

norm**NEN-EN 14792**

Emissies van stationaire bronnen -
Bepaling van massaconcentratie aan
stifstofoxiden - Referentiemethode:
Chemiluminescentie

Publicatie uitsluitend voor commentaar

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

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Voorbeeld
Preview

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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

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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.

prEN 14792:2014
Preview

prEN 14792:2014 (E)**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 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 mg/m³ to 1 300 mg/m³ of NO₂ for large combustion plants and 0 mg/m³ to 400 mg/m³ of NO₂ for waste incineration, according to emission limit values (ELV) laid down in the Directive 2010/75/EC.

The ELV for NO_x (NO + NO₂) in EU directives are expressed in mg/m³ of NO₂ 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, 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 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 NO₂ 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

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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

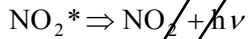
4 Principle**4.1 General**

This European Standard describes the standard reference method (SRM) for sampling and determining NO_x, NO and NO₂ 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 NO_x is based on the following reaction between nitrogen monoxide and ozone:



Some of the NO_2 created during the reaction of NO and O_3 is in an excited state. When returning to the basic state, these NO_2 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 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 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 NO and 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 NO_2 to NO . Therefore, NO and 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 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 CO_2 and H_2O 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 CO_2 as the sample gas.

NOTE 1 A vacuum chemiluminescent- NO_x analyser reduces the CO_2 and H_2O quenching error.

NOTE 2 A correction of the NO_x concentration may be necessary if the NH_3 concentration is higher than 20 mg/m^3 .

In flue gases from conventional combustion systems the nitrogen oxides consist of more than 95 % NO . The remaining oxide is predominantly NO_2 . These two oxides ($\text{NO} + \text{NO}_2$) 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.

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