



BSI Standards Publication

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

National foreword

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 It supersedes BS EN 14211:2005 which is withdrawn.

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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

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Contents

Contents.....	2
Foreword.....	4
1 Scope	5
2 Normative references	6
3 Terms and definitions.....	6
4 Abbreviated terms	11
5 Principle	11
5.1 General.....	11
5.2 Measuring principle	11
5.3 Type approval test	12
5.4 Field operation and quality control	12
6 Sampling	13
6.1 General.....	13
6.2 Sampling location	13
6.3 Sampling system.....	13
6.4 Control and regulation of sample flow rate.....	14
6.5 Sampling pump for the manifold.....	15
7 Analyser equipment.....	15
7.1 General.....	15
7.2 Converter	15
7.3 Ozone generator.....	16
7.4 Reaction chamber	16
7.5 Optical filter	16
7.6 Detector.....	16
7.7 Ozone removal device	16
7.8 Sampling pump for the analyser	16
7.9 Particle filter	16
8 Type approval of nitrogen dioxide and nitrogen monoxide analysers	16
8.1 General.....	16
8.2 Relevant performance characteristics and performance criteria	17
8.3 Design change.....	19
8.4 Procedures for determination of the performance characteristics during the laboratory test	20
8.5 Determination of the performance characteristics during the field test.....	32
8.6 Type approval and uncertainty calculation	35
9 Field operation and ongoing quality control.....	36
9.1 General.....	36
9.2 Suitability evaluation	36
9.3 Initial installation.....	38
9.4 Ongoing quality assurance/quality control	39
9.5 Calibration of the analyser.....	41
9.6 Checks	43
9.7 Maintenance	48
9.8 Data handling and data reports	48
9.9 Measurement uncertainty	49
10 Expression of results	49
11 Test reports and documentation	50
11.1 Type approval test	50
11.2 Field operation	51

Annex A (normative) Test of lack of fit	53
Annex B (informative) Sampling equipment	55
Annex C (informative) Types of chemiluminescence analysers	57
Annex D (informative) Manifold testing	60
Annex E (normative) Type approval	62
Annex F (informative) Calculation of uncertainty in field operation at the hourly limit value	81
Annex G (informative) Calculation of uncertainty in field operation at the annual limit value	89
Annex H (informative) Significant technical changes	99
Bibliography	100

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 $500 \mu\text{g}/\text{m}^3$. 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 $1\,200 \mu\text{g}/\text{m}^3$. 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 $\mu\text{g}/\text{m}^3$ (at 20°C and $101,3 \text{ kPa}$).

NOTE 3 $500 \mu\text{g}/\text{m}^3$ of NO_2 corresponds to $261 \text{ nmol}/\text{mol}$ of NO_2 at 20°C and $101,3 \text{ kPa}$. $1\,200 \mu\text{g}/\text{m}^3$ of NO corresponds to $962 \text{ nmol}/\text{mol}$ of NO at 20°C and $101,3 \text{ kPa}$.

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 NO₂ 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 NO₂ molecules decay to lower energy states.

This chemiluminescence method is based on the reaction



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:



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 $\mu\text{g}/\text{m}^3$ 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 $\leq 1,0\%$.

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 $5\text{ }\mu\text{m}$ 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 NO₂ and loss of NO

As O₃ is generally present in the sampled air, a change in concentrations of NO and NO₂ will occur due to the reaction of NO with O₃ in the sampling inlet and line or manifold, and in the analyser. In practice a significant change in the concentrations of NO and NO₂ may be avoided when the residence time in the sampling system is $\leq 3\text{ s}$. The requirement for the residence time in the analyser is $\leq 3\text{ s}$ (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 NO₂ 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 NO₂. 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 NO₂ 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 $\leq 1,0 \%$.

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 15267-2 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 NO ₂
				NO	NO ₂	NO	NO ₂	
1	Repeatability standard deviation at zero	$s_{r,z}$	8.4.5	x				$\leq 1,0$ nmol/mol
2	Repeatability standard deviation at concentration c_t	$s_{r,ct}$	8.4.5	x				$\leq 3,0$ 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				$\leq 4,0$ % of the measured value
3b	Residual at zero	r_z		x				$\leq 5,0$ nmol/mol
4	Sensitivity coefficient of sample gas pressure	b_{gp}	8.4.7	x				$\leq 8,0$ nmol/mol/kPa
5	Sensitivity coefficient of sample gas temperature	b_{gt}	8.4.8	x				$\leq 3,0$ nmol/mol/K
6	Sensitivity coefficient of surrounding temperature	b_{st}	8.4.9	x				$\leq 3,0$ nmol/mol/K
7	Sensitivity coefficient of electrical voltage	b_v	8.4.10	x				$\leq 0,30$ nmol/mol/V
8	Interferents at zero and at concentration c_t^a		8.4.11					
8a	H ₂ O with concentration 19 mmol/mol ^b	$X_{H_2O,z,ct}$		x				$\leq 5,0$ nmol/mol
8b	CO ₂ with concentration 500 µmol/mol	$X_{CO_2,z,ct}$		x				$\leq 5,0$ nmol/mol
8c	NH ₃ with concentration 200 nmol/mol ^c	$X_{NH_3,z,ct}$			x ^c			$\leq 5,0$ nmol/mol
9	Averaging effect	E_{av}	8.4.12	x	x			$\leq 7,0$ % of the measured value
10	Reproducibility standard deviation under field conditions	$s_{r,f}$	8.5.5				x	$\leq 5,0$ % of the average of a three month period
11	Long term drift at zero level	$D_{l,z}$	8.5.4			x		$\leq 5,0$ nmol/mol
12	Long term drift at span level	$D_{l,s}$	8.5.4			x		$\leq 5,0$ % of maximum of certification range
13	Short-term drift at zero level	$D_{s,z}$	8.4.4	x				$\leq 2,0$ nmol/mol over 12 h
14	Short-term drift at span level	$D_{s,s}$	8.4.4	x				$\leq 6,0$ 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			≤ 180 s
16	Response time (fall)	t_f	8.4.3	x	x			≤ 180 s
17	Difference between rise time and fall time	t_d	8.4.3	x	x			≤ 10 s
18	Difference sample/calibration port ^d	Δx_{sc}	8.4.13	x				≤ 1,0 %
19	Period of unattended operation		8.5.6			x		3,0 months or less if manufacturer indicates a shorter period
20	Availability of the analyser	A_a	8.5.7			x		≥ 90 %
21	Converter efficiency ^{e,f}	E_c	8.4.14		x			≥ 98 %
22	Residence time in the analyser		8.4.15		x			≤ 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)	$\pm 0,2$ 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: NO₂

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.

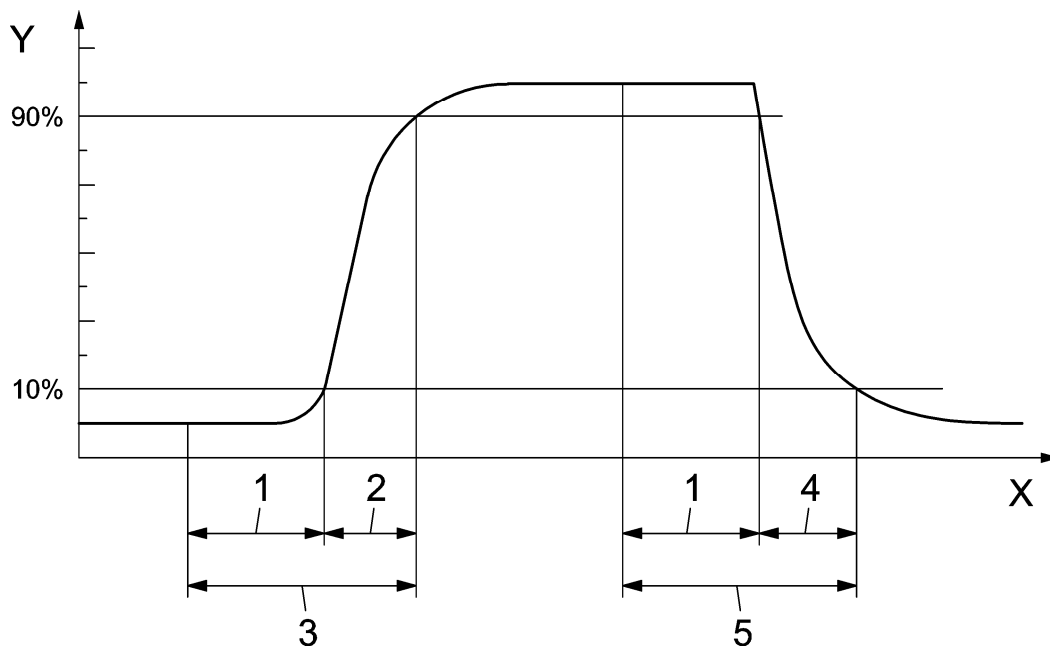
The sample flow rate shall be kept constant within the requirements as given in 8.4.2 ($\pm 1\%$) during the test. The test shall be performed with NO and with NO₂.

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 NO₂ at levels from less than 20 % to about 80 % of the maximum of the certification range of NO₂ and vice versa.

The difference in response times shall be calculated according to:

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

where

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

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

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

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

8.4.4 Short-term drift

After the required stabilisation period (8.4.2.1), the analyser shall be adjusted at zero and span level (around 70 % to 80 % of the maximum of the certification range of 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:

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

where

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

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

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

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

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

where

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

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

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

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

8.4.5 Repeatability standard deviation

After waiting the time equivalent of one independent reading, 20 individual measurements both at zero concentration and at 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:

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

where

- s_r is the repeatability standard deviation, in nmol/mol;
- x_i is the i th 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:

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

where

- l_{det} is the detection limit of 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:

$$b_{\text{gp}} = \frac{(C_{\text{p2}} - C_{\text{p1}})}{(P_2 - P_1)} \quad (9)$$

where

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

C_{p1} is the average concentration of the measurements at sampling gas pressure P_1 , in nmol/mol;

C_{p2} is the average concentration of the measurements at sampling gas pressure P_2 , in nmol/mol;

P_1 is the minimum sampling gas pressure, in kPa;

P_2 is the maximum sampling gas pressure, in kPa.

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

8.4.8 Sensitivity coefficient to sample gas temperature

Measurements shall be performed at sample gas temperatures of $T_{\text{G},1} = 0$ °C and $T_{\text{G},2} = 30$ °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:

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

where

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

$C_{\text{GT},1}$ is the average concentration of the measurements at sample gas temperature $T_{\text{G},1}$, 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:

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

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:

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

where

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

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

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

V_1 is the minimum voltage 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_i) 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_i and the interferent to be investigated. The influence quantities at zero and concentration c_i are calculated from:

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

(13)

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

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 NO₂ at a concentration c_{t,NO_2} which is about twice the hourly limit value; and
- b) a stepwise varied concentration of NO between zero and 600 nmol/mol (concentration $c_{t,\text{NO}}$).

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:

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

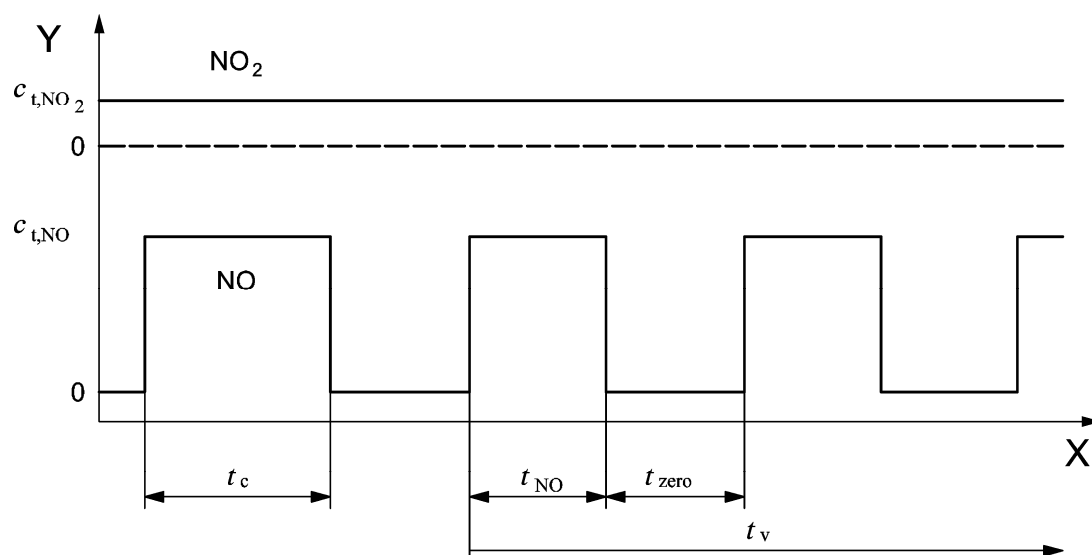
where

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

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

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

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



Key

Y concentration (nmol/mol)
X time

Figure 2 — Concentration variations for the averaging effect test

8.4.13 Difference sample/calibration port

If the analyser has different ports for feeding sample gas and calibration gas, the difference in response of the analyser to feeding through the sample or calibration port shall be tested. The test shall be carried out by feeding the analyser with a test gas with a concentration of 70 % to 80 % of the maximum of the certification range of 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:

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

where

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

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

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

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

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