

Stationary source emissions — Determination of mass concentration of nitrogen oxides (NO_x) — Reference method: Chemiluminescence

The European Standard EN 14792:2005 has the status of a
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National foreword

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The UK participation in its preparation was entrusted by Technical Committee EH/2, Air quality, to Subcommittee EH/2/1, Stationary source emissions, which has the responsibility to:

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- present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep UK interests informed;
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Foreword

This European Standard (EN 14792:2005) 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of an identical text or by endorsement, at the latest by May 2006, and conflicting national standards shall be withdrawn at the latest by May 2006.

This European Standard has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association, and supports essential requirements of EU Directive(s).

For relationship with EU Directive(s), see informative Annex ZA, which is an integral part of this European Standard.

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.

1 Scope

This European Standard describes the chemiluminescence method, including the sampling and the gas conditioning system, to determine the NO/NO₂/NO_x concentrations in flue gases emitted from ducts and stacks to atmosphere. This European Standard is the Standard Reference Method (SRM) for periodic monitoring and for calibration or control of Automatic Measuring Systems (AMS) permanently installed on a stack, for regulatory or other purposes such as calibration. To be used as the SRM, the user shall demonstrate that the performance characteristics of the method are better than the performance criteria defined in this European Standard and that the overall uncertainty of the method is less than $\pm 10\%$ relative at the daily Emission Limit Value (ELV).

NOTE When the chemiluminescence method is the measurement principle used for AMS, reference should be made to EN 14181 and other relevant standards provided by CEN TC 264.

An Alternative Method to this SRM may be used provided that the user can demonstrate equivalence according to the Technical Specification CEN TS 14793, to the satisfaction of his national accreditation body or law.

This SRM has been evaluated during field tests on waste incineration, co-incineration and large combustion installations. It has been validated for sampling periods of 30 min in the range of 0 mg NO₂/m³ to 1 300 mg NO₂/m³ for large combustion plants and 0 mg NO₂/m³ to 400 mg NO₂/m³ for waste incineration, according to emission limit values (ELVs) laid down in the following Council Directives:

- Council Directive 2001/80/EC on the limitation of emissions of certain pollutants into the air from large combustion plants;
- Council Directive 2000/76/EC on waste incineration plants.

The ELVs for NO_x (NO + NO₂) in EU directives are expressed in mg NO₂/m³, on dry basis, at a reference value for O₂ and at the reference conditions (273 K and 101,3 kPa).

2 Normative references

The following referenced documents are indispensable for the application of this European Standard. 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 14790:2003, *Stationary source emissions - Determination of the water vapour in ducts*.

CEN/TS 14793, *Stationary source emissions - Intralaboratory validation procedure for an alternative method compared to a reference method*.

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

3 Terms and definitions

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

NOTE In this European Standard, NO_x is defined as the sum of NO and NO_2 . The mass concentration of NO_x is expressed as the equivalent NO_2 concentration in milligrams per cubic metre at normal conditions.

3.1

adjustment (of a measuring system)

operation of bringing a measuring system into a state of performance suitable for its use

[VIM 4.30]

3.2

ambient temperature

temperature of the air around the measuring system

3.3

automatic measuring system (AMS)

measuring system permanently installed on site for continuous monitoring of emissions

NOTE 1 An AM is a method which is traceable to a reference method.

NOTE 2 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.

[EN 14181]

3.4

calibration

statistical relationship between values of the measurand indicated by the 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 sampling plane

NOTE The result of calibration permits to establish the relationship between the values of the SRM and the AMS (calibration function).

3.5

converter efficiency

percentage of NO_2 present in the sample gas converted to NO by the converter

3.6

drift

difference between two zero (zero drift) or span readings (span drift) at the beginning and at the end of a measuring period

3.7

emission limit value (ELV)

emission limit value according to EU Directives on the basis of 30 min, 1 hour or 1 day

3.8**influence quantity**

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

[adapted VIM 2.7]

NOTE Examples:

- ambient temperature;
- atmospheric pressure;
- presence of interfering gases in the flue gas matrix;
- pressure of the gas sample.

3.9**interference**

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

3.10**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 Lack of fit may be a function of the measurement result.

NOTE 2 The expression "lack of fit" is often replaced in everyday language by "linearity" or "deviation from linearity".

3.11**measurand**

particular quantity subject to measurement

[VIM 2.6]

3.12**measuring system**

complete set of measuring instruments and other equipment assembled to carry out specified measurements

[VIM 4.5]

3.13**performance characteristic**

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

3.14**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 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 Repeatability may be expressed quantitatively in terms of the dispersion characteristics of the results.

In this European Standard the repeatability is expressed as a value with a level of confidence of 95 %.

[VIM 3.6]

3.15

repeatability in the field

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

NOTE 1 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 Repeatability may be expressed quantitatively in terms of the dispersion characteristics of the results.

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

3.16

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 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 Reproducibility may be expressed quantitatively in terms of the dispersion characteristics of the results.

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

3.17

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

3.18**response time**

time interval between the instant when a stimulus is subjected to a specified abrupt change and the instant when the response reaches and remains within specified limits around its final steady value

NOTE By convention, time taken for the output signal to pass from 0 % to 90 % of the final change

[VIM 5.17]

3.19**sampling location**

specific area close to the sampling plane where the measurement devices are set up

3.20**sampling plane**

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

[EN 13284-1]

3.21**sampling point**

specific position on a sampling line at which a sample is extracted

[EN 13284-1]

3.22**span gas**

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

NOTE This concentration is often chosen around 80 % of the upper limit of the range or around the ELV.

3.23**standard reference method (SRM)**

measurement method recognised by experts and taken as a reference by convention, which gives, or is presumed to give, the accepted reference value of the concentration of the measurand (3.11) to be measured

3.24**uncertainty**

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

3.24.1**standard uncertainty u**

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

3.24.2**combined uncertainty u_c**

standard uncertainty u_c attached to the measurement result calculated by combination of several standard uncertainties according to GUM

3.24.3**expanded uncertainty U**

quantity defining a level of confidence about the result of a measurement that may be expected to encompass a specific fraction of the distribution of values that could reasonably be attributed to a measurand

$$U = k \times u$$

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

3.24.4

overall uncertainty U_c

expanded combined standard uncertainty attached to the measurement result calculated according to GUM

$$U_c = k \times u_c$$

3.25

uncertainty budget

calculation table combining all the sources of uncertainty according to EN ISO 14956 or ENV 13005 in order to calculate the overall uncertainty of the method at a specified value

4 Principle

4.1 General

This European Standard describes the SRM, based on the chemiluminescence principle for sampling and determining NO_x , NO and NO_2 concentrations in flue gases emitted to atmosphere from ducts and stacks. The specific components and the requirements for the sampling system and the chemiluminescence analyser are described. A number of performance characteristics, together with associated minimum performance criteria are specified for the analyser. These performance characteristics and the overall 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 table 1 in 7.2).

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 representative 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 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.

5 Description of measuring equipment - Sampling and sample gas conditioning systems

5.1 General

A representative volume of flue gas (see 8.2) is extracted from the emission source for a fixed period of time at a controlled flow rate. 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 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 A in EN 14790:2003).

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_x . 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 overall uncertainty of the measurement. In order to minimise this contribution to the overall measurement uncertainty, performance criteria for the sampling equipment and sampling conditions are specified in sections 5.2 and 7.2.

In order to minimise losses of NO_x in the sampling system, the use of configuration 1 shall be avoided when the measured ratio NO_2/NO_x represents more than 10 %.

5.2 Sampling line components

5.2.1 Sampling line

In order to access the representative measurement point(s) of the sampling plane, probes of different lengths and inner diameters may be used. The design and configuration of the sampling line used shall ensure the residence time of the sample gas is minimised in order to reduce the response time of the measuring system.

The procedure of clause 8.2 shall be used when the operator suspects that the flue gas is inhomogeneous.

NOTE 1 The probe may be marked before sampling in order to demonstrate that the representative measurement point(s) in the measurement plane has (have) been reached.

NOTE 2 A seal-able connection may be installed on the probe in order to introduce test gases for adjustment.

The line shall be made of 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_2/NO_x . In this case, ceramic, glass, quartz or titanium should be used. The use of any materials made from copper or copper based alloys are not permitted.

5.2.2 Filter

The particle filter 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 sampling 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 Sample cooler (configuration 1)

The design of the sample gas cooler shall be such that absorption of NO_2 in the condensates is minimised. Because overpressure in the cooling system increases losses of NO_2 in the condensates, the pump shall be situated between the cooling system and the analyser. In the case that the concentration of NO_2 in the sample gas becomes too high, the use of a gas cooler can produce errors on the NO_2 measurement. This can occur because of the solubility of NO_2 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_x in the sampling system, the use of configuration 1 shall be avoided when the measured ratio NO_2/NO_x represents more than 10 %.

NOTE The concentrations, provided by this sampling configuration, are considered to be given on dry basis. However, the user may correct the results for the remaining water (refer to the table of Annex A in EN 14790:2003).

5.2.4 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.

NOTE The concentrations, provided by this sampling configuration, are considered to be given on dry basis. However, the user may correct the results for the remaining water (refer to the table of Annex A in EN 14790:2003).

5.2.5 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 A of EN 14790:2003) 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/m³ - 1 mg/m³ - 5 mg/m³ - 10 mg/m³ - 25 mg/m³).

5.2.6 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).

5.2.7 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 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.

5.2.8 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.

5.2.9 Flow controller and flow meter

This apparatus sets the required flow. A corrosion resistant material shall be used. The sample 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.

6 Analyser equipment

6.1 General

Generally two configurations of analysers are available:

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

In the dual-chamber types the sample flow is divided into two streams, one passing directly to one of the reaction chambers for measurement of the nitrogen monoxide content. The other stream is fed through the converter for conversion of the nitrogen dioxide to nitrogen monoxide and then to the other reaction chamber for measurement of the total content of nitrogen dioxide and nitrogen monoxide.

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

A chemiluminescence apparatus consists of the principal components described in paragraphs 6.2 to 6.7.

6.2 Converter

An NO_2/NO converter shall be included in the measuring system. The converter converts nitrogen dioxide in the gas to nitrogen monoxide. It shall be capable of converting at least 95 % of the nitrogen dioxide to nitrogen monoxide. The converter efficiency shall be determined by one of the procedures described in Annex B. The converter shall consist of a heated furnace maintained at a constant temperature and is made of material such as stainless steel, molybdenum, tungsten, spectroscopically pure carbon or quartz.

NOTE 1 The converter can be bypassed with a changeover valve arrangement. If the sample gas flows through the converter, the total quantity ($\text{NO} + \text{NO}_2$) is determined; when the converter is by-passed, the NO content is determined. The amount of NO_2 can be calculated as the difference between NO_x and NO .

NOTE 2 If ammonia is present in the sample gas, interferences can occur depending on the operating temperature and the material of the converter.

NOTE 3 When using a stainless steel converter in a sample that is a reducing atmosphere, the NO in the sample can be disassociated to N_2 and O_2 . This leads to lower readings. Manufacturers of analysers that use stainless steel normally have an air bleed from the ozonator supply to the sample stream in order to avoid this effect.

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

6.3 Ozone generator

An ozone generator is required. Ozone is generated from oxygen by either ultra-violet radiation or by a high-voltage silent-electric discharge. If oxygen in ambient air is used for ozone generation by a high-voltage silent-electric-discharge, it is essential that the air is thoroughly dried and filtered before entering the generator. If the ozone is generated using oxygen of a recognised analytical grade from a compressed gas cylinder, this oxygen can be fed directly into the generator. The concentration of ozone produced shall be sufficiently high to maintain the required linearity of the analyser. If ozone concentration is too low, this can result in a non-linear response to the concentration of NO_2 and NO . It may be useful to check that the quantity of O_3 is sufficient by injecting a calibration gas of NO , which concentration is close to the upper limit of the measurement range.

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

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

6.4 Reaction chamber

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

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

6.5 Optical filter

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

6.6 Photomultiplier tube

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

6.7 Ozone removal

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

7 Determination of the characteristics of the SRM: analyser, sampling and conditioning line

7.1 General

When this European Standard is used as the SRM, the user shall demonstrate that:

- performance characteristics are better than the minimum performance criteria given in Table 1; and
- overall uncertainty calculated by combining values of standard uncertainties associated to the performance characteristics given in Table 1 is less than $\pm 10\%$ at the daily ELV expressed on dry basis and before correction to the O_2 reference concentration.

The values of the selected performance characteristics shall be evaluated by means of a laboratory test and a field test. An experienced laboratory recognised by the competent authority shall perform the laboratory tests according to the procedures described in the relevant CEN/TC264 standards or technical specifications. The user shall perform the field tests.

NOTE The performance characteristics and performance criteria given in this European Standard are not necessarily corresponding to those of an AMS. For AMS performance characteristics and performance criteria the user should refer to the relevant standards provided by CEN/TC 264.