



SLOVENSKI STANDARD

SIST EN 14211:2005

01-september-2005

Učinki bUčU UfU UĖGHUUXbUa YcXUnUXc`c UbY`cbWbUfUWY
Xi ý]_cj Y[UX]c_g]XU]b`Xi ý]_cj Y[Ua cbc_g]XUg`_Ya]i a]b]gWbWt

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

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

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

Ta slovenski standard je istoveten z: EN 14211:2005

ICS:

13.040.20 Kakovost okoljskega zraka Ambient atmospheres

SIST EN 14211:2005

en,fr,de

iTeh STANDARD PREVIEW
(standards.iteh.ai)

[SIST EN 14211:2005](https://standards.iteh.ai/catalog/standards/sist/55e46b86-1947-462d-9d6a-2f8fd21aecb7/sist-en-14211-2005)

<https://standards.iteh.ai/catalog/standards/sist/55e46b86-1947-462d-9d6a-2f8fd21aecb7/sist-en-14211-2005>

EUROPEAN STANDARD

EN 14211

NORME EUROPÉENNE

EUROPÄISCHE NORM

March 2005

ICS 13.040.20

English version

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

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

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

This European Standard was approved by CEN on 10 December 2004.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

<https://standards.iteh.ai/catalog/standards/sist/55e46b86-1947-462d-9d6a-2f8fd21aecb7/sist-en-14211-2005>



EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: rue de Stassart, 36 B-1050 Brussels

Contents

	Page
Foreword.....	4
1 Scope	5
2 Normative references	5
3 Terms and definitions	6
4 Symbols and abbreviated terms	10
5 Principle.....	12
5.1 General.....	12
5.2 Measuring principle	13
5.3 Type approval test	13
5.4 Field operation and quality control.....	14
6 Sampling equipment	14
6.1 General.....	14
6.2 Sampling location.....	14
6.3 Sample inlet and sampling line.....	14
6.4 Particulate filter.....	15
6.5 Control and regulation of sample flow rate.....	15
6.6 Sampling pump for the manifold.....	15
7 Analyser equipment	16
7.1 General.....	16
7.2 Converter	16
7.3 Ozone generator	16
7.4 Reaction chamber.....	17
7.5 Optical filter	17
7.6 Detector	17
7.7 Ozone removal device.....	17
7.8 Sampling pump for the analyser	17
7.9 Residence time inside the analyser	17
8 Type approval of nitrogen dioxide and nitrogen monoxide analysers	17
8.1 General.....	17
8.2 Relevant performance characteristics and performance criteria	18
8.3 Design change	20
8.4 Procedures for determination of the performance characteristics during the laboratory test	21
8.5 Determination of the performance characteristics during the field test.....	32
8.6 Expanded uncertainty calculation for type approval	36
9 Field operation and ongoing quality control	36
9.1 General.....	36
9.2 Suitability evaluation	37
9.3 Initial installation.....	38
9.4 Ongoing quality control	38
9.5 Calibration of the analyser.....	40
9.6 Checks	41
9.7 Maintenance	44
9.8 Data handling and data reports.....	44
10 Expression of results	45
11 Test reports and documentation.....	45
11.1 Type approval test	45

11.2	Field operation	45
Annex A (normative)	Calculation of residence times for a maximum allowable NO ₂ increase in the sampling line [ISO 13964]	47
Annex B (normative)	Test of lack of fit	48
Annex C (informative)	Sampling equipment	50
Annex D (informative)	Sampling on microscale [2]	52
Annex E (informative)	Types of chemiluminescence analysers	53
Annex F (informative)	Manifold testing equipment	56
Annex G (normative)	Type approval	57
Annex H (normative)	Calculation of uncertainty in field operation at the hourly limit value	76
Annex I (normative)	Calculation of uncertainty in field operation at the annual limit value	82
	Bibliography	92

iTeh STANDARD PREVIEW
(standards.iteh.ai)

[SIST EN 14211:2005](#)

<https://standards.iteh.ai/catalog/standards/sist/55e46b86-1947-462d-9d6a-2f8fd21aecb7/sist-en-14211-2005>

Foreword

This document (EN 14211:2005) 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 September 2005, and conflicting national standards shall be withdrawn at the latest by September 2005.

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

iTeh STANDARD PREVIEW (standards.iteh.ai)

[SIST EN 14211:2005](https://standards.iteh.ai/catalog/standards/sist/55e46b86-1947-462d-9d6a-2f8fd21aecb7/sist-en-14211-2005)

<https://standards.iteh.ai/catalog/standards/sist/55e46b86-1947-462d-9d6a-2f8fd21aecb7/sist-en-14211-2005>

1 Scope

This document specifies a continuous measurement method for the determination of the concentration of nitrogen dioxide and nitrogen monoxide present in ambient air based on the chemiluminescence measuring principle. This document 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 Directives data quality requirements and requirements during sampling, calibration and quality assurance.

The method is applicable to the determination of the concentration of nitrogen dioxide present in ambient air from $0 \mu\text{g}/\text{m}^3$ to $500 \mu\text{g}/\text{m}^3$. This concentration range represents the certification range for NO_2 for the type approval test.

NOTE 1 $0 \mu\text{g}/\text{m}^3$ to $500 \mu\text{g}/\text{m}^3$ of NO_2 corresponds to 0 nmol/mol to 261 nmol/mol of NO_2 .

The method is applicable to the determination of the concentration of nitrogen monoxide present in ambient air from $0 \mu\text{g}/\text{m}^3$ to $1\,200 \mu\text{g}/\text{m}^3$. This concentration range represents the certification range for NO for the type approval test.

NOTE 2 $0 \mu\text{g}/\text{m}^3$ to $1\,200 \mu\text{g}/\text{m}^3$ of NO corresponds to 0 nmol/mol to 962 nmol/mol of NO .

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.

NOTE 3 Lower ranges may be used for measurement systems applied at rural locations monitoring Ecosystems.

The results are expressed in $\mu\text{g}/\text{m}^3$ (at 293 K and 101,3 kPa).

When the standard is used for other purposes than the EU Directive, the range and uncertainty requirements need not apply.

[SIST EN 14211:2005](https://standards.iteh.ai/catalog/standards/sist/55e46b86-1947-462d-9d6a-2f8fd21aecb7/sist-en-14211-2005)

<https://standards.iteh.ai/catalog/standards/sist/55e46b86-1947-462d-9d6a-2f8fd21aecb7/sist-en-14211-2005>

2 Normative references

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

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

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

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

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

ISO 6144, *Gas analysis — Preparation of calibration gas mixtures — Static volumetric method*

ISO 6145 (all parts), *Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods*

ISO 13964:1998, *Air quality — Determination of ozone in ambient air — Ultraviolet photometric method*

EN 14211:2005 (E)

3 Terms and definitions

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

3.1

ambient air

outdoor air in the troposphere, excluding workplace air¹

3.2

sample gas temperature

temperature at the sample inlet outside the monitoring station

3.3

availability of the analyser

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

3.4

certification range

concentration range for which the analyser is type approved

3.5

calibration

comparison of the analyser response to a known gas concentration with a known uncertainty

3.6

combined standard uncertainty

calculation result of combining the uncertainties determined from all performance characteristics specified in this document according to the prescribed procedures given in this document

<https://standards.iteh.ai/catalog/standards/sist/55e46b86-1947-462d-9d6a-2f8fd21aecb7/sist-en-14211-2005>

3.7

converter efficiency

degree of conversion of NO₂ present in the sample gas into NO, given as a percentage

3.8

coverage factor

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

3.9

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

NOTE It is recommended that the designated body is accredited for the specific task according to EN ISO/IEC 17025.

3.10

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 for the purpose of this document 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 %

¹ As stated in the relevant EU legislation.

3.11**fall time**

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

3.12**independent measurement**

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

3.13**individual measurement**

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

3.14**influence quantity**

quantity that is not the measurand but that affects the result of the measurement (VIM 2.7), either an interferent influence quantity (i.e. the concentration of a substance in the air under investigation that is not the measurand), or an external influence quantity (i.e. a quantity that is not the measurand nor the concentration of a substance in the air mass under investigation)

NOTE Examples are:

- presence of interfering gases in the flue gas matrix (interferent influence quantity);
- temperature of the surrounding air (external influence quantity);
- atmospheric pressure (external influence quantity);
- pressure of the gas sample (external influence quantity).

iTeh STANDARD PREVIEW
(standards.iteh.ai)

3.15**interference**

response of the analyser to interferents

3.16**interferent**

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

[SIST EN 14211:2005](https://standards.iteh.ai/catalog/standards/sist/55e46b86-1947-462d-9d6a-2f8fd21aeb7/sist-en-14211-2005)

[https://standards.iteh.ai/catalog/standards/sist/55e46b86-1947-462d-9d6a-](https://standards.iteh.ai/catalog/standards/sist/55e46b86-1947-462d-9d6a-2f8fd21aeb7/sist-en-14211-2005)

[2f8fd21aeb7/sist-en-14211-2005](https://standards.iteh.ai/catalog/standards/sist/55e46b86-1947-462d-9d6a-2f8fd21aeb7/sist-en-14211-2005)

3.17**lag 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 10 % of the stable output reading

3.18**lag time (fall)**

lag time for a negative step change

3.19**lag time (rise)**

lag time for a positive step change

3.20**limit value**

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

3.21**lack of fit**

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

EN 14211:2005 (E)**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 NO_x analyser has been installed to monitor nitrogen monoxide and dioxide concentrations in such a way that its performance and operation complies with the prescribed requirements

3.24**parallel measurement**

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 is within 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 the same measurand carried out under the same conditions of measurement [1]

NOTE

- These conditions are called laboratory repeatability conditions and include:
- the same measurement procedure;
 - the same observer;
 - the same analyser, used under the same conditions;
 - at the same location;
 - repetition over a short period of time.

3.29**reproducibility under field conditions**

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

NOTE

- These conditions are called field reproducibility conditions and include:
- the same measurement procedure;
 - two identical analysers, used under the same conditions;
 - at the same monitoring station;
 - 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 transported from the sampling inlet (of the sampling system) 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 90 % of the stable output reading

3.33**response time (fall)**

response time to a negative step change

NOTE Response time (fall) is the sum of the lag time (fall) and the fall time.

3.34**response time (rise)**

response time to a positive step change

NOTE Response time (rise) is the sum of the lag time (rise) and the rise time.

3.35**rise time**

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

3.36**sampled air**

ambient air that has been sampled through the sampling inlet and sampling system

3.37**sampling inlet**

entrance to the sampling system where ambient air is collected from the atmosphere

3.38**short-term drift**

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

3.39**standard uncertainty**

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

[ENV 13005]

3.40**surrounding temperature**

temperature of the air directly surrounding the analyser (temperature inside the monitoring station or laboratory)

3.41**total residence time**

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

3.42**type approval**

decision taken by a designated body that the pattern of an analyser conforms to the requirements as laid down in this document

3.43**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

EN 14211:2005 (E)

3.44

uncertainty (of measurement)

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

4 Symbols and abbreviated terms

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

A_a	availability of the analyser
A_v	average concentration of the measurand during the field test
b_{gp}	sensitivity coefficient of the analyser to sample gas pressure change
b_{gt}	sensitivity coefficient of the analyser to sample gas temperature change
b_{st}	sensitivity coefficient of the analyser to surrounding air temperature change
b_v	sensitivity coefficient of the analyser to electrical voltage change
C	NO concentration of the applied gas
C_{P1}	average concentration of the measurements at sampling gas pressure P1
C_{P2}	average concentration of the measurements at sampling gas pressure P2
$C_{s,1}$	average concentration of the measurements at span level at the beginning of the drift period
$C_{s,2}$	average concentration of the measurements at span level at the end of the drift period
c_t	test gas concentration
C_{T1}	average concentration of the measurements at sample gas temperature T_1
C_{T2}	average concentration of the measurements at sample gas temperature T_2
C_{V1}	average concentration reading of the measurements at voltage V_1
C_{V2}	average concentration reading of the measurements at voltage V_2
$C_{z,1}$	average concentration of the measurements at zero at the beginning of the drift period
$C_{z,2}$	average concentration of the measurements at zero at the end of the drift period
C_{const}^{av}	average of at least four independent measurements during the constant concentration period (t_c)
C_{var}^{av}	average of at least four independent measurements during the variable concentration period (t_v)
\overline{d}_f	average difference of parallel measurements
$d_{f,i}$	the i th difference in a parallel measurement
$D_{l,s}$	long-term drift at span concentration c_t

$D_{l,z}$	long-term drift at zero
$D_{s,s}$	short-term drift at span level
$D_{s,z}$	short-term drift at zero
D_{sc}	difference sample/calibration port
E_{conv}	converter efficiency
E_{ss}	sample system collection efficiency
F_r	response factor in concentration units per voltage output of the analyser
P_1	sampling gas pressure P_1
P_2	sampling gas pressure P_2
R_d	mean analyser response to the test gas directly sampled by the analyser
R_m	mean analyser response to the test gas via the sample manifold
$s_{r,z}$	repeatability standard deviation at zero
$s_{r,ct}$	repeatability standard deviation at concentration c_t
$s_{r,f}$	reproducibility standard deviation under field conditions
s_l	repeatability standard deviation
T	surrounding air temperature
T_1	surrounding air temperature at the laboratory
T_1	sample gas temperature T_1
T_2	sample gas temperature T_2
t_d	relative difference between response time (rise) and response time (fall)
t_f	response time (fall)
t_r	response time (rise)
t_t	time period of the field test minus the time for calibration, conditioning and maintenance
t_u	total time period with validated measuring data
t_v	whole number of t_{NO} and t_{zero} pairs
V_1	minimum voltage V_{min} (V) specified by the manufacturer
V_2	maximum voltage V_{max} (V) specified by the manufacturer
\bar{x}	average of measurements
x_1	first average of the measurements at T_1 just after calibration

EN 14211:2005 (E)

x_z	average of the measurements at zero
x_2	second average of the measurements at T_1 just before calibration
x_{ct}	average of the measurements at concentration c_t
X_{av}	averaging effect
x_c	average of the measurements using the calibration port
$X_{CO_2,z,ct}$	influence quantity of CO_2 with concentration 500 $\mu\text{mol/mol}$
$X_{H_2O,z,ct}$	influence quantity of H_2O with concentration 19 mmol/mol
x_i	the i th measurement
$X_{int,ct}$	influence quantity of the interferent at concentration c_t
$X_{int,z}$	influence quantity of the interferent at zero
X_l	largest residual from the linear regression function at concentrations higher than zero
$X_{l,z}$	residual from the linear regression function at zero concentration
$X_{NH_3,z,ct}$	influence quantity of NH_3 with concentration 200 nmol/mol
$X_{O_3,z,ct}$	influence quantity of O_3 with concentration 200 nmol/mol
x_s	average of the measurements using the sample port
X_s	difference between the readings of two consecutive span checks
x_T	average of the measurements at T_{\min} or T_{\max}
X_z	difference between the readings of the recent zero check and the most recent calibration
$(x_{1,t})_i$	the i th measurement result of analyser 1;
$(x_{2,t})_i$	the i th measurement result of analyser 2 at the same time as the measurement of analyser 1;
Z_1	reading of the first zero check
Z_2	reading of the second zero check
ΔP_m	measured pressure drop induced by the manifold pump
ΔR_a	change in the analyser's response due to the influence of the pressure drop induced by the manifold pump, expressed as a percentage

5 Principle

5.1 General

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

Chemiluminescence is the emission of light during a chemical reaction. During the gas-phase reaction of NO and ozone light with an intensity proportional to the concentration of NO is produced when electrons of the excited NO₂ molecules decay to lower energy states.

This chemiluminescence method is based on the reaction



Excited nitrogen dioxide (NO₂^{*}) 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 µg/m³ 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 document test procedures are described for the determination of the actual values of the performance characteristics for at least two analysers in a laboratory and two analysers in the field. 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 relevant EU directives can be satisfied.