



**SLOVENSKI STANDARD**  
**oSIST prEN 14792:2015**  
**01-januar-2015**

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**Emisije nepremičnih virov - Določevanje masne koncentracije dušikovih oksidov - Standardna referenčna metoda: kemiluminiscenca**

Stationary source emissions - Determination of mass concentration of nitrogen oxides - Standard reference method: chemiluminescence

Emissionen aus stationären Quellen - Bestimmung der Massenkonzentration von Stickstoffoxiden - Standardreferenzverfahren: Chemilumineszenz

Emissions de sources fixes - Détermination de la concentration massique des oxydes d'azote - Méthode de référence normalisée : chimiluminescence

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**DRAFT**  
**prEN 14792**

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English Version

**Stationary source emissions - Determination of mass  
concentration of nitrogen oxides - Standard reference method:  
chemiluminescence**

Emissions de sources fixes - Détermination de la  
concentration massique des oxydes d'azote - Méthode de  
référence normalisée : chimiluminescence

Emissionen aus stationären Quellen - Bestimmung der  
Massenkonzentration von Stickstoffoxiden -  
Standardreferenzverfahren: Chemilumineszenz

This draft European Standard is submitted to CEN members for enquiry. It has been drawn up by the Technical Committee CEN/TC 264.

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

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## Foreword

This document (prEN 14792:2014) has been prepared by Technical Committee CEN/TC 264 "Air quality", the secretariat of which is held by DIN.

This document is currently submitted to the CEN Enquiry.

This document will supersede EN 14792:2005.

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

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SIST EN 14792:2017

<https://standards.iteh.ai/catalog/standards/sist/7f42411a-da58-423d-9c17-15ace02b6584/sist-en-14792-2017>

## 1 Scope

This European Standard specifies the standard reference method (SRM) based on the chemiluminescence principle for the determination of the nitrogen oxides ( $\text{NO}_x$ ) 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 measuring systems based on this measurement method. It applies for periodic monitoring and for the calibration or control of automatic 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 prEN 14793.

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  $0 \text{ mg/m}^3$  to  $1\,300 \text{ mg/m}^3$  of  $\text{NO}_2$  for large combustion plants and  $0 \text{ mg/m}^3$  to  $400 \text{ mg/m}^3$  of  $\text{NO}_2$  for waste incineration, according to emission limit values (ELV) laid down in the Directive 2010/75/EC.

The ELV for  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ) in EU directives are expressed in  $\text{mg/m}^3$  of  $\text{NO}_2$  on a dry basis, at a specified value for oxygen and at reference 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 F.

## 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.

prEN 14793:2014, *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 15267-3:2007, *Air quality — Certification of automated measuring systems — Part 3: Performance criteria and test procedures for automated measuring systems for monitoring 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/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,  $\text{NO}_x$  is defined as the sum of  $\text{NO}$  and  $\text{NO}_2$ . The mass concentration of  $\text{NO}_x$  is expressed as the equivalent  $\text{NO}_2$  concentration in milligrams per cubic metre at normal conditions.

**3.1****adjustment of a measuring system**

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

[SOURCE: JCGM 200:2012]

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

**3.2****ambient temperature**

temperature of the air around the measuring device

**3.3****automated measuring system****AMS**

measuring system permanently installed on site for continuous monitoring of emissions or measurement of peripheral parameters

Note 1 to entry: An AMS is a method which is traceable to a reference method.

Note 2 to entry: Apart from the analyser, an AMS includes facilities for taking samples (e.g. probe, sample gas lines, flow meters, regulators, delivery pumps) and for sample conditioning (e.g. dust filter, moisture removal devices, converters, diluters). This definition also includes testing and adjusting devices that are required for regular functional checks.

[SOURCE: FprEN 14181:2014]

**3.4****calibration of an AMS**

establishment of the statistical relationship between values of the measurand indicated by the automated measuring system (AMS) and the corresponding values given by the standard reference method (SRM) used during the same period of time and giving a representative measurement on the same measurement plane

Note 1 to entry: The result of calibration permits to establish the relationship between the values of the SRM and the AMS (calibration function).

**3.5****conversion efficiency**

percentage of NO<sub>2</sub> present in the sample gas converted to NO by the converter

**3.6****zero drift**

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

**3.7****span drift**

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

**3.8****emission limit value****ELV**

emission limit value according to EU Directives on the basis of 30 min, one hour or one day

**prEN 14792:2014 (E)****3.9****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. ambient temperature, atmospheric pressure, presence of interfering gases in the flue gas matrix or pressure of the gas sample.

**3.10****interference**

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

**3.11****lack of fit**

systematic deviation within the range of application 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 may 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".

**3.12****measurand**

quantity intended to be measured

[SOURCE: JCGM 200:2012]

**3.13****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]

**3.14****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]

**3.15****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]



**3.16****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]

**3.17****performance characteristic**

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

**3.18****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]

**3.19****standard reference method****SRM**

reference method prescribed by European or national legislation

[SOURCE: EN 15259:2007]

**3.20****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 procedure;
- same laboratory;
- same measuring instrument, 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 %.

**3.21****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

**prEN 14792:2014 (E)**

Note 1 to entry: These conditions include:

- same measurement procedure;
- two sets of equipment, the performance of which fulfils the requirements of the reference 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 %.

### **3.22 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 procedure;
- several sets of equipment, the performance of which fulfils the requirements of the reference 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 %.

### **3.23 residence time in the measuring system**

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

### **3.24 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 change.

[SOURCE: JCGM 200:2012]

**3.25****span gas**

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

Note 1 to entry: This concentration is often chosen around 80 % of the upper limit of the range.

**3.26****uncertainty**

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

**3.27****standard uncertainty**

$u$

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

**3.28****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)

**3.29****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

$$U = k \times u$$

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.

**3.30****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

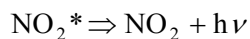
**4 Principle****4.1 General**

This European Standard describes the standard reference method (SRM) for sampling and determining NO<sub>x</sub>, NO and NO<sub>2</sub> 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. A number of performance characteristics, together with associated minimum performance criteria are specified for the analyser. These performance characteristics and the combined 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 for measurements in the field (see Clause 9).

## prEN 14792:2014 (E)

## 4.2 Measuring principle

The principle of chemiluminescence to measure  $\text{NO}_x$  is based on the following reaction between nitrogen monoxide and ozone:



Some of the  $\text{NO}_2$  created during the reaction of  $\text{NO}$  and  $\text{O}_3$  is in an excited state. When returning to the basic state, these  $\text{NO}_2$  molecules can radiate light, the intensity of which depends on the  $\text{NO}$  content and is influenced by the pressure and presence of other gases.

In a chemiluminescence analyser, gas is sampled through a sampling line 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 oxide only. The emitted radiation (chemiluminescence) is proportional to the amount of  $\text{NO}$  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 previously described. 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  $\text{NO}$  and  $\text{NO}_x$  results are determined continuously. On the contrary, with a single type analyser, the reaction chamber is alternatively fed with the raw gas and with the gas having passed the converter that reduces  $\text{NO}_2$  to  $\text{NO}$ . Therefore,  $\text{NO}$  and  $\text{NO}_x$  are determined alternately.

Chemiluminescence analysers are combined with an extractive sampling system and a gas conditioning system. A sample of gas is taken from the stack with a sampling probe and conveyed to the analyser through a sampling 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  $\text{CO}_2$  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  $\text{CO}_2$  and  $\text{H}_2\text{O}$  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  $\text{CO}_2$  as the sample gas.

NOTE 1 A vacuum chemiluminescent- $\text{NO}_x$  analyser reduces the  $\text{CO}_2$  and  $\text{H}_2\text{O}$  quenching error.

NOTE 2 A correction of the  $\text{NO}_x$  concentration may be necessary if the  $\text{NH}_3$  concentration is higher than  $20 \text{ mg/m}^3$ .

In flue gases from conventional combustion systems the nitrogen oxides consist of more than 95 %  $\text{NO}$ . The remaining oxide is predominantly  $\text{NO}_2$ . These two oxides ( $\text{NO} + \text{NO}_2$ ) are designated as  $\text{NO}_x$ .

It should be noted, that in other processes, the ratio of  $\text{NO}$  to  $\text{NO}_x$  may be different and other nitrogen oxides may be present.

## 5 Description of measuring equipment

### 5.1 General on sampling and sample gas conditioning systems

A volume of flue gas (see 8.2) is extracted from the emission source for a fixed period of time at a controlled flow rate. The sampling system consists of:

- a sampling probe;
- a filter;
- a sampling line;
- a conditioning system.

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

Four different sampling and conditioning configurations are available in order to avoid uncontrolled water condensation in the measuring system (see also Annex A). Each of the first three configurations requires that the user shall check that the dew point temperature is lower or equal to 4 °C at the outlet of the analyser. The user may correct the results for the remaining water content in order to report results on a dry basis (refer to the table of Annex B in prEN 14790).

These 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 characterised;
- Configuration 4: maintaining the temperature of the sampling line up to the heated analyser.

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<sub>x</sub>. Except for the cooling system of configuration 1, the temperature of the components likely to be in contact with the 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 minimise this contribution to the combined measurement uncertainty, performance criteria for the sampling equipment and sampling conditions are specified in 5.2 and Clause 6.

Some other 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 sampling line does not need to be heated and water vapour condensation is avoided.

In order to minimise losses of NO<sub>x</sub> in the sampling system, the use of configuration 1 shall be avoided when the NO<sub>2</sub> concentration represents more than 20 mg/m<sup>3</sup>. Configuration 1 shall be ordinarily avoided when the NO<sub>2</sub> / NO<sub>x</sub> represents more than 25 %, unless it is demonstrated that the losses of NO<sub>2</sub> were not significant within the gas cooler, at the concentrations of moisture and NO<sub>2</sub> expected in the field. In such cases, the losses of NO<sub>2</sub> in the sampling system shall not exceed 10%.

## 5.2 Sampling and conditioning system

### 5.2.1 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.

### 5.2.2 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. The particle filter shall be changed or cleaned periodically depending on the dust loading at the measuring site.

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

### 5.2.3 Sampling line

The sampling 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 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 NO<sub>2</sub>/NO<sub>x</sub>. In this case, ceramic, glass, quartz or titanium should be used.

Excessive temperatures should be avoided because this might alter the flue gas characteristics.

### 5.2.4 Conditioning system

#### 5.2.4.1 Sample cooler (configuration 1)

The design of the sample gas cooler shall be such that absorption of NO<sub>2</sub> in the condensates is minimised. Because overpressure in the cooling system increases losses of NO<sub>2</sub> in the condensates, the pump shall be situated between the cooling system and the analyser. In the case that the concentration of NO<sub>2</sub> in the sample gas becomes too high, the use of a gas cooler can produce errors on the NO<sub>2</sub> measurement. This can occur because of the solubility of NO<sub>2</sub> in the condensed water and shall also depend on the content of water vapour in the flue gas. A maximum dew-point temperature of 4 °C shall not be exceeded at the outlet of the sample cooler.

In order to minimise losses of NO<sub>x</sub> in the sampling system, the use of configuration 1 shall be ordinarily avoided when the NO<sub>2</sub> / NO<sub>x</sub> represents more than 25 %, unless there is verifiable evidence to show that the brand and type of gas cooler does not result in significant losses of NO<sub>2</sub> (see 5.1).

NOTE The concentrations, provided by this sampling configuration, are considered to be given on dry basis. However, the user can correct the results for the remaining water (refer to the table of Annex B in prEN 14790).

#### 5.2.4.2 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. A dew-point temperature of 4 °C shall not be exceeded at the outlet of the permeation drier.

Due to ammonium salts deposition on the permeation tube, the permeation system cannot be used when  $\text{NH}_3$  is present.

NOTE The concentrations, provided by this sampling configuration, are considered to be given on dry basis. However, the user can correct the results for the remaining water (refer to the table of Annex B in prEN 14790).

#### 5.2.4.3 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 dew point temperature at the outlet of the analyser shall be determined in order to correct the results and give them on a dry basis (refer to the table of Annex B of prEN 14790) if the dew-point temperature is higher than 4 °C.

NOTE Analysers that are used in combination with dilution probes, work with measuring ranges, which are typical for ambient air analysers (0 mg/m<sup>3</sup> – 1 mg/m<sup>3</sup> – 5 mg/m<sup>3</sup> – 10 mg/m<sup>3</sup> – 25 mg/m<sup>3</sup>).

#### 5.2.4.4 Heated line and heated analyser (configuration 4)

To avoid condensation, the user shall maintain the temperature of the sampling line up to the measuring cell. The analyser itself is 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 measured in the flue gases and the uncertainty attached to this correction shall be added to the uncertainty budget (see Clause 7).

#### 5.2.5 Sample pump

When a pump is not an integral part of the chemiluminescence analyser, an external pump is necessary to draw the sampled air 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  $\text{NO}_x$ . It shall be consistent with the requirements of the analyser to which it is connected.

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.

#### 5.2.6 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-fibre.

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

#### 5.2.7 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 instrument 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.