



BSI Standards Publication

**Stationary source emissions
— Determination of mass
concentration of nitrogen
oxides — Standard reference
method: Chemiluminescence**

National foreword

This British Standard is the UK implementation of EN 14792:2017. It supersedes BS EN 14792:2005 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee EH/2/1, Stationary source emission.

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European foreword

This document (EN 14792:2017) has been prepared by Technical Committee CEN/TC 264 "Air quality", the secretariat of which is held by DIN.

This document supersedes EN 14792:2005.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by July 2017, and conflicting national standards shall be withdrawn at the latest by July 2017.

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

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

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

1 Scope

This European Standard specifies the standard reference method (SRM) based on the chemiluminescence principle for the determination of the nitrogen oxides (NO_x) in flue gases emitted to the atmosphere from ducts and stacks. It includes the sampling and the gas conditioning system, as well as the analyser.

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

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

This European Standard has been validated during field tests on waste incineration, co-incineration and large combustion installations and on a recognized test-bench. It has been validated for sampling periods of 30 min in the range of 0 mg/m³ to 1 300 mg/m³ of NO_x for large combustion plants and 0 mg/m³ to 400 mg/m³ of NO_x for waste incineration, according to emission limit values (ELV) laid down in the Directive 2010/75/EU.

The ELV for NO_x (NO + NO₂) in EU Directives is expressed in mg/m³ of NO₂ on a dry basis, at a specified value for oxygen and at standard conditions (273 K and 101,3 kPa).

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

2 Normative references

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

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

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

EN 15267-4:2017, *Air quality — Certification of automated measuring systems — Part 4: Performance criteria and test procedures for automated measuring systems for periodic measurements of emissions from stationary sources*

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

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

3 Terms and definitions

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

NOTE In this European Standard, NO_x is defined as the sum of NO and NO₂. The mass concentration of NO_x is expressed as the equivalent NO₂ concentration in milligrams per cubic metre at standard conditions.

3.1 standard reference method SRM

reference method prescribed by European or national legislation

[SOURCE: EN 15259:2007]

3.2 reference method RM

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

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

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

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

[SOURCE: EN 15259:2007]

3.3 measurement method

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

[SOURCE: EN 14793:2017]

3.4 alternative method AM

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

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

[SOURCE: EN 14793:2017]

3.5 measuring system

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

[SOURCE: JCGM 200:2012]

3.6 automated measuring system AMS

entirety of all measuring instruments and additional devices for obtaining a result of measurement

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

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

[SOURCE: EN 15267-4:2017]

3.7 portable automated measuring system P-AMS

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

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

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

[SOURCE: EN 15267-4:2017]

3.8 calibration

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

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

Note 2 to entry: Calibration should not be confused with adjustment of a measuring system.

3.9 adjustment

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

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

3.10 span gas

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

3.11

measurand

particular quantity subject to measurement

[SOURCE: EN 15259:2007]

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

3.12

interference

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

3.13

influence quantity

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

Note 1 to entry: Influence quantities are e.g. presence of interfering gases; ambient temperature, pressure of the gas sample.

3.14

ambient temperature

temperature of the air around the measuring device

3.15

emission limit value

ELV

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

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

3.16

measurement site

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

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

[SOURCE: EN 15259:2007]

3.17

measurement plane

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

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

[SOURCE: EN 15259:2007]

3.18
measurement port

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

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

[SOURCE: EN 15259:2007]

3.19
measurement line

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

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

[SOURCE: EN 15259:2007]

3.20
measurement point

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

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

[SOURCE: EN 15259:2007]

3.21
performance characteristic

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

3.22
response time

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

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

3.23
short-term zero drift

difference between two zero readings at the beginning and at the end of the measurement period

3.24
short-term span drift

difference between two span readings at the beginning and at the end of the measurement period

3.25

lack of fit

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

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

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

3.26

repeatability in the laboratory

closeness of the agreement between the results of successive measurements of the same measurand carried out under the same conditions of measurement

Note 1 to entry: Repeatability conditions include:

- same measurement method;
- same laboratory;
- same measuring system, used under the same conditions;
- same location;
- repetition over a short period of time.

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

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

3.27

repeatability in the field

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

Note 1 to entry: These conditions include:

- same measurement method;
- two sets of equipment, the performance of which fulfils the requirements of the measurement method, used under the same conditions;
- same location;
- implemented by the same laboratory;
- typically calculated on short periods of time in order to avoid the effect of changes of influence parameters (e.g. 30 min).

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

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

3.28

reproducibility in the field

closeness of the agreement between the results of simultaneous measurements of the same measurand carried out using several sets of equipment under the same conditions of measurement

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

- same measurement method;
- several sets of equipment, the performance of which are fulfilling the requirements of the measurement method, used under the same conditions;
- same location;
- implemented by several laboratories.

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

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

3.29

residence time in the measuring system

time period for the sample gas to be transported from the inlet of the probe to the inlet of the measurement cell

3.30

conversion efficiency

percentage of NO₂ present in the sample gas converted to NO by the converter

3.31

uncertainty

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

3.32

standard uncertainty

u

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

3.33

combined uncertainty

u_c

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

3.34

expanded uncertainty

U

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

$$U = k \times u_c$$

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

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

3.35

uncertainty budget

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

4 Symbols and abbreviations

4.1 Symbols

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

$A(t_0)$	(result given by the analyser after adjustment at t_0 at span point – result given by the analyser after adjustment at t_0 at zero point) / (calibration gas concentration at span point – calibration gas concentration at zero point)
$B(t_0)$	result given by the analyser after adjustment at t_0 at zero point
C	measured concentration
C_{corr}	measured concentration corrected for drift
Drift(A)	{[(result given by the analyser during the drift check at t_{end} at span point – result given by the analyser during the drift check at t_{end} at zero point) / (calibration gas concentration at span point – calibration gas concentration at zero point)] – $A(t_0)$ } / ($t_{\text{end}} - t_0$)
Drift(B)	(result given by the analyser during the drift check at t_{end} at zero point – result

	given by the analyser after adjustment at t_0 at zero point) / $(t_{\text{end}} - t_0)$
f	volume fraction
k	coverage factor
M_{mol}	molar mass
s_R	reproducibility standard deviation
$s_{r,\text{limit}}$	maximum allowable repeatability standard deviation
t	time
t_0	time of adjustment
t_{end}	time of check for drift at the end of the measurement period
u	standard uncertainty
u_c	combined uncertainty
U	expanded uncertainty
V_{mol}	molar volume

4.2 Abbreviated terms

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

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

5 Principle

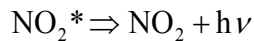
5.1 General

This European Standard describes the standard reference method (SRM) for sampling and determining NO_x (NO and NO_2) concentrations in flue gases emitted to atmosphere from ducts and stacks by means of an automatic analyser using chemiluminescence absorption principle. The specific components and the requirements for the sampling system and the chemiluminescence analyser are described in Clause 6 and Clause 7. A number of performance characteristics, together with associated performance criteria are specified for the analyser. These performance characteristics determined according to EN 15267-4:2017 and the expanded uncertainty of the method shall meet the performance criteria given in this European Standard. Requirements and recommendations for quality assurance and quality control are given in Clause 10 for measurements in the field.

5.2 Measuring principle

The principle of chemiluminescence to measure NO_x is based on the following reaction between nitrogen monoxide and ozone:





Some of the NO₂ created during the reaction of NO and O₃ is in an excited state. When returning to the basic state, these NO₂ molecules can radiate light, the intensity of which depends on the NO content and is influenced by the pressure and presence of other gases.

In a chemiluminescence analyser, gas is 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 oxide only. The emitted radiation (chemiluminescence) is proportional to the amount of NO present in the sampled gas. The emitted radiation is filtered by means of a selective optical filter and converted into an electric signal by means of a photomultiplier tube.

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

When a dual type analyser is used, both NO and NO_x results are determined continuously. On the contrary, with a single type analyser, the reaction chamber is alternatively fed with gas having not passed the converter and with the gas having passed the converter that reduces NO₂ to NO. Therefore, NO and NO_x are determined alternately.

Chemiluminescence analysers are associated to an extractive sampling system and a sample gas conditioning system. A sample of gas is taken from the stack with a sampling probe and conveyed to the analyser through a sample gas line and suitable gas conditioning system. The values from the analyser are recorded and/or stored by means of electronic data processing.

Interference due to CO₂ in the sample gas is possible, particularly in the presence of water vapour, due to quenching of the chemiluminescence. The extent of the quenching depends on the CO₂ and H₂O concentrations and the type of analyser used. Any necessary corrections may be made to the analyser output to increase its accuracy for example by reference to correction curves supplied by the manufacturers or by calibrating with gases containing approximately the same concentration of CO₂ as the sample gas.

NOTE 1 A vacuum chemiluminescent NO_x analyser reduces the CO₂ and H₂O quenching error.

NOTE 2 A correction of the NO_x concentration may be necessary if the NH₃ concentration is higher than 20 mg/m³.

In flue gases from conventional combustion systems the nitrogen oxides consist of more than 95 % NO. The remaining oxide is predominantly NO₂. These two oxides (NO + NO₂) are designated as NO_x.

It should be noted, that in other processes, the ratio of NO to NO_x may be different and other nitrogen oxides may be present.

6 Description of the measuring system

6.1 General

A volume is extracted from the flue gas for a fixed period of time at a controlled flow rate. The sampling system consists of:

- a sampling probe;
- a filter;

- a sample gas line;
- a conditioning system.

A filter removes the dust in the sampled volume before the sample is conditioned and passed to the analyser.

Different sampling and conditioning configurations are available in order to avoid water vapour condensation in the measuring system (see also Annex B).

Possible configurations are:

- Configuration 1: removal of water vapour by condensation using a cooling system;
- Configuration 2: removal of water vapour through elimination within a permeation drier;
- Configuration 3: dilution with dry, clean ambient air or nitrogen of the gas to be characterized;
- Configuration 4: heating of the complete sampling system from the inlet of the sample gas line to the heated analyser at a temperature above the dew point.

Configurations 1 to 3 require that the user shall check that the dew point temperature or the outlet temperature of the conditioning system is lower or equal to 4 °C at the inlet of the analyser.

For configuration 4 the user may correct the results for the remaining water content in order to report results on a dry basis (see Annex B in EN 14790:2017).

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

The temperature of all components of the sampling equipment coming into contact with the wet sample gas shall be maintained at a sufficiently high temperature to avoid any condensation.

Conditions and layout of the sampling equipment contribute to the combined uncertainty of the measurement. In order to minimize this contribution to the combined measurement uncertainty, performance criteria for the sampling equipment and sampling conditions are given in 6.2 and Clause 7.

Some other sample gas conditioning systems may exist and could be acceptable, provided they fulfil the requirements of this European Standard and have been validated with success during the certification process. For example, some systems put gas in depression using a simple Sonic nozzle in the collection probe in order to create a partial vacuum (between 50 hPa and 100 hPa absolute) so that the head of collection and the sample gas line does not need to be heated and water vapour condensation is avoided.

6.2 Sampling and sample gas conditioning system

6.2.1 Sampling probe

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

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

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

6.2.2 Filter

The filter and filter holder shall be made of an inert material (e.g. ceramic or sinter metal filter with an appropriate pore size). It shall be heated above the water or acid dew point, whichever is the greater. The particle filter shall be changed or cleaned periodically depending on the dust loading in the measurement plane.

NOTE Overloading of the particle filter can cause loss of nitrogen dioxide by sorption onto the particulate matter and can also increase the pressure drop in the sample gas line.

6.2.3 Sample gas line

The sample gas line shall be heated up to the conditioning system. It shall be made of a suitable corrosion resistant material (e.g. stainless steel, borosilicate glass, ceramic; PTFE or PFA is only suitable for flue-gas temperature lower than 200 °C). At temperatures greater than 250 °C, stainless steel and certain other materials can alter the ratio of NO₂/NO_x. In this case, ceramic, glass, quartz or titanium should be used.

6.2.4 Sample gas conditioning system

6.2.4.1 Sample gas cooler (configuration 1)

The design of the sample gas cooler shall be such that absorption of NO₂ in the condensates is minimised. Because overpressure in the cooling system increases losses of NO₂ in the condensates, the pump shall be situated between the cooling system and the analyser. In the case that the concentration of NO₂ in the sample gas becomes too high, the use of a sample gas cooler can produce errors on the NO₂ measurement. This can occur because of the solubility of NO₂ in the condensed water and shall also depend on the content of water vapour in the flue gas.

6.2.4.2 Permeation drier (configuration 2)

The permeation drier is used before the gas enters the analyser in order to separate water vapour from the flue gas. The dew point at the outlet of the system shall be sufficiently below the ambient temperature.

Due to ammonium salts deposition on the permeation tube, the permeation system shall not be used when the NH₃ concentration is outside the range specified by the manufacturer.

6.2.4.3 Dilution system (configuration 3)

The dilution technique is an alternative to hot-gas monitoring or sample gas drying. The flue gas is diluted with dry, clean, ambient air or nitrogen. The dilution gas shall be dry and free from nitrogen oxides. The dilution ratio shall be chosen according to the objectives of the measurement and shall be compatible with the range of the analytical unit. It shall remain constant through the period of the test. The water dew point shall be reduced so to avoid the risks of condensation.

The contribution of the dilution system to the uncertainty shall be added to the uncertainty budget.

NOTE 1 Configuration 3 was not included in the validation of the method in the field.

NOTE 2 Analysers that are used in combination with dilution probes, work with measurement ranges, which are typical for ambient air analysers (0 mg/m³ – 1 mg/m³ – 5 mg/m³ – 10 mg/m³ – 25 mg/m³).

6.2.4.4 Heated line and heated analyser (configuration 4)

To avoid condensation, the sample gas line up to the analyser and the analyser itself shall be heated.

The concentrations are given on wet basis and shall be corrected so that they are expressed on dry basis. The correction shall be made from the water vapour concentration in the flue gases and the uncertainty attached to this correction shall be added to the uncertainty budget (see Clause 8).

NOTE Configuration 4 was not included in the validation of the method in the field.

6.2.5 Sample gas pump

When a pump is not an integral part of the chemiluminescence analyser, an external pump is necessary to draw the sampled gas through the apparatus. It shall be capable of operating to the specified flow requirements of the manufacturer of the analyser and pressure conditions required for the reaction chamber. The pump shall be resistant to corrosion and shall be of materials that do not react with or absorb NO_x . It shall be consistent with the requirements of the analyser to which it is connected. The whole sampling system associated to the analyser, including the pump, has to meet the criterion in Table 1 related to the influence of gas pressure.

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

6.2.6 Secondary filter

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

NOTE No additional secondary filter is necessary when they are part of the analyser itself.

6.2.7 Flow controller and flow meter

This apparatus sets the required sample gas flow. A corrosion resistant material shall be used. The sample gas flow rate into the analyser shall be maintained according to the analyser manufacturer's requirements. A controlled pressure drop across restrictors is usually employed to maintain flow rate control into the chemiluminescence analyser.

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

6.3 Analyser equipment

6.3.1 General

Generally two configurations of analysers are available:

- dual type with two reaction chambers;
- single type with one reaction chamber.

In the dual-chamber types the sample flow 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 single-chamber type analyser the sample alternately bypasses or passes through the converter. This type of analyser sequentially measures the nitrogen monoxide of the sampled gas followed by the sum of nitrogen dioxide and nitrogen monoxide. If NO_2 and NO shall be measured, the cycle rate of switching between NO_x (through the converter) and NO (bypassing the converter) shall be faster than the rate of change of the NO_x in the sample stream (otherwise the subtraction can produce negative NO_2 readings).

A chemiluminescence apparatus consists of the principal components described in 6.3.2 to 6.3.7.

6.3.2 Converter

A NO₂/NO converter shall be included in the measuring system. The converter converts nitrogen dioxide in the sampled gas to nitrogen monoxide. It shall be capable of converting at least 95 % of the nitrogen dioxide to nitrogen monoxide. The conversion efficiency shall be determined by one of the procedures described in Annex C. The converter shall consist of a heated furnace maintained at a constant temperature.

NOTE 1 Relevant materials for a converter include stainless steel, molybdenum, tungsten, spectroscopically-pure carbon and quartz.

NOTE 2 The converter can be bypassed with a changeover-valve arrangement. If the sample gas flows through the converter, the total quantity (NO + NO₂) is determined; when the converter is by-passed, the NO content is determined. The amount of NO₂ can be calculated as the difference between NO_x and NO.

NOTE 3 If ammonia is present in the sample gas, interferences can occur depending on the operating temperature and the material of the converter.

NOTE 4 When using a stainless steel converter in a sample that is a reducing atmosphere, the NO in the sample can be disassociated to N₂ and O₂. This leads to lower readings. Manufacturers of analysers that use stainless steel normally have an air bleed from the ozonator supply to the sample stream in order to avoid this effect.

Examples of different types of converters are given in Annex D.

6.3.3 Ozone generator

An ozone generator is required. Ozone is generated from oxygen by either 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 is thoroughly dried and filtered before entering the generator. If the ozone is generated using oxygen of a recognized analytical grade from a compressed gas cylinder, this oxygen can be fed directly into the generator. The concentration of ozone produced shall be sufficiently high to maintain the required linearity of the analyser. If ozone concentration is too low, this can result in a nonlinear response to the concentration of NO₂ and NO. It may be useful to check that the quantity of ozone is sufficient by injecting a calibration gas of NO, which concentration is close to the upper limit of the measurement range.

WARNING — In order to minimize the risk of explosions, the necessary precautions shall be taken and safety regulations shall be applied when oxygen is used instead of air.

The flow rate of air or oxygen shall fulfil specifications given by the manufacturer of the analyser.

6.3.4 Reaction chamber

The reaction chamber shall be constructed of an inert material. The dimensions of the reaction chamber determine the characteristics of the chemiluminescence reaction (residence time, speed of reaction). The reaction chamber shall be heated at a constant temperature above the dew point of the sampled gases at the pressure conditions in this chamber.

The chemiluminescence reaction is carried out at reduced pressure to minimize quenching effects (interferences) and to increase sensitivity.

6.3.5 Optical filter

This filter shall remove radiation at wavelengths shorter than 600 nm, to minimize any interference produced by the chemiluminescence reaction with unsaturated hydrocarbons that radiate at these wavelengths.

6.3.6 Photomultiplier tube

The output of the analyser is affected by the characteristics of the photomultiplier tube(s). In order to reduce background noise and the effect of temperature changes, the tube is generally housed in a thermostatically controlled refrigerated-device (a Peltier cooler is commonly used.)

6.3.7 Ozone removal

The ozone shall be removed from the gas on leaving the reaction chamber by passage through an ozone removal device. This prevents contamination of the immediate surrounding air and protects the sampling pump.

7 Performance characteristics of the SRM

Table 1 gives an overview of the performance characteristics of the whole measurement method including the analyser with its sampling and sample gas conditioning system. These performance characteristics shall be determined in a general performance test according to the test procedures described in EN 15267-4:2017 by an independent test laboratory accredited or recognized by the competent authorities for the implementation of test procedures of EN 15267-4:2017.

The independent test laboratory shall check the conformity of the analyser with its sampling and sample gas conditioning system to fulfil the performance criterion attached to each performance characteristic. The maximum allowable deviations as absolute values of the measured values are given as mass concentrations or as percentages of the upper limit of the range.

Table 1 — Performance characteristics of the SRM and associated performance criteria

Performance characteristic	Performance criterion	Performance characteristic to be included in calculation of combined uncertainty
Response time	≤ 200 s	
Repeatability standard deviation at zero point	$\leq 2,0$ % ^a	X ^b
Repeatability standard deviation at span point	$\leq 2,0$ % ^a	X ^b
Reproducibility standard deviation	$\leq 3,3$ % ^a	X ^b
Lack of fit	$\leq 2,0$ % ^a	X
Short-term zero drift	$\leq 2,0$ % ^{a,c}	X
Short-term span drift	$\leq 2,0$ % ^{a,c}	X
Influence of ambient temperature change from 5 °C to 25 °C and from 40 °C to 20 °C at zero point	$\leq 5,0$ % ^{a,c}	X
Influence of ambient temperature change from 5 °C to 25 °C and from 40 °C to 20 °C at span point	$\leq 5,0$ % ^{a,c}	X
Influence of sample gas pressure at span point, for a pressure change Δp of 3 kPa	$\leq 2,0$ % ^a	X
Influence of sample gas flow on extractive AMS for a given specification by the manufacturer	$\leq 2,0$ % ^a	X
Influence of vibration	$\leq 2,0$ % ^a	X

Influence of voltage, at -15 % below and at +10 % above nominal supply voltage	$\leq 2,0 \%$ ^a	X
Cross-sensitivity	$\leq 4,0 \%$ ^{a,d}	X
Converter efficiency	$\geq 95 \%$	X ^e
Leakage in the sample gas line and sample gas conditioning system	$\leq 2,0 \%$ of the measured value	X ^f
<p>^a Percentage value of the upper limit of the certification range.</p> <p>^b The repeatability in the laboratory or the reproducibility in the field shall be used, whichever is greater. If the repeatability in the laboratory is used, only one of both values shall be included in the calculation: the first possibility is to choose the repeatability standard deviation got from laboratory tests corresponding to the closest concentration to the actual concentration in stack, or the higher (relative) standard deviation of repeatability independently of the concentration measured in stack.</p> <p>^c Consider either a combination of drift effect in the laboratory and effect of temperature in the laboratory or drift in the field whatever is the greatest, because drift in the field combines mainly intrinsic drift of the P-AMS and the drift due to temperature.</p> <p>^d The sums of contributions to uncertainty producing positive and negative effects are calculated separately. The maximum of their absolute value shall be compared with the performance criterion.</p> <p>^e NO₂ losses in the P-AMS should include the effect of lack of efficiency of the converter. For this reason the contribution of the efficiency should not be considered.</p> <p>^f If the leak test is performed under severe conditions of depression, then leak can be considered as negligible in normal conditions of use.</p>		

8 Suitability of the measuring system to the measurement task

An uncertainty budget shall be established by the user to determine for which measurement range the analyser and its associated sampling and sample gas conditioning system fulfil the requirements for a maximum allowable expanded uncertainty.

The relative expanded uncertainty, calculated on dry basis and before correction to the oxygen reference concentration shall not exceed 10,0 % of the daily emission limit value (ELV) or of the lowest limit value fixed to the plant by the local authorities.

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

Table 1 indicates which performance characteristics have to be included in the calculation of the combined uncertainty.

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

- determine the standard uncertainties attached to the performance characteristics to be included in the calculation of the uncertainty budget according to ISO/IEC Guide 98-3;
- calculate the uncertainty budget by combining all the standard uncertainties according to ISO/IEC Guide 98-3, including the uncertainty of the calibration gas;
- values of standard uncertainty that are less than 5 % of the maximum standard uncertainty may be neglected;
- calculate the combined uncertainty at the measured value, reported as a dry gas value at actual concentration of oxygen.

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

An example of an uncertainty budget is given in Annex F.

9 Field operation

9.1 Measurement planning

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

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

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

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

9.2 Sampling strategy

9.2.1 General

Sampling requires a suitable measurement section and measurement plane.

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

9.2.2 Measurement section and measurement plane

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

9.2.3 Minimum number and location of measurement points

It is necessary to ensure that the gas concentrations measured are representative of the average conditions inside the waste gas duct. Measurements may be performed at one representative measurement point or at any measurement point, if the corresponding requirements on the distribution of the NO_x concentration or any other relevant component specified in 8.3 of EN 15259:2007 are fulfilled. In all other cases the measurements shall be performed as grid measurements. In that case, EN 15259 specifies the minimum number of measurement points to be used and the location in the measurement plane for circular and rectangular ducts.

9.2.4 Measurement ports and working platform

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

Examples of suitable measurement ports are given in EN 15259.

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

9.3 Choice of the measuring system

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

- flue gas moisture content and dew point;
- temperature of exhaust gases;
- dust loading;
- expected concentration range of NO_x and emission limit values;
- NO₂/NO_x ratio;
- expected concentration of potentially interfering substances,

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

To avoid long response times, the sample gas line should be as short as possible. If necessary a bypass pump should be used.

Use a heated filter appropriate to the dust loading.

9.4 Setting of the measuring system on site

9.4.1 General

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

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

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

When both the analyser and the sampling system have been set-up, and before zero and span adjustments, the proper functioning of the instrument and sampling system shall be checked.

Any data recording and data processing system used shall be adapted to the measurement objective and to the response time of the measuring system; generally, data are recorded at least every 60 s.

9.4.2 Preliminary zero and span check, and adjustments

9.4.2.1 Test and supply gases

9.4.2.1.1 Oxygen

Oxygen or instrument air can be used to feed the ozone generator according to the manufacturer's instructions.

9.4.2.1.2 Zero gas

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

9.4.2.1.3 Span gases

The span gases used to adjust the analyser shall have concentrations traceable to SI units of NO or NO/NO₂. The expanded uncertainty on the analytical certificate of the span gas shall not exceed 2,0 % for NO or NO/NO₂.

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

NOTE Gas manufacturer's recommendations will be followed to avoid any diffusion back into the cylinder that can convert NO to NO₂.

9.4.2.2 Adjustment of the analyser

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

- check and adjust the zero value,
- check and adjust the span value,
- in case adjustments are made, check again zero to see if there is no significant change.

9.4.2.3 Check of the sampling system including the leak test

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

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

NOTE 1 Differences may be due to leakage or impurities in the sampling system leading to memory effects due to adsorption or desorption to or from the surfaces.

- assemble the complete sampling system; seal off the inlet of the probe and switch on the pump; after reaching minimum pressure, read or measure the flow rate with an appropriate measuring device; the leak flow rate shall not exceed 2,0 % of the expected sample gas flow rate used during measurement.

NOTE 2 The leak test can be carried out before the adjustment of the analyser.

9.4.3 Zero and span checks after measurement

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

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

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

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

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

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

where

- $A(t_0)$ is (result given by the analyser after adjustment at t_0 at span point – result given by the analyser after adjustment at t_0 at zero point) / (calibration gas concentration at span point – calibration gas concentration at zero point);
- $B(t_0)$ is the result given by the analyser after adjustment at t_0 at zero point;
- $\text{Drift}(A)$ is {[(result given by the analyser during the drift check at t_{end} at span point – result given by the analyser during the drift check at t_{end} at zero point) / (calibration gas concentration at span point – calibration gas concentration at zero point)] – $A(t_0)$ } / ($t_{\text{end}} - t_0$);
- $\text{Drift}(B)$ is (result given by the analyser during the drift check at t_{end} at zero point – result given by the analyser after adjustment at t_0 at zero point) / ($t_{\text{end}} - t_0$);
- $t_{\text{end}} - t_0$ is the duration of the measurement period in minutes (duration between adjustment and check for drift at the end of the measurement period).

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

10 Ongoing quality control

10.1 General

Quality control is critically important in order to ensure that the uncertainty of the measured values for NO and NO₂ are kept within the stated limits during extended automatic monitoring periods in the field. This means that maintenance, as well as zero and span adjustment procedures shall be followed, as they are essential for obtaining accurate and traceable data.

The losses of NO₂ in the P-AMS shall be checked every three months after adjustment of the analyser with NO by injecting calibration gas of NO₂ in N₂. Losses of NO₂ shall be lower than 20 % of the NO₂ value. The expanded uncertainty of the NO₂ value shall not exceed 2,0 %.

NOTE It is assumed that NO₂ losses do not have a insignificant influence on the measured value and on the measurement uncertainty, if the measuring system is kept under control by this procedure

10.2 Frequency of checks

Table 2 shows the required minimum frequency of checks. The test laboratory shall implement the relevant European Standards for determination of performance characteristics and procedure described in Annex C.

Table 2 — Frequency of checks

Checks	Frequency	Action criteria
Cleaning or changing of particulate filters ^a at the sampling inlet and at the monitor inlet	Every campaign, if needed ^a	
Leak test	Every campaign	As specified in 9.4.2.3
Zero and span adjustment	Every campaign	As specified in 9.4.2.2
Drift	Every campaign	As specified in 9.4.3
NO ₂ loss	Every three months	As specified in 10.1
Conversion efficiency of the NO _x converter (6.3.2)	At least every year ^b	Efficiency < 95 %
Checking or changing of ozone removal device (6.3.7), and if applicable: drying material and other consumables	At least every year ^c	As specified by the manufacturer
Regular maintenance of several parts of the monitor	As required by manufacturer	As specified by the manufacturer
Lack of fit	At least every year and after repair of the analyser	As specified in Table 1

a The particle filter shall be changed periodically depending on the dust loading at the measurement site. During this filter change the filter housing shall be cleaned. Overloading of the particle filter may cause losses of nitrogen dioxide by sorption on the particulate matter and may increase the pressure drop in the sampling line.

b Depending on the converting material and on NO₂ concentration. Frequency should be increased on the basis of the results of previous tests.

c Strongly dependent on site-specific conditions.

11 Expression of results

The measurement results shall be expressed as mass concentrations.

A volume fraction f (e.g. in 10⁻⁶ which is often expressed as ppm) is converted to a mass concentration C (e.g. in mg/m³) by Formula (2):

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

where:

$$M_{\text{mol}}(\text{NO}) = 30 \text{ g/mol}$$

$$M_{\text{mol}}(\text{NO}_2) = 46 \text{ g/mol}$$

$$M_{\text{mol}}(\text{NO}_x) = 46 \text{ g/mol} \text{ (NO and NO}_2\text{, expressed as NO}_2\text{)}$$

$$V_{\text{mol}} = 22,4 \text{ l/mol}$$

If the measurement result has to be converted to reference conditions the corresponding equations in Annex C of EN 15259:2007 shall be used.

12 Equivalence of an alternative method

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

The maximum allowable repeatability standard deviation (see Formula (3)) and the reproducibility standard deviation (see Formula (4)) defined in EN 14793:2017, expressed in mass concentration for this standard reference method are:

$$s_{r,\text{limit}}(C) = 0,016 C + 0,9 \frac{\text{mg}}{\text{m}^3} \quad (3)$$

$$s_R(C) = 0,0153 C + 2,12 \frac{\text{mg}}{\text{m}^3} \quad (4)$$

where C is the mass concentration in milligrams per cubic meter.

13 Measurement report

The measurement report shall fulfil the requirements of EN 15259 and shall include details of on-going quality controls:

- a) information about the personnel involved in the measurement;
- b) description of the location of the measurement points in the measurement plane;
- c) information about the analyser and description of the sampling and conditioning line;
- d) operating range;
- e) details of the quality and the concentration of the calibration gases used;
- f) details on the adjustment performed before and after actual sampling;
- g) measurement results with sampling date, time and duration;
- h) information on flue gas characteristics (temperature, velocity, moisture, pressure).

Annex A **(informative)**

Validation of the method in the field

A.1 General

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

A.2 Characteristics of installations

The following field tests were performed:

- 1st field test: INERIS bench-loop at Verneuil en Halatte (France); the bench-loop simulates combustion or waste incineration exhaust gases. Five teams took part in the 1st field test. Double measurements were not performed simultaneously but sequentially. Five different flue gas matrices were generated. Within each matrix, two sequential measurements were performed. Two additional sequential measurements were performed in flue gas matrices where the flue gas concentrations varied. There were a total of 12 measurements performed by all the teams.
- 2nd field test: waste incinerator in Denmark. Four teams took part to the field test and performed double measurements simultaneously. A total of 16 measurements were performed by all the teams.
- 3rd field test: waste incinerator in Italy. Four teams took part to the field test. Two pairs of two teams performed double measurements simultaneously and the four teams performed single measurements simultaneously. A total of six double measurements were performed by each pair of two teams while a total of 12 single measurements was performed by all teams.
- 4th field test: co-incinerator combined heat and power installation in Sweden. The fluidised bed boilers operate on fuel mixes of wood chips, demolition waste, peat and coal. Two pairs of two teams performed double measurements simultaneously and the four teams performed single measurements simultaneously. A total of six double measurements were performed by each pair of two teams while a total of 12 single measurements was performed by all the teams.
- 5th field test: co-incinerator cement plant in Germany. The fuel could be coal, heavy oil and secondary fuel (e.g. paper, plastics, textiles, and tires). Four teams took part to the field test and performed double measurements simultaneously. All the teams performed a total of 16 double measurements.
- 6th field test: coal fired power plant in Germany. Four teams performed their double measurements simultaneously. The total amount of double measurements performed by all teams was 12.

An overview of the flue gas characteristics is given in Table A.1.

Table A.1 — Flue gas characteristics during field tests

Field test	Installation	Fuel	Flue gas characteristics						
			T °C	O ₂ %	NO _x mg/m ³	SO ₂ mg/m ³	CO mg/m ³	H ₂ O %	PM mg/m ³
1	Power plant ^a	Natural gas	< 150	3 to 13	10 to 1 300	10 to 2 000	20 to 400	10 to 21	< 1
2	Waste incinerator	Municipal waste	90 to 110	8 to 11	180 to 250	25 to 250	5 to 15	13 to 19	1 to 5
3	Waste incinerator	Municipal waste	85 to 105	16 to 18	61 to 78	5 to 50	0 to 2	8 to 12	1 to 5
4	Co-incinerator	Wood, waste, coal	70 to 80	4 to 6	4 to 70	0 to 10	50 to 150	8 to 12	0 to 20
5	Co-incinerator	Coal, oil, waste	140 to 170	4 to 6	440 to 1060	60 to 170	260 to 740	23 to 26	5 to 10
6	Power plant	Coal	130 to 140	8,9 to 9,2	110 to 140	1 000 to 1 130	3 to 6	5,5 to 8	< 50

^a Bench-loop: flue gas simulation.

A.3 Repeatability and reproducibility in the field

A.3.1 General

Repeatability standard deviation s_r and reproducibility standard deviation s_R are determined from data obtained during inter-laboratory tests at the plants described in A.2.

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

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

$$r = \sqrt{2} t_{0,95;n-1} s_r \quad (\text{A.2})$$

where

s_r is the repeatability standard deviation;

x_i is the i^{th} measured signal;

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

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

r is the repeatability in the field.

Reproducibility standard deviation s_R used to estimate of the expanded uncertainty U (see Formula (A.3)) and reproducibility in the field R (see Formula (A.4)) are calculated according to

ISO 5725-2, from the results of parallel measurements performed simultaneously by several laboratories (see Table A.3):

$$U = t_{0,95;np-1} s_R \quad (\text{A.3})$$

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

where

U is an estimate of the expanded uncertainty;

s_R is the reproducibility standard deviation;

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

R is the reproducibility in the field.

A.3.2 Repeatability

Table A.2 — Repeatability in the field

Field test	Concentration		Number of teams	Number of double measurements	Repeatability standard deviation s_r mg/m ³	Repeatability r	
	Range mg/m ³	Average mg/m ³				mg/m ³	%
1A		30	5	2	0,44	1,4	4,8
1B		50	5	2	0,59	1,9	3,8
1C		90	5	2	0,83	2,7	3,0
1D		450	5	2	3,3	10,6	2,3
1E		1 350	5	2	9,4	30,1	2,2
1F	600 to 650	625	5	1	4,4	17,3	2,8
1G	87 to 98	92	5	1	0,88	3,5	3,8
2	187 to 243	217	4	16	3,6	10,7	5,0
3	61 to 78	68	4	12	2,4	7,4	10,3
4	4,5 to 67	35	4	12	0,61	2,0	7,3
5	448 to 1 065	634	3	12	9,2	28,3	4,5
6	118 to 137	126	4	12	2,3	7,1	5,6

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

$$s_r(C) = 0,0133C + 0,757 \frac{\text{mg}}{\text{m}^3} \quad (\text{A.5})$$

$$s_{r,\text{limit}}(C) = 0,016C + 0,9 \frac{\text{mg}}{\text{m}^3} \quad (\text{A.6})$$

$$r(C) = 0,041C + 2,8 \frac{\text{mg}}{\text{m}^3} \quad (\text{A.7})$$

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

A.3.3 Reproducibility

Table A.3 — Reproducibility in the field

Field test	Concentration		Number of teams	Number of double measurements	Reproducibility standard deviation s_R mg/m ³	Estimate of the expanded uncertainty U mg/m ³	Reproducibility R	
	Range mg/m ³	Average mg/m ³					mg/m ³	%
1A		30	5	2	0,59	1,3	1,9	6,4
1B		50	5	2	0,92	2,1	3,0	5,9
1C		90	5	2	1,0	2,3	3,2	3,6
1D		450	5	2	3,1	7,0	9,9	2,2
1E		1 350	5	2	19	44	61,6	4,6
1F	600 to 650	625	5	1	22	60	84,6	13,5
1G	87 to 98	92	5	1	4,0	11	15,9	17,2
2	187 to 243	217	4	16	4,6	9,7	13,8	6,3
3	61 to 78	68	4	12	4,6	10	14,2	21
4	4,5 to 67	35	4	12	a	4	5,8	16,6
5	448 to 1 065	634	3	12	12,0	27	38,2	6,0
6	118 to 137	126	4	12	4,1	9,0	12,7	10,1

^a $0,039 C + 0,52 \text{ mg}/\text{m}^3$

The following functions expressed as mass concentrations in mg/m^3 were determined:

$$s_R(C) = 0,0153C + 2,12 \frac{\text{mg}}{\text{m}^3} \quad (\text{A.8})$$

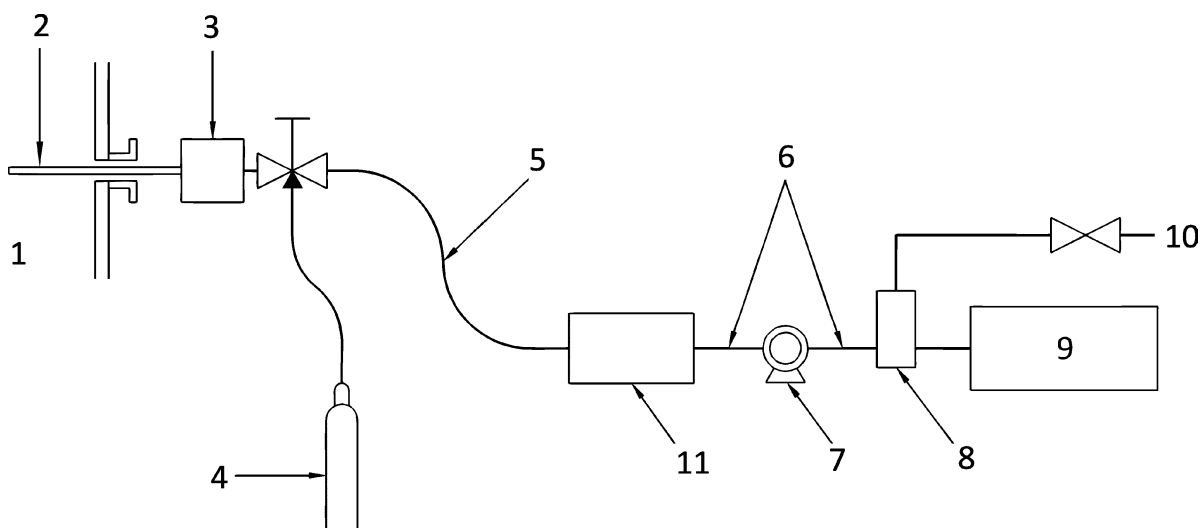
$$U(C) = 0,038C + 4,4 \frac{\text{mg}}{\text{m}^3} \quad (\text{A.9})$$

$$R(C) = 0,054C + 6,0 \frac{\text{mg}}{\text{m}^3} \quad (\text{A.10})$$

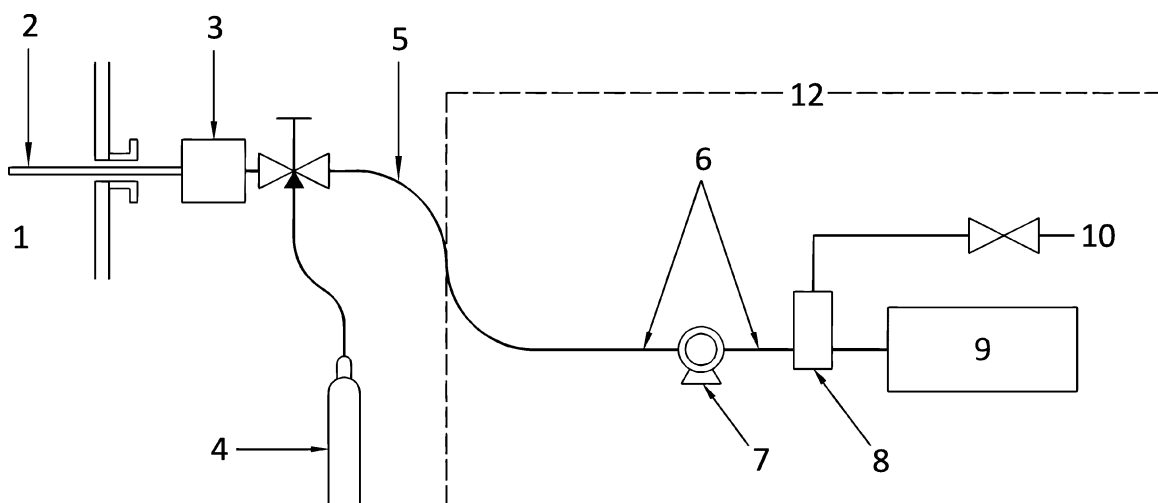
where C is the mass concentration expressed in mg/m^3 .

Annex B (informative)

Sampling and conditioning configurations



a) Configuration 1, 2, and 3



b) Configuration 4

Key

- | | | | |
|---|----------------------------------|----|--|
| 1 | stack | 9 | gas analyser |
| 2 | sampling probe | 10 | sample by-pass vent |
| 3 | heated filter | 11 | conditioning system for: |
| 4 | calibration gas | | configuration 1: condenser with a cooling system |
| 5 | heated sample gas line | | configuration 2: permeation drier |
| 6 | sample gas transport line (PTFE) | | configuration 3: dilution stage |
| 7 | sample gas pump | 12 | heated and temperature controlled zone for |
| 8 | sample gas manifold | | configuration 4 |

Figure B.1 — Examples of sampling and conditioning configurations

Annex C (normative)

Determination of conversion efficiency

C.1 General

The conversion efficiency is tested by means of measurements with known concentrations of NO₂ injected at the measuring inlet of the instrument. The NO₂ is delivered using a cylinder which contains a carrier gas such as nitrogen, and a known concentration of NO₂.

C.2 First method: cylinder gases for calibration

For analysers with two reaction chambers, adjust the analyser on the NO and NO_x channels with a NO concentration approximately equal to the ELV, ensuring that both channels give the same value. Then record the values.

Inject at the measuring inlet of the analyser with a known concentration of NO₂.

Record the NO_x and NO concentration. Wait at least four response times between the readings of the NO_x and NO concentrations. A measurement shall be taken as the average of a time period of at least three response times.

Calculate the conversion efficiency by Formula (C.1):

$$E = \frac{C_{\text{NO}_x, \text{u}} - C_{\text{NO}, \text{u}}}{C_{\text{NO}_2, \text{i}}} \times 100\% \quad (\text{C.1})$$

where

E is the conversion efficiency in percent;

$C_{\text{NO}_x, \text{u}}$ is the NO_x reading with NO₂ containing gas;

$C_{\text{NO}, \text{u}}$ is the NO reading with NO₂ containing gas;

$C_{\text{NO}_2, \text{i}}$ is the NO₂ concentration of the NO₂ containing gas applied to the analyser.

Perform the determination of the conversion efficiency three times and report the average of the three determinations.

C.3 Second method: gaseous phase titration

The following equipment is required:

- source of nitrogen monoxide such as a compressed gas cylinder containing nitrogen monoxide in nitrogen at a concentration of the order of 80 % of the certification range. The actual concentration does not need to be known provided that it remains constant throughout the test;
- source of oxygen, such as a compressed gas cylinder containing air or oxygen;
- ozone generator, capable of providing varying amounts of ozone from oxygen.

When using a corona-discharge ozone generator, pure oxygen should be used instead of air. Otherwise the corona-discharge ozone generator may oxidize the N₂ in the air to NO and result in a positive bias to the conversion efficiency calculations.

Ensure that the total flow rate of nitrogen monoxide and air (or oxygen) is greater than the flow rate of gas through the analyser.

In all of the following steps, determine the responses of the analyser to both the nitrogen monoxide and total NO_x.

This procedure evaluates the concentration of nitrogen dioxide being produced, which should be in the range 10 % to 90 % of the NO_x.

Turn off the ozone generator. Then the concentration $C_{NO_x,0}$ of total NO_x and the concentration $C_{NO,0}$ of NO shall be determined by waiting at least four response times, then recording three consecutive individual readings, each averaged over one response time, and averaging the three individual readings for each concentration.

Turn on the ozone generator and vary the output of the ozone generator to obtain at least five different ozone concentrations. Then the displayed concentrations of total NO_x ($C_{NO_x,1}, C_{NO_x,2}, \dots, C_{NO_x,n}$) and nitrogen monoxide ($C_{NO,1}, C_{NO,2}, \dots, C_{NO,n}$) shall be determined by waiting at least four response times, then recording three consecutive individual readings, each averaged over one response time, and averaging the three individual readings for each concentration.

NOTE Ozone is formed which reacts with the nitrogen monoxide to produce nitrogen dioxide before the gases enter the analyser.

The highest O₃ concentration shall be selected such that after the reaction a low level of NO remains to avoid reactions of ozone in the analyser.

Calculate the ratios $C_{NO_x,1}/C_{NO_x,0}, C_{NO_x,2}/C_{NO_x,0}, \dots, C_{NO_x,n}/C_{NO_x,0}$. Therefore, the concentration of total NO_x should be constant in each case and independent of the ratio of the concentrations of nitrogen dioxide to nitrogen monoxide.

Calculate the conversion efficiency E_i for each ozone concentration, expressed as a percentage, using Formula (C.2):

$$E_i = \frac{(C_{NO_x,i} - C_{NO,i}) - (C_{NO_x,0} - C_{NO,0})}{C_{NO,0} - C_{NO,i}} \times 100\% \quad (C.2)$$

where

E_i is the conversion efficiency at setting i of the ozone generator;

$C_{NO_x,0}$ is the concentration of total NO_x with ozone generator switched-off;

$C_{NO,0}$ is the concentration of NO with ozone generator switched-off;

$C_{NO_x,i}$ is the concentration of total NO_x with ozone generator at setting i ($i = 1$ to n);

$C_{NO,i}$ is the concentration of NO with ozone generator at setting i ($i = 1$ to n).

Annex D (informative)

Examples of different types of converters

D.1 Quartz converter

A silica coil heated and maintained at around 850 °C is used. The conversion efficiency is normally higher than 96 %.

Advantages: almost no maintenance.

Drawbacks: an unwieldy device, which needs to be thermally isolated to avoid the radiance effects.

Consumption of electricity.

Connections between metal and glass to be verified periodically.

D.2 Low temperature converter (molybdenum)

A cartridge in stainless steel with molybdenum cuttings, from which the grease has been removed, heated and adjusted typically in the range between 300 °C and 400 °C. The conversion efficiency should be above 97 %. Replacement can be based on the manufacturer's specifications for the capacity or on the results of the test of the conversion efficiency.

D.3 Stainless steel converter

A 316 L grade stainless steel coil is used. It is heated and maintained at around 650 °C. The conversion efficiency is normally higher than 97 %.

NOTE This type of converter can be combined with a molybdenum converter to measure NH₃.

Annex E (informative)

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

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

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

$$C_{\text{dry}} = C_{\text{wet}} \frac{100\%}{100\% - h_{\text{m}}} \quad (\text{E.1})$$

where

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

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

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

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

$$u^2(C_{\text{dry}}) = (C_{\text{dry}})^2 \times \left(\frac{u^2(C_{\text{wet}})}{(C_{\text{wet}})^2} + \frac{u^2(h_{\text{m}})}{(100\% - h_{\text{m}})^2} \right) \quad (\text{E.2})$$

where :

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

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

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

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

Concentration C_{wet} of the measured component:		100 mg/m ³ on wet basis	
Standard uncertainty of the concentration $u(C_{\text{wet}})$:		6 % of measured value	
Standard uncertainty of the water vapour content $u(h_m)$:		10 % of measured value	
Water vapour content h_m %	Concentration on dry basis C_{dry} mg/m ³	Standard uncertainty $u(C_{\text{dry}})$ mg/m ³	Relative standard uncertainty $u_{\text{rel}}(C_{\text{dry}})$ %
1	101,01	6,06	6,00
2	102,04	6,13	6,00
3	103,09	6,19	6,01
4	104,17	6,27	6,01
5	105,26	6,34	6,02
6	106,38	6,42	6,03
7	107,53	6,50	6,05
8	108,70	6,59	6,06
9	109,89	6,68	6,08
10	111,11	6,78	6,10
11	112,36	6,88	6,13
12	113,64	6,99	6,15
13	114,94	7,11	6,18
14	116,28	7,23	6,22
15	117,65	7,36	6,25
16	119,05	7,49	6,30
17	120,48	7,64	6,34
18	121,95	7,79	6,39
19	123,46	7,95	6,44
20	125,00	8,13	6,50
21	126,58	8,31	6,56
22	128,21	8,50	6,63
23	129,87	8,70	6,70
24	131,58	8,92	6,78
25	133,33	9,15	6,86
26	135,14	9,40	6,95
27	136,99	9,66	7,05

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

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

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

$$C_{\text{corr}} = C_{\text{m}} \times \frac{21\% - (o_{\text{ref}})_{\text{dry}}}{21\% - (o_{\text{m}})_{\text{dry}}} \quad (\text{E.3})$$

where

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

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

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

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

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

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

where

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

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

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

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

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

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

Annex F (informative)

Example of assessment of compliance of chemiluminescence method for NO_x with requirements on emission measurements

F.1 General

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

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

F.2 Elements required for the uncertainty determinations

F.2.1 Model equation

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

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

The model equation for the concentration C_{NO} can be generally expressed as a sum of individual contributions C_i as given by Formula (F.1):

$$C_{\text{NO}} = \sum_{i=1}^N C_i \quad (\text{F.1})$$

The individual contributions C_i represent the volume concentration indicated by the analyser and additional corrections due to deviations caused by the performance characteristics of the analyser and the influence quantities such as given by Table F.1.

Table F.1 — Parameters and signal and uncertainty contributions

Number <i>i</i>	Parameter	Signal contribution C_i	Uncertainty contribution u_i
1	volume concentration indicated by the analyser	C_{read}	u_{read}
2	repeatability	C_r	$u_r = s_r$
3	lack of fit	C_{lof}	u_{lof}
4	short-term zero drift	$C_{\text{d,z}}$	$u_{\text{d,z}}$
5	short-term span drift	$C_{\text{d,s}}$	$u_{\text{d,s}}$
6	influence of ambient temperature at zero ^a	$C_{\text{t,z}}$	$u_{\text{t,z}}$
7	influence of ambient temperature at span ^a	$C_{\text{t,s}}$	$u_{\text{t,s}}$
8	influence of sample gas pressure	C_p	u_p
9	influence of sample gas flow	C_f	u_f
10	influence of supply voltage	C_v	u_v
11	cross-sensitivity (interference)	C_i	u_i
12	adjustment (calibration gas)	C_{adj}	u_{adj}
^a choose the most appropriate of both according to the level of concentration measured			

F.2.2 Combined uncertainty

The combined uncertainty $u_c(C_{\text{NO}})$ of the concentration C_{NO} is obtained by application of the law of propagation of uncertainty on Formula (F.1) which leads to a quadratic summation of the uncertainty contributions u_i listed in Table F.1:

$$u_c(C_{\text{NO}}) = \sqrt{\sum_{i=1}^N \left[\left(\frac{\partial C_{\text{NO}}}{\partial C_i} \right)^2 u^2(C_i) \right]} = \sqrt{\sum_{i=1}^N u^2(C_i)} = \sqrt{\sum_{i=1}^N u_i^2} \quad (\text{F.2})$$

The uncertainty contributions u_i are quantified on the basis of available performance characteristics of the measurement system, data from the dispersion of repeated measurements, data describing the range of influence quantities or data provided in calibration certificates. If an uncertainty contribution is not expressed as a standard uncertainty (standard deviation), a conversion to a standard uncertainty is required.

F.2.3 Expanded uncertainty

In general, the uncertainty associated to a result of measurement is expressed as an expanded uncertainty which corresponds to the combined standard uncertainty multiplied by a coverage factor k . Since most of the values of the uncertainty components u_i are determined from test data, where the probability distribution of values is rectangular for most parameters and a normal distribution for a few parameters, a factor $k = 2,0$ is used for a level of confidence of approximately 95 % since the number of measurements to determine the uncertainty contributions and the associated number of degrees of freedom is sufficiently high or a rectangular distribution is assumed.

The expanded uncertainty $U(C_{NO})$ of the concentration C_{NO} is determined using Formula (F.3):

$$U(C_{NO}) = 2,0u_c(C_{NO}) \quad (F.3)$$

NO volume fraction and standard uncertainty are given by Formula (F.4) and Formula (F.5):

$$C_{NOx} = C_{NO} + C_{NO2} \quad (F.4)$$

$$u^2(C_{NOx}) = u^2(C_{NO}) + u^2(C_{NO2}) \quad (F.5)$$

If the conversion efficiency is not equal to 100 %, the NO_x concentration $C_{NOx,stack}$ in the stack is not equal to the NO_x concentration C_{NOx} given by the analyser. The concentration $C_{NOx,stack}$ is equal to the sum of the NO_2 concentration $C_{NO2,stack}$ and the NO concentration $C_{NO,stack}$ in stack. For the NO measurement, the converter has no effect and it can be considered that $C_{NO,stack} = C_{NO}$, where C_{NO} is the concentration given by the analyser. This leads to Formula (F.6) to Formula (F.8):

$$C_{NOx,stack} = C_{NO,stack} + C_{NO2,stack} \quad (F.6)$$

$$C_{NOx,stack} = C_{NO} + \frac{C_{NO2}}{\eta} \times 100\% \quad (F.7)$$

$$C_{NOx,stack} = C_{NO} + \frac{C_{NOx} - C_{NO}}{\eta} \times 100\% \quad (F.8)$$

The values C_{NO} and C_{NOx} are correlated. Then the standard uncertainty associated to the NO_x concentration is given by Formula (F.9):

$$u_c^2(C_{NOx,stack}) = \left(\frac{\partial C_{NOx,stack}}{\partial C_{NO}}\right)^2 \times u^2(C_{NO}) + \left(\frac{\partial C_{NOx,stack}}{\partial C_{NOx}}\right)^2 \times u^2(C_{NOx}) + \left(\frac{\partial C_{NOx,stack}}{\partial \eta}\right)^2 \times u^2(\eta) \\ + 2 \times \left(\frac{\partial C_{NOx,stack}}{\partial C_{NO}}\right) \times \left(\frac{\partial C_{NOx,stack}}{\partial C_{NOx}}\right) \times u(C_{NO}) \times u(C_{NOx}) \times r(C_{NO}, C_{NOx}) \quad (F.9)$$

where

$$\left(\frac{\partial C_{NOx,stack}}{\partial C_{NO}}\right) = \frac{\eta - 100\%}{\eta} \quad (F.10)$$

$$\left(\frac{\partial C_{NOx,stack}}{\partial C_{NOx}}\right) = \frac{100\%}{\eta} \quad (F.11)$$

$$\left(\frac{\partial C_{NOx,stack}}{\partial \eta}\right) = \frac{(-C_{NOx} + C_{NO}) \times 100\%}{\eta^2} \quad (F.12)$$

and

$r(C_{NO}, C_{NOx})$ is the correlation factor.

This leads to Formula (F.13):

$$\begin{aligned}
 u_c^2(C_{\text{NOx,stack}}) &= \left(\frac{\eta-100\%}{\eta}\right)^2 \times u^2(C_{\text{NO}}) + \left(\frac{100\%}{\eta}\right)^2 \times u^2(C_{\text{NOx}}) \\
 &+ \left(\frac{100\% \times (C_{\text{NO}} - C_{\text{NOx}})}{\eta^2}\right)^2 \times u^2(\eta) \\
 &+ 2 \times \left(\frac{\eta-100\%}{\eta}\right) \times \left(\frac{100\%}{\eta}\right) \times u(C_{\text{NO}}) \times u(C_{\text{NOx}}) \times r(C_{\text{NO}}, C_{\text{NOx}})
 \end{aligned} \tag{F.13}$$

where $u(C_{\text{NOx}})$ is calculated in the same way as $u(C_{\text{NO}})$.

As the variation in the NO_x concentration goes in the same direction as the variation of the NO concentration, the correlation factor $r(C_{\text{NO}}, C_{\text{NOx}})$ is positive or equal to zero. The value $((\eta-100\%)/\eta) \times (100\%/\eta)$ is negative. Then the last term of the equation is negative. The uncertainty is maximised by considering this term as equal to zero.

In this case the calculation is simplified and given by Formula (F.14):

$$u_c^2(C_{\text{NOx,stack}}) = \left(\frac{\eta-100\%}{\eta}\right)^2 \times u^2(C_{\text{NO}}) + \left(\frac{100\%}{\eta}\right)^2 \times u^2(C_{\text{NOx}}) + \left(\frac{100\% \times (C_{\text{NO}} - C_{\text{NOx}})}{\eta^2}\right)^2 \times u^2(\eta) \tag{F.14}$$

F.2.4 Determination of uncertainty contributions in case of rectangular distributions

In the case of rectangular distributions the standard uncertainty u_i is calculated according to EN ISO 14956 by Formula (F.15):

$$u_i = \sqrt{\frac{(C_{i,\text{max}} - C_{i,\text{adj}})^2 + (C_{i,\text{min}} - C_{i,\text{adj}})(C_{i,\text{max}} - C_{i,\text{adj}}) + (C_{i,\text{min}} - C_{i,\text{adj}})^2}{3}} \tag{F.15}$$

where

$C_{i,\text{min}}$ is the minimum value of the average reading influenced by parameter i ;

$C_{i,\text{max}}$ is the maximum value of the average reading influenced by parameter i ;

$C_{i,\text{adj}}$ is the value of the average reading during adjustment.

Equation (F.15) can be simplified in the following cases:

- if the value $C_{i,\text{adj}}$ is at the centre of the interval bounded by the maximum value $C_{i,\text{max}}$ and the minimum value $C_{i,\text{min}}$ of all values C_i , then the standard uncertainty u_i is given by Formula (F.16):

$$u_i = \frac{(C_{i,\text{max}} - C_{i,\text{min}})}{\sqrt{12}} \tag{F.16}$$

If the absolute value of the deviation above and below the central value is expressed by ΔC_i (see Formula (F.17)), then the standard uncertainty u_i is given by Formula (F.18)

$$|C_{i,\text{max}} - C_{i,\text{adj}}| = |C_{i,\text{min}} - C_{i,\text{adj}}| = \Delta C_i \tag{F.17}$$

$$u_i = \frac{\Delta C_i}{\sqrt{3}} \quad (\text{F.18})$$

— if the value of $C_{i,\text{adj}}$ is the same as either $C_{i,\text{min}}$ or $C_{i,\text{max}}$, then the standard uncertainty u_i is given by Formula (F.19):

$$u_i = \frac{(C_{i,\text{max}} - C_{i,\text{min}})}{\sqrt{3}} \quad (\text{F.19})$$

F.2.5 Determination of uncertainty contributions by use of sensitivity coefficients

The contribution C_i to the measured value caused by a parameter i can be calculated by use of the value X_i of the parameter and a corresponding sensitivity coefficient b_i of this parameter as shown by Formula (F.20):

$$C_i = b_i X_i \quad (\text{F.20})$$

The contribution of a variation of the parameter to the total uncertainty of the measured values can be calculated from the range of values of the parameter in the considered application and the sensitivity coefficient of this parameter determined in the laboratory test of the analyser by use of Formula (F.21):

$$u_i = |b_i| u(X_i) \quad (\text{F.21})$$

where

- u_i is the uncertainty contribution to the total uncertainty of the measured values caused by a variation of the parameter i ;
- b_i is the sensitivity coefficient of the parameter i ;
- $u(X_i)$ is the standard uncertainty due to variation of the parameter i .

The variation of the parameter i can be converted to a standard uncertainty by use of Formulae (F.15) to (F.19).

F.3 Example of an uncertainty calculation

F.3.1 Site specific conditions

Table F.2 gives the specific conditions at the site, that is to say the values and the variation ranges of the influence quantities used in this example.

Table F.2 — Site specific conditions and values or ranges of influence parameters applied for the example

Specific conditions	Value or range
Studied concentration of NO _x (limit value of NO _x for the site) expressed at standard conditions of temperature and pressure and at oxygen reference volume concentration	200 mg/m ³ expressed as NO ₂
Oxygen reference volume concentration	11 %
Ratio NO ₂ /NO _x	10 %
Conditions in the field	
Sample volume flow	60 l/h ± 5 l/h
Temperature during adjustment	285 K
Fluctuations of ambient temperature during measurement	283 K to 308 K
Voltage variation	230 V × (1 ± 5 %)
Gas pressure during adjustment	99 kPa
Gas pressure variation	99 kPa to 100 kPa
CO ₂ volume concentration variations	8 % to 15 %
NH ₃ mass concentration variations	0 mg/m ³ to 20 mg/m ³
Calibration gas (volume concentration of NO in N ₂ , without interferent)	180 × 10 ⁻⁶ × (1 ± 2 %)

F.3.2 Performance characteristics of the method

Table F.3 gives the performance characteristics of the method used in this example. These parameters can have an influence on the response of the analyser and include the metrological performance of the analyser and the effect of influence quantities (environmental conditions like ambient temperature, voltage, pressure and chemical interferents).

Table F.3 — Performance characteristics

Performance characteristic	Performance criterion	Results of laboratory and field tests
Response time	≤ 200 s	120 s
Repeatability standard deviation in the laboratory at zero point	$\leq 1,0$ % ^a	0,65 % ^a
Repeatability standard deviation in the laboratory at span point	$\leq 2,0$ % ^a	0,8 % ^a
Lack of fit	$\leq 2,0$ % ^a	0,7 % ^a
Short-term zero drift	$\leq 2,0$ % ^a	0,01 % ^a
Short-term span drift	$\leq 2,0$ % ^a	0,5 % ^a
Influence of ambient temperature change from 5 °C to 25 °C and from 40 °C to 20 °C at zero point	$\leq 5,0$ % ^a	0,5 % ^a
Influence of ambient temperature change from 5 °C to 25 °C and from 40 °C to 20 °C at span point	$\leq 5,0$ % ^a	1,0 % ^a
Influence of sample gas pressure at span point, for a pressure change Δp of 3 kPa	$\leq 2,0$ % ^a	1,6 % of the measured value
Influence of sample volume flow, for flow change of 10 l/h	$\leq 2,0$ % ^a	1,0 % ^a
Influence of voltage, for a voltage change of 10 V at span point	$\leq 2,0$ % ^a	0,12 % ^a
Cross-sensitivity CO ₂ (15 %) NH ₃ (20 mg/m ³)	total: $\leq 4,0$ % ^a	-2,6 mg/m ³ expressed as NO ₂ 1,5 mg/m ³ expressed as NO ₂
Losses of NO ₂ in the P-AMS	$< 10,0$ %	8 %
Drift of conversion efficiency between two calibrations		3 % (absolute)
Repeatability standard deviation of conversion efficiency		1,0 % (absolute)
Adjustment with calibration gases		2,0 % of the measured value
^a expressed in percent of the range		

F.3.3 Calculation of concentration values

Based on the studied concentration range of NO_x, the NO₂/NO_x ratio and the losses of NO₂ in the P-AMS given in Table F.2 and Table F.3, the following concentration values are calculated:

$$C_{\text{NOx,stack}} = C_{\text{NO,stack}} + C_{\text{NO}_2,\text{stack}} = C_{\text{NO}} + \frac{C_{\text{NO}_2}}{0,92} = C_{\text{NO}} + \frac{10}{90} \times C_{\text{NO}} = 1,1208 C_{\text{NO}}$$

$$C_{\text{NO}} = C_{\text{NO,stack}} = 178,4 \frac{\text{mg}}{\text{m}^3} \text{ expressed as NO}_2$$

$$C_{\text{NO}_2} = \frac{10}{90} \times 178,4 \frac{\text{mg}}{\text{m}^3} = 19,83 \frac{\text{mg}}{\text{m}^3} \text{ expressed as NO}_2$$

$$C_{\text{NO}_2,\text{stack}} = \frac{C_{\text{NO}_2}}{0,92} = 21,55 \frac{\text{mg}}{\text{m}^3} \text{ expressed as NO}_2$$

F.3.4 Determination of the uncertainty contributions

The relevant uncertainty contributions are determined as follows:

a) Volume concentration indicated by the analyser

The uncertainty u_{read} related to the reading of the concentration is due to the resolution of the analyser and of the data acquisition. It can be considered as negligible.

b) Repeatability

The standard uncertainty u_r due to repeatability is equal to the repeatability standard deviation s_r calculated from the results of the repetitions of the measurements.

Several tests can be carried out at different concentrations but only one of the values is included in the calculation of the uncertainty budget e.g.

- the repeatability standard deviation corresponding to the closest concentration measured in stack;
- the highest (relative) repeatability standard deviation whatever is the concentration measured in stack.

c) Lack of fit

If $C_{\text{lof,max}}$ is the maximum deviation between measured values and the corresponding values given by the linear regression achieved during the laboratory test, then it can be assumed that the lack of fit has an equal probability to take any value in the interval $[-C_{\text{lof,max}}; +C_{\text{lof,max}}]$. The standard uncertainty u_{lof} is calculated by application of a rectangular probability distribution according to Formula (F.22):

$$u_{\text{lof}} = \frac{C_{\text{lof,max}}}{\sqrt{3}} \tag{F.22}$$

d) Short-term zero drift

It can be assumed that the zero drift $C_{\text{d,z}}$ has an equal probability to take any value in the interval $[-C_{\text{d,z}}; +C_{\text{d,z}}]$. The standard uncertainty $u_{\text{d,z}}$ is calculated by application of a rectangular probability distribution according to Formula (F.23):

$$u_{d,z} = \frac{C_{d,z}}{\sqrt{3}} \quad (\text{F.23})$$

e) Short-term span drift

It can be assumed that the span drift $C_{d,s}$ has an equal probability to take any value in the interval $[-C_{d,s}; +C_{d,s}]$. The standard uncertainty $u_{d,s}$ is calculated by application of a rectangular probability distribution according to Formula (F.24):

$$u_{d,s} = \frac{C_{d,s}}{\sqrt{3}} \quad (\text{F.24})$$

f) Cross-sensitivity (interference)

Particularly with chemical components, deviations created by different interferences occur at the same time in the same proportion, i.e. the standard uncertainties of those substances are correlated. To avoid underestimation of additive effects and overestimation of effects by compensation, EN ISO 14956 recommends to determine the sum of all standard uncertainties of interferences with a positive impact on the measured value and the sum of all standard uncertainties of interferences with a negative impact on the measured value and to retain the highest sum as the representative value for all interferences.

Cross-sensitivity is tested in the laboratory test for one concentration of an interferent and is supposed to be proportional to the value of the interferent. The correction $C_{i,j}$ of the cross-sensitivity of an interferent j is also proportional to its variation $X_{i,j}$:

$$C_{i,j} = b_{i,j} X_{i,j} \quad (\text{F.25})$$

where $b_{i,j}$ is the (constant) sensitivity coefficient of interferent j determined in the laboratory test.

In general, the concentration of the interferent in the calibration gas used for adjustment of the analyser is equal to zero.

If the maximum deviation $C_{ip,j}$ of the measured value caused by interferent j or the maximum value $X_{ip,j}$ of interferent j with a positive impact on the measured value are known only, then it can be assumed that a deviation caused by this interferent has an equal probability to take any value in the interval between zero and the maximum value. In this case the corresponding standard uncertainty $u_{ip,j}$ is given by Formula (F.26):

$$u_{ip,j} = \frac{C_{ip,j}}{\sqrt{3}} = |b_{ip,j}| \frac{X_{ip,j}}{\sqrt{3}} \quad (\text{F.26})$$

If the value $X_{ip,j,adj}$ during the adjustment of the analyser and the minimum and maximum value, $X_{ip,j,min}$ and $X_{ip,j,max}$, during the measurement period are known, then the standard uncertainty of interferent j with a positive impact on the measured value can be calculated on the basis of Formulae (F.15) and (F.20) according to Formula (F.27):

$$u_{ip,j} = |b_{ip,j}| \sqrt{\frac{(X_{ip,j,max} - X_{ip,j,adj})^2 + (X_{ip,j,min} - X_{ip,j,adj})(X_{ip,j,max} - X_{ip,j,adj}) + (X_{ip,j,min} - X_{ip,j,adj})^2}{3}} \quad (\text{F.27})$$

If the value $X_{ip,j,adj}$ during the adjustment of the analyser is zero, then the standard uncertainty of interferent j with a positive impact on the measured value is given by Formula (F.28):

$$u_{ip,j} = |b_{ip,j}| \sqrt{\frac{(X_{ip,j,max})^2 + (X_{ip,j,min})(X_{ip,j,max}) + (X_{ip,j,min})^2}{3}} \quad (F.28)$$

The sum of all standard uncertainties of interferents with a positive impact on the measured value is calculated by Formula (F.29):

$$u_{ip} = \sum_{j=1}^p u_{ip,j} \quad (F.29)$$

The standard uncertainties $u_{in,j}$ and the sum u_{in} of all standard uncertainties of interferents with a negative impact on the measured value are calculated in the same manner as the uncertainties of interferents with a positive impact:

$$u_{in} = \sum_{j=1}^n u_{in,j} \quad (F.30)$$

The standard uncertainty u_i due to cross-sensitivity caused by correlated interferents is the maximum value of u_{ip} and u_{in} :

$$u_i = \max(u_{ip}; u_{in}) \quad (F.31)$$

Uncorrelated interferents are treated individually.

g) Influence quantities

Influence quantities such as ambient temperature, atmospheric pressure, sample gas flow and supply voltage are tested in the laboratory test for one value of the quantity and the effects of the influence quantities are supposed to be proportional to the value of the quantity. The correction C_i of the effect of an influence quantity i is also proportional to its variation X_i (see Formula (F.32)):

$$C_i = b_i X_i \quad (F.32)$$

where b_i is the (constant) sensitivity coefficient of influence quantity i determined in the laboratory test.

The calculation of the standard uncertainty associated with the correction of deviations caused by variations of influence quantities depends on the value $X_{i,adj}$ of the influence quantity during the adjustment of the analyser and the minimum and maximum value, $X_{i,min}$ and $X_{i,max}$, of the influence quantity during the measurement period. The uncertainty can be calculated by use of Formulae (F.4) to (F.10) either by use of the sensitivity coefficient and the deviations of the values of the influence quantity or directly from the deviations of the measured values.

h) Adjustment

The standard uncertainty u_{adj} is calculated from the uncertainty of the calibration gas. In general, the uncertainty given by manufacturer is an expanded uncertainty U_{cal} . For a level of confidence of 95 % the standard uncertainty u_{adj} is approximately given by Formula (F.33):

$$u_{\text{adj}} = \frac{U_{\text{cal}}}{2,0} \quad (\text{F.33})$$

If the expanded uncertainty is expressed as a relative uncertainty $U_{\text{cal,rel}}$ in form of a percentage value, the standard uncertainty of the correction at the concentration C_{NO} is given by Formula (F.34):

$$u_{\text{adj}} = \frac{U_{\text{cal,rel}} C_{\text{NO}}}{2,0} \quad (\text{F.34})$$

F.3.5 Result of uncertainty calculation

F.3.5.1 Standard uncertainties

Table F.4 presents the results of the uncertainty calculation based on the data presented in Table F.2 und Table F.3.

Table F.4 — Results of uncertainties calculation

Parameter	Standard uncertainty	Value of standard uncertainty at limit value (in mg/m ³)
Repeatability in laboratory at span level	u_r	$ 0,8\% \times 200 = 1,60$
Lack of fit	u_{lof}	$\frac{ 0,7\% \times 200}{\sqrt{3}} = 0,81$
Short-term zero drift	$u_{\text{d,z}}$	$\frac{ 0,01\% \times 200}{\sqrt{3}} = 0,01$
Short-term span drift	$u_{\text{d,s}}$	$\frac{ 0,5\% \times 200}{\sqrt{3}} = 0,58$
Influence of sample gas flow	u_f	$\left \frac{1\%}{10} \right \times 200 \times \frac{5}{\sqrt{3}} = 0,58$
Influence of sample gas pressure	u_p	$\left \frac{1,6\%}{3} \right \times 198,2 \times \frac{100-99}{\sqrt{3}} = 0,61$ for NO _x $\left \frac{1,6\%}{3} \right \times 178,4 \times \frac{100-99}{\sqrt{3}} = 0,55$ for NO
Influence of ambient temperature	$u_{\text{t,s}}$	$\left \frac{1\%}{20} \right \times 200 \times \sqrt{\frac{(308-285)^2 + (308-285)(283-285) + (283-285)^2}{3}} = 1,27$
Influence of supply voltage	u_v	$\left \frac{0,12\%}{10} \right \times 200 \times \frac{(230/100 \times 5)}{\sqrt{3}} = 0,16$
Interferent: NH ₃	$u_{\text{i,NH}_3}$	$\frac{1,5}{20} \times \sqrt{\frac{20^2}{3}} = 0,87$

Interferent: CO ₂	u_{i,CO_2}	$\frac{ -2,6 }{15} \times \sqrt{\frac{15^2 + 15 \times 8 + 8^2}{3}} = 2,03$
Uncertainty of calibration gas	u_{adj}	$\frac{2\% \times 198,2}{2} = 1,98$ for NO _x $\frac{2\% \times 178,4}{2} = 1,78$ for NO $\frac{2\% \times 19,83}{2} = 0,20$ for NO ₂
Conversion efficiency	u_{η}	$\sqrt{\left(\frac{3}{\sqrt{3}}\right)^2} + 1,0^2 = 2,00\%$ (absolute)

F.3.5.2 Combined uncertainty

The sum of the standard uncertainties of interferents with a negative impact on the measured value is greater than the sum of all standard uncertainties of interferents with a positive impact on the measured value:

$$u_i = \max(u_{ip}; u_{in}) = 2,03 \frac{\text{mg}}{\text{m}^3} \text{ expressed as NO}_2$$

According to Formula (F.2) and Formula (F.4) the combined uncertainties of the concentration values are given by:

$$\begin{aligned}
 u_c(C_{\text{NO}_x}) &= \sqrt{\sum_{i=1}^N u_i^2} = \sqrt{u_r^2 + u_{\text{lof}}^2 + u_{\text{d,z}}^2 + u_{\text{d,s}}^2 + u_i^2 + u_{\text{t,s}}^2 + u_p^2 + u_f^2 + u_v^2 + u_{\text{adj}}^2} \\
 &= \sqrt{1,60^2 + 0,81^2 + 0,01^2 + 0,58^2 + 2,03^2 + 1,27^2 + 0,61^2 + 0,58^2 + 0,16^2 + 1,98^2} \frac{\text{mg}}{\text{m}^3} \\
 &= \sqrt{13,94} \frac{\text{mg}}{\text{m}^3} \\
 &= 3,73 \frac{\text{mg}}{\text{m}^3} \text{ expressed as NO}_2
 \end{aligned}$$

$$\begin{aligned}
 u_c(C_{\text{NO}}) &= \sqrt{\sum_{i=1}^N u_i^2} \\
 &= \sqrt{u_r^2 + u_{\text{lof}}^2 + u_{\text{d,z}}^2 + u_{\text{d,s}}^2 + u_i^2 + u_{\text{t,s}}^2 + u_p^2 + u_f^2 + u_v^2 + u_{\text{adj}}^2} \\
 &= \sqrt{1,60^2 + 0,81^2 + 0,01^2 + 0,58^2 + 2,03^2 + 1,27^2 + 0,55^2 + 0,58^2 + 0,16^2 + 1,78^2} \frac{\text{mg}}{\text{m}^3} \\
 &= \sqrt{13,12} \frac{\text{mg}}{\text{m}^3}
 \end{aligned}$$

$$= 3,6 \frac{\text{mg}}{\text{m}^3} \text{ expressed as NO}_2$$

$$u_c^2(C_{\text{NOx,stack}}) = \left(\frac{\eta - 100\%}{\eta} \right)^2 \times u^2(C_{\text{NO}}) + \left(\frac{100\%}{\eta} \right)^2 \times u^2(C_{\text{NOx}}) + \left(\frac{100\% \times (C_{\text{NO}} - C_{\text{NOx}})}{\eta^2} \right)^2 \times u^2(\eta)$$

$$u(C_{\text{NOx,stack}}) = 4,10 \frac{\text{mg}}{\text{m}^3} \text{ expressed as NO}_2$$

F.3.5.3 Expanded uncertainty

The absolute and relative expanded uncertainty of the NO mass concentration for $k = 2$ are given by:

$$U(C_{\text{NO}}) = 7,2 \frac{\text{mg}}{\text{m}^3} \text{ expressed as NO}_2$$

$$U_{\text{rel}}(C_{\text{NO}}) = 4,0\%$$

The absolute and relative expanded uncertainty of the NO_x mass concentration for $k = 2$ are given by:

$$U(C_{\text{NOx}}) = 7,5 \frac{\text{mg}}{\text{m}^3} \text{ expressed as NO}_2$$

$$U_{\text{rel}}(C_{\text{NOx}}) = 3,8\%$$

F.3.5.4 Evaluation of the compliance with the required measurement quality

The performance criterion on cross-sensitivity is met for the sum of interferences with a positive impact on the measured values as well as for the sum of interferences with a negative impact:

$$C_{\text{ip}} = 0,87\% < 4\%$$

$$|C_{\text{in}}| = 2,031\% < 4\%$$

All values of the performance characteristics obtained in the laboratory and field tests comply with the performance criteria. Therefore, the measurement method fulfils the requirements.

Annex G (informative) Example of correction of data from drift effect

Table G.1 shows a spreadsheet example based on the correction procedure given in 9.4.3.

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

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

26	A (span point)	0,994444 (E15)	0,00001481 (G15/E10)			
27	B (zero point not corrected of span)	3,000000 (E7)	-0,006667 ((F7-E7)/E10)			
28						
29	$C_{corr} = [C - (B(t_0) + \text{Drift}(B) \times t)] / [A(t_0) + \text{Drift}(A) \times t]$					
30	$C_{corr} = [C - (E27 + F27 \times t)] / [E26 + F26 \times t]$					
31	:					
32	→ $C_{corr} = (C - (3,000000 - 0,006667 * t)) / (0,994444 + 0,00001481 * t)$					
33	To apply the formula in a calculation file:					
34	<ul style="list-style-type: none"> - copy cell C32 above; - in the calculation file click on "edition - special paste - values" in the first cell dedicated to a corrected value; - insert before formula "=" then the concentration value measured and replace "t" by its value in min. 					
35						

Annex H (informative)

Significant technical changes

Table H.1 — Significant technical changes

1	Directive 2000/76/EC has been replaced by Directive 2010/75/EU
2	Normative reference to EN 13284-1 has been replaced by EN 15259 related to requirements for measurement sections and sites and for the measurement objective, plan and report. Normative reference to EN 15267-4:2017 related to performance criteria and test procedures for portable automated measuring systems for monitoring emissions from stationary sources has been added.
3	Definitions have been reviewed taking into account EN 15259 definitions and new version of VIM (2012) Detection limit is no more considered in the list of definition and in performance characteristics (repeatability at zero is more suitable)
4	Symbols and abbreviations used in the main section of the document have been added.
6.1	The use of configuration 1 is avoided when the NO ₂ concentration represents more than 20 mg/m ³ . Configuration 1 shall be ordinarily avoided when the NO ₂ /NO _x represents more than 25 %, unless it is demonstrated that the losses of NO ₂ were not significant within the gas cooler.
6.3	This clause corresponds to the previous Clause 6.
7	The performance characteristics shall be determined in a general performance test according to the test procedures described in EN 15267-4:2017 instead EN 15267-3.
9.2	For determination of homogeneity reference to the EN 15259 has been added
9.4.2.1	The test gases shall have concentrations traceable to SI units
9.4.3	Equation to calculate the concentration corrected when drift occurs has been added
11	Expression of results have been modify to be in line with EN 15259
13	According to the new rules fixed in the EN 14793, $s_{r \text{ limit}}$ has been recalculated.
Annex A	An estimate of the uncertainty calculated through the determination of reproducibility has been added and replace the expression: "reproducibility confidence interval"
Annex F	An annex giving the procedure to calculate the uncertainty associated with a concentration expressed on dry gas and at an oxygen reference concentration, has been added
Annex G	The presentation of the calculation of the uncertainty budget has been improved
Annex H	Typing errors of the table to determine the drift have been corrected

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