BSI Standards Publication

Ambient air — Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide by chemiluminescence

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National foreword

This British Standard is the UK implementation of EN 14211:2012. It supersedes BS EN 14211:2005 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee EH/2/3, Ambient atmospheres.

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Ambient air - Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide by chemiluminescence

Air ambiant - Méthode normalisée pour le mesurage de la concentration en dioxyde d'azote et monoxyde d'azote par chimiluminescence

Luftqualität - Messverfahren zur Bestimmung der Konzentration von Stickstoffdioxid und Stickstoffmonoxid mit Chemilumineszenz

This European Standard was approved by CEN on 10 May 2012.

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Contents

Foreword

This document (EN 14211:2012) 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of an identical text or by endorsement, at the latest by February 2013, and conflicting national standards shall be withdrawn at the latest by February 2013.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 14211:2005.

The technical changes made since EN 14211:2005 are listed in Annex H 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 concentrations of nitrogen dioxide and nitrogen monoxide present in ambient air based on the chemiluminescence measuring principle. This standard describes the performance characteristics and sets the relevant minimum criteria required to select an appropriate chemiluminescence 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 concentration of nitrogen dioxide present in ambient air up to 500 µg/m^3. This concentration range represents the certification range for NO_2 for the type approval test.

The method is applicable to the determination of the concentration of nitrogen monoxide present in ambient air up to 1 200 µg/m^3. This concentration range represents the certification range for NO for the type approval test.

NOTE 1   It is possible to use other ranges depending on the levels present in ambient air.

NOTE 2   When this European 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 nitrogen dioxide and nitrogen monoxide in zones classified as rural areas, urban-background areas and traffic-orientated locations and locations influenced by industrial sources.

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

NOTE 3   500 µg/m^3 of NO_2 corresponds to 261 nmol/mol of NO_2 at 20 °C and 101,3 kPa. 1 200 µg/m^3 of NO corresponds to 962 nmol/mol of NO at 20 °C and 101,3 kPa.

This standard contains information for different groups of users.

Clauses 5 to 7 and Annexes B and C contain general information about the principles of NO_x measurement by chemiluminescence analyser and sampling equipment.

Clause 8 and Annex E are specifically directed towards test houses and laboratories that perform type-approval testing of NO_x 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 NO_x 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 NO_x 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 generally 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: Council Directive 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
converter efficiency
degree of conversion of NO_2 present in the sample gas into NO, given as a percentage

3.10
coverage factor
numerical factor used as a multiplier of the combined standard uncertainty in order to obtain an expanded uncertainty

[SOURCE: ENV 13005:1999]

3.11
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

3.12
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 $3,3 \times (s_z/B)$ 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].

3.13
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 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 %.

3.14
fall time
difference between the response time (fall) and the lag time (fall)

3.15
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.

3.16
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].

3.17
influence quantity
quantity that is not the measurand but that affects the result of the measurement

[SOURCE: ENV 13005:1999]

3.18
interferent
component of the air sample, excluding the measured constituent, that affects the output signal

3.19
lack of fit
maximum deviation from the linear regression line of the average of a series of measurement results at the same concentration

3.20
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

3.21
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: Council Directive 2008/50/EC [1]]

3.22
long term drift
difference between zero or span readings over a determined period of time (e.g. period of unattended operation)

3.23
monitoring station
enclosure located in the field in which an analyser has been installed to monitor concentrations of one or more ambient air pollutants

3.24
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

3.25
performance characteristic
one of the parameters assigned to equipment in order to define its performance

3.26
performance criterion
limiting quantitative numerical value assigned to a performance characteristic, to which conformance is tested

3.27
period of unattended operation
time period over which the drift complies with the performance criterion for long term drift

3.28
repeatability (of results of measurement)
closeness of the agreement between the results of successive individual measurements of nitrogen monoxide and nitrogen 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.

3.29
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.

3.30
residence time inside the analyser
time period for the sampled air to be transported from the inlet of the analyser to the reaction chamber for the NO-channel

3.31
residence time in the sampling system
time period for the sampled air to be transferred to the inlet of the analyser

3.32
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

3.33
sampled air
part of ambient air that is transferred through the sampling inlet and sampling system for subsequent measurement

3.34
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.

3.35
sampling system
the assembly of components needed to transfer ambient air to the analyser

3.36
short-term drift
difference between zero or span readings at the beginning and end of a 12 h period

3.37
standard uncertainty
uncertainty of the result of a measurement expressed as a standard deviation

[SOURCE: ENV 13005:1999]

3.38
surrounding temperature
temperature of the air directly surrounding the analyser

3.39
total residence time
sum of the residence time in the sampling system and the residence time inside the analyser

3.40
type approval
decision taken by a designated body that the pattern of an analyser conforms to specified requirements

3.41
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

3.42
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 concentrations of nitrogen dioxide and nitrogen monoxide in ambient air by means of chemiluminescence. The requirements, the specific components of the chemiluminescence 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

Chemiluminescence is based on the reaction of nitrogen monoxide with ozone. In a chemiluminescence analyser, air is sampled through a filter (to prevent contamination of the gas conveying system, especially the optical components of the analyser) and fed at a constant flow rate into the reaction chamber of the analyser, where it is mixed with an excess of ozone for the determination of nitrogen monoxide only. The emitted radiation (chemiluminescence) is proportional to the number of nitrogen monoxide molecules in the detection volume and thus proportional to the concentration of nitrogen monoxide. The emitted radiation is filtered by a selective optical filter and converted into an electric signal by a photomultiplier tube or a photodiode.

For the determination of nitrogen dioxide, the sampled air is fed through a converter where the nitrogen dioxide is reduced to nitrogen monoxide and analysed in the same way as previously described. The electrical signal obtained from the photomultiplier tube or photodiode is proportional to the sum of concentrations of nitrogen dioxide and nitrogen monoxide. The amount of nitrogen dioxide is calculated from the difference between this concentration and that obtained for nitrogen monoxide only (when the sampled air has not passed through the converter).

Chemiluminescence is the emission of light during a chemical reaction. During the gas-phase reaction of NO and ozone light with an intensity proportional to the concentration of NO is produced when electrons of the excited NO_2 molecules decay to lower energy states.

This chemiluminescence method is based on the reaction

$$NO + O_3 \rightarrow NO_2^* + O_2 \tag{1}$$

$$NO_2^* \rightarrow NO_2 + h\nu \tag{2}$$

Excited nitrogen dioxide (NO_2^*) emits radiation in the near infrared region (600 nm to 3 000 nm) with a maximum centered around 1 200 nm. For the determination of nitrogen dioxide, the nitrogen dioxide present in sampled air is converted to nitrogen monoxide in a converter as a result of the reaction:

$$NO_2 \xrightarrow{\;converter\;} NO \tag{3}$$
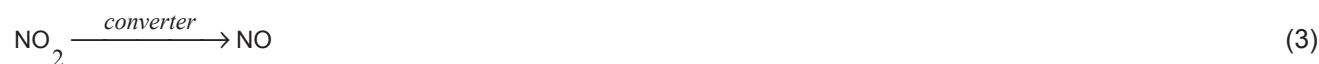
The NO is then analysed according to the reactions (1) and (2).

The concentrations of nitrogen dioxide and nitrogen monoxide are directly measured in volume/volume units (if the analyser is calibrated using a volume/volume standard), since the emitted radiation from the chemiluminescence reaction is proportional to the concentration of nitrogen monoxide in volume/volume units. The final results for reporting are expressed in µg/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 inlet, 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 chemiluminescence 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 subclauses.

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

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

— loss of nitrogen dioxide in the sampling system;

— loss of nitrogen dioxide in the particle filter;

— formation of nitrogen dioxide due to reaction of nitrogen monoxide with ozone in the sampling system and in the analyser.

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 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 (see also 6.3.3).

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 subclauses (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 nitrogen monoxide and nitrogen 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 nitrogen monoxide and nitrogen dioxide.

NOTE 1   The filter may be internal to the analyser (see 7.9) 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 nitrogen dioxide by adsorption on the particle matter and may increase the pressure drop in the sampling line.

6.3.3   Formation of NO_2 and loss of NO

As O_3 is generally present in the sampled air, a change in concentrations of NO and NO_2 will occur due to the reaction of NO with O_3 in the sampling inlet and line or manifold, and in the analyser. In practice a significant change in the concentrations of NO and NO_2 may be avoided when the residence time in the sampling system is ≤ 3 s. The requirement for the residence time in the analyser is ≤ 3 s (see Table 1). The residence time shall be evaluated for the NO channel. It is not necessary to evaluate the residence time for the NO_x channel (in which the converter is present) as all the NO_2 is converted to NO in the converter.

Consequently, the total residence time in the sampling system plus analyser shall comply with the performance criterion in Table 1.

Depending on the location of the particle filter, the sampling system can be contaminated by deposition of dust. This can induce losses of NO_2. The sampling system shall be cleaned (as stated in 9.4.1) 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 NO and NO_2 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 (see 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 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 chemiluminescence 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 fulfils the requirement given in 6.3.3. To verify the 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

Generally, three types of analysers are available, those with:

a)   two reaction chambers and one common photo multiplier or photodiode;

b)   two reaction chambers each with a separate photo multiplier or photodiode;

c)   one reaction chamber (with one photo multiplier or photodiode).

In Types a) and b) the airflow is divided into two streams, one passing directly to one of the reaction chambers for measurement of the nitrogen monoxide content. The other stream is fed through the converter for conversion of the nitrogen dioxide to nitrogen monoxide and then to the other reaction chamber for measurement of the total content of nitrogen dioxide and nitrogen monoxide.

In the Type c) analyser, the air sample alternately bypasses or passes through the converter. This type of analyser measures during a certain time period the amount of nitrogen monoxide and during the next time period the sum of nitrogen dioxide and nitrogen monoxide concentrations.

NOTE 1   Schematic diagrams of typical analysers are given in Figure C.1 and Figure C.2 (Types a) and b)) and Figure C.3 (Type c)).

NOTE 2   Some Type c) analysers do not fulfil the requirements for use at traffic-orientated locations, due to the rapid fluctuations of the nitrogen dioxide and nitrogen monoxide concentrations. These rapid fluctuations may result in erroneous determination of the NO_2 concentrations, as these are the result of the subtraction of two consecutive readings (NO_x and NO). The use of a delay loop reduces this problem. The averaging error is quantified in the type approval test.

A chemiluminescence analyser consists of the principal components which are described in 7.2 to 7.8.

7.2   Converter

The converter converts nitrogen dioxide in the sampled air into nitrogen monoxide.

Most converters use a heated furnace maintained at a constant temperature and are made of materials such as stainless steel, copper, molybdenum, tungsten or spectroscopically pure carbon. Other types are available, for example those based on photolysis of nitrogen dioxide.

The converter shall be capable of converting at least 95 % of the nitrogen dioxide to nitrogen monoxide. The conversion efficiency shall be checked according to 8.4.14. A mathematical correction for the NO_2 concentration shall be made when the converter efficiency is < 98 %.

NOTE   Heated-furnace converters are not specific for nitrogen dioxide but also convert other components such as nitric acid, nitrous acid, ammonia and PAN to nitrogen monoxide. This may be particularly relevant for rural sites. Photolytic converters are specific for nitrogen dioxide but have a low converter efficiency, e.g. around 50 %, that would need to be

established on a relatively frequent basis. Testing the effect of conversion of ammonia is part of the analyser type approval in this standard.

7.3   Ozone generator

Ozone is generated from oxygen either by ultraviolet radiation or by a high-voltage silent electric discharge. If oxygen in ambient air is used for ozone generation by a high-voltage silent electric discharge, it is essential that the air be thoroughly dried and filtered before entering the generator. If the ozone is generated from synthetic air of a recognised analytical grade from a compressed gas cylinder, this synthetic air can be fed directly into the generator. The concentration of ozone produced shall be sufficiently high to maintain the required lack of fit of the analyser. Too low an ozone concentration will result in a non-linear response to the concentration of nitrogen dioxide and nitrogen monoxide. The analyser shall fulfil the requirements for lack of fit as stated in 8.2.

7.4   Reaction chamber

The reaction chamber shall be constructed of an inert material. The reaction chamber shall be heated to a constant temperature above the surrounding temperature. The typical temperature in practice is 40 °C to 50 °C. The chemiluminescence reaction is carried out at reduced pressure to minimise quenching effects and to increase sensitivity.

7.5   Optical filter

The optical filter shall remove radiation at wavelengths shorter than 600 nm, to minimise any interference produced by the chemiluminescence reaction with unsaturated hydrocarbons, which radiate at these wavelengths.

7.6   Detector

The output of the analyser is affected by the characteristics of the detector. In order to reduce background noise and the effect of temperature changes, the detector can be housed in a thermostatically controlled refrigerated device (commonly cooled by means of a Peltier cooler).

7.7   Ozone removal device

The ozone shall be removed from the analysed sampled air at the exhaust of the reaction chamber by passage through an ozone removal device (e.g. cartridge filled with activated carbon). This prevents pollution of the immediate surrounding air and protects the sampling pump.

Some ozone scrubbers, e.g. iodide-based scrubbers, should not be used as explosive peroxides may be formed.

7.8   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 a 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.

7.9   Particle filter

An analyser will generally contain an internal particle filter. This filter shall be considered an integral part of the analyser in type-approval testing.

8   Type approval of nitrogen dioxide and nitrogen monoxide analysers

8.1   General

The determination of the concentration of nitrogen dioxide and nitrogen monoxide in ambient air shall fulfil the requirement of a maximum uncertainty in the measured values, which is prescribed by Directive 2008/50/EC. In order to achieve an uncertainty less than (or equal to) this required uncertainty, the chemiluminescence 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 uncertainties derived from the values of the selected performance characteristics in the expanded uncertainty calculation, a judgement shall be made whether or not the chemiluminescence analyser meets the criterion of maximum uncertainty prescribed by Directive 2008/50/EC.

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 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 15627-2 covers the supplementary requirements for an AMS manufacturer's management system to EN ISO 9001 [9], 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

nr	Performance characteristic	Symbol	Section	Lab. test		Field test		Performance criterion for NO and/or NO₂
				NO	NO₂	NO	NO₂	
1	Repeatability standard deviation at zero	$s_{r,z}$	8.4.5	x				≤ 1,0 nmol/mol
2	Repeatability standard deviation at concentration c_t	$s_{r,ct}$	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				≤ 8,0 nmol/mol/kPa
5	Sensitivity coefficient of sample gas temperature	b_{gt}	8.4.8	x				≤ 3, 0 nmol/mol/K
6	Sensitivity coefficient of surrounding temperature	b_{st}	8.4.9	x				≤ 3, 0 nmol/mol/K
7	Sensitivity coefficient of electrical voltage	b_V	8.4.10	x				≤ 0,30 nmol/mol/V
8	Interferents at zero and at concentration c_t [a]		8.4.11					
8a	H₂O with concentration 19 mmol/mol [b]	$X_{H2O,z,ct}$			x			≤ 5,0 nmol/mol
8b	CO₂ with concentration 500 µmol/mol	$X_{CO2,z,ct}$			x			≤ 5,0 nmol/mol
8c	NH₃ with concentration 200 nmol/mol [c]	$X_{NH3,z,ct}$			x [c]			≤ 5,0 nmol/mol
9	Averaging effect	E_{av}	8.4.12	x	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		≤ 5,0 nmol/mol
12	Long term drift at span level	$D_{l,s}$	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	$D_{s,s}$	8.4.4	x				≤ 6,0 nmol/mol over 12 h

nr	Performance characteristic	Symbol	Section	Lab. test		Field test		Performance criterion for NO and/or NO$_2$
				NO	NO$_2$	NO	NO$_2$	
15	Response time (rise)	t_r	8.4.3	x	x			$\leq$ 180 s
16	Response time (fall)	t_f	8.4.3	x	x			$\leq$ 180 s
17	Difference between rise time and fall time	t_d	8.4.3	x	x			$\leq$ 10 s
18	Difference sample/calibration port [d]	Δx_{sc}	8.4.13	x				$\leq$ 1,0 %
19	Period of unattended operation		8.5.6				x	3,0 months or less if manufacturer indicates a shorter period
20	Availability of the analyser	A_a	8.5.7				x	$\geq$ 90 %
21	Converter efficiency [e,f]	E_c	8.4.14		x			$\geq$ 98 %
22	Residence time in the analyser		8.4.15		x			$\leq$ 3,0 s

[a] Performance criterion is set both at zero and at test gas concentration level.
[b] A H$_2$O concentration of 19 mmol/mol equals 80 % RH at 20 °C and 101,3 kPa.
[c] To be determined using NO test gas by reading the NO$_2$ signal.
[d] If relevant.
[e] In NOx-analysers with a single reaction chamber, a leak in the switching valve between the NO and NOx channels can cause a degree of mixing of the NO$_2$ and NO components, causing an underreading of the NO$_2$ concentration.
[f] This requirement differs from the requirement in ongoing quality control (see Table 6 and 9.6.3). In the laboratory test the converter is new and therefore the requirement is more stringent.

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.

Most of the tests are performed with test gases containing nitrogen monoxide in specified concentrations by determining responses on the NO-channel. Reasons for this are:

— For most characteristics the effects on the NO- and NO_x-channels of an analyser will be the same.

— The generation of stable, low-concentration test gases of nitrogen dioxide with sufficiently low uncertainties is problematic.

Wherever differences may exist between responses of the NO- and NO_x-channels, the response of the NO_x-channel is used rather than that of the NO-channel.

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 shall 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 "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.

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. Various methods for the generation of test gases are given in Table 3.

Table 3 — Methods for preparation of test gases

Method	NO[a]	NO$_2$	Description	Standard to be used
Cylinder	+	+	Gas mixture of NO in N$_2$ or NO$_2$ gas mixture in (synthetic) air	EN ISO 6142 EN ISO 6143
Permeation tubes	-	+	Determination of the mass loss of a permeable tube containing NO$_2$ liquid and gas	EN ISO 6145-10
Static dilution	+	-	Preparation by means of injecting known amounts of NO into a known volume	EN ISO 6144
Dynamic dilution	+	+	Dynamic blending of cylinder gas with (synthetic) zero air	EN ISO 6145-6 EN ISO 6145-7
Gas phase titration	-	+	Conversion of NO containing gas with ozone to produce NO$_2$	
[a] +: appropriate method; - : not applicable.				

NOTE   Guidance to the correct application of gas-phase titration can be found in VDI 2453-2 [4] and ISO 15337 [5].

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 laboratory tests. Therefore the span gases and zero gas shall meet the specifications given in Tables 4a to 4d.

Table 4a — Specification for purity of test gas: NO

Pollutant	Concentration
CO_2	≤ 4,0 µmol/mol
O_3	≤ 2,0 nmol/mol
NH_3	≤ 1,0 nmol/mol
Water vapour	≤ 150 µmol/mol
NO_2	≤ 1,0 nmol/mol

Table 4b — Specification for purity of test gas: NO_2

Pollutant	Concentration
CO_2	≤ 4,0 µmol/mol
O_3	≤ 2,0 nmol/mol
NH_3	≤ 1,0 nmol/mol
Water vapour	≤ 150 µmol/mol
NO	≤ 1,0 nmol/mol

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

Pollutant	Concentration
CO_2	≤ 4,0 µmol/mol
O_3	≤ 2,0 nmol/mol
NH_3	≤ 1,0 nmol/mol
Water vapour	≤ 150 µmol/mol
NO	≤ 1,0 nmol/mol
NO_2	≤ 1,0 nmol/mol

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

Pollutant	Concentration
CO_2	≤ 400 µmol/mol
O_3	≤ 2,0 nmol/mol
NH_3	≤ 10 nmol/mol
Water vapour	≤ 150 µmol/mol
NO	≤ 1,0 nmol/mol
NO_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 ($\pm$ 1 %) during the test. The test shall be performed with NO and with NO_2.

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 NO 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 stable to within $\pm$ 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.
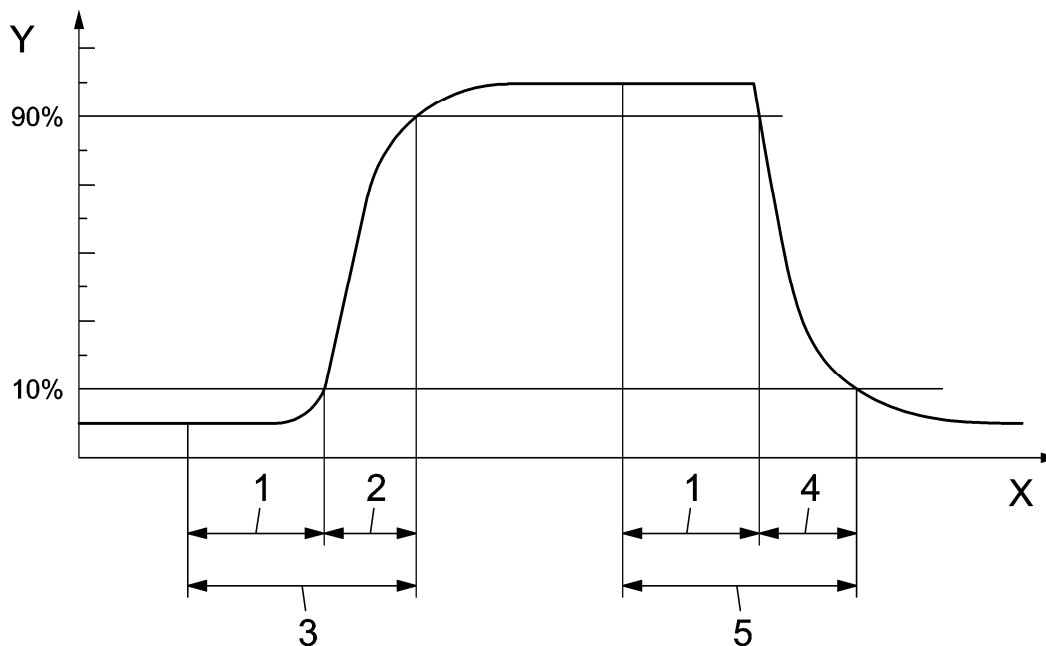
Key

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 test shall then be repeated with NO_2 at levels from less than 20 % to about 80 % of the maximum of the certification range of NO_2 and vice versa.

The difference in response times shall be calculated according to:

$$t_d = \bar{t}_r - \bar{t}_f \tag{4}$$

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 NO). 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 and 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:

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

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.

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

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 an NO test concentration (c_t) of (500 ± 50) nmol/mol shall be performed.

NOTE   This concentration has been chosen because no limit value exists for NO.

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

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

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 gas concentration c_t.

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 according to [3] as:

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

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 NO, 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 NO at an absolute pressure of about $(80 \pm 0{,}2)$ kPa and at an absolute pressure of about $(110 \pm 0{,}2)$ 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:

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

(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 NO shall be applied. Wait the time equivalent to one independent measurement 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:

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

(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 NO shall be applied. At each temperature setting after waiting the time equivalent to one independent measurement, 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.

The sequence of test temperatures is as follows: $T_{S,0}$, $T_{S,1}$, $T_{S,0}$ and $T_{S,0}$, $T_{S,2}$, $T_{S,0}$.

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 measurement procedure shall be repeated at the temperature sequence of $T_{S,0}$, $T_{S,2}$, and at $T_{S,0}$.

A stabilisation time of 4 h is recommended after changing the temperature of the surrounding air.

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:

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

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 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 voltage range specified by the manufacturer, V_1 and V_2, at zero concentration and at a concentration around 70 % to 80 % of the maximum of the certification range of NO. 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:

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

(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 in V specified by the manufacturer;

V_2 is the maximum voltage in V specified by the manufacturer.

For reporting the dependence on voltage, the higher 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 an NO test concentration (c_t) of (500 ± 50) nmol/mol.

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 of NO followed by two individual measurements of NO 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 quantities at zero and concentration c_t are calculated from:

$$X_{int,z} = x_z$$

(13)

$$X_{\text{int},c_t} = x_{c_t} - c_t \tag{14}$$

where

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

    x_z is the average of the measurements of NO 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 of NO at concentration c_t, in nmol/mol;

    c_t is the applied concentration of NO, in nmol/mol.

When testing the effect of interference of ammonia, the measured NO_x concentration shall be used instead of the NO concentration.

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)   a constant concentration of NO_2 at a concentration $c_{t,NO2}$ which is about twice the hourly limit value; and

b)   a stepwise varied concentration of NO between zero and 600 nmol/mol (concentration $c_{t,NO}$).

The time period (t_c) of the constant NO concentration shall be at least equal to a period necessary to obtain four independent readings (which is equal to at least sixteen response times). The time period (t_v) of the varying NO concentration shall be at least equal to a period to obtain four independent readings. The time period (t_{NO}) for the NO concentration shall be 45 s followed by a period (t_{zero}) of 45 s of zero concentration.

Further:

    c_t is the test concentration, in nmol/mol;

    t_V is a time period including a whole number of t_{NO} and t_{zero} pairs, and contains a minimum of 3 such pairs, in s.

The change from t_{NO} 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:

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

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.
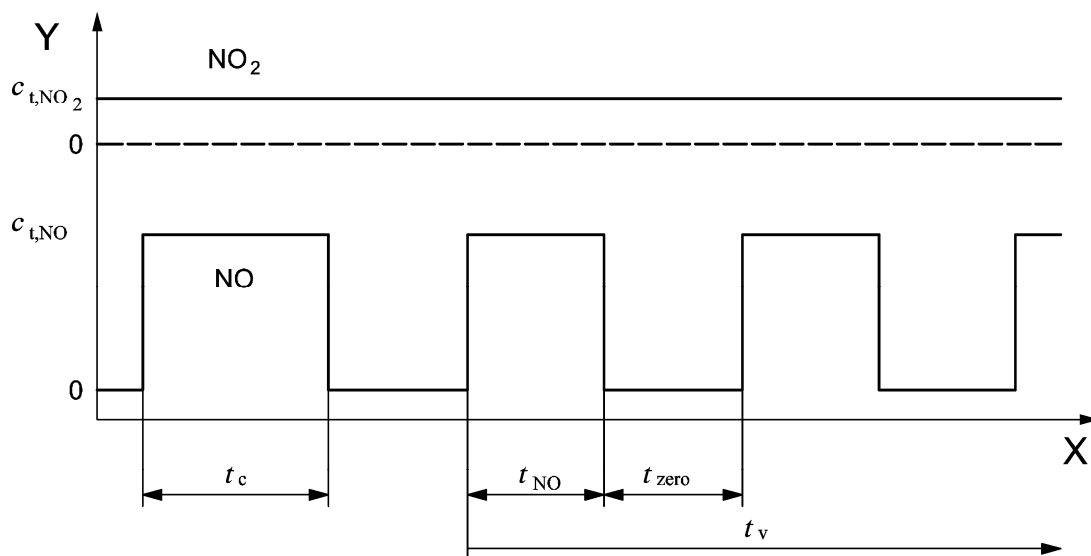
Key

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 NO through the sample port. The test shall consist of one independent measurement 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:

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

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.

8.4.14 Converter efficiency

The converter efficiency is determined by measurements with calculated amounts of NO_2. This can be achieved by means of gas-phase titration of NO to NO_2 with ozone.

NOTE   Guidance to the correct performance of gas-phase titration can be found in [4] and [5].

The test shall be performed at two concentration levels: at about 50 % and about 95 % of the maximum of the certification range of NO_2. Between these tests, the analyser shall be purged with zero gas for at least 30 min.

The procedure followed is as follows:

a) Calibration of both channels of the analyser with NO at 50 % to 80 % of the certification range of NO (~480 nmol/mol – 770 nmol/mol NO);

b) Application of 50 % of the NO certification range until a stable signal is obtained (at least 12 min) (~480 nmol/mol NO, no NO_2);

c) Addition of O_3 at the level of 50 % of the certification range of NO_2 (~480 nmol/mol NO_x, of which ~131 nmol/mol is NO_2) until a stable signal is obtained (at least 12 min);

d) Switch off addition of O_3. Application of 50 % of the NO certification range until a stable signal is obtained (at least 12 min) (~480 nmol/mol NO, no NO_2);

e) Addition of O_3 at the level of 95 % of the certification range of NO_2 (~480 nmol/mol NO_x, of which ~248 nmol/mol NO_2) until a stable signal is obtained (at least 12 min);

f) Switch off addition of O_3. Application of 50 % of the NO certification range until a stable signal is obtained (at least 12 min) (~480 nmol/mol NO, no NO_2).

Calculate the converter efficiency from:

$$E_c = \left(1 - \frac{C_{NOx,init} - C_{NOx,fin}}{C_{NO,init} - C_{NO,fin}} \right) \times 100 \tag{17}$$

where

E_c is the converter efficiency in %;

$C_{NOx,init}$ is the average of the four individual measurements at the NO_x channel at the initial NO_x concentration in nmol/mol;

$C_{NOx,fin}$ is the average of the four individual measurements at the NO_x channel at the resulting NO_x concentration after applying O_3 in nmol/mol;

$C_{NO,init}$ is the average of the four individual measurements at the NO channel at the initial NO concentration in nmol/mol;

$C_{NO,fin}$ is the average of the four individual measurements at the NO channel at the resulting NO concentration after applying O_3 in nmol/mol.

The lowest value of the two converter efficiencies shall be reported.

In some analyser designs, low converter efficiency can be a sign of NO to NO_x internal valve leakage. If low converter efficiency is determined, it is recommended that both converter and the internal valve are checked.

8.4.15 Residence time in the analyser

The residence time inside the analyser shall be calculated on the basis of the flow and the volumes of the tubing and other relevant components inside the analyser and the particle filter housing.

The calculated residence time shall fulfil the requirement given 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 ($\leq$ 10 m from kerb-side). Search for a location with a NO_2 concentration as high as practicable with an average concentration of NO_2 > 30 % of the hourly limit value of NO_2, unless the type approval is aimed at lower ranges.

b) Monitoring station facilities:

   1) sufficient capacity of the sampling system;

   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 $\pm$ 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, actual converter efficiency, 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 NO.

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 check. Filters that have been pre-conditioned in the laboratory using NO/NO_2 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 NO/NO_2 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 %;

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

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.

8.5.4 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 until 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.

The long-term drift is calculated as follows:

$$D_{l,z} = (C_{z,1} - C_{z,0}) \tag{18}$$

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 (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.

$$D_{l,s} = \frac{(C_{s,1} - C_{s,0}) - D_{l,z}}{C_{s,1}} \times 100 \qquad (19)$$

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.

In case of dual-detector analysers, the drifts of the NO and NO_x channels may be different when tested with NO as above. This may be evaluated by monitoring the long-term drift in both channels. If these drifts are significantly diffferent, an additional component to the uncertainty (Annex E) shall be added.

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 for NO_2 under field conditions

The reproducibility standard deviation for NO_2 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:

$$\Delta x_{f,i} = x_{f,1,l} - x_{f,2,i} \qquad (20)$$

where

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

$x_{f,1,l}$ 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:

$$s_{r,f} = \frac{\left(\sqrt{\dfrac{\sum_{i=1}^{n} \Delta x_{f,i}^2}{2n}} \right)}{c_f} \times 100 \qquad (21)$$

where

$s_{r,f}$ is the reproducibility standard deviation for NO_2 under field conditions, in %;

n is the number of parallel measurements;

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

The reproducibility standard deviation for NO_2 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 fourteen days. It is recommended to perform this check every day during the first fourteen days. These checks consists of plausibility checks on the measured values, as well as, when available, on status signals and other relevant parameters. 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 systems and filters (6.3) and maintenance shall not be included.

The availability of the analyser is calculated as:

$$A_a = \frac{t_u}{t_t} \times 100 \qquad (22)$$

where

A_a is the availability of the analyser;

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 8.2).

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 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 8.2).

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 individual measurements for continuous measurements at the hourly limit value. The relevant specific performance characteristics and the calculation procedures 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 Directive 2008/50/EC, quality assurance and quality control procedures for ongoing monitoring of nitrogen dioxide and nitrogen monoxide 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. Nitrogen monoxide or nitrogen 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 assessed.
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.
CO_2 concentration range	The range of hourly-average CO_2 concentrations during a whole period of a year shall be estimated.
NH_3 concentration range	The range of hourly-average NH_3 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 suitability evaluation 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.

NOTE 1   When very rapid fluctuations of levels of NO and NO_2 occur, the analyser may be equipped with a delay loop that enables the NO and NO_x to be analysed in the same air sample by sampling them simultaneously and injecting them sequentially in the reaction chamber [6].

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 2   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.

NOTE 3   At all levels of NO_2 other substances such as PAN (peroxyacetyl nitrate), nitrous acid and nitric acid may be measured as NO_2 by the analyser. This may be particularly relevant for rural sites when considering the annual limit value of nitrogen dioxide [7].

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.

The residence time of the sampled air in the total of sampling system and analyser shall be less than 6 s in order to avoid significant formation of nitrogen dioxide.

During the initial installation, a lack of fit test shall be performed according to 8.4.6. The analyser shall have its converter tested at initial installation according to the test procedure in 8.4.14.

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 nitrogen monoxide or nitrogen 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 nitrogen dioxide applied to the analyser with and without the filter. The concentration of nitrogen dioxide in the test gas shall be between 200 nmol/mol and 250 nmol/mol. The criterion for replacement is a loss of > 3 % of nitrogen 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 1   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 nitrogen dioxide at initial installation;
c)   After one week, again measure the concentration of nitrogen dioxide;

d) Replace the filter with a new filter and measure the concentration of nitrogen dioxide;

e) Calculate the loss of nitrogen 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 nitrogen 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 nitrogen monoxide and nitrogen 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 the 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 checks, 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 whether such violations occur.

Table 6 — Required frequency of calibration, checks and maintenance.

Calibration, checks and maintenance	Section	Frequency	Action criteria[d,h]
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: $\geq 1,0$ nmol/mol Repeatability standard deviation at span: $\geq 0,75\%$ of span concentration
Verification of gases used for zero and span checks	9.6.1	At least every six months	Zero: $\geq$ detection limit Span: $\geq 5,0\%$ of previous verification
Zero and span check	9.6.1	At least every two weeks[a]	Zero : $\leq$ -4 or $\geq$ 4 nmol/mol Span : $\geq 5,0\%$ of initial span value and actual difference between NOx and NO channels $\leq 5,0\%$
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 nmol/mol at zero
Converter efficiency	8.4.14 9.6.3	At least every year	$< 95\%$ [e,f,g]
Testing sample manifold - influence of pressure drop induced by the manifold pump - sample collection efficiency	 9.6.4.1 9.6.4.2	At least every three years	 influence $\geq 1,0\%$ of measured value influence $\geq 2,0\%$ 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]	Response to span gas passing the filter is $\leq 97,0\%$
Test of the sampling lines	6.3	At least every six months[c]	$\geq 2,0\%$ sample loss
Changing of consumables	6.4, 9.7.3	As required by manufacturer[c]	As required
Preventive/routine maintenance of components of the analyser	9.7.4	As required by manufacturer	As required

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

[a]   Recommended every 23 or 25 h. This enables the identification of unstable analysers in an early stage.

[b]   The particulate filter shall be changed periodically depending on the dust loading at the sampling site. Overloading of the particle filter may change the concentration of nitrogen monoxide and/or nitrogen dioxide. The filter housing shall be cleaned every 6 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]   At efficiency levels below 98 % a correction needs to be applied for the (lack of) converter efficiency. The uncertainty of the correction shall then be included in the uncertainty budget (see 9.6.3).

[f]   Analysers with non-thermal converters with efficiencies less than 95 % that are used at rural sites may be used provided that the uncertainty of the conversion factor is determined and the results from the analyser are shown to be equivalent [6].

[g]   In NO_x analysers with a single reaction chamber, a leak in the switching valve between the NO and NO_x channels can cause a degree of mixing of the NO_2 and NO components, causing an underreading of the NO_2 concentration. This may contribute to an underestimation of the converter efficiency.

[h]   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 (span concentration), 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 NO_x measured at a specific site (type) are significantly below the maximum of the certification range for NO of the analyser, e.g. below 20 %, the concentration at which the calibration is performed may be lowered accordingly. This also implies that the concentrations applied for span checks (9.6.1), lack of fit tests (9.6.2) and converter efficiency tests (9.6.3) should be lowered proportionally.

The three-monthly interval may be extended to six months when analyser stability has been demonstrated. A measure for this may be the results of zero and span checks over a three-month period being ≤ 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) at zero concentration and at span level ($s_{r,s}$) 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 tests:
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 nitrogen monoxide or nitrogen dioxide calibration gases 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 NO and NO_x readings of the analyser as logged by the data acquisition system shall be corrected in accordance with the following formulae:

$$c_{NO} = \left(y_{NO} - c_{NO,zero}\right) \times \frac{c_{calgas}}{\left(c_{NO,cal} - c_{NO,zero}\right)}$$

(23)

where

c_{NO} is the corrected NO reading, in nmol/mol;

c_{calgas} is the concentration of NO gas used for calibration of the analyser, in nmol/mol;

$c_{NO,cal}$ is the reading of the NO channel of the analyser during calibration as logged by the data acquisition system, in nmol/mol;

$c_{NO,zero}$ is the reading of the NO channel of the analyser during the zero check as logged by the data acquisition system, in nmol/mol;

y_{NO} is the reading of NO channel of the analyser during measurements, in nmol/mol.

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

(24)

where

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

c_{calgas} is the concentration of NO gas used for calibration of the analyser, in nmol/mol;

$c_{NOx,cal}$ is the reading of the NO$_x$ channel of the analyser during calibration as logged by the data acquisition system, in nmol/mol;

$c_{NOx,zero}$ is the reading of the NO$_x$ channel of the analyser during the zero check as logged by the data acquisition system, in nmol/mol;

y_{NOx} is the reading of NO$_x$ channel of the analyser during measurements, in nmol/mol.

NOTE   In order to avoid discontinuities in time series due to the establishment of a new calibration function, the calibration function may be linearised between calibrations, unless indications exist for discontinuities from zero and span checks.

The concentrations of NO$_2$ shall be calculated from concentrations of NO$_x$ and NO after the corrections as

$$c_{NO2} = \frac{c_{NOx} - c_{NO}}{E_c} \times 100$$ (25)

where

c_{NOx} is the corrected NO$_x$ reading, in nmol/mol;

c_{NO} is the corrected NO reading, in nmol/mol;

E_c is the analyser converter efficiency (9.6.3), in %.

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 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 certified 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, ammonia and carbon dioxide. In these cases, the uncertainty due to the presence of an excess of 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:

$$\Delta x_z = \left| Z_i - Z_0 \right|$$ (26)

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.

$$\Delta x_s = \frac{\left| S_i - S_0 \right| - \Delta x_z}{S_0} \times 100$$ (27)

where

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

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

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

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 $\leq$ -4 nmol/mol or $\geq$ 4 nmol/mol;
Span drift $\geq$ 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 NO 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 after 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 $\leq$ 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   Converter efficiency

The converter efficiency shall be tested at least every year according to the procedure described in 8.4.14. The test may be performed in the laboratory or at the site.

Frequency of test:
At least every year.

Action criterion:
< 95 %.

Appropriate action:
Replace converter after performance of a cross-port valve leak check, if appropriate.

When the current efficiency level is between 95 % and 98 %, a correction needs to be applied for the (lack of) converter efficiency to data collected between the previous and current converter efficiency tests as follows:

$$c_{NO_2} = \frac{c_{NOx} - c_{NO}}{\left(\dfrac{\overline{E_c}}{100}\right)} \tag{28}$$

where

c_{NO2} is the concentration of nitrogen dioxide, in nmol/mol;

c_{NOx} is the sum of the concentration of nitrogen dioxide and nitrogen monoxide, in nmol/mol;

c_{NO} is the concentration of nitrogen monoxide, in nmol/mol;

$\overline{E_c}$ is the average of the previous and current converter efficiencies, in %.

The standard uncertainty for this correction shall be included in the uncertainty budget for actual measurements. It is calculated as follows:

$$u_{EC,corr}^2 = \frac{\left(E_{c,i} - E_{C,i-1}\right)^2}{12} \tag{29}$$

where

$u_{EC,corr}$ is the uncertainty due to correction for changes in converter efficiency, in %;

$E_{c,i}$ is the converter efficiency determined in the current test, in %;

$E_{c,i-1}$ is the converter efficiency determined in the previous test, in %.

NOTE   Other methods for correction can be applied when their uncertainties are quantified and included in the uncertainty budget.

The correction also requires that NO_x concentrations (9.5.3) need to be re-calculated using the newly calculated NO_2 concentrations.

9.6.4   Testing the sample manifold

9.6.4.1   Procedure for measuring pressure drop induced by the manifold pump

Equipment required: Handheld manometer.

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

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

$$\Delta X_{\Delta Pm} = b_{gp} \Delta P_m \times 100 \qquad\qquad (30)$$

where

    $\Delta X_{\Delta Pm}$ 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.

9.6.4.2   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 manifolds (diameter ~30 mm, length 2 m) have a volume of ~1,5 l and shall have a maximum residence time of 3 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 nitrogen dioxide directly to the manifold and measuring the nitrogen 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 nitrogen dioxide to the ambient air sampled and measuring the concentrations of nitrogen 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.

9.6.5 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.
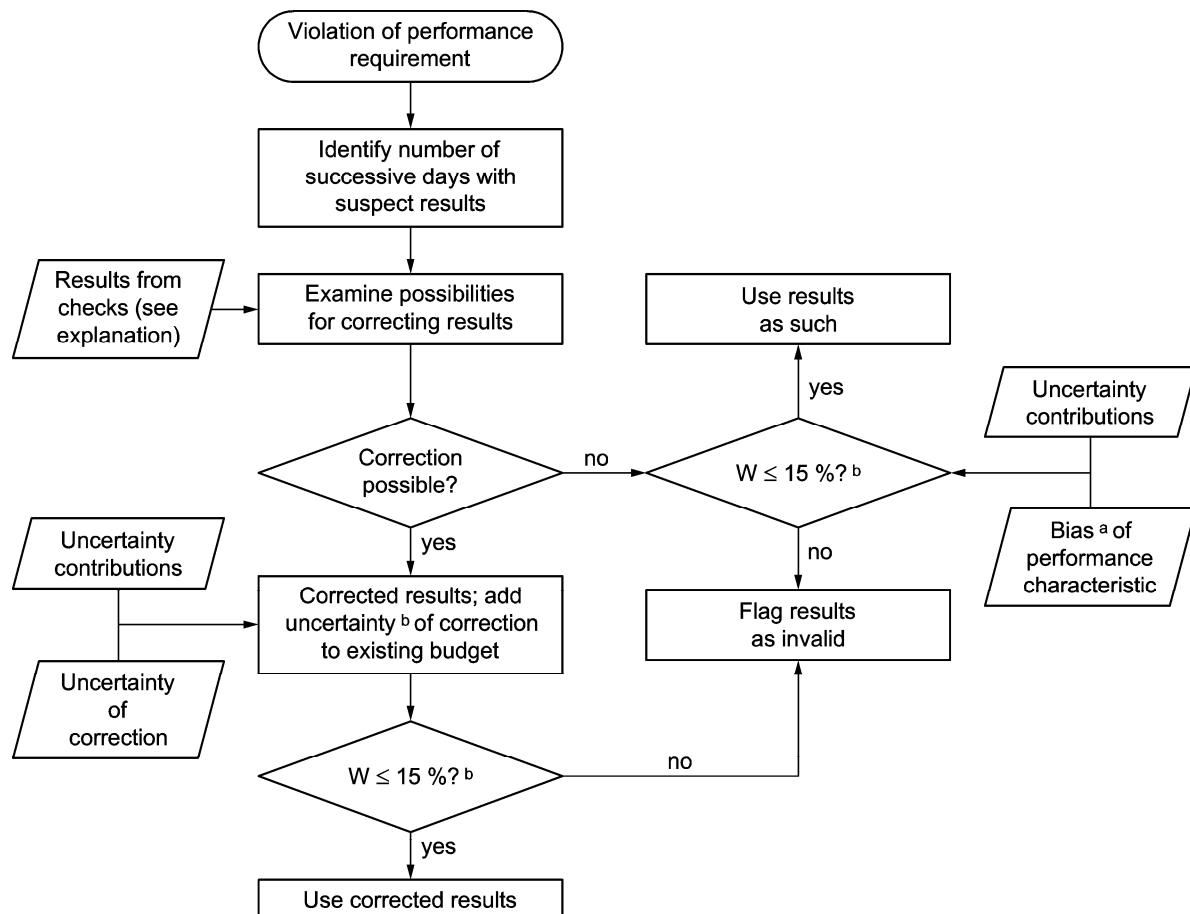
[a] The deviation of the value of the performance characteristic from its requirement.
[b] At the level of the hourly limit value.

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

Explanation

Checks that would in principle permit application of corrections include:

a)   Verification of test gases (9.6.1);

b)   Zero and/or span drift checks (9.6.2);

c)   Converter efficiency tests (9.6.3).

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 nitrogen dioxide levels at the site (type). As a consequence, the frequency of filter replacement may 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 nitrogen dioxide 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 6 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.

For analysers with a single reaction chamber, a leak in the valve switching the reaction chamber input from the NO to the NO_x channels and/or vice versa will lead to an underreading of the NO_2 concentration. If the valve leaks air from the NO channel when measuring the NO_x input the effect will be noticed as an apparent decrease in converter efficiency. If the valve leaks air from the NO_x channel when measuring the NO input the effect will not show up as an apparent decrease in converter efficiency.

NOTE 1   One way to test for leaks would be by supplying a test gas mixture with an accurately known concentration of NO_2 in the range of 200 to 250 nmol/mol. These may be prepared by one of the methods given in Table 3. However, the leakage to be established will never be less than the expanded uncertainty of the concentration of NO_2 in the test gas.

NOTE 2   Based on information from national metrology institutes, the lowest expanded uncertainty achievable for a nitrogen dioxide gas standard is estimated to be around 2 %. This implies that a leakage of < 2 % cannot be detected.

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 NO_2. For all measurements, basic values $\geq$ - (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 of 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 $\geq$ 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 and G describe the assessments of uncertainties of measurement results for hourly and annual averaging periods. 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 and G 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 [8], 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.

For nitrogen monoxide (NO) the conversion factors at 20 °C and 101,3 kPa are:
— 1 $\mu g/m^3$ NO   =   0,802 nmol/mol NO
— 1 nmol/mol NO   =   1,247 $\mu g/m^3$ NO

For nitrogen dioxide (NO_2) the conversion factors at 20 °C and 101,3 kPa are:
— 1 $\mu g/m^3$ NO_2 =   0,523 nmol/mol NO_2
— 1 nmol/mol NO_2 =   1,912 $\mu g/m^3$ NO_2

Methodology for converting NO_x expressed as NO_2 from nmol/mol to μg NO_x/m^3 for ecosystems:
— 1 $\mu g/m^3$ NO_x =   0,523 nmol/mol NO_x
— 1 nmol/mol NO_x =   1,912 $\mu g/m^3$ NO_x

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 (including detection limits) 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 gases, 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 nitrogen monoxide and nitrogen 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:

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

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:

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

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:

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

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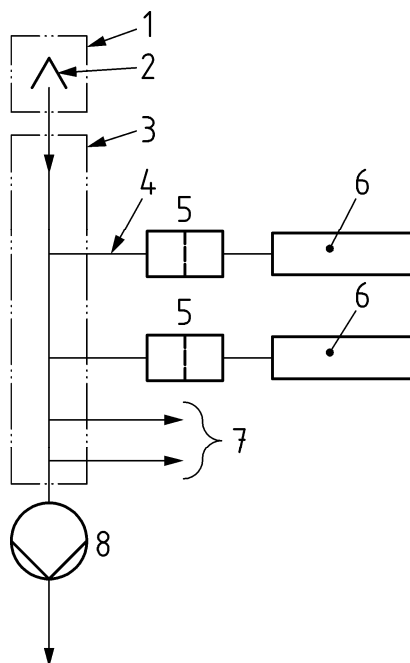
1	sample inlet
2	rain shield
3	manifold
4	sampling line
5	filter
6	analyser
7	connection for other analysers or equipment
8	sampling pump for the manifold

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

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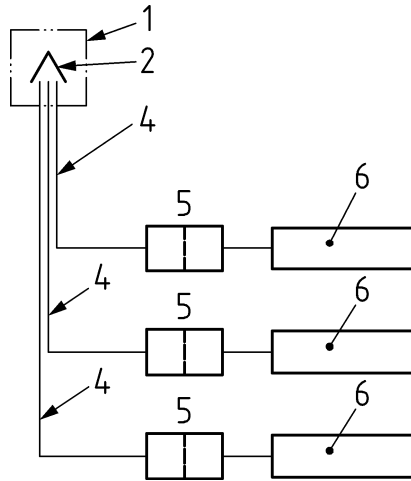
1   sample inlet
2   rain shield
4   sample line
5   filter
6   analyser

Figure B.2 — Sampling layout with individual lines

Annex C
(informative)

Types of chemiluminescence analysers
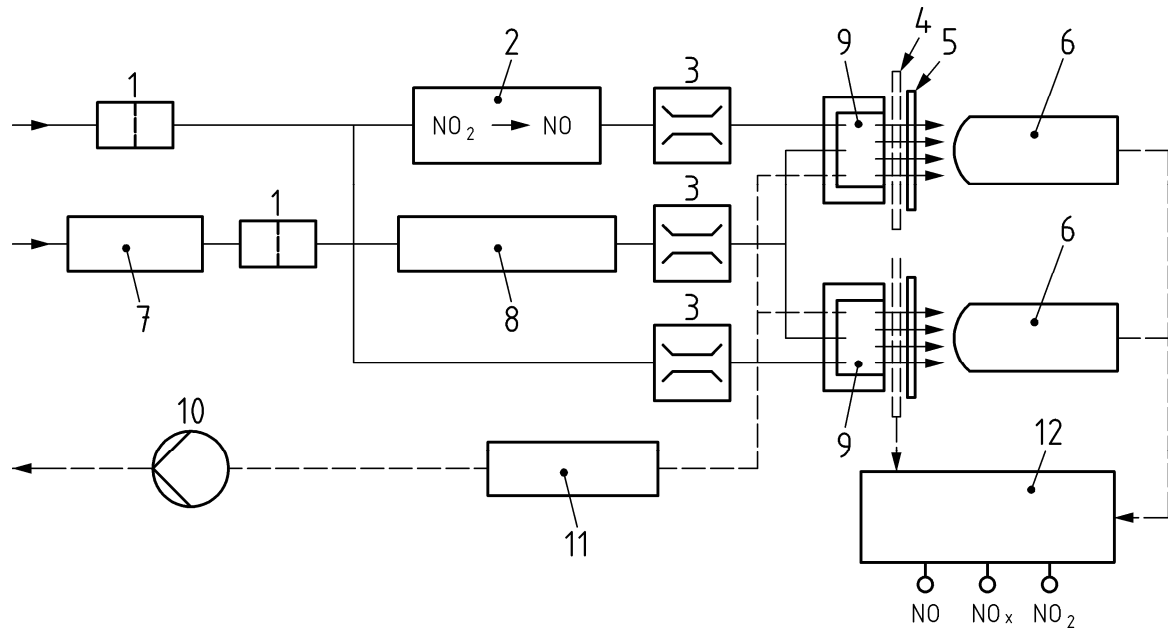
Key

1	particle filter
2	converter
3	flow rate controller
4	chopper
5	optical filter
6	photo multiplier tube
7	drier
8	ozone generator
9	reaction chamber
10	sampling pump
11	ozone filter
12	synchroniser output

Figure C.1 — Example of a dual cell, dual detector analyser
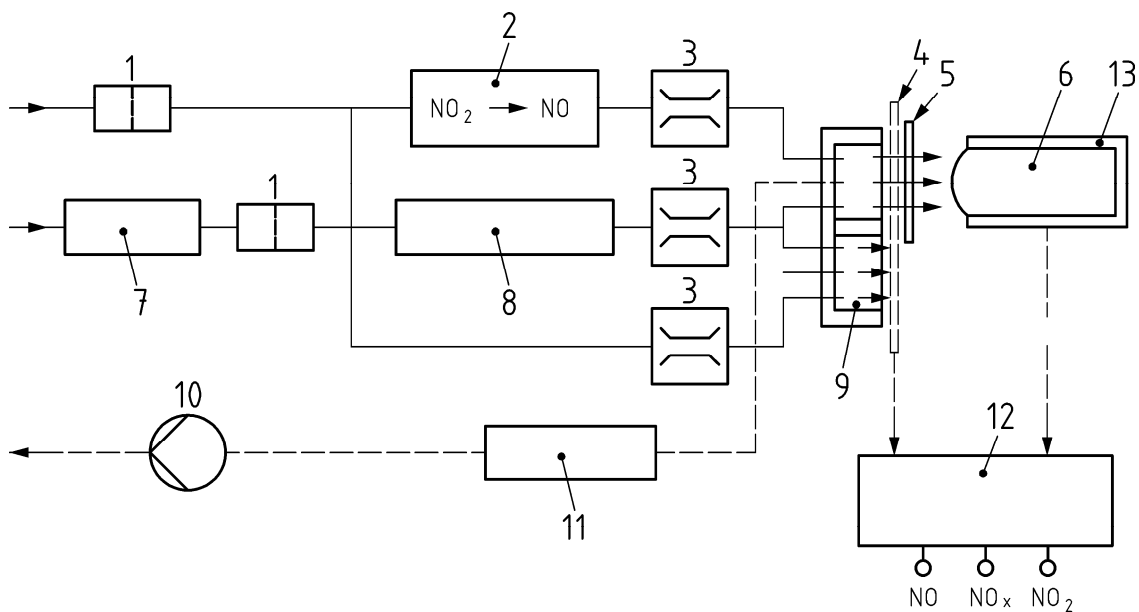
Key

1	particle filter
2	converter
3	flow rate controller
4	chopper
5	optical filter
6	photo multiplier tube
7	drier
8	ozone generator
9	double reaction chamber
10	sampling pump
11	ozone filter
12	synchroniser output
13	refrigerated housing

Figure C.2 — Example of a dual cell, single detector analyser

Key
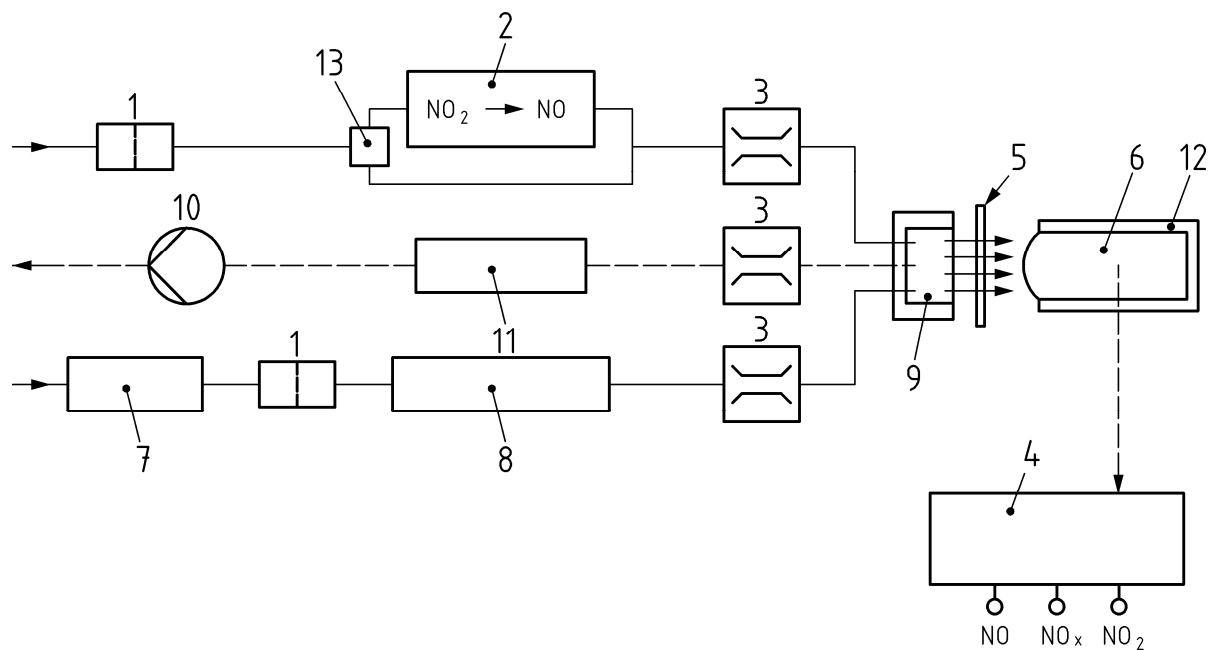
1	particle filter
2	converter
3	flow rate controller
4	controls NO-NOx cycling
5	optical filter
6	photo multiplier tube
7	drier
8	ozone generator
9	reaction chamber
10	sampling pump
11	ozone filter
12	refrigerated housing
13	sequential controller

Figure C.3 — Example of a single cell, single detector 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 nitrogen dioxide directly to the manifold and measuring the nitrogen 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 nitrogen 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:

$$E_{ss} = \frac{x_{man}}{x_{ref}} \times 100 \tag{D.1}$$

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 nitrogen dioxide delivered is not traceable, two measurements need to be performed, i.e., one by delivering the nitrogen 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:

$$E_{ss} = \frac{x_{man}}{x_{dir}} \times 100 \tag{D.2}$$

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.
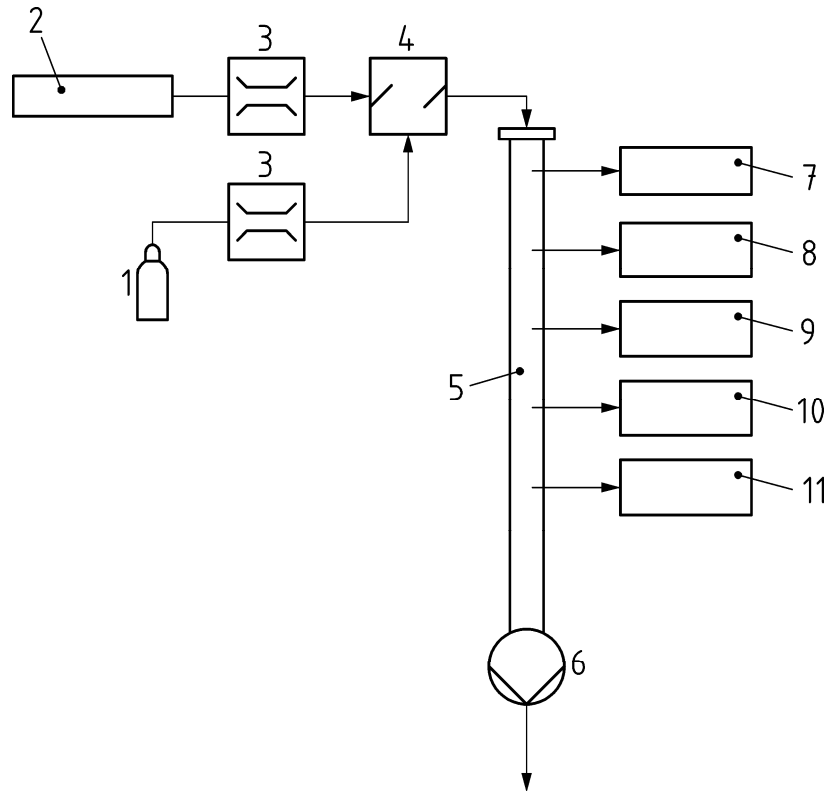
Key

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 analyser
10	sulphur dioxide analyser
11	nitrogen oxides analyser

NOTE   Target concentration nitrogen dioxide is 100 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.29).

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

nr	Performance characteristic	Symbol	Section	Performance criterion for NO/NO$_2$		Results lab. test[b]	[c]
1	Repeatability standard deviation at zero	$s_{r,z}$	8.4.5	≤ 1,0	nmol/mol	0,3	✓
2	Repeatability standard deviation at concentration c$_t$	$s_{r,ct}$	8.4.5	≤ 3,0	nmol/mol	1,5	✓
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	X_l		≤ 4,0	% of the measured value	1,5	✓
3b	Residual at zero	$X_{l,z}$	-	≤ 5,0	nmol/mol	0,5	✓
4	Sensitivity coefficient of sample gas pressure	b_{gp}	8.4.7	≤ 8,0	nmol/mol/kPa	0,10	✓
5	Sensitivity coefficient of sample gas temperature	b_{gt}	8.4.8	≤ 3,0	nmol/mol/K	0,10	✓
6	Sensitivity coefficient of surrounding temperature	b_{st}	8.4.9	≤ 3,0	nmol/mol/K	0,25	✓
7	Sensitivity coefficient of electrical voltage	b_V	8.4.10	≤ 0,30	nmol/mol/V	0,012	✓
8	Interferents at zero and concentration c$_t$ (at a level of the hourly limit value)		8.4.11				
8a	H$_2$O with concentration 19 mmol/mol [d]	$X_{H2O,z}$		≤ 5,0	nmol/mol	-1,25	✓
		$X_{H2O,ct}$		≤ 5,0	nmol/mol	0,75	✓
8b	CO$_2$ with concentration 500 µmol/mol	$X_{CO2,z}$		≤ 5,0	nmol/mol	-2,0	✓
		$X_{CO2,ct}$		≤ 5,0	nmol/mol	-0,1	✓
8c	NH$_3$ with concentration 200 nmol/mol	$X_{NH3,z}$		≤ 5,0	nmol/mol	-0,5	✓
		$X_{NH3,ct}$		≤ 5,0	nmol/mol	0,1	✓
9	Averaging effect	X_{av}	8.4.12	≤ 7,0	% of the measured value	4,5	✓
13	Short-term drift at zero	$D_{l,z}$	8.4.4	≤ 2,0	nmol/mol over 12 h	1,0	✓
14	Short-term drift at span level [a]	$D_{l,s}$	8.4.4	≤ 6,0	nmol/mol over 12 h	2,4	✓
15	Response time (rise)	$t_{r,NO}$	8.4.3	≤ 180	s	83	✓
		$t_{r,NO2}$		≤ 180	s	85	✓

nr	Performance characteristic	Symbol	Section	Performance criterion for NO/NO$_2$		Results lab. test[b]	c
16	Response time (fall)	$t_{f,NO}$	8.4.3	≤ 180	s	80	✓
		$t_{,NO2}$		≤ 180	s	81	✓
17	Difference between rise time and fall time	$t_{d,NO}$	8.4.3	≤ 10	s	3	✓
		$t_{d,NO2}$		≤ 10	s	4	✓
18	Difference sample/calibration port [e]	Δx_{sc}	8.4.13	≤ 1,0	%	1,0	✓
21	Converter efficiency	E_c	8.4.14	≥ 98	%	99	✓
22	Residence time in the analyser		8.4.15	≤ 3	s	2,5	✓

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$_2$O-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 of nitrogen dioxide.

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:

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

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:

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

Since the concentration of NO$_2$ is measured as the difference of measured concentrations of NO$_x$ and NO, the above calculation should be applied both for NO$_x$ and NO, and the results combined. However, because measurements of NO$_x$ and NO are performed (almost) simultaneously, the bias components of the measurement uncertainty need only to be accounted for once. Uncertainty components that are random in nature (precision-

related) need to be included twice (in quadrature). Of course, uncertainty components specific for NO_2 (e.g. converter efficiency) shall be included.

Consequently, 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

nr	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-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 at the hourly limit value		
8a	H_2O with concentration 19 mmol/mol	u_{H2O}	E.19, E.20
8b	CO_2 with concentration 500 µmol/mol	u_{CO2}	E.21, E.22
8c	NH3 with concentration 200 nmol/mol	u_{NH3}	E.21, E.22
9	Averaging effect	u_{av}	E.25
18	Difference sample/calibration port	$u_{\Delta sc}$	E.27
21	Converter efficiency	U_{EC}	E.28

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).

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

nr	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 shall be calculated according to:

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

where

u_c is the combined standard uncertainty under laboratory conditions, 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_{H_2O} 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_{EC} is the standard uncertainty for converter efficiency, in nmol/mol;

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

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

$$U = ku_c \qquad (E.4)$$

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:

$$W = \frac{U}{l_h} \cdot 100 \qquad (E.5)$$

where

W   is the relative expanded uncertainty, in %;

U   is the expanded uncertainty, in nmol/mol;

l_h is the hourly limit value of NO_2, in nmol/mol.

Requirement b) 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:

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

with

$$m = \frac{t}{2(t_r + t_f)}$$ (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 NO_2

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

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

with

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

and

$$s_{r,lh} = \frac{l_h}{c_t} s_{r,ct} \tag{E.10}$$

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 3 600 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 of nitrogen dioxide, in nmol/mol;

c_t is the NO test gas concentration applied, 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:

$$u_{l,lh} = \frac{r_{max}}{100} \frac{l_h}{\sqrt{3}} \tag{E.11}$$

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 nitrogen 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

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

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

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

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

$$u(c_q) = b_q \sqrt{\frac{q_{max}^2 + q_{max}q_{min} + q_{min}^2}{3}}$$
(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 according to (E.13) as:

$$u_{gp} = \frac{l_h}{c_t} b_{gp} \sqrt{\frac{(P_2 - P_1)^2}{3}}$$
(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 nitrogen dioxide, in nmol/mol;

c_t is the test gas concentration (70 % to 80 % of the certification range of NO), 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 according to (E.13) as:

$$u_{gt} = \frac{l_h}{c_t} b_{gt} \sqrt{\frac{(T_{G,2} - T_{G,1})^2}{3}}$$
(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 nitrogen dioxide, in nmol/mol;

c_t is the test gas concentration (70 % to 80 % of the certification range of NO), 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 according to (E.13) as:

$$u_{st} = \frac{l_h}{c_t} b_{st} \sqrt{\frac{(T_{S,2} - T_{S,1})^2}{3}}$$ (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 nitrogen dioxide, in nmol/mol;

c_t is the test gas concentration (70 % to 80 % of the certification range of NO), 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 according to (E.13) as:

$$u_V = \frac{l_h}{c_t} b_V \sqrt{\frac{(V_2 - V_1)^2}{3}}$$ (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 nitrogen dioxide, in nmol/mol;

c_t is the test gas concentration (70 % to 80 % of the certification range of NO), in nmol/mol;

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

V_1 is the minimum electrical voltage in V;

V_2 is the maximum electrical voltage 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:

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

$$u_{H_2O} = b_{H_2O} \sqrt{\frac{c_{H_2O,max}^2 + c_{H_2O,max} c_{H_2O,min} + c_{H_2O,min}^2}{3}} \tag{E.20}$$

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 gas concentration of NO, in nmol/mol (500 ± 50);

l_h is the hourly limit value of nitrogen 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 **interferent at the hourly limit value** (other than water vapour) is calculated according to:

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

$$u_{int} = b_{int} \sqrt{\frac{c_{int,max}^2 + c_{int,max} c_{int,min} + c_{int,min}^2}{3}} \tag{E.22}$$

where

X_{int,c_t} is the influence quantity of the maximum concentration in nmol/mol or µmol/mol of the relevant interferent 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 interferent 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 in (nmol/mol)/(μmol/mol);

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

c_t is the test concentration of NO, in nmol/mol (500 ± 50);

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

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

$c_{int,min}$ is the minimum concentration of 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 shall be calculated as:

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

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

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 nth 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 nth 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:

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

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 of nitrogen dioxide, in nmol/mol.

Calibration gas

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

$$u_{cg} = \frac{W_{cg}}{2 \times 100} l_h$$

(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 nitrogen dioxide, in nmol/mol.

Difference sample/calibration port

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

$$u_{\Delta sc} = \frac{\Delta x_{sc}}{100} l_h$$

(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 nitrogen dioxide, in nmol/mol.

Converter efficiency

The standard uncertainty due to the **converter efficiency** is calculated according to:

$$u_{EC} = \left(1 - \frac{E_c}{100}\right) l_h$$

(E.28)

where

u_{EC} is the standard uncertainty due to the converter efficiency, in nmol/mol;

E_c is the converter efficiency, in %;

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

E.3.3 Example calculation

Nr	Parameter	C_t		Unit	Value		X-	X+	u	u^2
	NO$_2$ hourly limit value	104		nmol/mol						
Nr	Parameter	C_t		Unit	Value		X-	X+	u	u^2
1	Repeatability at zero			nmol/mol	0,30				0,09	0,02
2	Repeatability at C_t	500		nmol/mol	1,50				0,09	0,02
3	Lack-of-fit			%	1,50				0,90	0,81
4	Sample gas pressure	700		nmol/mol/kPa	0,10		80	110	0,26	0,07
5	Sample gas temperature	700		nmol/mol/K	0,10		273	303	0,26	0,07
6	Surrounding temperature	700		nmol/mol/K	0,25		273	303	0,64	0,41
7	Electrical voltage	700		nmol/mol/V	0,012		210	240	0,03	0,00
8	Interferents	C_t	Cint			Xint	X-	X+	u	u^2
8a	- H$_2$O 19 mmol/mol span	500	19	nmol/mol	-1,25	0,018	6	21	0,249	0,06
	- H$_2$O 19 mmol/mol zero				0,75					
8b	- CO$_2$ 500 µmol/mol span	500	500	nmol/mol	-2,0	-0,001	0	500	-0,286	
	- CO$_2$ 500 µmol/mol zero				-0,1					
8c	- NH$_3$ 200 nmol/mol span	500	200	nmol/mol	-0,5	0,000	0	200	-0,014	
	- NH$_3$ 200 nmol/mol zero				0,1					
	Sum interferents (without water)								0,30	0,09
9	Averaging effect			%	4,5				2,70	7,30
18	Difference sample/calibration port			%	1,0				1,04	1,08
21	Converter efficiency			%	99				2,08	4,33
22	Calibration gas			%	4,0				2,08	4,33
	Sum of variances									18,6
	Combined uncertainty (nmol/mol)									4,3
	Expanded uncertainty (%)									8,3

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

nr	Performance characteristic	Symbol	Section	Performance criterion for NO_x		Results field test	[b]
10	Reproducibility standard deviation for NO_2 under field conditions	$s_{r,f}$	8.5.5	≤ 5,0	% of the average of a three month period	3,1	✓
11	Long term drift at zero	$D_{l,z}$	8.5.4	≤ 5,0	nmol/mol	1,0	✓
12	Long term drift at span level [a]	$D_{l,s}$	8.5.4	≤ 5,0	% of maximum of certification range	2,4	✓
19	Period of unattended operation		8.5.6	> 3,0	months or less if manufacturer indicates a shorter period	3	✓
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 of nitrogen dioxide.

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

nr	Standard uncertainty due to	Symbol	Formula
1	Repeatability at zero	$u_{r,z}$	E.6, E.7
2	Repeatability at the hourly limit value	$u_{r,lh}$	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	CO_2 with concentration 500 µmol/mol	u_{CO2}	E.21, E.22
8c	NH_3 with concentration 200 nmol/mol	u_{NH3}	E.21, E.22
9	Averaging effect	u_{av}	E.25
10	Reproducibility under field conditions [a]	$u_{r,f}$	E.30
11	Long term drift at zero	$u_{d,l,z}$	E.31
12	Long term drift at the hourly limit value	$u_{d,l,lh}$	E.32
18	Difference sample/calibration port	$u_{\Delta sc}$	E.27
21	Converter efficiency	u_{EC}	E.28

[a] Take for the calculation of the combined standard uncertainty $\sqrt{2}$ times the uncertainty due to the repeatability at the hourly 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

nr	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:

$$u_c = \sqrt{2u_{r,z}^2 + u_{r,C}^2 + u_{l,lh}^2 + u_{gp}^2 + u_{gt}^2 + u_{st}^2 + u_V^2 + u_{H_2O}^2 + u_{int}^2 + u_{av}^2 + u_{d,l,z}^2 + u_{d,l,lh}^2 + u_{\Delta sc}^2 + u_{EC}^2 + u_{cg}^2}$$

(E.29)

where

u_c is the standard 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 √2 times the standard uncertainty for laboratory repeatability for NO ($\sqrt{2}u_{r,lh}$) or the field reproducibility for NO_2 $u_{r,f}$, in nnmol/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_{EC} is the standard uncertainty for converter efficiency, 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:

$$U = ku_c$$

(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:

$$W = \frac{U}{l_h} \cdot 100 \tag{E.5}$$

where

W is the relative expanded uncertainty, in %;

U is the expanded uncertainty, in nmol/mol;

l_h is the hourly limit value of NO_2, in nmol/mol.

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** are 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 due to 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:

$$u_{r,f} = \frac{s_{r,f}}{100} l_h$$ (E.30)

where

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

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

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

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

$$u_{d,l,z} = \frac{D_{l,z}}{\sqrt{3}}$$ (E.31)

where

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

$D_{l,z}$ 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:

$$u_{d,l,lh} = \frac{D_{l,lh}}{100} \frac{l_h}{\sqrt{3}}$$ (E.32)

where

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

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

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

The standard uncertainty due to the **converter efficiency** is calculated according to Formula (E.28).

E.5.3 Example calculation

	NO$_2$ hourly limit value	104		nmol/mol					
Nr	Parameter	C$_t$		Unit	Value	X-	X+	u	u^2
1	Repeatability at zero			nmol/mol	0,30			0,09	0,00
2	Repeatability at C$_t$	500		nmol/mol	1,50			0,09	
3	Lack-of-fit			%	1,50			0,90	0,81
4	Sample gas pressure	700		nmol/mol/kPa	0,10	80	110	0,26	0,07
5	Sample gas temperature	700		nmol/mol/K	0,10	0	30	0,26	0,07
6	Surrounding temperature	700		nmol/mol/K	0,25	0	30	0,64	0,41
7	Electrical voltage	700		nmol/mol/V	0,012	210	240	0,03	0,00
8	Interferents	Ct	Cint		Xint				
8a	- H$_2$O 19 mmol/mol span	500	19	nmol/mol	-1,25	0,018	6	21	0,249	0,06
	- H$_2$O 19 mmol/mol zero				0,75					
8b	- CO$_2$ 500 µmol/mol span	500	500	nmol/mol	-2,0	-0,001	0	500	-0,286	
	- CO$_2$ 500 µmol/mol zero				-0,1					
8c	- NH$_3$ 200 nmol/mol span	500	200	nmol/mol	-0,5	0,000	0	200	-0,014	
	- NH$_3$ 200 nmol/mol zero				0,1					
	Sum interferents (without water)							0,30	0,09
9	Averaging effect			%	4,5			2,70	7,30
10	Field reproducibility			%	3,1			3,22	10,39
11	Long term zero drift			nmol/mol	1,0			0,58	0,33
12	Long term span drift			%	2,4			1,44	2,08
18	Difference sample/calibration port			%	1,0			1,04	1,08
21	Converter efficiency			%	99			2,08	4,33
22	Calibration gas			%	4,0			2,08	4,33
	Sum of variances								31,4
	Combined uncertainty (nmol/mol)								5,6
	Expanded uncertainty (%)								10,8

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.4. 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:

$$u_{c,act} = \sqrt{2u_{r,z}{}^2 + u_{r,C}{}^2 + u_{l,lh}^2 + u_{gp,act}^2 + u_{gt,act}^2 + u_{st,act}^2 + u_{V,act}^2 + u_{H_2O,act}^2 + u^2{}_{int,act} + u_{av}{}^2 + u_{d,l,z}{}^2 + u_{d,l,lh}{}^2 + u_{\Delta sc}{}^2 + u_{EC}{}^2 + u_{zg}{}^2 + u_{cg}{}^2}$$

(F. 1)

where

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

$u_{r,C}$　　is the highest value of √2 times the standard uncertainty for laboratory repeatability for NO (√2$u_{r,lh}$) or the field reproducibility for NO_2 $u_{r,f}$, 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_{EC}　　is the standard uncertainty for actual converter efficiency, 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 for calibration gas, in nmol/mol.

The absolute **expanded uncertainty** is calculated according to:

$$U = k u_{c,act} \tag{F.2}$$

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:

$$W = \frac{U}{l_h} \times 100 \tag{F.3}$$

where

     W is the relative expanded uncertainty, in %;

     U is the expanded uncertainty, in nmol/mol;

     l_h is the hourly limit value of NO_2, 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} from linearity tests.

Influence quantities

General

In general, the principal approach described in this Annex 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.

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:

$$u_{gp,act} = \frac{l_h}{c_t} b_{gp} \sqrt{\frac{(P_{max} - P_{cal})^2 + (P_{max} - P_{cal})(P_{min} - P_{cal}) + (P_{min} - P_{cal})^2}{3}} \qquad (F.4)$$

where

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

l_h is the hourly limit value of NO_2, in nmol/mol;

c_t is the test gas concentration (70 % to 80 % of the certification range of NO), 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

$$u_{gp,act} = \frac{l_h}{c_t} b_{gp} \sqrt{\frac{(P_{max} - P_{min})^2}{3}} \qquad (F.4a)$$

Sample gas temperature

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

$$u_{gt,act} = \frac{l_h}{c_t} b_{gt} \sqrt{\frac{(T_{G,max} - T_{G,cal})^2 + (T_{G,max} - T_{G,cal})(T_{G,min} - T_{G,cal}) + (T_{G,min} - T_{G,cal})^2}{3}} \qquad (F.5)$$

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 NO_2, in nmol/mol;

c_t is the test gas concentration (70 % to 80 % of the certification range of NO), 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.8) reduces to

$$u_{gt,act} = \frac{l_h}{c_t} b_{gt} \sqrt{\frac{\left(T_{G,max} - T_{G,min}\right)^2}{3}} \tag{F.5a}$$

Surrounding temperature

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

$$u_{st,act} = \frac{l_h}{c_t} b_{st} \sqrt{\frac{\left(T_{S,max} - T_{S,cal}\right)^2 + (T_{S,max} - T_{S,cal})(T_{S,min} - T_{S,cal}) + \left(T_{S,min} - T_{S,cal}\right)^2}{3}} \tag{F.6}$$

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 NO_2, in nmol/mol;

c_t is the test gas concentration (70 % to 80 % of the certification range of NO), 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

$$u_{st,act} = \frac{l_h}{c_t} b_{st} \sqrt{\frac{\left(T_{S,max} - T_{S,min}\right)^2}{3}} \tag{F.6a}$$

Electrical voltage

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

$$u_{V,act} = \frac{l_h}{c_t} b_V \sqrt{\frac{(V_{max} - V_{cal})^2 + (V_{max} - V_{cal})(V_{min} - V_{cal}) + (V_{min} - V_{cal})^2}{3}} \qquad \text{(F.7)}$$

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 NO_2, in nmol/mol;

c_t is the test gas concentration (70 % to 80 % of the certification range of NO), 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

$$u_{,Vact} = \frac{l_h}{c_t} b_V \sqrt{\frac{(V_{max} - V_{min})^2}{3}} \qquad \text{(F.7a)}$$

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 interferents.

Water vapour

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

$$u_{H_2O,act} = b_{H_2O} \cdot \sqrt{\frac{c_{H_2O,max,act}^2 + c_{H_2O,max,act} c_{H_2O,min,act} + c_{H_2O,min,act}^2}{3}} \qquad \text{(F.8)}$$

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 **interferent at the hourly limit value** (other than water vapour) is calculated according to:

$$u_{int,act} = b_{int} \cdot \sqrt{\frac{c_{int,max,act}^2 + c_{int,max,act}c_{int,min,act} + c_{int,min,act}^2}{3}}$$ (F.9)

where

$u_{int,act}$ 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 in (nmol/mol)/(µmol/mol), see Formula (E.21);

$c_{int,max,act}$ is the actual maximum hourly average concentration of the interferent, in nmol/mol or µmol/mol;

$c_{int,min,act}$ 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 are calculated as:

$$u_{int,act,pos} = \sqrt{\left(u_{int,act,1,pos} + \ldots\ldots + u_{int,act,n,pos}\right)^2}$$ (F.10)

$$u_{int,act,neg} = \sqrt{\left(u_{int,act,1,neg} + \ldots\ldots + u_{int,act,n,neg}\right)^2}$$ (F.11)

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 nth 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 nth interferent with negative impact, in nmol/mol.

The highest value of (F.10) or (F.11) is taken as value for $u_{int,act}$ 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 NO$_2$** is calculated according to Formula (E.30).

Long term drift at zero

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

$$u_{D_{l,z}} = \frac{D_{l,z}}{\sqrt{3}}$$
(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 of NO$_2$** is calculated according to:

$$u_{d,l,lh} = \frac{D_{l,span}}{100} \frac{l_h}{\sqrt{3}}$$
(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 NO$_2$, 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 nitrogen dioxide as:

$$u_{zg} = \frac{1}{\sqrt{3}}$$
(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).

Converter efficiency

In actual practice, a correction needs to be applied for (lack of) converter efficiency when 95 % $\leq E_c$ <98 % (7.2).

Actual calculation of the standard uncertainty for this correction should be based on the use of Formula (17) as a model formula. For practical purposes, the default relative standard uncertainty for the **converter efficiency** is set to 2 %.

Consequently:

$$u_{EC} = 0,02 \times l_h \qquad\qquad\qquad (F.15)$$

where

u_{EC} is the standard uncertainty for converter efficiency, in nmol/mol;

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

Correction for converter efficiencies between 95 % and 98 % is performed by applying Formula (28). The uncertainty associated with the correction is calculated using Formula (29).

F.4   Example calculation

NO$_2$ hourly limit value	104		nmol/mol								

Parameter	C_t		Unit	Value	X-	Xcal	X+	q_{min}	q_{max}	u	u^2
Repeatability at zero			nmol/mol	0,30						0,09	0,00
Repeatability at C_t	500		nmol/mol	1,50						0,09	
Lack-of-fit			%	1,50						0,90	0,81
Sample gas pressure	700		nmol/mol/kPa	0,10	97	97	104	0	7	0,06	0,00
Sample gas temperature	700		nmol/mol/K	0,10	0	0	30	0	30	0,26	0,07
Surrounding temperature	700		nmol/mol/K	0,25	0	23	30	-23	7	0,44	0,19
Electrical voltage	700		nmol/mol/V	0,012	210	230	240	-20	10	0,02	0,00
Interferents	C_t	C_{int}			*Xint*						
- H$_2$O 19 mmol/mol span	500	19	nmol/mol	-1,25	0,024	6	0	21	6	21	0,249	0,06
- H$_2$O 19 mmol/mol zero				0,75							
- CO$_2$ 500 µmol/mol span	500	500	nmol/mol	-2,0	-0,001	340	0	360	340	360	-0,347	
- CO$_2$ 500 µmol/mol zero				-0,1							
- NH$_3$ 200 nmol/mol span	500	200	nmol/mol	-0,5	0,000	0	0	50	0	50	-0,004	
- NH$_3$ 200 nmol/mol zero				0,1							
Sum interferents (without water)										0,35	0,12
Averaging effect			%	4,5						2,70	7,30
Field reproducibility			%	3,1						3,22	10,4
Long term zero drift			nmol/mol	1,0						0,58	0,33
Long term span drift			%	2,4						1,44	2,08
Difference sample/calibration port			%	1,0						1,04	1,08
Converter efficiency			%	99						2,08	4,33
Calibration gas			%	4,0						2,08	4,33
Zero gas			nmol/mol	0,6						0,60	0,36
Sum of variances											30,4
Combined uncertainty (nmol/mol)											5,5
Expanded uncertainty (%)											10,6

Annex G
(informative)

Calculation of uncertainty in field operation at the annual 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 annual average at the annual limit value. This result 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 .

G.2   Combined standard uncertainty

The **combined standard uncertainty** in an annual average at the level of the annual limit value during field operation of a measuring system is calculated using the following formula:

$$u_{c,act} = \sqrt{2u_{r,z,la}^2 + u_{r,C}^2 + u_{l,la}^2 + u_{gp,act}^2 + u_{gt,act}^2 + u_{st,act}^2 + u_{V,act}^2 + u_{H_2O,act}^2 + u_{int,act}^2 + u_{av}^2 + u_{d,l,z}^2 + u_{d,l,la}^2 + u_{\Delta sc}^2 + u_{EC}^2 + u_{zg}^2 + u_{cg}^2}$$

(G.1)

where

$u_{r,z,la}$ is the standard uncertainty for repeatability at zero, in nmol/mol, at the level of the annual limit value;

$u_{r,C}$ is the highest value of $\sqrt{2}$ times the standard uncertainty for laboratory repeatability for NO ($\sqrt{2}u_r$) or the field reproducibility for NO_2 $u_{r,f}$, in nnmol/mol;

$u_{l,la}$ is the standard uncertainty for actual lack of fit at the annual 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;

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

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

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

The absolute **expanded uncertainty** is calculated according to:

$$U = ku_{c,act}$$ (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:

$$W = \frac{U}{l_a} \times 100$$ (G.3)

where

W is the relative expanded uncertainty, in %;

U is the expanded uncertainty, in nmol/mol;

l_a is the annual limit value of NO_2, in nmol/mol.

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:

$$u_{r,z,la} = \frac{u_{r,z}}{\sqrt{n_a}}$$ (G.4)

where

$u_{r,z,la}$ 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 Formulae (E.6) to (E.7), in nmol/mol;

n_a is the number of valid hourly measurements in the year ($n_a \geq 7884$).

Repeatability at the annual limit value

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

$$u_{r,la} = \frac{s_{r,ct}}{c_t} l_a \frac{1}{\sqrt{mn_a}}$$

(G.5)

where

$u_{r,la}$ is the standard uncertainty in the annual average due to repeatability at the level of the annual limit value, in nmol/mol;

n_a is the number of valid hourly measurements in the year ($\geq$ 7884);

m is the number of independent measurements in 3 600 s, taking response (rise) and response time (fall) for half that time period respectively (see Formula (E.9));

$s_{r,ct}$ is the repeatability standard deviation at the test gas concentration c_t;

l_a is the annual limit value, in nmol/mol;

c_t is the applied NO test gas concentration, in nmol/mol.

Lack of fit

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

$$u_{l,la} = \frac{r_{max}}{100} \frac{l_a}{\sqrt{3}}$$

(G.6)

where

$u_{l,la}$ 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 limit value, in nmol/mol.

Influence quantities

General

In general, the principal approach described in this Annex 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.

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 limit value** is calculated according to:

$$u_{\text{gp,act}} = \frac{l_a}{c_t} b_{\text{gp}} \sqrt{\frac{\left(P_{\max} - P_{\text{cal}}\right)^2 + \left(P_{\max} - P_{\text{cal}}\right)\left(P_{\min} - P_{\text{cal}}\right) + \left(P_{\min} - P_{\text{cal}}\right)^2}{3}} \qquad (\text{G.7})$$

where

$u_{\text{gp,act}}$ is the standard uncertainty due to the influence of actual pressure variations, in nmol/mol;

l_a is the annual limit value, in nmol/mol;

c_t is the test gas concentration (70 % to 80 % of the certification range of NO), 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

$$u_{\text{gp,act}} = \frac{l_a}{c_t} b_{\text{gp}} \sqrt{\frac{\left(P_{\max} - P_{\min}\right)^2}{3}} \qquad (\text{G.7a})$$

Sample gas temperature

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

$$u_{\text{gt,act}} = \frac{l_a}{c_t} b_{\text{gt}} \sqrt{\frac{\left(T_{\text{G,max}} - T_{\text{G,cal}}\right)^2 + \left(T_{\text{G,max}} - T_{\text{G,cal}}\right)\left(T_{\text{G,min}} - T_{\text{G,cal}}\right) + \left(T_{\text{G,min}} - T_{\text{G,cal}}\right)^2}{3}} \qquad (\text{G.8})$$

where

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

l_a is the annual limit value, in nmol/mol;

c_t is the test gas concentration (70 % to 80 % of the certification range of NO), in nmol/mol;

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

$T_{\text{G,max}}$ is the upper level of the site-specific range of the variation of the sample gas temperature, in °C;

$T_{\text{G,min}}$ is the lower level of the site-specific range of the variation of the sample gas temperature, in °C.

When $T_{G,cal}$ is not known, (G.8) reduces to

$$u_{\text{gt,act}} = \frac{l_a}{c_t} b_{\text{gt}} \sqrt{\frac{\left(T_{\text{G,max}} - T_{\text{G,min}}\right)^2}{3}} \qquad (\text{G.8a})$$

Surrounding temperature

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

$$u_{st,act} = \frac{l_a}{c_t} b_{st} \sqrt{\frac{\left(T_{S,max} - T_{S,cal}\right)^2 + \left(T_{S,max} - T_{S,cal}\right)\left(T_{S,min} - T_{S,cal}\right) + \left(T_{S,min} - T_{S,cal}\right)^2}{3}} \quad (G.9)$$

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 limit value of NO_2, in nmol/mol;

c_t is the test gas concentration (70 % to 80 % of the certification range of NO), 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

$$u_{st,act} = \frac{l_a}{c_t} b_{st} \sqrt{\frac{\left(T_{S,max} - T_{S,min}\right)^2}{3}} \quad (G.9a)$$

Electrical voltage

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

$$u_{V,act} = \frac{l_a}{c_t} b_V \sqrt{\frac{\left(V_{max} - V_{cal}\right)^2 + \left(V_{max} - V_{cal}\right)\left(V_{min} - V_{cal}\right) + \left(V_{min} - V_{cal}\right)^2}{3}} \quad (G.10)$$

where

$u_{V,act}$ is the standard uncertainty due to the influence of actual voltage variations, in nmol/mol;

l_a is the annual limit value of NO_2, in nmol/mol;

c_t is the test gas concentration (70 % to 80 % of the certification range of NO), 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, (G.10) reduces to

$$u_{V,act} = \frac{l_a}{c_t} b_V \sqrt{\frac{(V_{max} - V_{min})^2}{3}}$$

(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 chemical interferents.

Water vapour

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

$$b_{H_2O} = \frac{1}{c_{H_2O}} \left[X_{H_2O,z} + \left(X_{H_2O,C_t} - X_{H_2O,z} \right) \frac{l_a}{c_t} \right]$$

(G.11)

$$u_{H_2O,act} = b_{H_2O} \sqrt{\frac{c_{H_2O,max}^2 + c_{H_2O,max} c_{H_2O,min} + c_{H_2O,min}^2}{3}}$$

(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 NO, in nmol/mol, in the type-approval test;

l_a is the annual limit value, 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 interferent at the annual limit value** (other than water vapour) is calculated according to:

$$b_{\text{int}} = \frac{1}{c_{\text{int}}} \left[X_{\text{int,z}} + \left(X_{\text{int,C}_t} - X_{\text{int,z}} \right) \frac{l_a}{c_t} \right] \qquad \text{(G.13)}$$

$$u_{\text{int,act}} = b_{\text{int}} \cdot \sqrt{\frac{c_{\text{int,act,max}}^2 + c_{\text{int,act,max}} c_{\text{int,act,min}} + c_{\text{int,act,min}}^2}{3}} \qquad \text{(G.14)}$$

where

X_{int,c_t} is the influence quantity of the maximum concentration, in nmol/mol or µmol/mol of the relevant interferent 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 interferent 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 in (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 NO, in nmol/mol;

l_a is the annual limit value, in nmol/mol;

$c_{\text{int,act,max}}$ is the actual maximum hourly average concentration of interferent, in nmol/mol or µmol/mol;

$c_{\text{int,act,min}}$ is the actual minimum hourly average concentration of 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 are calculated as:

$$u_{\text{int,act,pos}} = \sqrt{\left(u_{\text{int,act,1,pos}} + \ldots\ldots + u_{\text{int,act, n,pos}} \right)^2} \qquad \text{(G.15)}$$

$$u_{\text{int,act,neg}} = \sqrt{\left(u_{\text{int,act,1,neg}} + \ldots\ldots + u_{\text{int,act,n,neg}} \right)^2} \qquad \text{(G.16)}$$

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 nth 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 nth 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:

$$u_{av} = \frac{E_{av}}{100} \frac{l_a}{\sqrt{3}}$$ (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_a is the annual limit value, 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 nitrogen dioxide using Formula (F.14).

Calibration gas

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

$$u_{cg} = \frac{W_{cg}}{2 \times 100} l_a$$ (G.18)

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 limit value, in nmol/mol.

Difference sample/calibration port

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

$$u_{\Delta sc} = \frac{\Delta x_{sc}}{100} l_a$$ (G.19)

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 limit value, in nmol/mol.

Converter efficiency

In actual practice, a correction needs to be applied for (lack of) converter efficiency when 95 % ≤ E_c < 98 % (7.2).

Actual calculation of the standard uncertainty for this correction should be based on the use of Formula (17) as a model formula. For practical purposes, the relative standard uncertainty for the **converter efficiency** is set to 2 %.

Consequently:

$$u_{EC} = 0{,}02 \times l_a$$

(G.20)

where

u_{EC} is the uncertainty for converter efficiency, in nmol/mol;

l_a is the annual limit value, in nmol/mol.

Correction for converter efficiencies between 95 % and 98 % is performed by applying Formula (28). The uncertainty associated with the correction is calculated using Formula (29). The correction is applied to hourly average values.

Reproducibility under field conditions

The standard uncertainty due to the **reproducibility under field conditions** is calculated according to:

$$u_{r,f,la} = \frac{s_{r,f}}{100\sqrt{n_a}} l_a$$

(G.21)

where

$u_{r,f,la}$ is the standard uncertainty at the annual limit value due to reproducibility under field conditions, in nmol/mol;

n_a is the number of valid hourly measurements in the year (≥ 7884);

$s_{r,f}$ is the reproducibility standard deviation for NO_2 from the field test, in %;

l_a is the annual limit value, in nmol/mol.

Long term drift at zero

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

$$u_{D_{l,z}} = \sqrt{\frac{1}{k}\sum_{i=1}^{k}\frac{D_{l,z,i}}{3}}$$

(G.22)

where

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

$D_{l,z,i}$ is the long term zero drift, in nmol/mol, determined from periodic calibrations, for period l;

k is the number of calibrations / adjustments performed within the annual period.

Long term drift at level of the annual limit value

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

$$u_{\mathrm{D,l,la}} = \frac{l_{\mathrm{a}}}{100} \sqrt{\frac{1}{k} \sum_{i=1}^{n} \frac{D_{\mathrm{l,span,}i}^2}{3}} \qquad\qquad (G.23)$$

where

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

$D_{\mathrm{l,span,}i}$ is the long term span drift, in %, determined from periodic calibrations, for period l;

k is the number of calibrations / adjustments performed within the annual period;

l_{a} is the annual limit value, in nmol/mol.

G.4 Example calculation

NO_2 annual limit value	21		nmol/mol								
Number of hourly values	7884										
Number of yearly calibrations	4										
Parameter	C_t		Unit	Value	X-	Xcal	X+	q_{min}	q_{max}	u	u^2
Repeatability at zero			nmol/mol	0,30						0,00	0,00
Repeatability at C_t	500		nmol/mol	1,50						0,00	
Lack-of-fit			%	1,50						0,18	0,03
Sample gas pressure	700		nmol/mol/kPa	0,10	97	97	104	0	7	0,01	0,00
Sample gas temperature	700		nmol/mol/K	0,10	273	273	303	0	30	0,05	0,00
Surrounding temperature	700		nmol/mol/K	0,25	273	273	303	0	30	0,13	0,02
Electrical voltage	700		nmol/mol/V	0,012	210	230	240	-20	10	0,00	0,00
Interferences	C_t	$Cint$		$Xint$							
- H_2O 19 mmol/mol span	500	19	nmol/mol	-1,25	0,036	6	0	21	6	21	0,50	0,25
- H_2O 19 mmol/mol zero				0,75							
- CO_2 500 μmol/mol span	500	500	nmol/mol	-2,0	0,000	340	0	360	340	360	-0,126	
- CO_2 500 μmol/mol zero				-0,1							
- NH_3 200 nmol/mol span	500	200	nmol/mol	-0,5	0,000	0	0	50	0	50	0,011	
- NH_3 200 nmol/mol zero				0,1							
Sum interferents (without water)										0,13	0,02
Averaging effect			%	4,5						0,55	0,30
Field reproducibility			%	3,1						0,01	0,00
Long term zero drift			nmol/mol	1,0						0,58	0,33
Long term span drift			%	2,4						0,29	0,08
Difference sample/calibration port			%	1						0,21	0,04
Converter efficiency			%	99						0,42	0,18
Calibration gas			%	4,0						0,42	0,18
Zero gas			nmol/mol	0,6						0,60	0,36
Sum of variances											1,7
Combined uncertainty (nmol/mol)											1,32
Expanded uncertainty (%)											12,5

Annex H
(informative)

Significant technical changes

Details of significant technical changes between this European Standard and the previous edition are:

Clause	Technical change
6.3; Annex A	Residence time is no longer calculated from reaction kinetics as prescribed in Annex A. Annex A has been removed.
8.4.2.3, Table 4	Requirements for impurities in zero gas have been relaxed for other than interferents tests.
8.4.11	Test of ozone interference has been removed as ozone is not an interferent.
8.4.11	Determination of the effect of interference of ammonia is performed by reading the NO_x signal instead of the NO signal.
8.4.5; 9.3	A formula has been introduced for calculation of the detection limit of an analyser. Information about its applications has been added.
9.4; 9.6	Performance requirements have been tightened for some performance characteristics in field operation.
9.4; 9.6	Additional performance criteria and tests have been introduced for repeatability at zero and span levels in field operation.
9.5	Formulae have been introduced for software adjustment of the raw analyser signal after calibration.
9.6	Formulae have been introduced to calculate average converter efficiency between checks and the resulting uncertainty of the average efficiency.
Annexes F and G	Uncertainty calculations have been modified to be in conformity with EN ISO 14956.

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