criterion stated in Table 1 (see 8.3).

b) The expanded uncertainty calculated from the standard uncertainties due to the values of the specific performance characteristics obtained in the laboratory tests shall fulfil the criterion as stated in Annex I of Directive 2008/50/EC (15% for fixed measurements or 25 % for indicative measurements). This criterion is the maximum uncertainty of individual measurements for continuous measurements at the hourly limit value. The relevant specific performance characteristics and the calculation procedure are given in Annex E.

c) The value of each of the individual performance characteristics tested in the field shall fulfil the criterion stated in Table 1 (see 8.3).

d) The expanded uncertainty calculated from the standard uncertainties due to the values of the specific performance characteristics obtained in the laboratory and field tests shall fulfil the criterion as stated in Annex I of Directive 2008/50/EC (15% for fixed measurements or 25 % for indicative measurements). This criterion is the maximum uncertainty of individual measurements for continuous measurements at the hourly limit value. The relevant specific performance characteristics and the calculation procedure are given in Annex E.

The analyser can be type-approved when all four requirements are met.

9 Field operation and ongoing quality control

9.1 General

When a type-approved analyser has been chosen for a particular measuring task, the suitability of this analyser shall be evaluated at a specific measuring location. This shall be performed by means of a suitability evaluation as described in 9.2.

The analyser shall be installed at a monitoring station in such a way that normal operation of the analyser is not compromised. This implies that the analyser is sheltered and shielded from dust, rain and snow, direct sun radiation, strong temperature fluctuations etc. An enclosure (container or building) with temperature control or air conditioning usually fulfils these requirements. At some locations voltage stabilisers for the power supply may be considered, when voltage fluctuations are expected.

After installation of the analyser at the measuring station, the analyser shall be tested for proper operation. This is described in 9.3 (initial installation).

Subsequently, once the analyser at the specific site has been judged to conform with the EU data quality objectives of Annex I in Directive 2008/50/EC, quality assurance and quality control procedures for ongoing monitoring of sulphur dioxide concentrations shall be followed (as described in 9.4 to 9.6) in order to ascertain that the measured data comply with the uncertainty requirements as given in Annex I of Directive 2008/50/EC (15% for fixed measurements or 25 % for indicative measurements).

9.2 Suitability evaluation

9.2.1 General

When a type-approved analyser has been chosen, the suitability of this analyser shall be evaluated for the site-specific conditions at the monitoring site. For example, temperature fluctuations might be such that the type-approved analyser does not fulfil the uncertainty requirements under these conditions. Consequently, it may be necessary to control the temperature of the air directly surrounding the analyser. Sulphur dioxide test gases that are used for the calibration of the analyser shall be traceable to (inter)nationally accepted standards.

9.2.2 Analyser for a monitoring station or task

An uncertainty assessment for the type-approved analyser shall be made according to 9.9.The site-specific conditions which shall be assessed, are given in Table 5.

Table 5 — Site-specific conditions to be evaluated

Parameters	**Remarks**
Sample pressure range	The range of sample gas pressures expected during a whole period of a year shall be estimated.
Sample gas temperature range	The range of sample gas temperatures expected during a whole period of a year shall be estimated. Sample gas temperature may be controlled by heating or thermostating.
Surrounding temperature range	The range of temperatures expected shall be within the range specified in the type approval test. Temperature may be controlled thermostatically.
Line voltage range[a]	The range of line voltages expected shall be within the range specified in the type approval test. Voltage fluctuations may be controlled by means of voltage stabilisers.
H_2O concentration range	The range of hourly-average H_2O concentrations during a whole period of a year shall be estimated.
H_2S concentration range	The range of hourly-average H_2S concentrations during a whole period of a year shall be estimated.
NH_3 concentration range	The range of hourly averaged NH_3 concentrations during a whole period of a year shall be estimated.
NO concentration range	The range of hourly-average NO concentrations during a whole period of a year shall be estimated.
NO_2 concentration range	The range of hourly-average NO_2 concentrations during a whole period of a year shall be estimated.
m-Xylene concentration range	The range of hourly-average m-xylene concentrations during a whole period of a year shall be estimated.
Expanded uncertainty of the calibration gas	The expanded uncertainty of the calibration gas shall be included. This implies the uncertainty of the calibration gas itself as well as the uncertainty of any dilution system (where applicable)
Calibration frequency	The intended calibration frequency shall be used for the calculation of the influence of the drift.
[a] For an analyser operating on direct current the type approval test of voltage variation shall be carried out over the range of ± 10 % of the nominal voltage.	

As a “default” input the extreme conditions from the type-approval may be used.

If the site-specific conditions are outside the conditions for which the analyser is type-approved, then either:

a) the analyser is subjected to supplementary tests by a designated body under these site-specific conditions;

b) the analyser is tested by the network under these site-specific conditions when the number of sites under concern is limited; or

c) the uncertainty assessment is performed by extrapolation of the conditions under concern.

In each case, the uncertainty shall be recalculated and a report shall be issued. If the analyser complies with the requirements laid down in Annex I of Directive 2008/50/EC (15% for fixed measurements or 25 % for indicative

measurements), then that particular analyser may be installed and used at that monitoring station. The decision on the permission for its use rests with the National Competent Authority.

If the site-specific conditions are inside the conditions for which the analyser is type-approved, then the uncertainty may be calculated using these site-specific conditions. The evaluations shall be documented.

The analyser shall only be used in the tested configuration.

NOTE EN ISO 14956 gives information about typical levels of air pollutants. However, these should be used with proper care for their representativeness for the situations under consideration.

9.3 Initial installation

When the analyser and the sampling system have been set up at the monitoring station, proper functioning of the analyser and sampling system shall be checked. The results of these checks shall fulfil the requirements and limitations as set out by the manufacturer of the analyser as well as the requirements (such as materials used, residence times and so on) given in this standard. The compliance with the requirements of the manufacturer and requirements set out in this standard shall be documented.

During the initial installation, a lack of fit test shall be performed according to 8.4.6.

In addition, the repeatability standard deviation ($s_{r,z}$) at zero concentration shall be determined. After waiting the time equivalent of one independent measurement, 10 individual measurements at zero concentration shall be performed to calibrate the analyser. From these measurements, the repeatability standard deviation ($s_{r,z}$) at zero concentration shall be calculated according to Formula (7).

The results shall fulfil the criteria in Table 6.

The repeatability standard deviation shall be combined with the slope of the calibration function to calculate the detection limit of the analyser using Formula (8). The detection limit is used:

a) to define the maximum level of sulphur dioxide in zero gas used for calibration (see 9.5.2);

b) when processing data as described in 9.8.

It is permitted that these tests be carried out in the laboratory directly before installation at the site or at installation at the site.

The shortest expected lifetime of a particle filter (6.3.2) at a particular site type shall be tested by measuring the loss of sulphur dioxide applied to the analyser with and without the filter. The concentration of sulphur dioxide in the test gas shall be about 100 nmol/mol. The criterion for replacement is a loss of > 3 % of sulphur dioxide.

The test may be performed at a number of monitoring sites representative of other sites in a network. The results are then generalised for other sites of the same type.

The complete test may be performed before putting the analyser into routine operation. Alternatively, the first test is a part of the initial installation, with following tests performed as a part of routine QA/QC. Consideration should be given to the fact that the latter approach may lead to loss of data that will affect data capture.

NOTE A relatively simple test procedure is the following.

a) Supply an overflow of test gas to the analyser, passing the filter, using a t-piece;
b) Measure the concentration of sulphur dioxide at initial installation;
c) After 1 week, again measure the concentration of sulphur dioxide;
d) Replace the filter with a new filter and measure the concentration of sulphur dioxide;
e) Calculate the loss of sulphur dioxide from the relative differences in the two concentrations;
f) Repeat the procedure after 2 weeks, 4 weeks, 8 weeks, 16 weeks etc. until the loss of sulphur dioxide exceeds the criterion of 3 %;
g) Establish the maximum lifetime of the filter from the calculated losses.

When the concentrations measured by an analyser at a monitoring station are collected by a data-logger/computer system, then the proper functioning of the data collection shall be checked. When the measured data are transmitted to a central computer system, the transmission process shall be checked as well. Checks shall be performed to an extent ensuring that the actual concentrations measured by the analyser are properly recorded in any data collection system.

Subsequently, each time parts of the data registration/transmission process are changed, the proper function of the complete process shall be rechecked.

All checks on the proper function of the data collection/transmission system(s) shall be documented.

9.4 Ongoing quality assurance/quality control

9.4.1 General

Quality control is necessary in order to ensure that the uncertainties of the measured values for sulphur dioxide in ambient air are kept within the stated limits during extended continuous monitoring periods in the field. This requires that maintenance, test and calibration procedures shall be followed which are essential for obtaining accurate and traceable air quality data. In this section, procedures for maintenance, checks and calibration are given. These procedures are regarded as a minimum necessary for maintaining the required quality level.

The quality of the materials and equipment used in the described test procedures shall be in accordance with the requirements given in this standard and shall not significantly influence the results of these procedures.

If a National Reference Laboratory performs the ongoing quality control procedures it shall be accredited according to EN ISO/IEC 17025.

It is recommended that other designated bodies that perform ongoing quality control procedures are accredited according to EN ISO/IEC 17025 or work in accordance with its requirements.

9.4.2 Frequency of calibrations, checks and maintenance

The checks and calibrations together with their frequency are summarised in Table 6. Criteria are also given for readjustment, calibration or maintenance of the analyser.

In applying these criteria, the user shall be aware that the combination of a number of performance characteristics being close to their respective action criteria may lead to a violation of the measurement uncertainty data quality objective specified in Annex I of Directive 2008/50/EC (15% for fixed measurements or 25 % for indicative measurements). The approach to the assessment of measurement uncertainty described in Annex F can be used to check when such violations occur.

Table 6 — Required frequency of calibration, checks and maintenance

Calibration, checks and maintenance	Section	Frequency	Action criteria[d,e]
Calibration of the analyser	9.5.1	At least every three months and after repair	Zero or span drift beyond the tolerances set by the user
Repeatability at zero and span of the analyser	9.5.1	In combination with calibration, using the data from the calibration	Repeatability standard deviation at zero: ≥ 1,0 nmol/mol Repeatability standard deviation at span: ≥ 1,5 % of span concentration
Verification of gases used for zero and span checks	9.5.2	At least every six months	Zero: ≥ detection limit Span: ≥ 5,0 % of previous verification
Zero and span check	9.6.1	At least every two weeks[a]	Zero : ≤ -4,0 or ≥ 4,0 nmol/mol Span : ≥ 5,0 % of initial span value
Lack of fit check (to be performed in laboratory or in field)	9.6.2, Annex A	Within one year after initial installation and after repair Further frequency depending on the results of the previous test	Lack of fit > 4,0 % of the measured value Lack of fit > 5,0 nmol/mol at zero
Testing sample manifold - influence of pressure drop induced by the manifold pump - sample collection efficiency	 9.6.3.1 9.6.3.2	At least every three years	 influence ≥ 1,0 % of measured value influence ≥ 2,0 % of the measured value
Change of particle filters[b] of the sampling system at the sampling inlet and/or at the analyser inlet	9.3, 9.7.1	Depending on the results of a test as prescribed in 9.3, but at least every three months[c]	
Test of the sampling lines	6.3	At least every six months[c]	≥ 2,0 % sample loss
Changing of consumables	9.7.2	As required by manufacturer[c]	As required
Preventive/routine maintenance of components of the analyser	9.7.3	As required by manufacturer	As required

Calibration, checks and maintenance	Section	Frequency	Action criteria[d,e]

[a] Recommended every 23 or 25 h.

[b] The particle filter shall be changed periodically depending on the dust loading at the sampling site. Overloading of the particle filter may change the concentration of sulphur dioxide. The filter housing shall be cleaned every six months.

[c] Dependent on site-specific conditions as established at initial installation.

[d] If infringement of an action criterion occurs, corrective actions shall be taken as soon as possible. An evaluation of the influence of the detected infringement on the measurement data produced before the actual correction of the infringement took place shall be given and taken into account during data validation. To ensure that the data capture criterion is met, data will need to be inspected by a trained operator every working day.

[e] The combination of a number of performance characteristics being close to their respective action criteria may lead to a violation of the measurement uncertainty data quality objective specified in Directive 2008/50/EC. In this case, the measurement uncertainty shall be re-assessed to ensure conformity with the uncertainty requirements. The approach to the assessment of measurement uncertainty described in Annex F can be used to check when such violations occur.

9.5 Calibration of the analyser

9.5.1 General

Calibration shall be performed at least every three months at a recommended concentration of 70 % to 80 % of the certification range, to determine analyser response and drift. Calibrations at higher frequencies will give a better indication of drift and analyser performance.

When the maximum concentrations of SO_2 measured at a specific site (type) are significantly below the maximum of the certification range for SO_2 of the analyser, e.g. below 20 %, the concentration at which the calibration is performed may be lowered accordingly. This implies that also the concentrations applied for span checks (9.6.1), lack of fit tests (9.6.2) and converter efficiency tests should be lowered proportionally.

The three-monthly interval may be extended to six months when analyser stability can be demonstrated. A measure for this may be the results of zero and span checks over a three-month period being $\leq$ 2 %. However, in order to use this criterion the demonstration of stability of zero and span test gases over this period is a prerequisite.

Calibration gases shall be introduced before the filter to check and, if necessary, to correct for contamination of the filter.

After waiting the time equivalent of one independent measurement, 10 individual measurements both at zero concentration and at span concentration shall be performed to calibrate the analyser. In addition, from these measurements the repeatability standard deviation ($s_{r,z}$) at zero concentration and at span level shall be calculated according to Formula (7).

Repeatability may be determined either in the laboratory or on site.

The standard deviations shall comply with the performance criterion in Table 6, both at zero and at the span level.

Frequency of test:
At least every three months and after repair.

Action criterion:
Zero or span drift beyond the tolerances set by the user.

Action:
Service the analyser.

If servicing includes manual adjustment to the analyser, this shall only be performed by competent personnel, following strict QA/QC procedures to guarantee documentation and traceability of any adjustment.

After servicing the analyser shall be recalibrated.

9.5.2 Calibration gases

For the calibration of the analyser, several methods are available to generate calibration gases. In Table 3 the various methods are given.

The concentrations of the sulphur dioxide calibration gases that are used to calibrate the analyser shall be traceable to (inter)nationally accepted standards. Maximum permitted uncertainty in the concentration of gases used for ongoing quality control is 5 % with a level of confidence of 95 %. The zero gas shall give no analyser reading higher than the detection limit. The gases shall be different from those used for the zero and span checks. The user shall demonstrate that the uncertainty of the calibration gas does not add to the uncertainty budget in such a way that data quality uncertainty requirements are exceeded.

9.5.3 Data adjustment function

After calibration the readings of the analyser as logged by the data acquisition system shall be corrected in accordance with the following formula:

$$c_{SO2} = \left(y_{SO2} - c_{SO2,zero}\right) \times \frac{c_{calgas}}{\left(c_{SO2,cal} - c_{SO2,zero}\right)} \quad (22)$$

where

c_{SO2} is the corrected reading, in nmol/mol;

c_{calgas} is the concentration of SO_2 gas used for calibration of the analyser, in nmol/mol;

$c_{SO2,cal}$ is the reading of the analyser during calibration as logged by the data acquisition system, in nmol/mol;

$c_{SO2,zero}$ is the reading of the analyser during the zero check as logged by the data acquisition system, in nmol/mol;

y_{SO2} is the reading of the analyser during measurements, in nmol/mol.

9.6 Checks

9.6.1 Zero and span checks

9.6.1.1 Zero and span gases

Zero and span gas can be supplied by gas cylinder, or generated by an external calibrator unit or internally in the analyser. The concentration c_t of the span gas shall be around 70 % to 80 % of the maximum of the certification range or the user-defined range (see 9.5.1).

The stability of the gases used for span and zero checks shall be verified at least every six months with use of reference gases traceable to (inter)nationally accepted standards. These gases shall fulfil the specifications in Table 4. The zero gas shall give no measurement result higher than that specified in Table 6, and the gas used for daily span checks shall not differ by more than 5 % of the last measured value.

The purity of the gases may be as specified in Table 4. However, it is possible to relax the impurity specifications in the gases for water vapour and ammonia. In these cases the uncertainty due to the presence of excess impurities shall be included in the uncertainty budget, where significant.

Action criteria:
Zero ≥ detection limit;
Span ≥ 5 % of previous verification.

Appropriate action:
Service the span or zero gas generation unit.

9.6.1.2 Performance of zero and span checks

Zero and span gas shall be introduced into the analyser for a period sufficient to get a stable reading and with the objective of achieving 75 % of valid data each hour.

The timing may also be arranged that zero gas and span gas are injected during consecutive hourly periods.

For zero and span checks the gases should pass through the particle filter, whenever possible.

The differences between two zero or two span values obtained from the following formulae shall be calculated to determine if the action criteria have been exceeded:

$$\Delta x_z = \left| Z_i - Z_0 \right| \tag{23}$$

where

Δx_z is the difference between the readings of the current zero check and the most recent zero check after calibration;

Z_i is the reading of the current zero check of the analyser;

Z_0 is the reading of the most recent zero check after calibration of the analyser.

$$\Delta x_s = \frac{\left| S_i - S_0 \right| - \Delta x_z}{S_0} \times 100 \tag{24}$$

where

Δx_s is the difference between the readings of the current span check and the span check after calibration, in %;

Δx_z is the difference between the readings of the current zero check and the most recent zero check after calibration;

S_i is the reading of the current span check of the analyser;

S_0 is the reading of the most recent span check after calibration of the analyser.

Frequency of test:
At least every two weeks. Recommended every 23 or 25 h.

Action criteria:
Zero drift ≤ -4 nmol/mol or ≥ 4 nmol/mol;
Span drift ≥ 5 %.

Appropriate action:
The analyser shall be recalibrated.

9.6.2 Lack of fit

The lack of fit of the analyser shall be tested using at minimum the following concentrations: 0 %, 60 %, 20 %, and 95 % of the maximum of the certification range of sulphur dioxide or the user-defined range (see 9.5.1). At each concentration (including zero) at least two individual readings shall be performed. After each change in concentration at least four response times shall be taken into account before the next measurement is performed.

Frequency of test:
a) Within one year of the test at initial installation; subsequently;

   1) within one year after test if the lack-of-fit is within 2,0% to 4,0 %;

   2) within three years if the lack of fit is ≤ 2,0 %;

b) After repair.

Action criteria:
> 4,0 % of the measured value;

> 5,0 nmol/mol for residual at zero.

Appropriate action:

Remove analyser from site for further testing and repair if necessary.

NOTE Lack of fit may be checked either in the laboratory or on site.

9.6.3 Testing the sample manifold

9.6.3.1 Procedure for measuring pressure drop induced by the manifold pump

Equipment required: Handheld manometer.

Attach the inlet of manometer to sample port on manifold, leave outlet open to atmospheric pressure; record measured pressure drop.

The resulting pressure drop should be used to calculate the induced effect on the analyser's response using the following formula:

$$\Delta X_{\Delta \mathrm{Pm}} = b_{\mathrm{gp}} \Delta P_{\mathrm{m}} \times 100 \qquad (25)$$

where

$\Delta X_{\Delta \mathrm{Pm}}$ is the change in the analyser response due to the influence of the pressure drop induced by the manifold pump, in %;

b_{gp} is the sensitivity coefficient of the analyser to sample gas pressure change expressed as a percentage of the measured value, obtained during the laboratory type approval test;

ΔP_{m} is the measured pressure drop induced by the manifold pump.

Action criteria:
Influence of the pressure drop induced by the manifold sampling pump on the measured concentration ≥ 1,0 %.

Appropriate action:
Reduce flow through manifold to reduce the induced pressure drop so that the criterion is met.

9.6.3.2 Procedure for testing the sample collection efficiency of the sampling manifold

The flow rate of the test gas in the sampling manifold should be such that the residence time is greater than or equal to that found under normal operating conditions as assessed by the user. Typical manifold (diameter ~30 mm, length 2 m) have a volume of ~1,5 l and shall have a maximum residence time of 5 s.

Frequency of test:
At least every three years.

Action criteria:
Sample loss ≥ 2,0 %.

Appropriate action:
Clean/replace/repair manifold as necessary and re-test.

Possible test procedures for the sample collection efficiency include:

— delivering a test gas containing a known concentration of sulphur dioxide directly to the manifold and measuring the sulphur dioxide concentrations directly in the test gas and at the sampling port of the manifold;

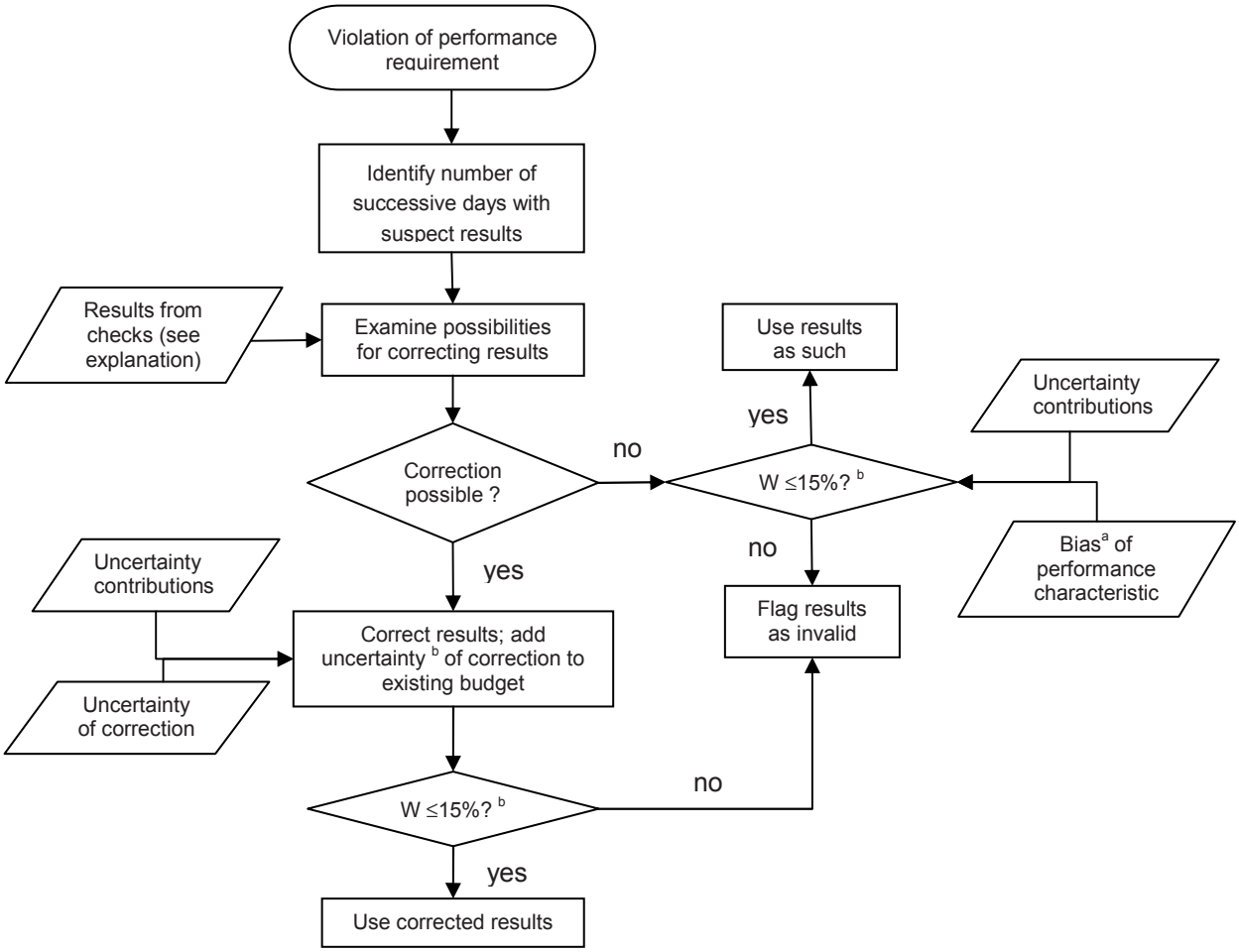
— adding a known flow of a test gas containing a known concentration of sulphur dioxide to the ambient air sampled and measuring the concentrations of sulphur dioxide at the top and sampling port of the manifold using two separate analysers.

In Annex D, an example is given of a possible manifold test performance using the first setup.

9.6.4 Treatment of data after exceedance of performance criteria

If in one of the above checks a violation of a performance criterion occurs, the effect of this violation on the measurement results obtained between the previous and the current check shall be evaluated. The aim of this evaluation is to attempt to optimise the time coverage and data capture. In principle, the first shall be 100 %; the second shall be ≥ 90 % of measurement time excluding periods of calibration and normal maintenance.

A flow scheme for the performance of this evaluation and for the evaluation of possibilities for correcting data is given below in Figure 3.



[a] The deviation of the value of the performance characteristic from its requirement.
[b] At the level of the hourly limit value.

Figure 3 — Flow scheme for performance of evaluation of effects of violation of performance requirements and possibilities for data correction

EXAMPLE Checks that would in principle permit application of corrections include:

— verification of test gases (9.6.1);

— zero and/or span drift checks (9.6.2).

9.7 Maintenance

9.7.1 Change of particle filters

The effective filter lifetime shall be determined as described in 9.3. Filters may be changed at a frequency higher than that determined from the test results, but shall be changed at least every three months.

When replacing filters contamination should be avoided. This may be achieved by wearing gloves or using suitable tweezers.

NOTE The lifetime of the filter will be affected by changes particle composition and/or concentration level and changes in sulphur dioxide levels at the site (type). As a consequence, the frequency of filter replacement might need to be increased.

New filters shall be conditioned with ambient air for 30 min before any ambient data is considered valid. This conditioning is considered a part of normal maintenance.

Action criteria:
Response to sulphur dioxide gas mixture passing the filter is ≤ 97 %.

Appropriate action:
Replace the filter.

9.7.2 Change of sampling lines

Sampling lines shall be changed or cleaned at least every six months.

9.7.3 Change of consumables as applicable

Generally, the requirements of the manufacturer can be followed. However, at the initial installation, the effects of site-specific conditions on consumables' lifetimes shall be established. Site-specific maintenance periods shall then be devised for the replacement of such consumables.

9.7.4 Preventive/routine maintenance of components of the analyser

The manufacturer's recommendations should be followed for the routine maintenance of the analyser.

9.8 Data handling and data reports

The designated body responsible for QA/QC of the monitoring station is responsible for producing valid data. This implies that the collected data shall be free from data acquired during normal maintenance, faulty data, zero and span checks and calibrations.

Data used for aggregation purposes shall have at least one digit more than the numerical value of the hourly limit value for SO_2. For all measurements, basic values ≥ - *(detection limit)* shall be accepted for aggregations and calculations. Values < - *(detection limit)* shall be discarded.

When a datum that is larger than the maximum of the certification range is reported, this datum shall be used in the calculation of averages. However, these averages shall be flagged in the data report to indicate that these averages may have exceeded the uncertainty requirement in Annex I of Directive 2008/50/EC (15% for fixed measurements or 25 % for indicative measurements).

Rounding of results shall be the last step of any calculation, i.e., immediately before comparing the result with the limit value. For rounding, the so-called "commercial rounding" shall be used.

Data collection from the analyser shall be done at a frequency of at least twice per response time period.

Data capture shall be ≥ 75 % of the averaging time.

The response of the analyser to zero or span test gases shall be recorded before and after the adjustment of the analyser. Measured drift in the analyser's response that is less than the action criteria in Table 6 may be corrected for in data processing.

9.9 Measurement uncertainty

Annexes F to H describe the assessment of uncertainties of measurement results for hourly, daily and annual averaging periods, respectively. These assessments are based on combining uncertainty contributions derived from actual values of the performance characteristics obtained from the type-approval tests with practical values obtained as a result of evaluation of QA/QC data, e.g., for zero and span drift, actual ranges of influence characteristics and actual uncertainties of calibration gas mixtures. The assessment does not include the uncertainty contribution of the sampling process. The contribution of data transmission is not considered in the final uncertainty budget.

The assessment shall be repeated at least every year using actual values of uncertainty contributions estimated from information gained during ongoing QA/QC.

NOTE 1 The approach described in Annexes F to H allows the user to compare uncertainty contributions and target QA/QC towards reduction of the largest contributions to uncertainty (see also the note under Table 6, 9.4.2).

NOTE 2 Other approaches, such as those described in EN ISO 20988 [4], may also be used. These may be particularly useful for analysers for which currently no values of performance characteristics from type-approval tests are available.

10 Expression of results

The readings from the analyser are converted to concentrations using the appropriate conversion factors and the results expressed in micrograms per cubic metre.

The conversion factors at 20 °C and 101,3 kPa are:

— 1 $\mu g/m^3$ SO_2 = 0,376 nmol/mol SO_2;

— 1 nmol/mol SO_2 = 2,66 $\mu g/m^3$ SO_2.

NOTE For conversion at different atmospheric pressures and/or temperatures, factors may be derived from the ideal gas law.

11 Test reports and documentation

11.1 Type approval test

The designated body shall prepare a type approval report, which shall contain at least the following information:

a) General:

1) certification proposal;

2) unambiguous analyser designation;

3) measured component(s);

4) device manufacturer together with full address;

5) field of application;

6) measuring range for type-approval test;

7) restrictions: restrictions shall be formulated if testing shows that the analyser does not cover the full scope of possible application fields;

8) notes: in the event of supplementary or extended testing, reference shall be made to all preceding test reports. Attention shall de drawn to main equipment peculiarities;

9) test laboratory;

10) test report number and date of compilation.

b) Task definition:

1) nature of test: first test or supplementary testing;

2) objective: specification of which performance criteria were tested; bibliography; scope of any supplementary tests.

c) Description of the analyser tested:

1) measuring principle: description of metrological and scientific relationships;

2) analyser scope and set-up: description of all parts of the analyser covered in the scope of testing, if possible including a copy of an illustration or flow diagram showing the analyser; statement of technical specifications, if appropriate, in tabular form.

d) Test program: details shall be provided on the test program, in relation to the analyser under test; in the case of supplementary or extended testing, the additional scope of testing shall be detailed and substantiated; particularities of the test shall be documented:

1) laboratory test: statement of test steps involved;

2) field test: details on: test steps involved; site type at which the field test examinations were carried out; operating conditions for the analyser under test;

3) any deviations from test steps and/or conditions prescribed in this standard; these shall also be reported on the approval certificate summary page.

e) Test results: comparison of the performance criteria placed on the analyser in the performance test with the results attained. The information below shall be stated for each individual test point in the following order of sequence:

1) citation of performance criterion;

2) equipment;

3) method;

4) evaluation;

5) assessment of measurement uncertainty;

6) detailed presentation of test results allowing for the respective section of the documentation.

The type approval report shall be made available to the (potential) user.

11.2 Field operation

11.2.1 Suitability evaluation

The user and/or operator of an analyser or monitoring station shall prepare a report on the suitability evaluation (9.2, 9.3) of the analyser at the monitoring site. The suitability test report shall contain at least the following information:

a) reference to this European Standard;

b) complete identification of the analyser and monitoring site;

c) results of the suitability evaluation of the analyser at the monitoring site, including the calculated measurement uncertainty;

d) proof of the compliance of the sampling system to this European Standard;

e) checks on the initial installation.

11.2.2 Documentation

The user and/or operator shall document all maintenance, repairs, calibrations, change of calibration units, malfunctionings, etc. for each individual analyser, sampling system and monitoring site, and any deviations from the requirements of this European Standard, provided that these have significant consequences for the quality of the results.

11.2.3 Ambient air quality data reports

Ambient air data reports for sulphur dioxide shall be prepared according to Chapter V, Information and reporting of Directive 2008/50/EC. The report shall contain at least the following information:

a) reference to this European Standard;

b) percentage of data capture;

c) air quality data presented in the required format;

d) a statement on the measurement uncertainty of the data reported, including:

   1) the type of analyser used;

   2) whether it has been type-approved;

   3) a reference to the approach used for uncertainty assessment (e.g. this European Standard).

Annex A
(normative)

Test of lack of fit

A.1 Establishment of the regression line

A linear regression function in the form of $y_i = A + B\,x_i$ is made through calculation of the following formula:

$$y_i = a + B\,(x_i - x_z) \tag{A.1}$$

For the regression calculation, all measuring points (including zero) are taken into account. The total number of measuring points (n) is equal to the number of concentration levels (at least six including zero) times the number of repetitions (at least five) at a particular concentration level.

The coefficient a is obtained from:

$$a = \sum y_i / n \tag{A.2}$$

where

a is the average value of the Y-values;

y_i is the individual Y-value;

n is the number of measuring points.

The coefficient B is obtained from:

$$B = \left(\sum y_i \left(x_i - x_z\right)\right) / \sum \left(x_i - x_z\right)^2 \tag{A.3}$$

where

x_z is the average of the x-values ($=\Sigma\, x_i/n$);

x_i is the individual x-value.

The function $y_i = a + B\,(x_i - x_z)$ is converted to $y_i = A + B\,.x_i$ through the calculation of A:

$$A = a - B\,x_z \tag{A.4}$$

A.2 Calculation of the residuals of the averages

The residuals of the averages of each calibration point (including the zero point) are calculated as follows.

The average of each calibration point (including the zero point) at one and the same concentration c is calculated according to:

$$(y_a)_c = \sum (y_i)_c / m \tag{A.5}$$

where

$(y_a)_c$ is the average y-value at concentration level c;

$(y_i)_c$ is the individual y-value at concentration level c;

m is the number of repetitions at one and the same concentration level $c = (\Sigma\, y_i/m)_c$.

The residual of each average (r_c) at each concentration level is calculated according to:

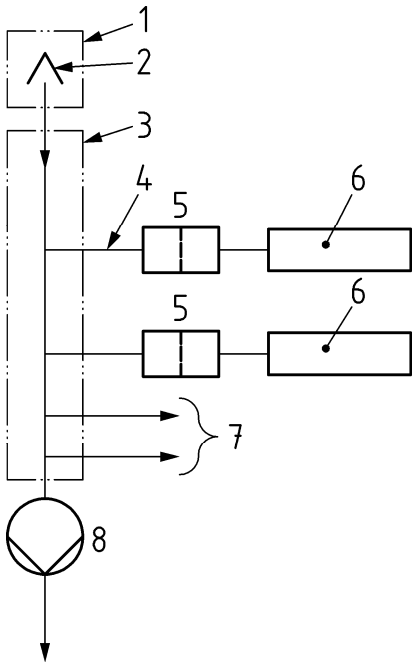
$$r_c = (y_a)_c - (A + B\,c) \tag{A.6}$$

Each residual to a value relative to its own concentration level c is expressed, in %, as:

$$r_{c,rel} = \frac{r_c}{c} \times 100 \tag{A.7}$$

Annex B
(informative)

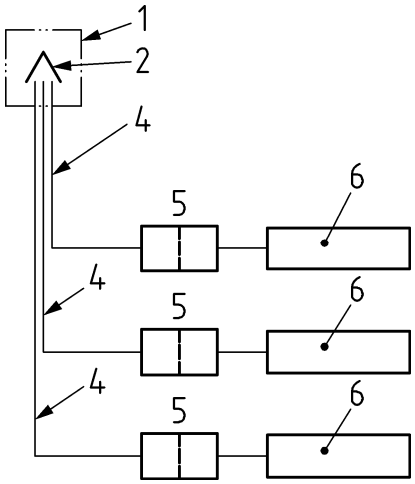
Sampling equipment



Key

1 sample inlet
2 rain shield
3 manifold
4 sampling line
5 filter
6 analyser
7 connection for other analysers or equipment
8 sampling pump for the manifold

Figure B.1 — Sampling layout with a main sampling manifold



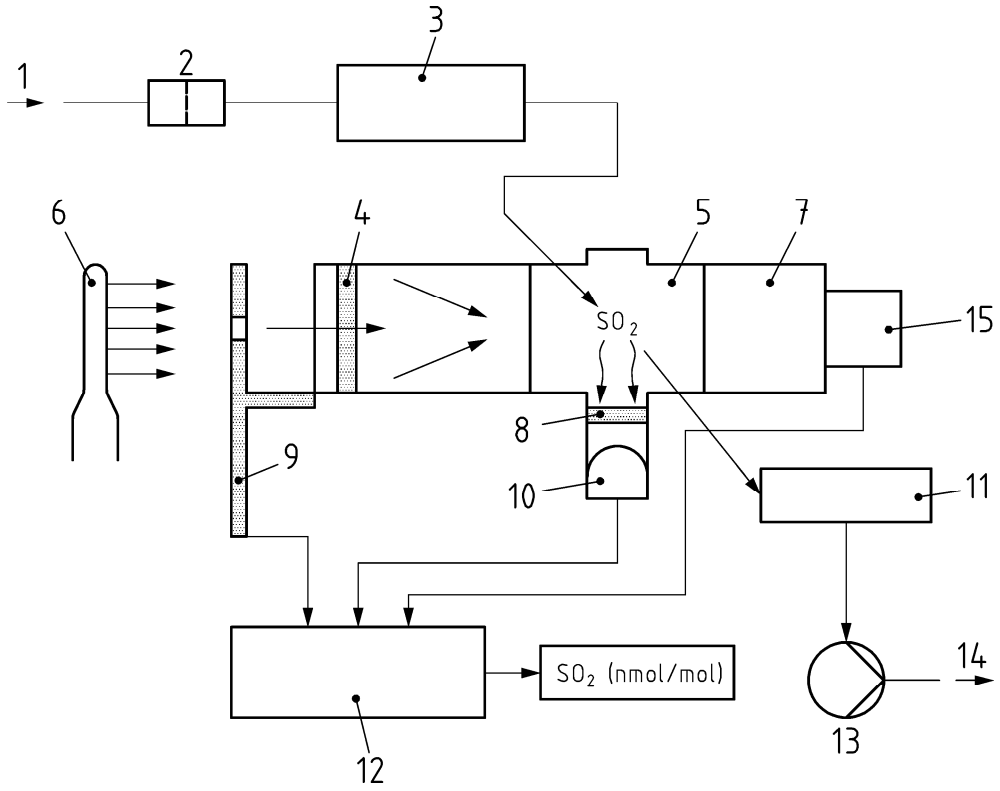
Key

1 sample inlet
2 rain shield
4 sample line
5 filter
6 analyser

Figure B.2 — Sampling layout with individual lines

Annex C
(informative)

Ultraviolet fluorescence analyser



Key

1 sample
2 sampling inlet filter
3 selective traps for interfering agents
4 optical filter
5 reaction chamber
6 UV lamp
7 optical trap
8 optical outlet filter
9 modulator
10 photomultiplier tube
11 compensation pressure flow rate
12 synchronous electronic amplification
13 pump
14 exhaust
15 reference detector

Figure C.1 — Schematic diagram of a UV fluorescence sulphur dioxide analyser

Annex D
(informative)

Manifold testing

Figure D.1 gives the setup for the performance of a manifold test by delivering a test gas containing a known concentration of sulphur dioxide directly to the manifold and measuring the sulphur dioxide concentrations directly in the test gas and at the end of the manifold. The flow of the test gas should be sufficient to keep its residence time within 6 s.

When the concentration of the sulphur dioxide delivered is traceable to (inter)nationally accepted standards, only one test needs to be performed using a calibrated analyser. The sample collection efficiency may then be directly calculated as the ratio of the measured and delivered concentrations.

The sample system collection efficiency, E_{ss}, is then calculated as follows:

$$E_{ss} = \frac{x_{man}}{x_{ref}} \times 100 \quad \text{(D.1)}$$

where

E_{ss} is the sample system collection efficiency, in %;

X_{ref} is reference concentration delivered to the sample manifold;

x_{man} is the mean measured analyser concentration.

When the concentration of the sulphur dioxide delivered is not traceable, two measurements need to be performed, i.e., one by delivering the sulphur dioxide gas mixture directly to the analyser, and one in which the mixture is delivered through the manifold. In this case, the correct calibration of the analysers is not necessary, nor is the exact knowledge of the concentration of the test gas. The concentration of the test gas shall be stable.

During testing, the analyser output is collected through the data collection system at the monitoring site under normal site operating procedures.

Data averaged over periods of 10 min are recorded for each stage of the test.

Sample system collection efficiency, E_{ss}, is then calculated as follows:

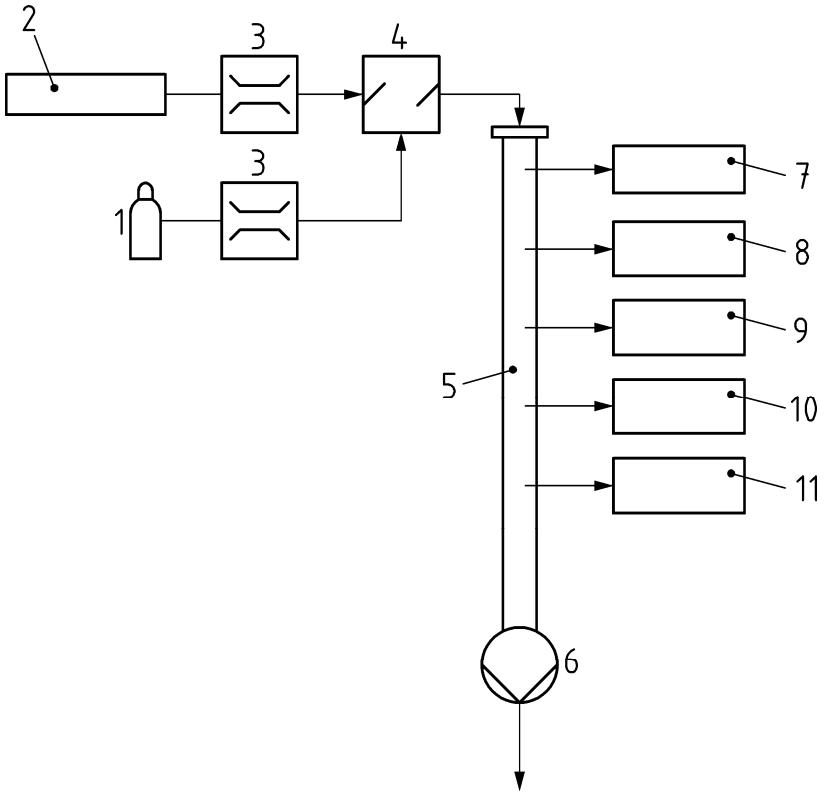
$$E_{ss} = \frac{x_{man}}{x_{dir}} \times 100 \quad \text{(D.2)}$$

where

E_{ss} is the sample system collection efficiency, in %;

x_{dir} is the mean analyser response to the test gas directly sampled by the analyser;

x_{man} is the mean analyser response to the test gas via the sample manifold.



Key

1 source gas
2 zero-air supply
3 mass-flow controllers
4 mixing chamber
5 sampling manifold
6 sampling pump
7 overflow
8 ozone analyser
9 carbon monoxide analyzer
10 sulphur dioxide analyser
11 nitrogen oxides analyser

NOTE Target concentration sulphur dioxide is 134 nmol/mol.

Figure D.1 – Schematic diagram of manifold testing equipment

Annex E
(normative)

Type approval

E.1 Type approval and uncertainty calculation

E.1.1 Type approval

The type approval of the analyser consists of the following steps (see 8.6):

a) The value of each individual performance characteristic tested in the laboratory shall fulfil the criterion stated in Table 1 (see 8.2).

b) The expanded uncertainty calculated from the standard uncertainties due to the values of the specific performance characteristics obtained in the laboratory tests shall fulfil the criterion as stated in Annex I of Directive 2008/50/EC (15% for fixed measurements or 25 % for indicative measurements). This criterion is the maximum uncertainty of hourly values of continuous measurements at the hourly limit value. The relevant specific performance characteristics and the calculation procedure are given in this annex.

c) The value of each of the individual performance characteristics tested in the field shall fulfil the criterion stated in Table 1 (see 8.2).

d) The expanded uncertainty calculated from the standard uncertainties due to the values of the specific performance characteristics obtained in the laboratory and field tests shall fulfil the criterion as stated in Annex I of Directive 2008/50/EC (15% for fixed measurements or 25 % for indicative measurements). This criterion is the maximum uncertainty of hourly values of continuous measurements at the hourly limit value. The relevant specific performance characteristics and the calculation procedure are given in this annex.

The analyser is type-approved when all four requirements are met.

E.1.2 Uncertainty calculation

For the purpose of application of this European Standard, the combined uncertainty resulting from the laboratory type approval tests is calculated using Formula (E.3).

The combined uncertainty resulting after the additional data from the field tests are available is calculated using Formula (E.28).

E.2 Type approval Requirement a)

Table E.1 gives the performance characteristics that shall be considered in demonstrating compliance with Requirement a) in the type approval procedure and an example of laboratory results.

Table E.1 — Relevant performance characteristics and criteria

No.	Performance characteristic	Symbol	Section	Performance criterion for SO_2		Results lab. test [b]	[c]
1	Repeatability standard deviation at zero	$s_{r,z}$	8.4.5	≤ 1,0	nmol/mol	0,002	✓
2	Repeatability standard deviation at concentration c_t (at a level of the hourly limit value)	$s_{r,ct}$	8.4.5	≤ 3,0	nmol/mol	0,001	✓
3	Lack of fit (residual from the linear regression function at concentrations higher than zero)		8.4.6				
3a	Largest residual from the linear regression function at concentrations higher than zero	r_{max}		≤ 4,0	% of the measured value	0,38	✓
3b	Residual at zero	r_z	8.4.6	≤ 5,0	nmol/mol	0,30	✓
4	Sensitivity coefficient of sample gas pressure	b_{gp}	8.4.7	≤ 2,0	nmol/mol/kPa	0,05	✓
5	Sensitivity coefficient of sample gas temperature	b_{gt}	8.4.8	≤ 1,0	nmol/molK	0,41	✓
6	Sensitivity coefficient of surrounding temperature	b_{st}	8.4.9	≤ 1,0	nmol/molK	0,35	✓
7	Sensitivity coefficient of electrical voltage	b_V	8.4.10	≤ 0,30	nmol/mol/V	0,01	✓
8	Interferents at zero and concentration c_t (at a level of the hourly limit)	$X_{H2O,z}$	8.4.11				
8a	H_2O with concentration 19 mmol/mol [d]	$X_{H2O,ct}$		≤ 10	nmol/mol	-2,3	✓
		$X_{H2O,z}$		≤ 10	nmol/mol	-0,17	✓
8b	H_2S with concentration 200 nmol/mol			≤ 5,0	nmol/mol	-0,67	✓
				≤ 5,0	nmol/mol	-0,07	✓
8c	NH_3 with concentration 200 nmol/mol	$X_{NH3,z,ct}$		≤ 5,0	nmol/mol	-0,70	✓
		$X_{NH3,z}$		≤ 5,0	nmol/mol	0,10	✓
8d	NO with concentration 500 nmol/mol	$X_{NO,z,ct}$		≤ 5,0	nmol/mol	4,0	✓
		$X_{NO,z}$		≤ 5,0	nmol/mol	3,3	✓
8e	NO_2 with concentration 200 nmol/mol	$X_{NO2,z,ct}$		≤ 5,0	nmol/mol	1,0	✓

No.	Performance characteristic	Symbol	Section	Performance criterion for SO_2		Results lab. test [b]	[c]
		$X_{NO2,z}$		≤ 5,0	nmol/mol	0,23	✓
8f	m-xylene with concentration 1,0 µmol/mol	$X_{xyl,ct}$		≤ 10,0	nmol/mol	1,0	✓
		$X_{xyl,z}$		≤ 10,0	nmol/mol	0,07	✓
9	Averaging effect	E_{av}	8.4.12	≤ 7,0	% of the measured value	4,0	✓
13	Short term drift at zero	$\langle AC_1 \rangle D_{s,z} \langle AC_1 \rangle$	8.4.4	≤ 2,0	nmol/mol over 12 h	0,007	✓
14	Short term drift at span level [a]	$\langle AC_1 \rangle D_{s,s} \langle AC_1 \rangle$	8.4.4	≤ 6,0	nmol/mol over 12 h	0,20	✓
15	Response time (rise)	t_r	8.4.3	≤ 180	s	52	✓
16	Response time (fall)	t	8.4.3	≤ 180	s	55	✓
17	Difference rise time and fall time	t_d	8.4.3	≤ 10	s	3	✓
18	Difference sample/calibration port [e]	ΔX_{sc}	8.4.13	≤ 1,0	%	0	✓

[a] Span level is 70 % to 80 % of the certification range.

[b] To demonstrate compliance the absolute value of the performance characteristic shall be taken.

[c] ✓ : requirement is met.

[d] A H_2O-concentration of 19 mmol/mol equals 80 % RH at 20 °C and 101,3 kPa.

[e] If relevant.

Conclusion: All values of the performance characteristics obtained in the laboratory tests comply with the requirements. Requirement a) is fulfilled.

E.3 Type approval Requirement b)

E.3.1 General

In type approval Requirement b), the expanded uncertainty calculated from the standard uncertainties due to the values of the specific performance characteristics obtained in the laboratory tests shall fulfil the criterion as stated in Annex I of Directive 2008/50/EC (15% for fixed measurements or 25 % for indicative measurements). This criterion is the maximum uncertainty of hourly values of continuous measurements at the hourly limit value.

The model formula for the measurement is based on the assumption that the measured value c consists of signal contribution from the concentration of the measurand, c^*, and a sum of signal contributions c_K (in units of the measured value) caused by the influence of the considered performance characteristics K of the measuring system:

$$c = c^* + \sum_k c_k \qquad \text{(E.1)}$$

From this model formula the following variance formula is derived which describes the uncertainty of the measured value, $u(c)$, under the conditions of the type approval test:

$$u^2(c) = \sum_k u^2(c_k) \qquad \text{(E.2)}$$

The values of the following uncertainties (Table E.2) shall be included in the calculation of the expanded uncertainty after the laboratory tests.

Table E.2 — Standard uncertainties to be incorporated in the calculation of the expanded uncertainty after the laboratory tests

No.	Standard uncertainty due to	Symbol	Formula
1	Repeatability standard deviation at zero	$u_{r,z}$	E.6, E.7
2	Repeatability standard deviation at the hourly limit value	$u_{r,lh}$	E.8 to E.10
3	Lack of fit at the hourly limit value	$u_{l,lh}$	E.11
4	Variation in sample gas pressure at the hourly limit value	u_{gp}	E.15
5	Variation in sample gas temperature at the hourly limit value	u_{gt}	E.16
6	Variation in surrounding temperature at the hourly limit value	u_{st}	E.17
7	Variation in electrical voltage at the hourly limit value	u_{V}	E.18
8	Interferences at the hourly limit value		
8a	H_2O with concentration 19 mmol/mol	u_{H2O}	E.19, E.20
8b	H_2S with concentration 200 nmol/mol	u_{tol}	E.21, E.22
8c	NH_3 with concentration 200 nmol/mol	u_{NH3}	E.21, E.22
8d	NO with concentration 500 nmol/mol	u_{NO}	E.21, E.22
8e	NO_2 with concentration 200 nmol/mol	u_{NO2}	E.21, E.22
8f	m-xylene with concentration 1,0 µmol/mol	u_{xyl}	E.21, E.22
9	Averaging effect	u_{av}	E.25
18	Difference sample/calibration port	$u_{\Delta sc}$	E.27

In addition to the uncertainties due to these performance characteristics, the uncertainty in the concentration of calibration gas and in the calibration itself are incorporated in the uncertainty calculation.

Table E.3 — Standard uncertainty of the calibration gas to be incorporated in the calculation of the expanded uncertainty after the laboratory tests

No.	Standard uncertainty due to	Symbol	Formula
21	Uncertainty in calibration gas	u_{cg}	E.26

The calculation of standard uncertainties is based on the procedures laid down in EN ISO 14956. The uncertainty calculation shall be carried out with the values of the performance characteristics at the concentration of the hourly limit value (if relevant).

The combined standard uncertainty shall be calculated according to:

$$u_c = \sqrt{u_{r,z}^2 + u_{r,lh}^2 + u_{l,lh}^2 + u_{gp}^2 + u_{gt}^2 + u_{st}^2 + u_V^2 + u_{H_2O}^2 + u_{int}^2 + u_{av}^2 + u_{\Delta sc}^2 + u_{cg}^2} \quad \text{(E.3)}$$

where

u_c is the combined standard uncertainty in nmol/mol;

$u_{r,z}$ is the standard uncertainty for repeatability at zero, in nmol/mol;

$u_{r,lh}$ is the standard uncertainty for repeatability at level of the hourly limit value, in nmol/mol;

$u_{l,lh}$ is the standard uncertainty for lack of fit at level of the hourly limit value, in nmol/mol;

u_{gp} is the standard uncertainty for sample gas pressure variation, in nmol/mol;

u_{gt} is the standard uncertainty for sample gas temperature variation, in nmol/mol;

u_{st} is the standard uncertainty for surrounding temperature variation, in nmol/mol;

u_V is the standard uncertainty for electrical voltage variation, in nmol/mol;

u_{H2O} is the standard uncertainty for the presence of water vapour, in nmol/mol;

u_{int} is the standard uncertainty for interferents (except water vapour), in nmol/mol;

u_{av} is the standard uncertainty for averaging, in nmol/mol;

$u_{\Delta sc}$ is the standard uncertainty for difference sample/calibration port, in nmol/mol;

u_{cg} is the standard uncertainty for calibration gas, in nmol/mol.

The absolute **expanded uncertainty** shall be calculated according to:

$$U = k u_c \quad \text{(E.4)}$$

with $k = 2$

where

U is the expanded uncertainty, in nmol/mol;

k is the coverage factor of approximately 95 %;

u_c is the combined standard uncertainty, in nmol/mol.

The relative **expanded uncertainty** shall be calculated according to:

$$W = \frac{U}{l_h} \times 100 \quad \text{(E.5)}$$

where

W is the relative expanded uncertainty, in %;

U is the expanded uncertainty, in nmol/mol;

l_h is the hourly limit value of sulphur dioxide, in nmol/mol.

Requirement 2 is fulfilled when: $W \leq W_{req.}$

E.3.2 Calculation of standard uncertainties

For the calculation of the standard uncertainties, the following formulae shall be used.

Repeatability at zero

The standard uncertainty for **repeatability at zero** is calculated according to:

$$u_{r,z} = \frac{s_{r,z}}{\sqrt{m}} \tag{E.6}$$

with

$$m = \frac{t}{2(t_r + t_f)} \tag{E.7}$$

where

$u_{r,z}$ is the standard uncertainty for repeatability at zero, in nmol/mol;

t is 3 600 s;

t_r is the response time (rise), in s;

t_f is the response time (fall), in s;

$s_{r,z}$ is the repeatability standard deviation at zero according to 8.4.5, in nmol/mol;

m is the number of independent measurements in 3 600 s, taking response (rise) and response time (fall) for half that time period respectively.

Repeatability at the hourly limit value of sulphur dioxide

The standard uncertainty for **repeatability at the hourly limit value** is calculated according to:

$$u_{r,lh} = \frac{s_{r,lh}}{\sqrt{m}} \tag{E.8}$$

with

$$m = \frac{t}{2(t_r + t_f)} \tag{E.9}$$

and

$$s_{r,lh} = \frac{l_h}{c_t} s_{r,ct} \quad \text{(E.10)}$$

where

$u_{r,lh}$ is the standard uncertainty for repeatability at the hourly limit value, in nmol/mol;

$s_{r,lh}$ is the repeatability standard deviation at the hourly limit value, in nmol/mol;

m is the number of independent measurements in 3 600 s, taking response (rise) and response time (fall) for half that time period respectively;

t is 3600 s;

t_r is the response time (rise), in s;

t_f is the response time (fall), in s;

l_h is the hourly limit value, in nmol/mol;

c_t is the test gas concentration (at the level of the hourly limit value), in nmol/mol;

$s_{r,ct}$ is the repeatability standard deviation at the test gas concentration, in nmol/mol.

Lack of fit

The standard uncertainty due to **lack of fit at the hourly limit value** is calculated according to:

$$u_{l,lh} = \frac{r_{max}}{100} \frac{l_h}{\sqrt{3}} \quad \text{(E.11)}$$

where

$u_{l,lh}$ is the standard uncertainty due to lack of fit at the hourly limit value, in nmol/mol;

r_{max} is the maximum residual from a linear regression function, in %, calculated according to Annex A;

l_h is the hourly limit value of sulphur dioxide, in nmol/mol.

Influence quantities

General

The approach taken to quantify the uncertainty contributions due to influence quantities (physical and chemical) is taken directly from EN ISO 14956.

In short: an analyser is calibrated at an influence quantity value q_{cal} and is adjusted before being put into operation.

Subsequently, the analyser is used in the field where ambient values of q may vary between q_{min} and q_{max}. The distribution of the values of q is unknown. The sensitivity coefficient of the variation of response with variations in q has been determined in the type approval test to be b_q nmol/mol/unit.

The maximum positive and negative changes in q are $\Delta q_{max} = q_{max} - q_{cal}$ and $\Delta q_{min} = q_{min} - q_{cal}$

where

q_{max} is the maximum practical value of the influence quantity;

q_{min} is the minimum practical value of the influence quantity.

NOTE Δq_{min} is usually negative.

If the distribution of values of q is assumed to be uniform, the uncertainty in the concentration due to the variations in q is

$$u(c_q) = b_q \sqrt{\frac{\Delta q_{max}^2 + \Delta q_{max}\Delta q_{min} + \Delta q_{min}^2}{3}} \quad \text{(E.12)}$$

When q_{cal} is unknown, but varies between q_{min} and q_{max}, (E.12) reduces to

$$u(c_q) = b_q \sqrt{\frac{(q_{max} - q_{min})^2}{3}} \quad \text{(E.13)}$$

When q_{cal} is zero, as is usually the case for chemical influence quantities, (E.12) reduces to

$$u(c_q) = b_q \sqrt{\frac{q_{max}^2 + q_{max}q_{min} + q_{min}^2}{3}} \quad \text{(E.14)}$$

For calculation of uncertainties within the frame of the type-approval test (E.13) and (E.14) are used.

Sample gas pressure

The standard uncertainty due to variation of **sample gas pressure at the hourly limit value** is calculated as:

$$u_{gp} = \frac{l_h}{c_t} b_{gp} \sqrt{\frac{(P_2 - P_1)^2}{3}} \quad \text{(E.15)}$$

where

u_{gp} is the standard uncertainty due to the influence of pressure, in nmol/mol;

b_{gp} is the sensitivity coefficient of sample gas pressure variation, in nmol/mol/kPa;

l_h is the hourly limit value of sulphur dioxide, in nmol/mol;

c_t is the test gas concentration (70 % to 80 % of the certification range of SO_2), in nmol/mol;

P_1 is the minimum sample gas pressure, in kPa;

P_2 is the maximum sample gas pressure, in kPa.

Sample gas temperature

The standard uncertainty due to variation of **sample gas temperature at the hourly limit value** is calculated as:

$$u_{gt} = \frac{l_h}{c_t} b_{gt} \sqrt{\frac{(T_{G2} - T_{G,1})^2}{3}} \quad \text{(E.16)}$$

where

u_{gt} is the standard uncertainty due to the variation of sample gas temperature, in nmol/mol;

l_h is the hourly limit value of sulphur dioxide, in nmol/mol;

c_t is the test gas concentration (70 % to 80 % of the certification range of SO_2), in nmol/mol;

b_{gt} is the sensitivity coefficient of sample gas temperature variation, in nmol/mol/K;

$T_{G,1}$ is the minimum sample gas temperature, in °C;

$T_{G,2}$ is the maximum sample gas temperature, in °C.

Surrounding temperature

The standard uncertainty due to variation of **surrounding temperature at the hourly limit value** is calculated as:

$$u_{st} = \frac{l_h}{c_t} b_{st} \sqrt{\frac{(T_{S,2} - T_{S,1})^2}{3}} \quad \text{(E.17)}$$

where

u_{st} is the standard uncertainty due to the variation of the surrounding temperature, in nmol/mol;

l_h is the hourly limit value of sulphur dioxide, in nmol/mol;

c_t is the test gas concentration (70 % to 80 % of the certification range of SO_2), in nmol/mol;

b_{st} is the sensitivity coefficient of the surrounding temperature variation, in nmol/mol/K;

$T_{S,1}$ is the minimum surrounding temperature, in °C;

$T_{S,2}$ is the maximum surrounding temperature, in °C.

Electrical voltage

The standard uncertainty due to variation of **electrical voltage at the hourly limit value** is calculated as:

$$u_V = \frac{l_h}{c_t} b_V \sqrt{\frac{(V_2 - V_1)^2}{3}} \quad \text{(E.18)}$$

where

u_V is the standard uncertainty due to the variation of electrical voltage, in nmol/mol;

l_h is the hourly limit value of sulphur dioxide, in nmol/mol;

c_t is the test gas concentration (70 % to 80 % of the certification range of SO_2), in nmol/mol;

b_V is the sensitivity coefficient of electrical voltage variation, in nmol/mol/V;

V_1 is the minimum electrical voltage V_1, in V;

V_2 is the maximum electrical voltage V_2, in V.

Water vapour

The standard uncertainty due to **interference by the presence of water vapour at the hourly limit value** is calculated according to:

$$b_{H_2O} = \frac{1}{c_{H_2O}}\left[X_{H_2O,z} + \left(X_{H_2O,C_t} - X_{H_2O,z}\right)\frac{l_h}{c_t} \right] \quad \text{(E.19)}$$

$$u_{H_2O} = b_{H_2O}\sqrt{\frac{c^2_{H_2O,max} + c_{H_2O,max}c_{H_2O,min} + c^2_{H_2O,min}}{3}} \quad \text{(E.20)}$$

where

$X_{H_2O,z}$ is the influence quantity of an H_2O concentration of 19 mmol/mol at zero concentration of the measurand, in nmol/mol;

X_{H_2O,c_t} is the influence quantity of an H_2O concentration of 19 mmol/mol at the test concentration c_t of the measurand, in nmol/mol;

u_{H_2O} is the standard uncertainty due to interference by the presence of water vapour, in nmol/mol;

b_{H_2O} is the sensitivity coefficient due to interference by the presence of water vapour, in (nmol/mol)/(mmol/mol);

c_{H_2O} is the test concentration of H_2O (19 mmol/mol);

c_t is the test concentration of SO_2 at the level of the hourly limit value, in nmol/mol;

l_h is the hourly limit value of sulphur dioxide, in nmol/mol;

$c_{H_2O,max}$ is the maximum concentration of water vapour, in mmol/mol (= 21 mmol/mol);

$c_{H_2O,min}$ is the minimum concentration of water vapour, in mmol/mol (= 6 mmol/mol).

Other interferents

The standard uncertainty due to each **interfering compound at the hourly limit value** (other than water vapour) is calculated according to:

$$b_{int} = \frac{1}{c_{int}}\left[X_{int,z} + \left(X_{int,C_t} - X_{int,z}\right)\frac{l_h}{c_t} \right] \quad \text{(E.21)}$$

$$u_{int} = b_{int}\sqrt{\frac{c^2_{int,max} + c_{int,max}c_{int,min} + c^2_{int,min}}{3}} \quad \text{(E.22)}$$

where

X_{int,c_t} is the influence quantity of the maximum concentration, in nmol/mol or µmol/mol, of the relevant interfering compound at the test concentration c_t of the measurand, in nmol/mol

$X_{int,z}$ is the influence quantity of the maximum concentration, in nmol/mol or µmol/mol, of the relevant interfering compound at zero concentration of the measurand, in nmol/mol;

u_{int} is the standard uncertainty due to the presence of the interferent, in nmol/mol;

b_{int} is the sensitivity coefficient due to the presence of the interferent, in (nmol/mol)/(nmol/mol) or (nmol/mol)/(µmol/mol);

c_{int} is the test concentration of the relevant interfent, in nmol/mol or µmol/mol;

c_t is the test concentration of SO_2 at the level of the hourly limit value, in nmol/mol;

l_h is the hourly limit value of sulphur dioxide, in nmol/mol;

$c_{int,max}$ is the maximum concentration of interfering compound, in nmol/mol or µmol/mol;

$c_{int,min}$ is the minimum concentration of interfering compound, in nmol/mol or µmol/mol.

According to EN ISO 14956, the summed uncertainties due to the interferents with positive impact and the summed uncertainties of the interferents with negative impact shall be calculated as:

$$u_{int,pos} = \sqrt{(u_{int,1,pos} + u_{int,2,pos} + ... + u_{int,n,pos})^2} \quad \text{(E.23)}$$

$$u_{int,neg} = \sqrt{(u_{int,1,neg} + u_{int,2,neg} + ... + u_{int,n,neg})^2} \quad \text{(E.24)}$$

where

$u_{int,pos}$ is the sum of uncertainties due to interferents with positive impact, in nmol/mol;

$u_{int,1,pos}$ is the uncertainty due to the 1th interferent with positive impact, in nmol/mol;

$u_{int,n,pos}$ is the uncertainty due to the *n*th interferent with positive impact, in nmol/mol;

$u_{int,neg}$ is the sum of uncertainties due to interferents with negative impact, in nmol/mol;

$u_{int,1,neg}$ is the uncertainty due to the 1th interferent with negative impact, in nmol/mol;

$u_{int,n,neg}$ is the uncertainty due to the *n*th interferent with negative impact, in nmol/mol.

The highest value of (E.23) and (E.24) shall be taken as value for u_{int} in (E.3).

Averaging effect

The standard uncertainty due to the **averaging effect** is calculated according to:

$$u_{av} = \frac{E_{av}}{100} \frac{l_h}{\sqrt{3}} \quad \text{(E.25)}$$

where

u_{av} is the standard uncertainty due to the averaging effect, in nmol/mol;

E_{av} is the averaging error, in % of the measured value;

l_h is the hourly limit value, in nmol/mol.

Calibration gas

The standard uncertainty due to the **calibration gas** is calculated according to:

$$u_{cg} = \frac{W_{cg}}{2 \times 100} l_h \quad \text{(E.26)}$$

where

u_{cg} is the standard uncertainty due to the calibration gas, in nmol/mol;

W_{cg} is the relative expanded uncertainty of the calibration gas, in %;

l_h is the hourly limit value of sulphur dioxide, in nmol/mol.

Difference sample/calibration port

The standard uncertainty due to the **difference sample/calibration port** is calculated according to:

$$u_{\Delta sc} = \frac{\Delta x_{sc}}{100} l_h \quad \text{(E.27)}$$

where

$u_{\Delta sc}$ is the standard uncertainty due to the difference sample/calibration port, in nmol/mol;

Δx_{sc} is the difference sample/calibration port, in %;

l_h is the hourly limit value of sulphur dioxide, in nmol/mol.

E.3.3 Example calculation

	SO_2 hlv	133		nmol/mol					
No	Parameter	*Ct*		Unit	Value		X-	X+	u	u^2
1	Repeatability at zero			nmol/mol	0,002				0,00	0,00
2	Repeatability at C_t	300		nmol/mol	0,001				0,00	0,00
3	Lack-of-fit			%	0,38				0,29	0,09
4	Sample gas pressure	300		nmol/mol/kPa	0,05		80	110	0,38	0,15
5	Sample gas temperature	300		nmol/mol/K	0,41		273	303	3,15	9,91
6	Surrounding temperature	300		nmol/mol/K	0,35		273	303	2,69	7,22
7	Electrical voltage	300		nmol/mol/V	0,01		210	240	0,08	0,01
8	Interferences		*Cint*			*Xint*				
8a	- H_2O 19 mmol/mol span	300	19	nmol/mol	-2,33	-0,06	6	21	-0,84	0,71
	- H_2O 19 mmol/mol zero				-0,17					
8b	- H_2S 200 nmol/mol span	300	200	nmol/mol	-0,67	0,00	1	3	0,00	
	- H_2S 200 nmol/mol zero				-0,07					
8c	- NO 500 nmol/mol span	300	500	nmol/mol	4	0,01	50	300	1,37	
	- NO 500 nmol/mol zero				3,3					
8d	- NO_2 200 nmol/mol span	300	200	nmol/mol	1	0,00	5	100	0,17	
	- NO_2 200 nmol/mol zero				0,23					
8e	- m-X 1000 nmol/mol span	300	1000	nmol/mol	1	0,00	0	1	0,00	
	- m-X 1000 nmol/mol zero				0,07					
8f	- NH_3 200 nmol/mol span	300	200	nmol/mol	-0,7	0,00	0	5	0,00	
	- NH_3 200 nmol/mol zero				0,1					
	Sum interferents (without water)								1,54	2,36
9	Averaging effect			%	4				3,07	9,4
18	Difference sample/calibration port			%	0					
21	Calibration gas			%	5				3,33	11,1
	Sum of variances									40,9
	Combined uncertaint (nmol/mol)									6,4
	Expanded uncertainty (%)									9,6

Conclusion: W ≤ 15 %. Requirement b) is met.

E.4 Type approval Requirement c)

Table E.4 gives the performance characteristics that shall be considered in demonstrating compliance with Requirement c) in the type approval procedure.

Table E.4 — Relevant performance characteristics and criteria

No.	Performance characteristic	Symbol	Section	Performance criterion for SO_2		Results field test	[b]
10	Reproducibility standard deviation under field conditions	$s_{r,f}$	8.5.5	≤ 5,0	% of the average of a three month period	2,0	✓
11	Long term drift at zero	$D_{l,z}$	8.5.4	≤ 5,0	nmol/mol	0,56	✓
12	Long term drift at span level [a]	$D_{l,s}$	8.5.4	≤ 4,0	% of maximum of certification range	1,0	✓
19	Period of unattended operation		8.5.6	> 3,0	months or less if manufacturer indicates a shorter period	4	✓
20	Availability of the analyser	A_a	8.5.7	> 90	%	100	✓

[a] Span level is 70 % to 80 % of the certification range.

[b] ✓ : requirement is met.

Conclusion: All values of the performance characteristics obtained in the field tests comply with the requirements. Requirement c) is fulfilled.

E.5 Type approval Requirement d)

E.5.1 General

In type approval Requirement d), the expanded uncertainty calculated from the standard uncertainties due to the values of the specific performance characteristics obtained in the laboratory and field tests shall fulfil the criterion as stated in Annex I of Directive 2008/50/EC (15% for fixed measurements or 25 % for indicative measurements). This criterion is the maximum uncertainty of hourly values of continuous measurements at the hourly limit value.

The calculation of the expanded uncertainty is based on Formulae (E.1) and (E.2).

The values of the following uncertainties (Table E.5) shall be included in the calculation of the expanded uncertainty after the laboratory and field tests.

Table E.5 — Standard uncertainties to be incorporated in the calculation of the expanded uncertainty after the laboratory and field tests

No.	Standard uncertainty due to	Symbol	Formula
1	Repeatability at zero	$u_{r,z}$	E.6, E.7
2	Repeatability at the hourly limit value [a]	$u_{r,lh}$	E.8 – E.10
3	Lack of fit at the hourly limit value	$u_{l,lh}$	E.11
4	Variation in sample gas pressure at the hourly limit value	u_{gp}	E.15
5	Variation in sample gas temperature at the hourly limit value	u_{gt}	E.16
6	Variation in surrounding temperature at the hourly limit value	u_{st}	E.17
7	Variation in electrical voltage at the hourly limit value	u_{V}	E.18
8	Interferents		
8a	H_2O with concentration 19 mmol/mol	u_{H2O}	E.19,E.20
8b	H_2S with concentration 200 nmol/mol	u_{tol}	E.21, E.22
8c	NH_3 with concentration 200 nmol/mol	u_{NH3}	E.21, E.22
8d	NO with concentration 500 nmol/mol	u_{NO}	E.21, E.22
8e	NO_2 with concentration 200 nmol/mol	u_{NO2}	E.21, E.22
8f	m-xylene with concentration 1,0 µmol/mol	u_{xyl}	E.21, E.22
9	Averaging error	u_{av}	E.25
10	Reproducibility under field conditions [a]	$u_{r,f}$	E.29
11	Long term drift at zero	$u_{d,l,z}$	E.30
12	Long term drift at the hourly limit value	$u_{d,l,lh}$	E.31
18	Difference sample/calibration port	$u_{\Delta sc}$	E.27

[a] Take for the calculation of the combined standard uncertainty the uncertainty due to the repeatability at the limit value or the uncertainty due to the reproducibility under field conditions, whichever is greater.

In addition to the uncertainties due to these performance characteristics, the uncertainty in the concentration of calibration gas and in the calibration itself are incorporated in the uncertainty calculation (Table E.6).

Table E.6 — Standard uncertainty of the calibration gas to be incorporated in the calculation of the expanded uncertainty after the laboratory and field tests

No.	Standard uncertainty due to	Symbol	Formula
22	Uncertainty in calibration gas	u_{cg}	E.26

The calculation of standard uncertainties is based on the procedures laid down in EN ISO 14956.The uncertainty calculation shall be carried out with the values of the performance characteristics at the concentration of the hourly limit value (if relevant).

The **combined standard uncertainty** is calculated using the formula:

$$u_c = \sqrt{u_{r,z}^2 + u_{r,C}^2 + u_{l,lh}^2 + u_{gp}^2 + u_{gt}^2 + u_{st}^2 + u_V^2 + u_{H_2O}^2 + u_{int}^2 + u_{av}^2 + u_{d,l,z}^2 + u_{d,l,lh}^2 + u_{\Delta sc}^2 + u_{cg}^2} \quad \text{(E.28)}$$

where

u_c is the combined uncertainty under field conditions, in nmol/mol;

$u_{r,z}$ is the standard uncertainty for repeatability at zero, in nmol/mol;

$u_{r,C}$ is the highest value of the standard uncertainty for repeatability at the hourly limit value $u_{r,lh}$ and the field reproducibility $u_{r,f}$, in nmol/mol;

$u_{l.lh}$ is the standard uncertainty for lack of fit at the hourly limit value, in nmol/mol;

u_{gp} is the standard uncertainty for sample gas pressure variation, in nmol/mol;

u_{gt} is the standard uncertainty for sample gas temperature variation, in nmol/mol;

u_{st} is the standard uncertainty for surrounding temperature variation, in nmol/mol;

u_V is the standard uncertainty for electrical voltage variation, in nmol/mol;

u_{H2O} is the standard uncertainty for the presence of water vapour, in nmol/mol;

u_{int} is the standard uncertainty for interferents (except water vapour), in nmol/mol;

u_{av} is the standard uncertainty for averaging, in nmol/mol;

$u_{d,l,z}$ is the standard uncertainty for long term drift at zero, in nmol/mol;

$u_{d,l,lh}$ is the standard uncertainty for long term drift at level of the hourly limit value, in nmol/mol;

$u_{\Delta sc}$ is the standard uncertainty for difference sample/calibration port, in nmol/mol;

u_{cg} is the standard uncertainty for calibration gas, in nmol/mol.

The absolute **expanded uncertainty** shall be calculated according to:

$$U = ku_c \quad \text{(E.4)}$$

with $k = 2$

where

U is the expanded uncertainty, in nmol/mol;

k is the coverage factor of approximately 95 %;

u_c is the combined standard uncertainty, in nmol/mol.

The relative **expanded uncertainty** shall be calculated according to:

$$W = \frac{U}{l_h} \times 100 \quad \text{(E.5)}$$

where

W is the relative expanded uncertainty, in %;

U is the expanded uncertainty, in nmol/mol;

l_h is the hourly limit value, in nmol/mol.

Conclusion: Requirement d) is fulfilled when: $W \leq W_{req}$.

E.5.2 Calculation of standard uncertainties

For the calculation of the standard uncertainties, the test values as given in E.4 have been used.

The standard uncertainty for **repeatability at zero** is calculated according to Formulae (E.6) to (E.7).

The standard uncertainty for **repeatability at the hourly limit value** is calculated according to Formulae (E.8) to (E.10).

The standard uncertainty due to **lack of fit at the hourly limit value** is calculated according to Formula (E.11).

The standard uncertainty due to variation of **sample gas pressure at the hourly limit value** is calculated according to Formula (E.15).

The standard uncertainty due to variation of **sample gas temperature at the hourly limit value** is calculated according to Formula (E.16).

The standard uncertainty due to variation of **surrounding temperature at the hourly limit value** is calculated according to Formula (E.17).

The standard uncertainty due to variation of **electrical voltage at the hourly limit value** is calculated according to Formula (E.18).

The standard uncertainty due to **interference by the presence of water vapour** is calculated according to Formulae (E.19) to (E.20).

The standard uncertainties due to **other interferents** is calculated according to Formulae (E.21) to (E.22).

According to EN ISO 14956, the summed uncertainties due to the interferents with positive impact and the summed uncertainties of the interferents with negative impact shall be calculated. Take the highest sum as the representative value for all interferents (see Formulae (E.23) and (E.24)).

The standard uncertainty due to the **averaging effect** is calculated according to Formula (E.25).

The standard uncertainty due to the **calibration gas** is calculated according to Formula (E.26).

The standard uncertainty due to the **difference sample/calibration port** is calculated according to Formula (E.27).

The standard uncertainty due to the **reproducibility under field conditions at the hourly limit value** is calculated according to:

$$u_{\mathrm{r,f}} = \frac{s_{\mathrm{r,f}}}{100} l_{\mathrm{h}} \tag{E.29}$$

where

$u_{\mathrm{r,f}}$ is the standard uncertainty due to reproducibility under field conditions, in nmol/mol;

l_{h} is the hourly limit value of sulphur dioxide, in nmol/mol;

$s_{\mathrm{r,f}}$ is the standard uncertainty for reproducibility under field conditions, in %.

The standard uncertainty due the **long term drift at zero** is calculated according to:

$$u_{\mathrm{d,l,z}} = \frac{D_{\mathrm{l,z}}}{\sqrt{3}} \tag{E.30}$$

where

$u_{\mathrm{d,l,z}}$ is the standard uncertainty due to long term drift at zero, in nmol/mol;

$D_{\mathrm{l,z}}$ is the long term drift at zero, in nmol/mol.

The standard uncertainty due to the **long term drift at level of the hourly limit value** is calculated according to:

$$u_{\mathrm{d,l,lh}} = \frac{D_{\mathrm{l,lh}}}{100} \frac{l_h}{\sqrt{3}} \tag{E.31}$$

where

$u_{\mathrm{d,l,lh}}$ is the standard uncertainty due to long term drift at the hourly limit value, in nmol/mol;

$D_{\mathrm{l,lh}}$ is the long term drift at level of the hourly limit value, in %;

l_{h} is the hourly limit value of sulphur dioxide, in nmol/mol.

E.5.3 Example calculation

	SO_2 hlv	133		nmol/mol					
No	Parameter	*Ct*		Unit	Value		X-	X+	u	u^2
1	Repeatability at zero			nmol/mol	0,002				0,00	0,00
2	Repeatability at C_t	300		nmol/mol	0,001				0,00	0,00
3	Lack-of-fit			%	0,38				0,29	0,09
4	Sample gas pressure	300		nmol/mol/kPa	0,05		80	110	0,38	0,15
5	Sample gas temperature	300		nmol/mol/K	0,41		273	303	3,15	9,91
6	Surrounding temperature	300		nmol/mol/K	0,35		273	303	2,69	7,22
7	Electrical voltage	300		nmol/mol/V	0,01		210	240	0,08	0,01
8	Interferences		*Cint*			*Xint*				
8a	- H_2O 19 mmol/mol span	300	19	nmol/mol	-2,33	-0,06	6	21	-0,84	0,71
	- H_2O 19 mmol/mol zero				-0,17					
8b	- H_2S 200 nmol/mol span	300	200	nmol/mol	-0,67	0,00	1	3	0,00	
	- H_2S 200 nmol/mol zero				-0,07					
8c	- NO 500 nmol/mol span	300	500	nmol/mol	4	0,01	50	300	1,37	
	- NO 500 nmol/mol zero				3,3					
8d	- NO_2 200 nmol/mol span	300	200	nmol/mol	1	0,00	5	100	0,17	
	- NO_2 200 nmol/mol zero				0,23					
8e	- m-X 1 000 nmol/mol span	300	1000	nmol/mol	1	0,00	0	1	0,00	
	- m-X 1 000 nmol/mol zero				0,07					
8f	- NH_3 200 nmol/mol span	300	200	nmol/mol	-0,7	0,00	0	5	0,00	
	- NH_3 200 nmol/mol zero				0,1					
	Sum interferents (without water)								1,54	2,36
9	Averaging effect			%	4				3,07	9,4
10	Field reproducibility			%	2				2,66	14,2
11	Long term zero drift			nmol/mol	0,023				0,01	0,00
12	Long term span drift			%	1,0				0,77	0,59
18	Difference sample/calibration port			%	0					
21	Calibration gas			%	5				3,33	11,1
	Sum of variances									48,6
	Combined uncertainty (nmol/mol)									7,0
	Expanded uncertainty (%)									10,5

Conclusion: W ≤ 15 %. Requirement d) is met.

Annex F
(informative)

Calculation of uncertainty in field operation at the hourly limit value

F.1 General

This uncertainty evaluation may be applied for the suitability evaluation after initial installation of an analyser (9.2) and for the periodic compliance check of the measurement uncertainty (9.9).

F.2 Combined standard uncertainty

In principle, the approach to uncertainty calculation does not differ from that given in E.5. The difference here is that, where possible, practical (actual) values are used for the values of influence quantities.

The **combined standard uncertainty** in an hourly measurement at the hourly limit value during actual field operation of a measuring system is calculated using the following formula:

$$u_{c,act} = \sqrt{u_{r,z}^{\ 2} + u_{r,C}^{\ 2} + u_{l,lh}^2 + u_{gp,act}^2 + u_{gt,act}^2 + u_{st,act}^2 + u_{V,act}^2 + u_{H_2O,act}^2 + u_{int,act}^{\ 2} + u_{av}^{\ 2} + u_{d,l,z}^{\ 2} + u_{d,l,lh}^{\ 2} + u_{\Delta sc}^{\ 2} + u_{zg}^2 + u_{cg}^{\ 2}} \quad \text{(F. 1)}$$

where

$u_{c,act}$ is the combined uncertainty under actual conditions, in nmol/mol;

$u_{r,z}$ is the standard uncertainty for repeatability at zero, in nmol/mol;

$u_{r,C}$ is the highest value of the standard uncertainty for repeatability at the hourly limit value $u_{r,lh}$ and the field reproducibility $u_{r,f}$, in nmol/mol;

$u_{l,lh}$ is the standard uncertainty for actual lack of fit at the hourly limit value, in nmol/mol;

$u_{gp,act}$ is the standard uncertainty for actual sample gas pressure variation, in nmol/mol;

$u_{gt,act}$ is the standard uncertainty for actual sample gas temperature variation, in nmol/mol;

$u_{st,act}$ is the standard uncertainty for actual surrounding temperature variation, in nmol/mol;

$u_{V,act}$ is the standard uncertainty for actual electrical voltage variation, in nmol/mol;

$u_{H2O,act}$ is the standard uncertainty for the actual presence of water vapour, in nmol/mol;

$u_{int,act}$ is the standard uncertainty for the actual presence of interferents (except water vapour), in nmol/mol;

u_{av} is the standard uncertainty for averaging, in nmol/mol;

$u_{d,l,z}$ is the standard uncertainty for actual long term drift at zero, in nmol/mol;

$u_{d,l,lh}$ is the standard uncertainty for actual long term drift at level of the hourly limit value, in nmol/mol;

$u_{\Delta sc}$ is the standard uncertainty for difference sample/calibration port, in nmol/mol;

u_{zg} is the standard uncertainty of the composition of the zero gas used for calibration, in nmol/mol

u_{cg} is the standard uncertainty of the calibration gas, in nmol/mol.

The absolute **expanded uncertainty** is calculated according to:

$$U = ku_c \quad \text{(F.2)}$$

with $k = 2$

where

U is the expanded uncertainty, in nmol/mol;

k is the coverage factor of approximately 95 %;

u_c is the combined standard uncertainty, in nmol/mol.

The relative **expanded uncertainty** is calculated according to:

$$W = \frac{U}{l_h} \times 100 \quad \text{(F.3)}$$

where

W is the relative expanded uncertainty, in %;

U is the expanded uncertainty, in nmol/mol;

l_h is the hourly limit value of sulphur dioxide, in nmol/mol.

F.3 Standard uncertainties

The standard uncertainties are calculated with the formulae given in Annex E, using the relevant values of the performance characteristics, the values of the site-specific conditions related to physical and chemical influences, the value of the site-specific conditions related to operational parameters and the actual values of test gas concentrations during the type approval test.

Repeatability at zero

The standard uncertainty for **repeatability at zero** is calculated according to Formulae (E.6) to (E.7).

Repeatability at the hourly limit value

The standard uncertainty for **repeatability at the hourly limit value** is calculated according to Formulae (E.8) to (E.10).

Lack of fit

The standard uncertainty due to **lack of fit at the hourly limit value** is calculated according to Formula (E.11) using actual values for r_{max} obtained from recent linearity tests.

Influence quantities

General

In general, the principal approach described in Annex E applies to the calculation of the uncertainties due to effects of influence quantities (physical and chemical). In short: if the value of the influence quantity q_{cal} at calibration is known and differs from q_{max} or q_{min}, Formula (E.12) applies.

When q_{cal} is unknown, but varies between q_{min} and q_{max}, Formula (E.13) applies. The uncertainty calculations presented here are based on the application of Formula (E.12).

NOTE If it can be demonstrated that a triangular distribution of values of q is appropriate rather than a uniform distribution, the denominator value will be 6 instead of 3.

Sample gas pressure

The standard uncertainty due to variation of **sample gas pressure at the hourly limit value** is calculated according to:

$$u_{\mathrm{gp,act}} = \frac{l_h}{c_t} b_{\mathrm{gp}} \sqrt{\frac{\left(P_{\max} - P_{\mathrm{cal}}\right)^2 + \left(P_{\max} - P_{\mathrm{cal}}\right)\left(P_{\min} - P_{\mathrm{cal}}\right) + \left(P_{\min} - P_{\mathrm{cal}}\right)^2}{3}} \quad \text{(F.4)}$$

where

$u_{\mathrm{gp,act}}$ is the standard uncertainty due to the influence of actual pressure variations, in nmol/mol;

l_h is the hourly limit value of sulphur dioxide, in nmol/mol;

c_t is the test gas concentration (70 % to 80 % of the certification range of sulphur dioxide), in nmol/mol;

b_{gp} is the sensitivity coefficient of sample gas pressure variation, in nmol/mol/kPa;

$P_{\max}$ is the maximum level of the site-specific range of the variation of the sample gas pressure, in kPa;

P_{cal} is the sample gas pressure at which the calibration is performed, in kPa;

$P_{\min}$ is the minimum level of the site-specific range of the variation of the sample gas pressure, in kPa.

When P_{cal} is not known, (F.4) reduces to

$$u_{\mathrm{gp,act}} = \frac{l_{\mathrm{h}}}{c_{\mathrm{t}}} b_{\mathrm{gp}} \sqrt{\frac{\left(P_{\max} - P_{\min}\right)^2}{3}} \quad \text{(F.4a)}$$

Sample gas temperature

The standard uncertainty due to variation of **sample gas temperature at the hourly limit value** is calculated according to:

$$u_{\mathrm{gt,act}} = \frac{l_{\mathrm{h}}}{c_{\mathrm{t}}} b_{\mathrm{gt}} \sqrt{\frac{\left(T_{\mathrm{G,max}} - T_{\mathrm{G,cal}}\right)^2 + \left(T_{\mathrm{G,max}} - T_{\mathrm{G,cal}}\right)\left(T_{\mathrm{G,min}} - T_{\mathrm{G,cal}}\right) + \left(T_{\mathrm{G,min}} - T_{\mathrm{G,cal}}\right)^2}{3}} \quad \text{(F.5)}$$

where

$u_{gt,act}$ is the standard uncertainty due to the influence of actual sample gas temperature variations, in nmol/mol;

l_h is the hourly limit value of sulphur dioxide, in nmol/mol;

c_t is the test gas concentration (70 % to 80 % of the certification range of sulphur dioxide), in nmol/mol;

b_{gt} is the sensitivity coefficient of sample gas temperature variation, in nmol/mol/K;

$T_{G,max}$ is the maximum level of the site-specific range of the variation of the sample gas temperature, in °C;

$T_{G,cal}$ is the sample gas temperature at which the calibration is performed, in °C;

$T_{G,min}$ is the minimum level of the site-specific range of the variation of the sample gas temperature, in °C.

When $T_{G,cal}$ is not known, (F.5) reduces to

$$u_{gt,act} = \frac{l_h}{c_t} b_{gt} \sqrt{\frac{\left(T_{G,max} - T_{G,min}\right)^2}{3}} \quad \text{(F.5a)}$$

Surrounding temperature

The standard uncertainty due to variation of **surrounding temperature at the hourly limit value** is calculated according to:

$$u_{st,act} = \frac{l_h}{c_t} b_{st} \sqrt{\frac{\left(T_{S,max} - T_{S,cal}\right)^2 + \left(T_{S,max} - T_{S,cal}\right)\left(T_{S,min} - T_{S,cal}\right) + \left(T_{S,min} - T_{S,cal}\right)^2}{3}} \quad \text{(F.6)}$$

where

$u_{st,act}$ is the standard uncertainty due to the influence of actual surrounding temperature variations, in nmol/mol;

l_h is the hourly limit value of sulphur dioxide, in nmol/mol;

c_t is the test gas concentration (70 % to 80 % of the certification range of sulphur dioxide), in nmol/mol;

b_{st} is the sensitivity coefficient of surrounding temperature variation, in nmol/mol/K;

$T_{S,max}$ is the maximum level of the site-specific range of the variation of the surrounding temperature, in °C;

$T_{S,cal}$ is the surrounding temperature at which the calibration is performed, in °C;

$T_{S,min}$ is the minimum level of the site-specific range of the variation of the surrounding temperature, in °C.

When $T_{S,cal}$ is not known, (F.6) reduces to

$$u_{st,act} = \frac{l_h}{c_t} b_{st} \sqrt{\frac{\left(T_{S,max} - T_{S,min}\right)^2}{3}} \quad \text{(F.6a)}$$

Electrical voltage

The standard uncertainty due to variation of **electrical voltage at the hourly limit value** is calculated according to:

$$u_{V,act} = \frac{l_h}{c_t} b_V \sqrt{\frac{(V_{max} - V_{cal})^2 + (V_{max} - V_{cal})(V_{min} - V_{cal}) + (V_{min} - V_{cal})^2}{3}} \quad \text{(F.7)}$$

where

$u_{V,act}$ is the standard uncertainty due to the influence of actual voltage variations, in nmol/mol;

l_h is the hourly limit value of sulphur dioxide, in nmol/mol;

c_t is the test gas concentration (70 % to 80 % of the certification range of sulphur dioxide), in nmol/mol;

b_V is the sensitivity coefficient of voltage variation, in nmol/mol/V;

V_{max} is the maximum level of the site-specific range of the variation of the voltage, in V;

V_{cal} is the voltage at which the calibration is performed, in V;

V_{min} is the minimum level of the site-specific range of the variation of the voltage, in V.

When V_{cal} is not known, (F.7) reduces to

$$u_{V,act} = \frac{l_h}{c_t} b_V \sqrt{\frac{(V_{max} - V_{min})^2}{3}} \quad \text{(F.7a)}$$

Interferents

The calculation of the uncertainty due to interferents is based on the actual concentration of the chemical interferents during field operation. Therefore the following formulae are used for calculating the uncertainty due to water vapour and other interfering chemical compounds.

Water vapour

The standard uncertainty due to the actual **presence of water vapour at the hourly limit value** is calculated according to:

$$u_{H_2O,act} = b_{H_2O} \sqrt{\frac{c^2_{H_2O,max,act} + c_{H_2O,max,act} c_{H_2O,min,act} + c^2_{H_2O,min,act}}{3}} \quad \text{(F.8)}$$

where

$u_{H_2O,act}$ is the standard uncertainty due to actual interference by the presence of water vapour, in nmol/mol;

b_{H_2O} is the sensitivity coefficient due to interference by the presence of water vapour, in (nmol/mol)/(mmol/mol), see Formula (E.19);

$c_{H_2O,max,act}$ is the actual maximum hourly average concentration of water vapour, in mmol/mol;

$c_{H_2O,min,act}$ is the actual minimum hourly average concentration of water vapour, in mmol/mol.

Other interferents

The standard uncertainty due to each **interfering compound at the hourly limit value** (other than water vapour) is calculated according to:

$$u_{\text{int,act}} = b_{\text{int}} \sqrt{\frac{c_{\text{int,max,act}}^2 + c_{\text{int,max,act}} c_{\text{int,min,act}} + c_{\text{int,min,act}}^2}{3}} \quad \text{(F.9)}$$

where

$u_{\text{int,act}}$ is the standard uncertainty due to actual presence of the interferent, in nmol/mol;

b_{int} is the sensitivity coefficient due to the presence of the interferent, in nmol/mol)/(nmol/mol) or (nmol/mol)/(µmol/mol), see Formula (E.21);

$c_{\text{int,max,act}}$ is the actual maximum hourly average concentration of the interferent, in nmol/mol or µmol/mol;

$c_{\text{int,min,act}}$ is the actual minimum hourly average concentration of the interferent, in nmol/mol or µmol/mol.

According to EN ISO 14956, the summed uncertainties due to the interferents with positive impact and the summed uncertainties of the interferents with negative impact is calculated as:

$$u_{\text{int,act,pos}} = \sqrt{(u_{\text{int,act,1,pos}} + ... + u_{\text{int,act, n,pos}})^2} \quad \text{(F.10)}$$

$$u_{\text{int,act,neg}} = \sqrt{(u_{\text{int,act,1,neg}} + ... + u_{\text{int,act,n,neg}})^2} \quad \text{(F.11)}$$

where

$u_{\text{int,act, pos}}$ is the sum of uncertainties due to interferents with positive impact, in nmol/mol;

$u_{\text{int,act,1,pos}}$ is the uncertainty due to the 1th interferent with positive impact, in nmol/mol;

$u_{\text{int,act,n,pos}}$ is the uncertainty due to the *n*th interferent with positive impact, in nmol/mol;

$u_{\text{int,act,neg}}$ is the sum of uncertainties due to interferents with negative impact, in nmol/mol;

$u_{\text{int,act,1,neg}}$ is the uncertainty due to the 1th interferent with negative impact, in nmol/mol;

$u_{\text{int,act,n,neg}}$ is the uncertainty due to the *n*th interferent with negative impact, in nmol/mol.

The highest value of (F.10) and (F.11) is taken as value for $u_{\text{int,act}}$ in (F.1).

Averaging effect,

The standard uncertainty due to the **averaging effect** is calculated according to Formula (E.25).

Reproducibility under field conditions

The standard uncertainty due to the **reproducibility under field conditions for sulphur dioxide** is calculated according to Formula (E.29).

Long term drift at zero

The standard uncertainty due the **long term drift at zero** is calculated according to:

$$u_{D_{l,z}} = \frac{D_{l,z}}{\sqrt{3}} \quad \text{(F.12)}$$

where

$u_{D_{l,z}}$ is the uncertainty due to long term drift at zero, in nmol/mol;

$D_{l,z}$ is the actual long term drift at zero, in nmol/mol, determined from periodic calibrations over the period of re-assessment of the measurement uncertainty.

Long term drift at level of the hourly limit value

The standard uncertainty due to the **long term span drift at level of the hourly limit value** is calculated according to:

$$u_{d,l,lh} = \frac{D_{l,span}}{100} \frac{l_h}{\sqrt{3}} \quad \text{(F.13)}$$

where

$u_{d,l,lh}$ is the standard uncertainty due to long term drift at the hourly limit value, in nmol/mol;

$D_{l,span}$ is the long term span drift, in %, determined from periodic calibrations over the period of re-assessment of the measurement uncertainty;

l_h is the hourly limit value of sulphur dioxide, in nmol/mol.

Zero gas

The uncertainty related to the composition of the zero gas used for calibration is calculated from its specifications (Table 4) for sulphur dioxide as:

$$u_{zg} = \frac{1}{\sqrt{3}} \text{ nmol/mol} \quad \text{(F.14)}$$

where

u_{zg} is the standard uncertainty related to the composition of the zero gas in nmol/mol.

Calibration gas

The standard uncertainty due to the **calibration gas** is calculated according to Formula (E.26), with the actual uncertainty of the calibration gas.

Difference sample/calibration port

The standard uncertainty due to the **difference sample/calibration port** is calculated according to Formula (E.27).

F.4 Example calculation

SO_2 hlv	133		nmol/mol								
Parameter	*Ct*		Unit	Value		X-	Xcal	X+	DX-	DX+	u	u^2
Repeatability at zero			nmol/mol	0,00							0,00	0,00
Repeatability at C_t	300		nmol/mol	0,00							0,00	
Lack-of-fit			%	0,38							0,29	0,09
Sample gas pressure	300		nmol/mol/kPa	0,05		97	101	104	-4	3	0,05	0,00
Sample gas temperature	300		nmol/mol/K	0,41		273	293	303	-20	10	1,82	3,30
Surrounding temperature	300		nmol/mol/K	0,35		273	293	303	-20	10	1,55	2,41
Electrical voltage	300		nmol/mol/V	0,01		215	220	230	-5	10	0,02	0,00
Interferences		*Cint*			*Xint*							
- H_2O 19 mmol/mol span	300	19	nmol/mol	-2,3	-0,06	6	0	21	6	21	-0,84	0,71
- H_2O 19 mmol/mol zero				-0,2								
- H_2S 200 nmol/mol span	300	200	nmol/mol	-0,7	0,00	1	0	3	1	3	0,00	
- H_2S 200 nmol/mol zero				-0,1								
- NO 500 nmol/mol span	300	500	nmol/mol	4	0,01	50	0	300	50	300	1,37	
- NO 500 nmol/mol zero				3,3								
- NO_2 200 nmol/mol span	300	200	nmol/mol	1	0,00	5	0	100	5	100	0,17	
- NO_2 200 nmol/mol zero				0,23								
- m-X 1 000 nmol/mol span	300	1000	nmol/mol	1	0,00	0	0	1	0	1	0,00	
- m-X 1 000 nmol/mol zero				0,07								
- NH_3 200 nmol/mol span	300	200	nmol/mol	-0,7	0,00	0	0	5	0	5	0,00	
- NH_3 200 nmol/mol zero				0,1								
Sum interferents (without water)											1,54	2,36
Averaging effect			%	4							3,07	9,4
Field reproducibility			%	2							2,66	7,1
Long term zero drift			nmol/mol	0,02							0,01	0,00
Long term span drift			%	1,0							0,77	0,59
Difference sample/calibration port			%	0								
Calibration gas			%	5							3,33	11,1
Zero gas			nmol/mol	0,6							0,6	0,36
Sum of variances												37,4
Combined uncertainty (nmol/mol)												6,1
Expanded uncertainty (%)												9,2

Annex G
(informative)

Calculation of uncertainty in field operation at the daily limit value

G.1 General

The calculation given here is used to demonstrate whether the measurements with a type-approved analyser can fulfil the data quality objective for an average at the daily limit value. This result can differ from a calculation to establish the uncertainty in an actual daily average.

In principle, the approach to uncertainty calculation does not differ from that given in Annex F. The difference here is that, where appropriate, contributions of uncertainty sources that have a random effect are reduced.

G.2 Combined standard uncertainty

The **combined standard uncertainty** of a daily average at the daily limit value during field operation of a measuring system may be calculated using the following formula:

$$u_{c,act} = \sqrt{u_{r,d,z}^2 + u_{r,C}^2 + u_{l,ld}^2 + u_{gp,act}^2 + u_{gt,act}^2 + u_{st,act}^2 + u_{V,act}^2 + u_{H_2O,act}^2 + u_{int,act}^2 + u_{av}^2 + u_{d,l,z}^2 + u_{d,l,ld}^2 + u_{\Delta sc}^2 + u_{zg}^2 + u_{cg}^2} \quad \text{(G.1)}$$

where

$u_{c,act}$ is the combined uncertainty under actual conditions, in nmol/mol;

$u_{r,d,z}$ is the standard uncertainty for repeatability at zero, in nmol/mol, at the level of the daily limit value;

$u_{r,C}$ is the highest value of the standard uncertainty for repeatability at the hourly limit value $u_{r,lh}$ and the field reproducibility $u_{r,f}$, in nmol/mol;

$u_{l,ld}$ is the standard uncertainty for actual lack of fit at the daily limit value, in nmol/mol;

$u_{gp,act}$ is the standard uncertainty for actual sample gas pressure variation, in nmol/mol;

$u_{gt,act}$ is the standard uncertainty for actual sample gas temperature variation, in nmol/mol;

$u_{st,act}$ is the standard uncertainty for actual surrounding temperature variation, in nmol/mol;

$u_{V,act}$ is the standard uncertainty for actual electrical voltage variation, in nmol/mol;

$u_{H2O,act}$ is the standard uncertainty for the actual presence of water vapour, in nmol/mol;

$u_{int,act}$ is the standard uncertainty for the actual presence of interferents (except water vapour), in nmol/mol;

u_{av} is the standard uncertainty for averaging, in nmol/mol;

$u_{d,l,z}$ is the standard uncertainty for long term drift at zero, in nmol/mol;

$u_{d,l,ld}$ is the standard uncertainty for long term drift at level of the daily limit value, in nmol/mol

$u_{\Delta sc}$ is the standard uncertainty for difference sample/calibration port, in nmol/mol;

u_{zg} is the standard uncertainty of the composition of the zero gas used for calibration;

u_{cg} is the standard uncertainty of the calibration gas.

The absolute **expanded uncertainty** is calculated according to:

$$U = ku_{c,act} \quad \text{(G.2)}$$

with $k = 2$

where

U is the expanded uncertainty, in nmol/mol;

k is the coverage factor of approximately 95 %;

$u_{c,act}$ is the combined standard uncertainty, in nmol/mol.

The relative **expanded uncertainty** is calculated according to:

〈AC1〉 $$W = \frac{U}{l_d} \times 100 \quad \text{(G.3)}$$

where

W is the relative expanded uncertainty, in %;

U is the expanded uncertainty, in nmol/mol;

l_d is the daily limit value of SO_2, in nmol/mol; 〈AC1〉

G.3 Standard uncertainties

The standard uncertainties are calculated with the following formulae, using the relevant values of the performance characteristics, the values of the site-specific conditions related to physical and chemical influences, the value of the site-specific conditions related to operational parameters and the default value for uncertainty due to the calibration procedure.

Repeatability at zero

The standard uncertainty for **repeatability at zero** is calculated according to:

$$u_{r,d,z} = \frac{u_{r,z}}{\sqrt{n_d}} \quad \text{(G.4)}$$

where

$u_{r,d,z}$ is the standard uncertainty in the daily average value due to repeatability at zero, in nmol/mol;

$u_{r,z}$ is the standard uncertainty for repeatability at zero calculated according to Formula (E.9), in nmol/mol;

n_d is the number of valid hourly measurements in a day ($n_d \geq 18$).

Repeatability at the daily limit value

The standard uncertainty for **repeatability at the daily limit value** is calculated according to:

$$u_{\mathrm{r,d,ld}} = \frac{s_{\mathrm{r,ct}}}{c_{\mathrm{t}}} l_{\mathrm{d}} \frac{1}{\sqrt{m n_{\mathrm{d}}}} \quad \text{(G.5)}$$

where

$u_{\mathrm{r,d,ld}}$ is the standard uncertainty in the daily average due to repeatability at the level of the daily limit value, in nmol/mol;

n_{d} is the number of valid hourly measurements in a day (≥ 18);

m is the number of independent measurements in 3 600 s, calculated by taking the average of response (rise) and response time (fall) for half that time period (see Formula (E.10));

$s_{\mathrm{r,ct}}$ is the repeatability standard deviation at the test gas concentration c_t;

l_d is the daily limit value of sulphur dioxide, in nmol/mol;

c_{t} is the applied SO_2 test gas concentration, in nmol/mol.

Lack of fit

The standard uncertainty due to **lack of fit at the daily limit value** is calculated according to:

$$u_{\mathrm{l,ld}} = \frac{r_{\max}}{100} \frac{l_{\mathrm{d}}}{\sqrt{3}} \quad \text{(G.6)}$$

where

$u_{\mathrm{l,ld}}$ is the standard uncertainty due to lack of fit at the hourly limit value, in nmol/mol;

$r_{\max}$ is the maximum residual from a linear regression function in % resulting from actual linearity tests, calculated according to Annex A;

l_{d} is the daily limit value of sulphur dioxide, in nmol/mol.

Influence quantities

General

In general, the principal approach described in Annex F applies to the calculation of the uncertainties due to effects of influence quantities (physical and chemical). In short: if the value of the influence quantity q_{cal} at calibration is known and differs from $q_{\max}$ or $q_{\min}$, Formula (E.12) applies.

When q_{cal} is unknown, but varies between $q_{\min}$ and $q_{\max}$, Formula (E.13) applies. The uncertainty calculations presented here are based on the application of Formula (E.12).

NOTE If it can be demonstrated that a triangular distribution of values of q is appropriate rather than a uniform distribution, the denominator value will be 6 instead of 3.

Sample gas pressure

The standard uncertainty due to variation of **sample gas pressure at the daily limit value** is calculated according to:

$$u_{\mathrm{gp,act}} = \frac{l_{\mathrm{d}}}{c_{\mathrm{t}}} b_{\mathrm{gp}} \sqrt{\frac{\left(P_{\max} - P_{\mathrm{cal}}\right)^2 + \left(P_{\max} - P_{\mathrm{cal}}\right)\left(P_{\min} - P_{\mathrm{cal}}\right) + \left(P_{\max} - P_{\mathrm{cal}}\right)^2}{3}} \quad \text{(G.7)}$$

where

$u_{\mathrm{gp,act}}$ is the standard uncertainty due to the influence of actual pressure variations, in nmol/mol;

l_{d} is the daily limit value of sulphur dioxide, in nmol/mol;

c_{t} is the test gas concentration (70 % to 80 % of the certification range of SO_2), in nmol/mol;

b_{gp} is the sensitivity coefficient of sample gas pressure variation, in nmol/mol/kPa;

$P_{\max}$ is the upper level of the site-specific range of the variation of the sample gas pressure, in kPa;

$P_{\min}$ is the lower level of the site-specific range of the variation of the sample gas pressure, in kPa.

When P_{cal} is not known, (G.7) reduces to

$$u_{\mathrm{gp,act}} = \frac{l_{\mathrm{d}}}{c_{\mathrm{t}}} b_{\mathrm{gp}} \sqrt{\frac{\left(P_{\max} - P_{\min}\right)^2}{3}} \quad \text{(G.7a)}$$

Sample gas temperature

The standard uncertainty due to variation of **sample gas temperature at the daily limit value** is calculated according to:

$$u_{\mathrm{gt,act}} = \frac{l_{\mathrm{d}}}{c_{\mathrm{t}}} b_{\mathrm{gt}} \sqrt{\frac{\left(T_{\mathrm{G,max}} - T_{\mathrm{G,cal}}\right)^2 + \left(T_{\mathrm{G,max}} - T_{\mathrm{G,cal}}\right)\left(T_{\mathrm{G,min}} - T_{\mathrm{G,cal}}\right) + \left(T_{\mathrm{G,max}} - T_{\mathrm{G,cal}}\right)^2}{3}} \quad \text{(G.8)}$$

where

$u_{\mathrm{gt,act}}$ is the standard uncertainty due to actual variation of sample gas temperature, in nmol/mol;

l_{d} is the daily limit value of sulphur dioxide, in nmol/mol;

c_{t} is the test gas concentration (70 % to 80 % of the certification range of SO_2), in nmol/mol;

b_{gt} is the sensitivity coefficient of sample gas temperature variation, in nmol/mol/K;

$T_{\mathrm{G,max}}$ is the upper level of the site-specific range of the variation of the sample gas temperature, in °C;

$T_{\mathrm{G,min}}$ is the lower level of the site-specific range of the variation of the sample gas temperature, in °C.

When $T_{\mathrm{G,cal}}$ is not known, (G.8) reduces to

$$u_{\mathrm{gt,act}} = \frac{l_{\mathrm{d}}}{c_{\mathrm{t}}} b_{\mathrm{gt}} \sqrt{\frac{\left(T_{\mathrm{G,max}} - T_{\mathrm{G,min}}\right)^2}{3}} \quad \text{(G.8a)}$$

Surrounding temperature

The standard uncertainty due to variation of **surrounding temperature at the daily limit value** is calculated according to:

$$u_{st,act} = \frac{l_d}{c_t} b_{st} \sqrt{\frac{\left(T_{S,max} - T_{S,cal}\right)^2 + \left(T_{S,max} - T_{S,cal}\right)\left(T_{S,min} - T_{S,cal}\right) + \left(T_{S,max} - T_{S,cal}\right)^2}{3}} \quad \text{(G.9)}$$

where

$u_{st,act}$ is the standard uncertainty due to the influence of actual surrounding temperature variations, in nmol/mol;

l_d is the daily limit value of sulphur dioxide, in nmol/mol;

c_t is the test gas concentration (70 % to 80 % of the certification range of SO_2), in nmol/mol;

b_{st} is the sensitivity coefficient of surrounding temperature variation, in nmol/mol/K;

$T_{S,max}$ is the maximum level of the site-specific range of the variation of the surrounding temperature, in °C;

$T_{S,cal}$ is the surrounding temperature at which the calibration is performed, in °C;

$T_{S,min}$ is the minimum level of the site-specific range of the variation of the surrounding temperature, in °C.

When $T_{S,cal}$ is not known, (G.9) reduces to

$$u_{st,act} = \frac{l_d}{c_t} b_{st} \sqrt{\frac{\left(T_{S,max} - T_{S,min}\right)^2}{3}} \quad \text{(G.9a)}$$

Electrical voltage

The standard uncertainty due to variation of **electrical voltage at the daily limit value** is calculated according to:

$$u_{V,act} = \frac{l_d}{c_t} b_V \sqrt{\frac{\left(V_{max} - V_{cal}\right)^2 + \left(V_{max} - V_{cal}\right)\left(V_{min} - V_{cal}\right) + \left(V_{max} - V_{cal}\right)^2}{3}} \quad \text{(G.10)}$$

where

$u_{V,act}$ is the standard uncertainty due to the influence of actual voltage variations, in nmol/mol;

l_d is the daily limit value of sulphur dioxide, in nmol/mol;

c_t is the test gas concentration (70 % to 80 % of the certification range of SO_2), in nmol/mol;

b_V is the sensitivity coefficient of voltage variation, in nmol/mol/V;

V_{max} is the maximum level of the site-specific range of the variation of the voltage, in V;

V_{cal} is the voltage at which the calibration is performed, in V;

V_{min} is the minimum level of the site-specific range of the variation of the voltage (V).

When V_{cal} is not known, (G.10) reduces to

$$u_{V,act} = \frac{l_d}{c_t} b_V \sqrt{\frac{\left(V_{max} - V_{min}\right)^2}{3}} \quad \text{(G.10a)}$$

Interferents

The calculation of the uncertainty due to interferents is based on the actual concentration of the chemical interferents during field operation. Therefore, the following formulae are used for calculating the uncertainty due to water vapour and other interfering chemical compounds.

Water vapour

The standard uncertainty due to the **presence of water vapour at the daily limit value** is calculated according to:

$$b_{H_2O} = \frac{1}{c_{H_2O}} \left[X_{H_2O,z} + \left(X_{H_2O,C_t} - X_{H_2O,z} \right) \frac{l_d}{c_t} \right] \quad \text{(G.11)}$$

$$u_{H_2O,act} = b_{H_2O} \times \sqrt{\frac{c^2_{H_2O,max} + c_{H_2O,max} c_{H_2O,min} + c^2_{H_2O,min}}{3}} \quad \text{(G.12)}$$

where

$X_{H_2O,z}$ is the influence quantity of an H_2O concentration of 19 mmol/mol at zero concentration of the measurand, in nmol/mol;

X_{H_2O,c_t} is the influence quantity of an H_2O concentration of 19 mmol/mol at the test concentration c_t of the measurand, in nmol/mol;

$u_{H_2O,act}$ is the standard uncertainty due to interference by the actual presence of water vapour, in nmol/mol;

b_{H_2O} is the sensitivity coefficient due to interference by the presence of water vapour, in (nmol/mol)/(mmol/mol);

c_{H_2O} is the test concentration of H_2O in the type-approval test (19 mmol/mol);

c_t is the test gas concentration of SO_2, in nmol/mol;

l_d is the daily limit value of sulphur dioxide, in nmol/mol;

$c_{H_2O,max}$ is the maximum hourly average concentration of water vapour, in mmol/mol;

$c_{H_2O,min}$ is the minimum hourly average concentration of water vapour, in mmol/mol.

Other interferents

The standard uncertainty due to **each interfering compound at the daily limit value** (other than water vapour) is calculated according to:

$$b_{int} = \frac{1}{c_{int}} \left[X_{int,z} + \left(X_{int,C_t} - X_{int,z} \right) \frac{l_d}{c_t} \right] \quad \text{(G.13)}$$

$$u_{int,act} = b_{int} \sqrt{\frac{c^2_{int,act,max} + c_{int,act,max} c_{int,act,min} + c^2_{int,act,min}}{3}} \quad \text{(G.14)}$$

where

X_{int,c_t} is the influence quantity of the maximum concentration, in nmol/mol or µmol/mol, of the relevant interfering compound at the test concentration c_t of the measurand, in nmol/mol;

$X_{int,z}$ is the influence quantity of the maximum concentration, in nmol/mol or µmol/mol, of the relevant interfering compound at zero concentration of the measurand, in nmol/mol;

u_{int} is the standard uncertainty due to the presence of the interferent, in nmol/mol;

b_{int} is the sensitivity coefficient due to the presence of the interferent, in (nmol/mol)/(nmol/mol) or (nmol/mol)/(µmol/mol);

c_{int} is the test concentration of the relevant interfent, in nmol/mol or µmol/mol;

c_t is the test gas concentration of SO_2, in nmol/mol;

l_d is the daily limit value of sulphur dioxide, in nmol/mol;

$c_{int,act,max}$ is the actual maximum hourly average concentration of interfering compound, in nmol/mol or µmol/mol;

$c_{int,act,\ min}$ is the actual minimum hourly average concentration of interfering compound, in nmol/mol or µmol/mol.

According to EN ISO 14956, the summed uncertainties due to the interferents with positive impact and the summed uncertainties of the interferents with negative impact are calculated as:

$$u_{int,act,pos} = \sqrt{(u_{int,act,1,pos} + ... + u_{int,act,\ n,pos})^2} \quad \text{(G.15)}$$

$$u_{int,act,neg} = \sqrt{(u_{int,act,1,neg} + ... + u_{int,act,n,neg})^2} \quad \text{(G.16)}$$

where

$u_{int,act,\ pos}$ is the sum of uncertainties due to interferents with positive impact, in nmol/mol;

$u_{int,act,1,pos}$ is the uncertainty due to the 1th interferent with positive impact, in nmol/mol;

$u_{int,act,n,pos}$ is the uncertainty due to the *n*th interferent with positive impact, in nmol/mol;

$u_{int,act,neg}$ is the sum of uncertainties due to interferents with negative impact, in nmol/mol;

$u_{int,act,1,neg}$ is the uncertainty due to the 1th interferent with negative impact, in nmol/mol;

$u_{int,act,n,neg}$ is the uncertainty due to the *n*th interferent with negative impact, in nmol/mol.

The highest value of (G.15) and (G.16) is taken as value for $u_{int,act}$ in (G.1).

Averaging effect

The standard uncertainty due to the **averaging effect** is calculated according to:

$$u_{av} = \frac{E_{av}}{100}\frac{l_d}{\sqrt{3}} \quad \text{(G.17)}$$

where

u_{av} is the standard uncertainty due to the averaging effect, in nmol/mol;

E_{av} is the averaging effect, in % of the measured value;

l_d is the daily limit value of sulphur dioxide, in nmol/mol.

Zero gas

The uncertainty related to the composition of the zero gas used for calibration is calculated from its specifications (Table 4) for sulphur dioxide as:

$$u_{zg} = \frac{1}{\sqrt{3}} \text{ nmol/mol} \quad \text{(G.18)}$$

where

u_{zg} is the standard uncertainty due to the zero gas in nmol/mol.

Calibration gas

The standard uncertainty due to the **calibration gas** is calculated according to:

$$u_{cg} = \frac{W_{cg}}{2 \times 100} l_d \quad \text{(G.19)}$$

where

u_{cg} is the standard uncertainty due to the calibration gas, in nmol/mol;

W_{cg} is the relative expanded uncertainty of the calibration gas, in %;

l_d is the daily limit value of sulphur dioxide, in nmol/mol.

Difference sample/calibration port

The standard uncertainty due to the **difference sample/calibration port** is calculated according to:

$$u_{\Delta sc} = \frac{\Delta x_{sc}}{100} l_d \quad \text{(G.20)}$$

where

$u_{\Delta sc}$ is the standard uncertainty due to the difference sample/calibration port, in nmol/mol;

Δx_{sc} is the difference sample/calibration port, in %;

l_d is the daily limit value of sulphur dioxide, in nmol/mol.

Reproducibility under field conditions

The standard uncertainty due to the **reproducibility under field conditions** is calculated according to:

$$u_{\mathrm{r,f,ld}} = \frac{l_d \times s_{\mathrm{r,f}}}{100\sqrt{n_{\mathrm{d}}}} \quad \text{(G.21)}$$

where

$u_{\mathrm{r,f,ld}}$ is the standard uncertainty at the daily limit value due to reproducibility under field conditions, in nmol/mol;

n_{d} is the number of valid hourly measurements in a day (≥ 18);

$s_{\mathrm{r,f}}$ is the reproducibility standard deviation for SO_2 from the field test, in %;

l_{d} is the daily limit value of sulphur dioxide, in nmol/mol.

Long term drift at zero

The standard uncertainty due the **long term drift at zero** is calculated according to:

$$u_{\mathrm{D_{l,z}}} = \frac{D_{\mathrm{l,z}}}{\sqrt{3}} \quad \text{(G.22)}$$

where

$u_{\mathrm{D_{l,z}}}$ is the uncertainty due to long term drift at zero, in nmol/mol;

$D_{\mathrm{l,z}}$ is the actual long term drift at zero, in nmol/mol, determined from periodic calibrations over the period of re-assessment of the measurement uncertainty.

Long term drift at level of the daily limit value

The standard uncertainty due to the **long term span drift at level of the daily limit value**, $u_{\mathrm{d,l,ld}}$, is calculated according to:

$$u_{\mathrm{d,l,ld}} = \frac{D_{\mathrm{l,span}}}{100}\frac{l_{\mathrm{d}}}{\sqrt{3}} \quad \text{(G.23)}$$

where

$u_{\mathrm{d,l,ld}}$ is the standard uncertainty due to long term drift at the daily limit value, in nmol/mol;

$D_{\mathrm{l,span}}$ is the long term span drift, in %, determined from periodic calibrations over the period of re-assessment of the measurement uncertainty;

l_{d} is the daily limit value of sulphur dioxide, in nmol/mol.

G.4 Example calculation

SO_2 dlv	47		nmol/mol								
Number of hourly values	18										
Parameter	*Ct*		Unit	Value		X-	Xcal	X+	DX-	DX+	u	u^2
Repeatability at zero			nmol/mol							0,00	0,00	
Repeatability at C_t	300		nmol/mol							0,00		
Lack-of-fit			%							0,10	0,01	
Sample gas pressure	300		nmol/mol/kPa		97	101	104	-4	3	0,02	0,00	
Sample gas temperature	300		nmol/mol/K		273	293	303	-20	10	0,64	0,41	
Surrounding temperature	300		nmol/mol/K		273	293	303	-20	10	0,55	0,30	
Electrical voltage	300		nmol/mol/V		215	220	230	-5	10	0,01	0,00	
Interferences		*Cint*		*Xint*								*Xint*
- H_2O 19 mmol/mol span - H_2O 19 mmol/mol zero	300	19	nmol/mol	-0,03	6	0	21	6	21	-0,38	0,14	-0,03
- H_2S 200 nmol/mol span - H_2S 200 nmol/mol zero	300	200	nmol/mol	0,00	1	0	3	1	3	0,00		0,00
- NO 500 nmol/mol span - NO 500 nmol/mol zero	300	500	nmol/mol	0,01	50	0	300	50	300	1,29		0,01
- NO_2 200 nmol/mol span - NO_2 200 nmol/mol zero	300	200	nmol/mol	0,00	5	0	100	5	100	0,10		0,00
- m-X 1 000 nmol/mol span - m-X 1 000 nmol/mol zero	300	1000	nmol/mol	0,00	0	0	1	0	1	0,00		0,00
- NH_3 200 nmol/mol span - NH_3 200 nmol/mol zero	300	200	nmol/mol	0,00	0	0	5	0	5	0,00		0,00
Sum interferents (without water)											1,39	1,95
Averaging effect			%								1,08	1,17
Field reproducibility			%								0,22	0,05
Long term zero drift			nmol/mol								0,01	0,00
Long term span drift			%								0,27	0,07
Difference sample/calibration port			%	0								
Calibration gas			%	5							3,33	11,1
Zero gas			nmol/mol	0,6							0,6	0,36
Sum of variances												5,8
Combined uncertainty (nmol/mol)												2,4
Expanded uncertainty (%)												10,3

Annex H
(informative)

Calculation of uncertainty in field operation at the annual critical level

H.1 General

The calculation given here is to demonstrate if the measurements with a type-approved analyser can fulfil the data quality objective for an annual average at the annual critical level. The result of this calculation can differ from a calculation to establish the uncertainty in an actual annual average.

In principle, the approach to uncertainty calculation does not differ from that given in Annex F. The difference here is that, where appropriate, contributions of uncertainty sources that have a random effect are reduced.

H.2 Combined standard uncertainty

The **combined standard uncertainty** in an annual average at the annual critical level during field operation of a measurement system may be calculated using the following formula:

$$u_{c,act} = \sqrt{u_{r,a,z}^2 + u_{r,a,C}^2 + u_{l,la}^2 + u_{gp,act}^2 + u_{gt,act}^2 + u_{st,act}^2 + u_{V,act}^2 + u_{H_2O,act}^2 + u_{int,act}^2 + u_{av}^2 + u_{d,l,z}^2 + u_{d,l,la}^2 + u_{\Delta sc}^2 + u_{zg}^2 + u_{cg}^2} \quad \text{(H.1)}$$

where

$u_{c,act}$ is the combined uncertainty under actual conditions, in nmol/mol;

$u_{r,a,z}$ is the standard uncertainty for repeatability at zero, in nmol/mol, applied at the level of the annual limit value;

$u_{r,a,C}$ is the highest value of the standard uncertainty for repeatability at the hourly limit value $u_{r,lh}$ and the field reproducibility $u_{r,f}$, in nmol/mol;

$u_{l,la}$ is the standard uncertainty for actual lack of fit at the annual critical level, in nmol/mol;

$u_{gp,act}$ is the standard uncertainty for actual sample gas pressure variation, in nmol/mol;

$u_{gt,act}$ is the standard uncertainty for actual sample gas temperature variation, in nmol/mol;

$u_{st,act}$ is the standard uncertainty for actual surrounding temperature variation, in nmol/mol;

$u_{V,act}$ is the standard uncertainty for actual electrical voltage variation, in nmol/mol;

$u_{H2O,act}$ is the standard uncertainty for the actual presence of water vapour, in nmol/mol;

$u_{int,act}$ is the standard uncertainty for the actual presence of interferents (except water vapour), in nmol/mol;

u_{av} is the standard uncertainty for averaging, in nmol/mol;

$u_{d,l,z}$ is the standard uncertainty for long term drift at zero, in nmol/mol;

$u_{d,l,la}$ is the standard uncertainty for long term drift at level of the annual critical level, in nmol/mol;

$u_{\Delta sc}$ is the standard uncertainty for difference sample/calibration port, in nmol/mol;

u_{zg} is the standard uncertainty of the composition of the zero gas used for calibration;

u_{cg} is the standard uncertainty of the calibration gas.

The absolute **expanded uncertainty** is calculated according to:

$$U = ku_c \quad \text{(H.2)}$$

with $k = 2$

where

U is the expanded uncertainty, in nmol/mol;

k is the coverage factor of approximately 95 %;

u_c is the combined standard uncertainty, in nmol/mol.

The relative **expanded uncertainty** is calculated according to:

$$W = \frac{U}{l_a} \times 100 \quad \text{(H.3)}$$

where

W is the relative expanded uncertainty, in %;

U is the expanded uncertainty, in nmol/mol;

l_a is the annual critical level of SO_2, in nmol/mol.

H.3 Standard uncertainties

The standard uncertainties may be calculated with the following formulae, using the relevant values of the performance characteristics, the values of the site-specific conditions related to physical and chemical influences, the value of the site-specific conditions related to operational parameters and the default value for uncertainty due to the calibration procedure.

Repeatability at zero

The standard uncertainty for **repeatability at zero** is calculated according to:

$$u_{r,a,z} = \frac{u_{r,z}}{\sqrt{n_a}} \quad \text{(H.4)}$$

where

$u_{r,a,z}$ is the standard uncertainty in the annual average value due to repeatability at zero, in nmol/mol;

$u_{r,z}$ is the standard uncertainty for repeatability at zero calculated according to Formula (E.9), in nmol/mol;

n_a is the number of valid hourly measurements in the year ($n_a \geq 7884$).

Repeatability at the annual critical level

The standard uncertainty for **repeatability at the annual critical level** is calculated according to:

$$u_{\mathrm{r,la}} = \frac{s_{\mathrm{r,ct}}}{c_{\mathrm{t}}} l_a \frac{1}{\sqrt{mn_{\mathrm{a}}}} \quad \text{(H.5)}$$

where

$u_{\mathrm{r,la}}$ is the standard uncertainty in the annual average due to repeatability at the level of the annual critical level, in nmol/mol;

n_{a} is the number of valid hourly measurements in the year (≥ 7884);

m is the number of individual measurements in 3 600 s, calculated by taking the average of response (rise) and response time (fall) for half the period (see Formula (E.10));

$s_{\mathrm{r,ct}}$ is the repeatability standard deviation at the test gas concentration c_t;

l_{a} is the annual critical level of sulphur dioxide, in nmol/mol;

c_{t} is the applied SO_2 test gas concentration, in nmol/mol.

Lack of fit

The standard uncertainty due to **lack of fit at the annual critical level** is calculated according to:

$$u_{\mathrm{l,la}} = \frac{r_{\mathrm{max}}}{100} \frac{l_{\mathrm{a}}}{\sqrt{3}} \quad \text{(H.6)}$$

where

$u_{\mathrm{l,la}}$ is the standard uncertainty due to lack of fit at the hourly limit value, in nmol/mol;

r_{max} is the maximum residual from a linear regression function, in %, resulting from actual linearity tests, calculated according to Annex A;

l_{a} is the annual critical level of sulphur dioxide, in nmol/mol;

Influence quantities

General

In general, the principal approach described in Annex F applies to the calculation of the uncertainties due to effects of influence quantities (physical and chemical). In short: if the value of the influence quantity q_{cal} at calibration is known and differs from q_{max} or q_{min}, Formula (E.12) applies.

When q_{cal} is unknown, but varies between q_{min} and q_{max}, Formula (E.13) applies. The uncertainty calculations presented here are based on the application of Formula (E.12).

NOTE If it can be demonstrated that a triangular distribution of values of q is appropriate rather than a uniform distribution, the denominator value will be 6 instead of 3.

Sample gas pressure

The standard uncertainty due to variation of **sample gas pressure at the annual critical level** is calculated according to:

$$u_{\mathrm{gp,act}} = \frac{l_{\mathrm{h}}}{c_{\mathrm{t}}} b_{\mathrm{gp}} \sqrt{\frac{\left(P_{\max} - P_{\mathrm{cal}}\right)^2 + \left(P_{\max} - P_{\mathrm{cal}}\right)\left(P_{\min} - P_{\mathrm{cal}}\right) + \left(P_{\max} - P_{\mathrm{cal}}\right)^2}{3}} \quad \text{(H.7)}$$

where

$u_{\mathrm{gp,act}}$ is the standard uncertainty due to the influence of actual pressure variations, in nmol/mol;

l_{a} is the annual critical level of sulphur dioxide, in nmol/mol;

c_{t} is the test gas concentration (70 % to 80 % of the certification range of SO_2), in nmol/mol;

b_{gp} is the sensitivity coefficient of sample gas pressure variation, in nmol/mol/kPa;

$P_{\max}$ is the upper level of the site-specific range of the variation of the sample gas pressure, in kPa;

$P_{\min}$ is the lower level of the site-specific range of the variation of the sample gas pressure, in kPa.

When P_{cal} is not known, (H.7) reduces to

$$u_{\mathrm{gp,act}} = \frac{l_{\mathrm{a}}}{c_{\mathrm{t}}} b_{\mathrm{gp}} \sqrt{\frac{\left(P_{\max} - P_{\min}\right)^2}{3}} \quad \text{(H.7a)}$$

Sample gas temperature

The standard uncertainty due to variation of **sample gas temperature at the annual critical level**, $u_{\mathrm{gt,act}}$, is calculated according to:

$$u_{\mathrm{gt,act}} = \frac{l_{\mathrm{a}}}{c_{\mathrm{t}}} b_{\mathrm{gt}} \sqrt{\frac{\left(T_{\mathrm{G,max}} - T_{\mathrm{G,cal}}\right)^2 + \left(T_{\mathrm{G,max}} - T_{\mathrm{G,cal}}\right)\left(T_{\mathrm{G,min}} - T_{\mathrm{G,cal}}\right) + \left(T_{\mathrm{G,max}} - T_{\mathrm{G,cal}}\right)^2}{3}} \quad \text{(H.8)}$$

where

$u_{\mathrm{gt,act}}$ is the standard uncertainty due to actual variation of sample gas temperature, in nmol/mol;

l_{a} is the annual critical level of sulphur dioxide, in nmol/mol;

c_{t} is the test gas concentration (70 % to 80 % of the certification range of SO_2), in nmol/mol;

b_{gt} is the sensitivity coefficient of sample gas temperature variation, in nmol/mol/K;

$T_{\mathrm{G,max}}$ is the upper level of the site-specific range of the variation of the sample gas temperature, in °C;

$T_{\mathrm{G,min}}$ is the lower level of the site-specific range of the variation of the sample gas temperature, in °C.

When $T_{\mathrm{G,cal}}$ is not known, (H.8) reduces to

$$u_{\mathrm{gt,act}} = \frac{l_{\mathrm{a}}}{c_{\mathrm{t}}} b_{\mathrm{gt}} \sqrt{\frac{\left(T_{\mathrm{G,max}} - T_{\mathrm{G,min}}\right)^2}{3}} \quad \text{(H.8a)}$$

Surrounding temperature

The standard uncertainty due to variation of **surrounding temperature at the annual critical level** is calculated according to:

$$u_{st,act} = \frac{l_a}{c_t} b_{st} \sqrt{\frac{(T_{S,max} - T_{S,cal})^2 + (T_{S,max} - T_{S,cal})(T_{S,min} - T_{S,cal}) + (T_{S,max} - T_{S,cal})^2}{3}} \quad \text{(H.9)}$$

where

$u_{st,act}$ is the standard uncertainty due to the influence of actual surrounding temperature variations, in nmol/mol;

l_a is the annual critical level of sulphur dioxide, in nmol/mol;

c_t is the test gas concentration (70 % to 80 % of the certification range of SO_2), in nmol/mol;

b_{st} is the sensitivity coefficient of surrounding temperature variation, in nmol/mol/K;

$T_{S,max}$ is the maximum level of the site-specific range of the variation of the surrounding temperature, in °C;

$T_{S,cal}$ is the surrounding temperature at which the calibration is performed, in °C;

$T_{S,min}$ is the minimum level of the site-specific range of the variation of the surrounding temperature, in °C.

When $T_{S,cal}$ is not known, (H.9) reduces to

$$u_{st,act} = \frac{l_a}{c_t} b_{st} \sqrt{\frac{(T_{S,max} - T_{S,min})^2}{3}} \quad \text{(H.9a)}$$

Electrical voltage

The standard uncertainty due to variation of **electrical voltage at the annual critical level** is calculated according to:

$$u_{V,act} = \frac{l_a}{c_t} b_V \sqrt{\frac{(V_{max} - V_{cal})^2 + (V_{max} - V_{cal})(V_{min} - V_{cal}) + (V_{max} - V_{cal})^2}{3}} \quad \text{(H.10)}$$

where

$u_{V,act}$ is the standard uncertainty due to the influence of actual voltage variations, in nmol/mol;

l_a is the annual critical level of sulphur dioxide, in nmol/mol;

c_t is the test gas concentration (70 % to 80 % of the certification range of SO_2), in nmol/mol;

b_V is the sensitivity coefficient of voltage variation, in nmol/mol/V;

V_{max} is the maximum level of the site-specific range of the variation of the voltage, in V;

V_{cal} is the voltage at which the calibration is performed, in V;

V_{min} is the minimum level of the site-specific range of the variation of the voltage, in V.

When V_{cal} is not known, (H.10) reduces to

$$u_{V,act} = \frac{l_a}{c_t} b_V \sqrt{\frac{(V_{max} - V_{min})^2}{3}} \quad \text{(H.10a)}$$

Interferents

The calculation of the uncertainty due to interferents is based on the actual concentration of the chemical interferents during field operation. Therefore, the following formulae are used for calculating the uncertainty due to water vapour and other interfering chemical compounds.

Water vapour

The standard uncertainty due to the **presence of water vapour at the annual critical level** is calculated according to:

$$b_{H_2O} = \frac{1}{c_{H_2O}}\left[X_{H_2O,z} + \left(X_{H_2O,C_t} - X_{H_2O,z}\right)\frac{l_a}{c_t}\right] \quad \text{(H.11)}$$

$$u_{H_2O,act} = b_{H_2O} \cdot \sqrt{\frac{c^2_{H_2O,max} + c_{H_2O,max}c_{H_2O,min} + c^2_{H_2O,min}}{3}} \quad \text{(H.12)}$$

where

$X_{H_2O,z}$ is the influence quantity of an H_2O concentration of 19 mmol/mol at zero concentration of the measurand, in nmol/mol;

X_{H_2O,c_t} is the influence quantity of an H_2O concentration of 19 mmol/mol at the test concentration c_t of the measurand, in nmol/mol;

$u_{H_2O,act}$ is the standard uncertainty due to interference by the actual presence of water vapour, in nmol/mol;

b_{H_2O} is the sensitivity coefficient due to interference by the presence of water vapour, in (nmol/mol)/(mmol/mol);

c_{H_2O} is the test concentration of H_2O in the type-approval test (19 mmol/mol);

c_t is the test gas concentration of SO_2, in nmol/mol;

l_a is the annual critical level of sulphur dioxide, in nmol/mol;

$c_{H_2O,max}$ is the maximum hourly average concentration of water vapour, in mmol/mol;

$c_{H_2O,min}$ is the minimum hourly average concentration of water vapour, in mmol/mol.

Other interferents

The standard uncertainty due to **each interfering compound at the annual critical level** (other than water vapour) is calculated according to:

$$b_{int} = \frac{1}{c_{int}}\left[X_{int,z} + \left(X_{int,C_t} - X_{int,z}\right)\frac{l_a}{c_t}\right] \quad \text{(H.13)}$$

$$u_{int,act} = b_{int} \cdot \sqrt{\frac{c^2_{int,act,max} + c_{int,act,max}c_{int,act,min} + c^2_{int,act,min}}{3}} \quad \text{(H.14)}$$

where

X_{int,c_t} is the influence quantity of the maximum concentration, in nmol/mol or µmol/mol, of the relevant interfering compound at the test concentration c_t of the measurand, in nmol/mol;

$X_{\text{int,z}}$ is the influence quantity of the maximum concentration, in nmol/mol or µmol/mol, of the relevant interfering compound at zero concentration of the measurand, in nmol/mol;

u_{int} is the standard uncertainty due to the presence of the interferent, in nmol/mol;

b_{int} is the sensitivity coefficient due to the presence of the interferent, in (nmol/mol)/(nmol/mol) or (nmol/mol)/(µmol/mol);

c_{int} is the test concentration of the relevant interfent, in nmol/mol or µmol/mol;

c_t is the test gas concentration of SO_2, in nmol/mol;

l_a is the annual critical level of sulphur dioxide, in nmol/mol;

$c_{\text{int,act,max}}$ is the actual maximum hourly average concentration of interfering compound, in nmol/mol or µmol/mol;

$c_{\text{int,act, min}}$ is the actual minimum hourly average concentration of interfering compound, in nmol/mol or µmol/mol.

According to EN ISO 14956, the summed uncertainties due to the interferents with positive impact and the summed uncertainties of the interferents with negative impact are calculated as:

$$u_{\text{int,act,pos}} = \sqrt{(u_{\text{int,act,1,pos}} + ... + u_{\text{int,act, n,pos}})^2} \quad \text{(H.15)}$$

$$u_{\text{int,act,neg}} = \sqrt{(u_{\text{int,act,1,neg}} + ... + u_{\text{int,act,n,neg}})^2} \quad \text{(H.16)}$$

where

$u_{\text{int,act, pos}}$ is the sum of uncertainties due to interferents with positive impact, in nmol/mol;

$u_{\text{int,act,1,pos}}$ is the uncertainty due to the 1th interferent with positive impact, in nmol/mol;

$u_{\text{int,act,n,pos}}$ is the uncertainty due to the *n*th interferent with positive impact, in nmol/mol;

$u_{\text{int,act,neg}}$ is the sum of uncertainties due to interferents with negative impact, in nmol/mol;

$u_{\text{int,act,1,neg}}$ is the uncertainty due to the 1th interferent with negative impact, in nmol/mol;

$u_{\text{int,act,n,neg}}$ is the uncertainty due to the *n*th interferent with negative impact, in nmol/mol.

The highest value of (H.15) and (H.16) is taken as value for $u_{\text{int,act}}$ in (H.1).

Averaging effect

The standard uncertainty due to the **averaging effect** is calculated according to:

$$u_{\text{av}} = \frac{E_{\text{av}}}{100} \frac{l_{\text{a}}}{\sqrt{3}} \quad \text{(H.17)}$$

where

u_{av} is the standard uncertainty due to the averaging effect, in nmol/mol;

E_{av} is the averaging effect, in % of the measured value;

l_a is the annual critical level of sulphur dioxide, in nmol/mol.

Zero gas

The uncertainty related to the composition of the zero gas used for calibration is calculated from its specifications (Table 4) for sulphur dioxide as:

$$u_{zg} = \frac{1}{\sqrt{3}} \text{ nmol/mol} \quad \text{(H.18)}$$

where

u_{zg} is the standard uncertainty due to the zero gas in nmol/mol.

Calibration gas

The standard uncertainty due to the **calibration gas** is calculated according to:

$$u_{cg} = \frac{W_{cg}}{2 \times 100} l_a \quad \text{(H.19)}$$

where

u_{cg} is the standard uncertainty due to the calibration gas, in nmol/mol;

W_{cg} is the relative expanded uncertainty of the calibration gas, in %;

l_a is the annual critical level of sulphur dioxide, in nmol/mol.

Difference sample/calibration port

The standard uncertainty due to the **difference sample/calibration port** is calculated according to:

$$u_{\Delta sc} = \frac{\Delta x_{sc}}{100} l_a \quad \text{(H.20)}$$

where

$u_{\Delta sc}$ is the standard uncertainty due to the difference sample/calibration port, in nmol/mol;

Δx_{sc} is the difference sample/calibration port, in %;

l_a is the annual critical level of sulphur dioxide, in nmol/mol.

Reproducibility under field conditions

The standard uncertainty due to the **reproducibility under field conditions** is calculated according to:

$$u_{r,f,la} = \frac{s_{r,f} \cdot l_a}{100 \cdot \sqrt{n_a}} \quad \text{(H.21)}$$

where

$u_{r,f,la}$ is the standard uncertainty at the annual critical level due to reproducibility under field conditions, in nmol/mol;

n_a is the number of valid hourly measurements in the year (≥ 7 884);

$s_{r,f}$ is the reproducibility standard deviation for SO_2 from the field test, in %;

l_a is the annual critical level of sulfur dioxide, in nmol/mol.

Long term drift at zero

The standard uncertainty due the **long term drift at zero** is calculated according to:

$$u_{D_{l,z}} = \frac{D_{l,z}}{\sqrt{3}} \quad \text{(H.22)}$$

where

$u_{D_{l,z}}$ is the uncertainty due to long term drift at zero, in nmol/mol;

$D_{l,z}$ is the actual long term drift at zero, in nmol/mol, determined from periodic calibrations over the period of re-assessment of the measurement uncertainty.

Long term drift at level of the annual critical level

The standard uncertainty due to the **long term span drift at level of the annual critical level** is calculated according to:

$$u_{D,l,la} = \frac{l_a}{100} \cdot \sqrt{\frac{1}{k} \sum_{i=1}^{n} \frac{D_{l,span,i}^2}{3}} \quad \text{(H.23)}$$

where

$u_{D,l,la}$ is the standard uncertainty due to long term drift at the annual critical level, in nmol/mol;

$D_{l,span,i}$ is the long term span drift, in %, determined from periodic calibrations over the period of re-assessment of the measurement uncertainty, for period *i;*

k is the number of calibrations performed within the annual period;

l_a is the annual critical level of sulphur dioxide, in nmol/mol.

H.4 Example calculation

SO_2 acl	8		nmol/mol								
Number of hourly values	7884										
Number of yearly calibrations	4										
Parameter	*Ct*		Unit	Value		X-	Xcal	X+	DX-	DX+	u	u^2
Repeatability at zero			nmol/mol	0							0,00	0,00
Repeatability at C_t	300		nmol/mol	0							0,00	
Lack-of-fit			%	0,38							0,02	0,00
Sample gas pressure	300		nmol/mol/kPa	0,05		97	101	104	-4	3	0,00	0,00
Sample gas temperature	300		nmol/mol/°C	0,41		273	293	303	-20	10	0,10	0,01
Surrounding temperature	300		nmol/mol/°C	0,35		273	293	303	-20	10	0,09	0,01
Electrical voltage	300		nmol/mol/V	0,01		215	220	230	-5	10	0,00	0,00
Interferences		*Cint*			*Xint*							
- H_2O 19 mmol/mol span	300	19	nmol/mol	-2,3	-0,01	6	0	21	6	21	-0,17	0,03
- H_2O 19 mmol/mol zero				-0,2								
- H_2S 200 nmol/mol span	300	200	nmol/mol	-0,7	0,00	1	0	3	1	3	0,00	
- H_2S 200 nmol/mol zero				-0,1								
- NO 500 nmol/mol span	300	500	nmol/mol	4	0,01	0	0	50	0	50	0,19	
- NO 500 nmol/mol zero				3,3								
- NO_2 200 nmol/mol span	300	200	nmol/mol	1	0,00	5	0	100	5	100	0,07	
- NO_2 200 nmol/mol zero				0,23								
- m-X 1 000 nmol/mol span	300	1000	nmol/mol	1	0,00	0	0	1	0	1	0,00	
- m-X 1 000 nmol/mol zero				0,07								
- NH_3 200 nmol/mol span	300	200	nmol/mol	-0,7	0,00	0	0	5	0	5	0,00	
- NH_3 200 nmol/mol zero				0,1								
Sum interferents (without water)											0,27	0,07
Averaging effect			%								0,17	0,03
Field reproducibility			%	4							0,00	0,00
Long term zero drift			nmol/mol	2							0,00	0,00
Long term span drift			%	0,02							0,01	0,00
Difference sample/calibration port			%	0								
Calibration gas			%	5							0,19	0,04
Zero gas			nmol/mol	0,6							0,6	0,36
Sum of variances												0,54
Combined uncertainty (nmol/mol)												0,74
Expanded uncertainty (%)												19,7

NOTE Due to the uncertainty in the level of SO_2 in the zero gas, the 15 % uncertainty requirement cannot be met. Reducing the uncertainty to 0,3 nmol/mol would lead to a reduction of the expanded uncertainty to 14,0%.

Annex I
(informative)

Significant technical changes

Details of significant technical changes between this European Standard and the previous edition are:

Clause	*Technical change*
8.4.2.3, Table 4	Requirements for impurities in zero gas have been relaxed for other than interferents tests.
9.4; 9.6	Performance requirements have been tightened for some performance characteristics.
9.4; 9.6	Additional performance criteria and tests have been introduced for repeatability at zero and span levels.
9.5	Formulae have been introduced for software adjustment of the raw analyser signal after calibration.
Annexes F to H	Uncertainty calculations have been modified to be in conformity with EN ISO 14956.

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