



# SLOVENSKI STANDARD

## SIST EN 14211:2012

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Nadomešča:  
SIST EN 14211:2005

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### Zunanji zrak - Standardna metoda za določevanje koncentracije dušikovega dioksida in dušikovega monoksida s kemiluminiscenco

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

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

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

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EUROPEAN STANDARD

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

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

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

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

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**EN 14211:2012 (E)****Foreword**

This document (EN 14211:2012) has been prepared by Technical Committee CEN/TC 264 "Air quality", the secretariat of which is held by DIN.

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of an identical text or by endorsement, at the latest by February 2013, and conflicting national standards shall be withdrawn at the latest by February 2013.

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

This document supersedes EN 14211:2005.

The technical changes made since EN 14211:2005 are listed in Annex H of this European Standard.

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

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## 1 Scope

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

The method is applicable to the determination of the concentration of nitrogen dioxide present in ambient air up to  $500 \mu\text{g}/\text{m}^3$ . This concentration range represents the certification range for  $\text{NO}_2$  for the type approval test.

The method is applicable to the determination of the concentration of nitrogen monoxide present in ambient air up to  $1\,200 \mu\text{g}/\text{m}^3$ . This concentration range represents the certification range for  $\text{NO}$  for the type approval test.

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

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

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

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

NOTE 3  $500 \mu\text{g}/\text{m}^3$  of  $\text{NO}_2$  corresponds to  $261 \text{ nmol}/\text{mol}$  of  $\text{NO}_2$  at  $20^\circ\text{C}$  and  $101,3 \text{ kPa}$ .  $1\,200 \mu\text{g}/\text{m}^3$  of  $\text{NO}$  corresponds to  $962 \text{ nmol}/\text{mol}$  of  $\text{NO}$  at  $20^\circ\text{C}$  and  $101,3 \text{ kPa}$ .

This standard contains information for different groups of users.

Clauses 5 to 7 and Annexes B and C contain general information about the principles of  $\text{NO}_x$  measurement by chemiluminescence analyser and sampling equipment.

Clause 8 and Annex E are specifically directed towards test houses and laboratories that perform type-approval testing of  $\text{NO}_x$  analysers. These sections contain information about:

- Type-approval test conditions, test procedures and test requirements;
- Analyser performance requirements;
- Evaluation of the type-approval test results;
- Evaluation of the uncertainty of the measurement results of the  $\text{NO}_x$  analyser based on the type-approval test results.

Clauses 9 to 11 and Annexes F and G are directed towards monitoring networks performing the practical measurements of  $\text{NO}_x$  in ambient air. These sections contain information about:

- Initial installation of the analyser in the monitoring network and acceptance testing;
- Ongoing quality assurance/quality control;
- Calculation and reporting of measurement results;
- Evaluation of the uncertainty of measurement results under practical monitoring conditions.

## EN 14211:2012 (E)

## 2 Normative references

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

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

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

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

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

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

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

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

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

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

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

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

## 3 Terms and definitions

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

### 3.1 adjustment

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

Note 1 to entry: Types of adjustment of a measuring system include zero adjustment of a measuring system, offset adjustment, and span adjustment (sometimes called gain adjustment).

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

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

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



### 3.2

#### **ambient air**

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

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

### 3.3

#### **analyser**

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

### 3.4

#### **availability of the analyser**

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

### 3.5

#### **calibration**

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

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

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

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

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

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

### 3.6

#### **certification range**

concentration range for which the analyser is type-approved

### 3.7

#### **check**

verification that the analyser is still operating within specified performance limits

### 3.8

#### **combined standard uncertainty**

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

[SOURCE: ENV 13005:1999]

### 3.9

#### **converter efficiency**

degree of conversion of NO<sub>2</sub> present in the sample gas into NO, given as a percentage

**EN 14211:2012 (E)****3.10****coverage factor**

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

[SOURCE: ENV 13005:1999]

**3.11****designated body**

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

**3.12****detection limit**

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

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

**3.13****expanded uncertainty**

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

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

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

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[SOURCE: ENV 13005:1999] <https://standards.iteh.ai/catalog/standards/sist/a88b57c2-898f-4fd9-986b-d2d11f059431/sist-en-14211-2012>

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

**3.14****fall time**

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

**3.15****independent measurement**

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

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

**3.16****individual measurement**

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

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

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

**3.17****influence quantity**

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

[SOURCE: ENV 13005:1999]

**3.18****interferent**

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

**3.19****lack of fit**

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

**3.20****lag time**

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

**3.21****limit value**

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

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

**3.22****long term drift**

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

**3.23****monitoring station**

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

**3.24****parallel measurements**

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

**3.25****performance characteristic**

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

**3.26****performance criterion**

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

**3.27****period of unattended operation**

time period over which the drift complies with the performance criterion for long term drift

**3.28****repeatability (of results of measurement)**

closeness of the agreement between the results of successive individual measurements of nitrogen monoxide and nitrogen dioxide carried out under the same conditions of measurement

Note 1 to entry: These conditions include:

- a) the same measurement procedure;
- b) the same observer;
- c) the same analyser, used under the same conditions;
- d) at the same location;
- e) repetition over a short period of time.

**EN 14211:2012 (E)****3.29****reproducibility under field conditions**

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

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

- a) the same measurement procedure;
- b) two identical analysers, used under the same conditions;
- c) at the same monitoring station;
- d) the period of unattended operation.

**3.30****residence time inside the analyser**

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

**3.31****residence time in the sampling system**

time period for the sampled air to be transferred to the inlet of the analyser

**3.32****response time**

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

**3.33****sampled air**

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

**3.34****sample gas temperature**

temperature of the sampled gas at the sample inlet

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

**3.35****sampling system**

the assembly of components needed to transfer ambient air to the analyser

**3.36****short-term drift**

difference between zero or span readings at the beginning and end of a 12 h period

**3.37****standard uncertainty**

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

[SOURCE: ENV 13005:1999]

**3.38****surrounding temperature**

temperature of the air directly surrounding the analyser

**3.39****total residence time**

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

**3.40****type approval**

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

**3.41****type approval test**

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

**3.42****uncertainty (of measurement)**

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

[SOURCE: ENV 13005:1999]

**4 Abbreviated terms**

FEP perfluoro-ethylene-propylene

MFC mass flow controller

PTFE polytetrafluoroethylene

**5 Principle****5.1 General**

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

**5.2 Measuring principle**

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

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

Chemiluminescence is the emission of light during a chemical reaction. During the gas-phase reaction of NO and ozone light with an intensity proportional to the concentration of NO is produced when electrons of the excited NO<sub>2</sub> molecules decay to lower energy states.

**EN 14211:2012 (E)**

This chemiluminescence method is based on the reaction



Excited nitrogen dioxide ( $\text{NO}_2^*$ ) emits radiation in the near infrared region (600 nm to 3 000 nm) with a maximum centered around 1 200 nm. For the determination of nitrogen dioxide, the nitrogen dioxide present in sampled air is converted to nitrogen monoxide in a converter as a result of the reaction:



The NO is then analysed according to the reactions (1) and (2).

The concentrations of nitrogen dioxide and nitrogen monoxide are directly measured in volume/volume units (if the analyser is calibrated using a volume/volume standard), since the emitted radiation from the chemiluminescence reaction is proportional to the concentration of nitrogen monoxide in volume/volume units. The final results for reporting are expressed in  $\mu\text{g}/\text{m}^3$  using standard conversion factors (see Clause 10).

**5.3 Type approval test**

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

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

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

Appropriate experimental evidence shall be provided by

- type approval tests performed under conditions of intended use of the specified method of measurement, and
- calculation of expanded uncertainty of results of measurement by reference to ENV 13005.

**5.4 Field operation and quality control**

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

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

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

## 6 Sampling

### 6.1 General

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

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

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

- loss of nitrogen dioxide in the sampling system;
- loss of nitrogen dioxide in the particle filter;
- formation of nitrogen dioxide due to reaction of nitrogen monoxide with ozone in the sampling system and in the analyser.

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

### 6.2 Sampling location

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

### 6.3 Sampling system

#### 6.3.1 Construction

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

- a sampling line or manifold;
- a particle filter placed between the sampling line or manifold and the analyser;
- a sampling pump in case a sampling manifold is used.

The sample inlet shall be constructed in such a way that ingress of rainwater into the sampling line or manifold is prevented. The sampling line or manifold shall be as short as practical to minimise the residence time (see also 6.3.3).

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

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