INTERNATIONAL
STANDARD

ISO
10849

First edition
1996-04-15

Stationary source emissions — Determination of the mass concentration of nitrogen oxides — Performance characteristics of automated measuring systems

Émissions de sources fixes — Détermination de la concentration en masse des oxydes d'azote — Caractéristiques de performance des systèmes de mesurage automatiques

Reference number
ISO 10849:1996(E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 10849 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 1, *Stationary source emissions*.

Annex A forms an integral part of this International Standard. Annexes B and C are for information only.

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Case Postale 56 • CH-1211 Genève 20 • Switzerland

Printed in Switzerland

Introduction

Nitrogen oxides are produced during most combustion processes. In fossil fuel combustion, nitrogen oxides are produced from nitrogen combined in the fuel and from the oxidation of nitrogen in the air used for combustion. The quantity of nitrogen oxides produced depends upon the nitrogen content of the fuel, the boiler design, the burner design and the boiler operating conditions.

In flue gases from conventional combustion systems, the nitrogen oxides consist of approximately 95 % nitrogen monoxide (NO). The remaining oxide is predominantly nitrogen dioxide (NO_2) formed from the oxidation of NO when the flue gas temperature decreases. These two oxides (NO + NO_2) are generally designated as NO_x. It should be noted that in other processes the ratio of NO to NO_2 may be different and other nitrogen oxides may be present.

There are numerous ways of determining nitrogen oxides in the gases of combustion plants, both wet chemical/analytical methods and instrumental techniques.

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Stationary source emissions — Determination of the mass concentration of nitrogen oxides — Performance characteristics of automated measuring systems

1 Scope

This International Standard specifies the fundamental structure and the most important performance characteristics of automated measuring systems for oxides of nitrogen to be used on stationary source emissions, for example combustion plants. The procedures to determine the performance characteristics are also specified. Furthermore, it describes methods and equipment to determine NO or NO_x ($NO + NO_2$) in flue gases including the sampling system and sample gas conditioning system. Dinitrogen monoxide (N_2O) is not determined by the methods described in this International Standard. The given performance characteristics refer to the complete measuring system, from sampling to analyser.

This International Standard describes extractive and non-extractive systems in connection with a range of analysers that operate using, for example, the following principles:

— chemiluminescence;

— non-dispersive infrared spectroscopy;

— non-dispersive ultraviolet spectroscopy;

— differential optical absorption spectrometry.

NOTE 1 Commercial devices using the described techniques, that meet the requirements of this International Standard, are available.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 6879:1995, *Air quality — Performance characteristics and related concepts for air quality measuring methods.*

ISO 7996:1985, *Ambient air — Determination of the mass concentration of nitrogen oxides — Chemiluminescence method.*

ISO 9096:1992, *Stationary source emissions — Determination of concentration and mass flow rate of particulate material in gas-carrying ducts — Manual gravimetric method.*

ISO 9169:1994, *Air quality — Determination of performance characteristics of measurement methods.*

ISO 10396:1993, *Stationary source emissions — Sampling for the automated determination of gas concentrations.*

3 Definitions

For the purposes of this International Standard, the following definitions apply.

3.1 automated measuring system (AMS): System that may be attached to a chimney to continuously measure and record the mass concentration of nitrogen oxides passing through the chimney.

3.2 analyser: Analytical part in an extractive AMS.

3.3 verified (AMS): AMS previously verified against this International Standard.

3.4 calibration gas: Gas of known, reliable and stable composition that may be used to check the response of the AMS and should be used for the calibration of the AMS.

3.5 comparative measurements: Measurements that are taken on the same chimney in the same sampling plane for the same period of time, with the AMS under test and with the comparative method providing pairs of measured values.

3.6 comparative method: Defined test method for the comparative measurements of stationary source emissions containing nitrogen oxides. This can be a manual method or an AMS verified according to this International Standard, with a different measuring principle.

NOTE 2 The naphthylethylenediamine (NEDA) method according to ISO 11564, has been proven to be a suitable manual method. Also, validated national standards with known performance characteristics (standard deviation, lower detection limit, effect of interfering substances) may be applied.

3.7 standard deviation, s_A: Measure of the working precision of the AMS.

The standard deviation, s_A, is derived from the difference in the pairs of measured values of nitrogen oxides by the AMS under test and the comparative method, on the basis of a sufficient number of comparative measurements spread over the period of unattended operation (see annex A).

s_c is the standard deviation of the comparative method.

s_D is the standard deviation of the paired values.

s_x is the standard deviation of the blank readings.

NOTES

3 It is not possible to determine directly the standard deviation, s_A, of an AMS under repeatable working conditions or in a laboratory, because:

- commercially available calibration gas mixtures containing nitrogen monoxide do not have all the properties of actual waste gas and do not cover all possible influences;
- the mass concentration of nitrogen oxides in waste gas usually varies with time;
- it is not possible to maintain the properties of a waste gas present in the waste gas flue in a waste gas sample transferred into a vessel.

Therefore, the evaluation of the standard deviation, s_A, is performed by comparison with an independent manual method or an analyser with a different principle of detection.

Applying the comparative method in combination with the test for systematic errors ensures a satisfying accuracy of the automated measuring system.

4 The standard deviation, s_A, is a measure of the working precision under site conditions. Therefore, it contains, in addition to random errors, the effects of interfering substances, the effects of temperature changes and of any zero and span drifts, because they cannot be eliminated in practice.

The standard deviation, s_A, is an upper limiting value for the AMS. Known systematic errors of the measured values of the independent comparative method are to be taken into account.

5 This procedure is suitable for finding the precision of the measuring result of the automated measuring method, as long as the standard deviation, s_c, of the measured values of the comparative method is significantly smaller than the standard deviation, s_D, of the difference in pairs of measured values.

If the AMS under investigation has a substantially smaller standard deviation, s_A, than the comparative method, s_c, the method above can still be used, although the value of s_A will have a large uncertainty. If the uncertainty in s_c is unknown and hence the limits of s_A cannot be established, the value of s_A can be used as a qualitative rather than a quantitative assessment of the AMS performance.

3.8 chimney: Stack or final exit duct on a stationary process used for the dispersion of residual process gases.

3.9 mass concentration: Concentration of a substance in an emitted waste gas, expressed in milligrams per cubic metre.

NOTE 6 The concentration of nitrogen oxides can be expressed as ppm, as milligrams of NO per cubic metre or as milligrams of NO_2 per cubic metre.

NO: 1 ppm $(V/V) = 1{,}34$ mg/m^3

NO_2: 1 ppm $(V/V) = 2{,}05$ mg/m^3

Concentrations should be related to standard atmospheric conditions (273 K, 101,3 kPa) and dry gas.

Depending on national regulations, the concentrations should be referred to defined oxygen or carbon dioxide concentrations.

In this International Standard, all concentrations of nitrogen oxides are expressed as milligrams of NO_2 per cubic metre.

3.10 stationary source emissions: Those gases that have been emitted by a stationry plant or process and are transported to a chimney for dispersion into the atmosphere.

3.11 calibration curve: Curve describing the dependence of the measured signal on a given calibration gas.

3.12 period of unattended operation: Maximum admissible interval of time for which the performance characteristics will remain within a predefined range without external servicing, e.g. refill, calibration, adjustment. [ISO 6879]

NOTE 7 For long-term monitoring installations a minimum of 7 d of unattended operation is required.

3.13 calibration: Setting and checking of the AMS before determining the performance characteristics or before beginning any measurement of NO_x. Further steps of the calibration of an AMS, like comparative measurements, may be part of national regulations.

4 Principle

With extractive systems, a representative sample of gas is taken from the stack with a sampling probe and conveyed to the analyser through the sample line and sample gas conditioning system.

Non-extractive systems do not require any sampling transfers out of the stack. For the installation of these systems, a representative place in the stack is to be chosen. *In-situ* systems may sample a larger part of the flue gas.

The values from the analyser are recorded and/or stored by means of electronic data processing.

The systems described here basically only measure nitrogen monoxide. If, with the systems, the nitrogen dioxide content or the total quantity of the nitrogen oxides ($NO + NO_2$) is to be determined, a converter to reduce nitrogen dioxide to nitrogen monoxide is to be used. The converter may be a separate piece of equipment or incorporated into the NO analyser.

Systems also exist, mainly using ultraviolet techniques, that can monitor nitrogen dioxide directly. These systems are mostly combined with NO analysers.

In most of the cases, it is considered that only nitrogen monoxide has to be measured, because the NO_2 content is negligible. However, in some cases nitrogen dioxide may occur in large quantities and has to be taken into account, either by direct measurement or by using a converter. The sampling will, however, be difficult, due to the high reactivity of nitrogen dioxide.

5 Description of the measuring equipment

5.1 Sampling and sample gas conditioning systems for extractive systems

5.1.1 General

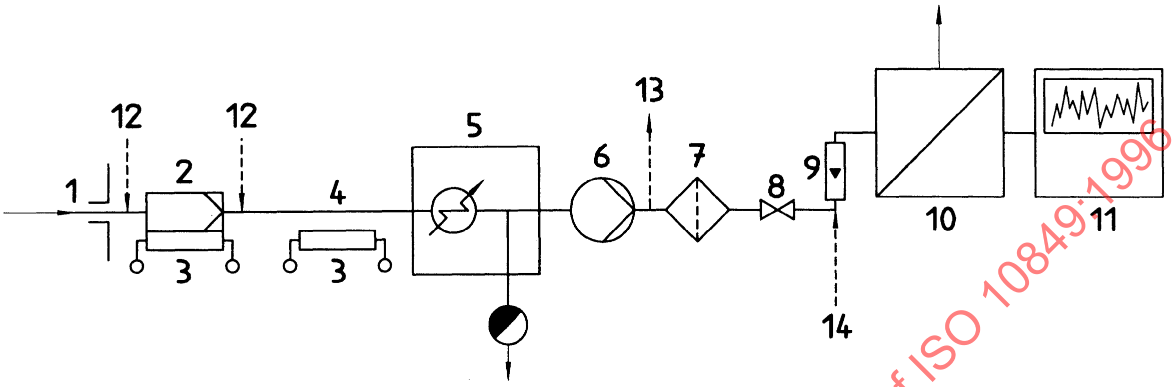
A more detailed description of sampling and sample gas conditioning systems for extractive methods is given in ISO 10396.

Figure 1 a) shows a typical arrangement of a complete measuring system for NO. This system is suitable for use with all the analysers that are described in 5.2.

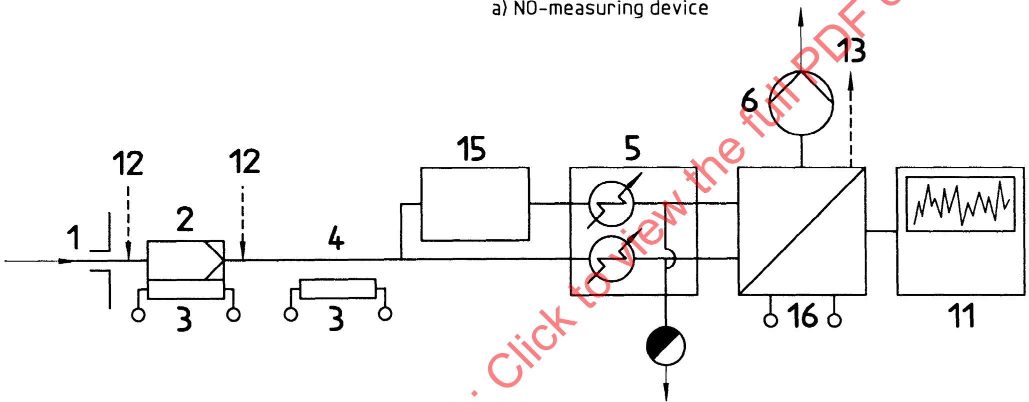
In addition to this arrangement, there are also automated measuring systems for the NO_x measurement that heat the sample gas to above water and acid dew-points (or the dew-point of other condensable substances) to avoid losses of NO_2. In this case, the system can be simplified. It is important that all the components carrying the sample gas to the analyser are also heated above water and acid dew-points.

In the case that higher amounts of NO_2 are in the sample gas, the use of a gas cooler can produce errors on the NO_2 measurement due to the solubility of NO_2 in the condensed water and depending on the content of water vapour in the flue gas. A possible arrangement to avoid losses of NO_2 is shown in figure 1 b).

The sampling of gas shall be representative, that is, the sampling location shall be typical of the entire duct. The representativeness of the sampling location requires confirmation by means of a network measurement in accordance with the guidelines given in ISO 10396. The sampling points for the network measurement shall be located in accordance with ISO 9096. Checking of representativeness shall be done before the first installation of a measuring system and shall be repeated in the case of uncertainty.



a) NO-measuring device



b) NO/NO$_x$-measuring device

Key:

1	Gas sampling probe	9	Flowmeter
2	Particulate filter	10	NO-analyser
3	Heating	11	Recorder
4	Sampling line (heated if necessary)	12	Inlet for zero and calibration gas (preferably in front of the filter) to check the complete system
5	Sample cooler with condensate separator	13	Bypass for excess gas
6	Sample pump	14	Inlet for zero and span gas to check the analyser
7	Filter	15	Converter
8	Needle valve	16	NO/NO$_x$-analyser

Figure 1 — Examples of the installation of measuring devices

The components described in 5.1.2.1 to 5.1.2.8 have, for example, proven to be successful for measurements at gas-, oil- and coal-fired plants (precautions need be observed because of the high corrosiveness of condensable acid gases, e.g. HCl, SO_3 or NO_2).

5.1.2 Components

5.1.2.1 Sampling probe, made of suitable, corrosion-resistant material. For gas temperatures up to 220 °C, polytetrafluoroethylene (PTFE) is an acceptable material. At temperatures > 250 °C, stainless steel and certain other materials can alter the ratio of $NO:NO_2$. In this case, ceramic or glass material is required, if it is necessary to determine the ratio. Cooling may be considered necessary in order to maintain the gas concentrations in the flue gas.

5.1.2.2 Filter, made of ceramic or sinter metal with 10 µm pore size. The filter shall be heated above the water or acid dew-point.

5.1.2.3 Sample line, made of PTFE or stainless steel. The lines shall be operated 15 K above the dew-point of condensable substances (generally the water or acid dew-point). The inner diameter of the line depends on the quantity of sample gas required, with 4 mm as a minimum (and preferably 4 mm to 8 mm).

5.1.2.4 Sample cooler or permeation drier, to separate water vapour from the flue gas. The dew-point shall be sufficiently below the ambient temperature. A cooling temperature of 2 °C to 5 °C is convenient. Sufficient cooling is required for the volume of gas being sampled and the amount of water vapour that it contains.

The design of the sample gas cooler shall be such that absorption of NO_2 in the condensate is restricted to a minimum. This ensures that loss of NO_2 dissolved in the condensate, which is drained from the sample cooler, is at a minimum.

The use of a permeation drier also ensures that NO_2 losses are negligible.

5.1.2.5 Sampling pump (corrosion-resistant), of which the performance shall be such that it can supply the connected analyser with its required gas flow. The quantity of sample gas required can vary between 30 l/h and 500 l/h, dependent upon the analyser and the expected response time.

5.1.2.6 Secondary filter, to separate fine dust, with a pore size of 1 µm to 2 µm, made for example from glass fibre, sintered ceramics, stainless steel or PTFE fibre.

5.1.2.7 Flow controller and flowmeter, to set the required flow and constructed of corrosion-resistant material.

5.1.2.8 NO_2/NO converter, necessary if NO_2 has to be measured with a NO analyser (only possible in combination with extractive systems).

Different types of converters exist, for example:

— carbon converters;

— carbon-molybdenum converters;

— stainless steel converters;

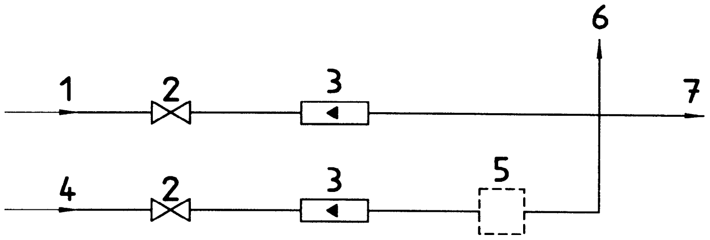
— thermal converters.

In some situations (e.g. when ammonia is present in the sample gas) interferences can occur depending on the operating temperature of the converter. In these cases, it is necessary to take into account such possibilities when selecting the converter type.

The converter can be bypassed with a three-way valve. If the sample gas flows through the converter, the total quantity ($NO + NO_2$) is obtained; when the converter is bypassed, the NO content is obtained. The amount of NO_2 can be calculated as the difference between NO_x and NO.

The converter shall have an efficiency > 95 %, which can be tested using calibration gases containing NO_2 in synthetic air, or with a converter efficiency tester. This method is described in detail in ISO 7996 and it is not suitable if the NO analyser is prone to interference by ozone.

The principle of an efficiency tester is shown in figure 2. A constant flow of a NO-calibration gas is mixed with a constant flow of air or oxygen, that contains different amounts of ozone, produced by an adjustable ozone generator. Ozone reacts with NO to produce NO_2. Thus the total amount of nitrogen oxides ($NO + NO_2$) remains constant, while the ratio ($NO:NO_2$) changes.



Key:

1	NO-calibration gas
2	Needle valve
3	Flowmeter
4	Oxygen
5	Ozone generator (adjustable)
6	Bypass for excess test gas
7	Test gas for converter + analyser

Figure 2 — Principle of an efficiency tester for NO_2/NO converters

If the converter efficiency is > 95 %, the signal of the analyser, combined with the tested converter, remains nearly constant. The signal of every different concentration is compared with the signal of the gas mixture containing NO only (with the ozone generator switched off). At each different ozone concentration, the concentration of NO and (NO + NO_2) of the gas mixture shall be determined. N_2O is not converted to NO. Dinitrogen pentoxide (N_2O_5) is converted to NO.

5.1.3 Dilution

The dilution technique is an alternative to hot gas monitoring or sample gas drying. The flue gas is diluted with a dilution gas which shall be 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 throughout the period of the test. The water dew-point shall be reduced so as to reduce the risks of condensation in the gas loops. The measured values always refer to the wet gas.

Analysers which are used in combination with dilution probes have measuring ranges which are typical for ambient air analysers (0 mg/m^3 to 1 mg/m^3, 5 mg/m^3, 10 mg/m^3 or 25 mg/m^3).

5.2 Measuring principles of analysers

The following examples describe typical principles found in existing analysers. The performance characteristics described in clause 6 are applicable both to existing equipment and to future developments.

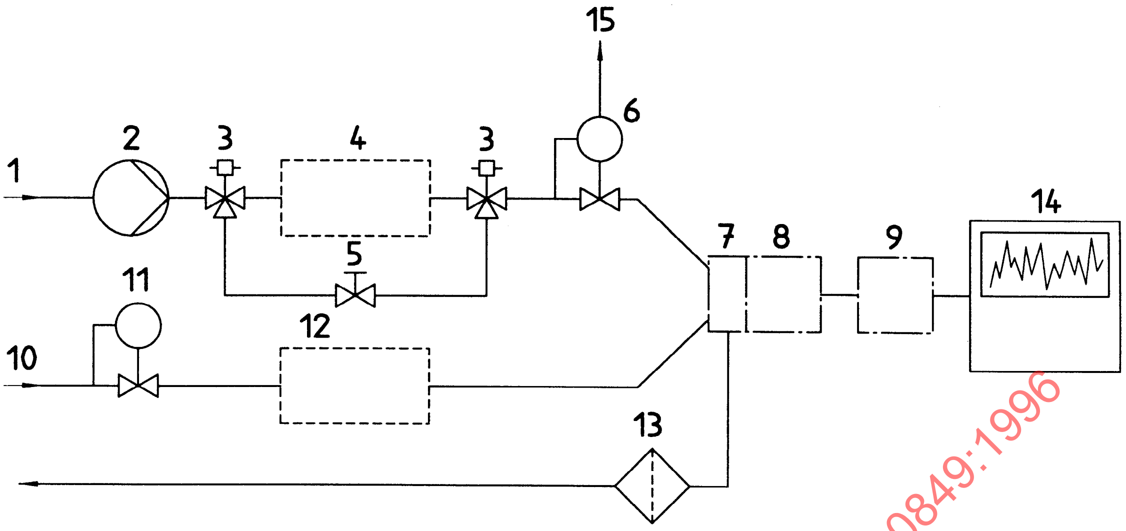
5.2.1 Chemiluminescence method

The principle of the chemiluminescence method for the determination of the mass concentration of nitrogen oxides in ambient air is described in ISO 7996.

If NO reacts with ozone (O_3), NO_2 is formed. Part of this NO_2 is in a photochemically excited state. When returning to the basic state, these NO_2 molecules can radiate light in the wavelength range of 590 nm to 3 000 nm. The intensity of this light depends on the NO content and is influenced by the pressure and presence of other gases.

Figure 3 shows the basic arrangement of a chemiluminescence analyser.

There are atmospheric pressure and low pressure analysers, depending on the pressure in the reaction chamber. Some analysers have built-in NO_2/NO converters and, because of their structure, give signals for NO, NO_x and NO_2 either simultaneously or in sequence.



Key:

1	Sample inlet
2	Sample pump
3	Magnetic valve
4	NO_2/NO converter
5	Flow regulator
6	Pressure regulator
7	Reaction chamber
8	Photomultiplier
9	Electronics
10	Oxygen inlet
11	Pressure regulator
12	Ozone regulator
13	Ozone filter
14	Signal
15	Bypass

Figure 3 — Basic arrangement of a chemiluminescence analyser

The measuring range of chemiluminescence analysers used for emission measurements extends from 10 mg/m^3 to 20 000 mg/m^3. The minimum measuring range that is known to meet the performance characteristics of this International Standard is 0 mg/m^3 to 200 mg/m^3.

Interference due to carbon dioxide (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 shall be made to the analyser output either 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.

5.2.2 Non-dispersive infrared (NDIR) method

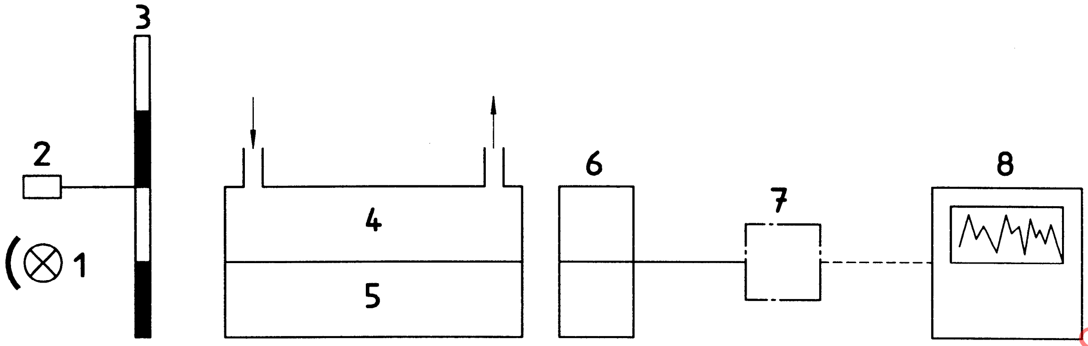
The most common application of the IR method are analysers working according to the NDIR method.

Gases which consist of molecules of different atoms absorb light of the characteristic wavelength in the infrared spectral region. With the NDIR method, spectral analysis of the IR radiation is omitted and the total absorption of the NO molecule at ν_{max} = 1 876 cm^{-1} (= 5,3 µm) is used for the measurement.

Figure 4 shows an example of a typical NDIR analyser.

The radiation emitted from the IR source is divided into two beams and then modulated, one beam passing through the measuring cell and the other through the reference cell containing an IR inactive gas, usually nitrogen. If the sample gas contains NO, some of the IR energy is absorbed and the difference in IR energy reaching the detector is proportional to the amount of NO present. The detector is designed so that it is only sensitive to the NO-specific wavelengths.

A special arrangement of the NDIR method is the gas filter correlation method.



Key:

1	Light source
2	Chopper motor
3	Chopper wheel
4	Measuring cell
5	Reference cell
6	Detector
7	Electronics
8	Signal

Figure 4 — Example of a NDIR analyser

A minimum measuring range of 0 mg/m^3 to 200 mg/m^3 is possible. Each analyser can be used only for the scheduled concentration range.

Interference is possible, particularly with water vapour.

5.2.3 Non-dispersive ultraviolet (NDUV) method

The described system is a typical example of the application of the NDUV method. However, other systems exist.

This method is based on the resonance absorption of a line multiplet emerging from a hollow-cathode discharge lamp through the NO monoxide in the sample gas.

Figure 5 shows the basic arrangement of the analyser.

A hollow-cathode discharge lamp filled with nitrogen and oxygen emits a line multiplet which is characteristic of NO in the range of 226 nm. This beam consists of resonant lines which are absorbed by NO and also of non-resonant lines. A rotary chopper wheel with two cells is connected to the hollow-cathode discharge lamp. One of the cells is filled with concentrated NO, the other is empty. The resonant lines of the beam are filtered through the cell filled with NO. Thus, two beams are obtained alternately: a measuring beam of resonant and non-resonant lines and a reference beam of non-resonant lines. Only the range around 226 nm is transmitted through a subsequent interference filter with a bandwidth of several nanometres. The two beams meet alternately via a semipermeable mirror on the reference detector and the measuring detector. NO in the sample gas absorbs resonant lines from the measuring beam and this absorption depends on the concentration of NO. Thus, there are four signals at the two detectors and they are processed in a microcomputer. The resultant signal represents a measure for the concentration of NO. The microcomputer also converts the signals to give a linear output.

A minimum measuring range of 0 mg/m^3 to 200 mg/m^3 is possible with this method.

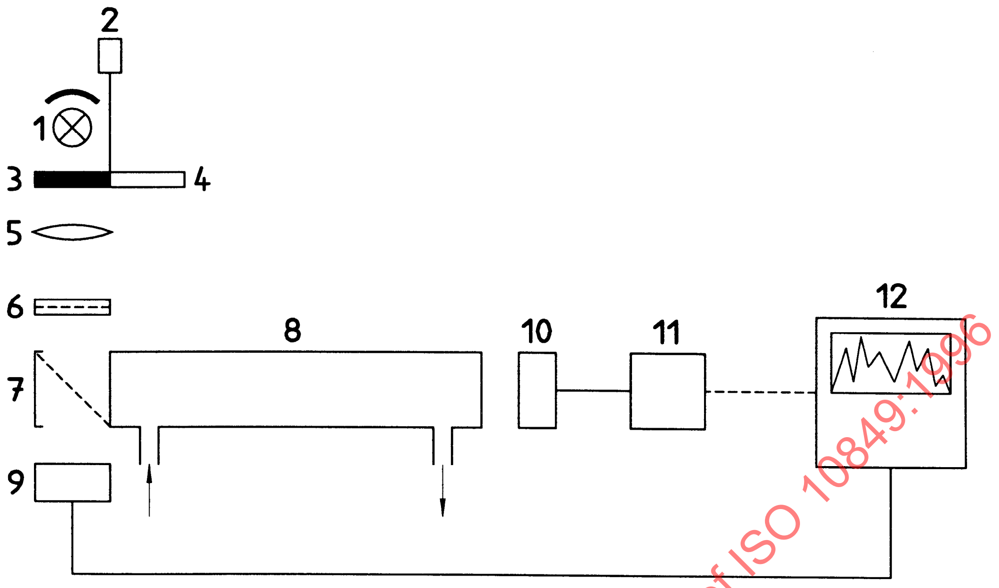
These UV instruments can suffer from interference due to SO_2 in the flue gas sample. This interference can be minimized by internal adjustments in the analysers. In addition, the presence of NO_2 or aromatic compounds in the sample may cause slight interference.

5.2.4 Non-extractive method *(in situ)*

There are two different kinds of *in situ* methods:

- — traversal method (path monitor);
- — point method.

The signals from the *in situ* instruments always refer to the wet gas. If the result of the measurement has to be referred to dry gas, a correction factor is needed.



Key:

1	Hollow-cathode discharge lamp	7	Semipermeable mirror
2	Motor	8	Measuring cell
3	NO cell	9	Reference detector
4	Empty cell	10	Measuring detector
5	Collimator	11	Electronics
6	Interference filter	12	Signal

Figure 5 — Example of a NDUV analyser

5.2.4.1 Traversal method

The traversal method takes into consideration a larger volume of the waste gas than the point method. It uses an optical mode directly in the duct of gaseous effluents. It includes two modules, the first is a radiation emission module, the second ensures reception of these radiations after passing through the gas containing nitrogen oxides.

The examples given in 5.2.4.1.1 and 5.2.4.1.2 briefly describe two instruments which meet the performance characteristics of this International Standard.

5.2.4.1.1 Figure 6, which is typical for path monitors, shows the principle of the first instrument.

This instrument uses the ultraviolet part of the spectrum, namely the range 218 nm to 233 nm. Gases other than NO and SO_2 do not absorb at all in this wavelength range, or only with very small or constant absorption coefficients.

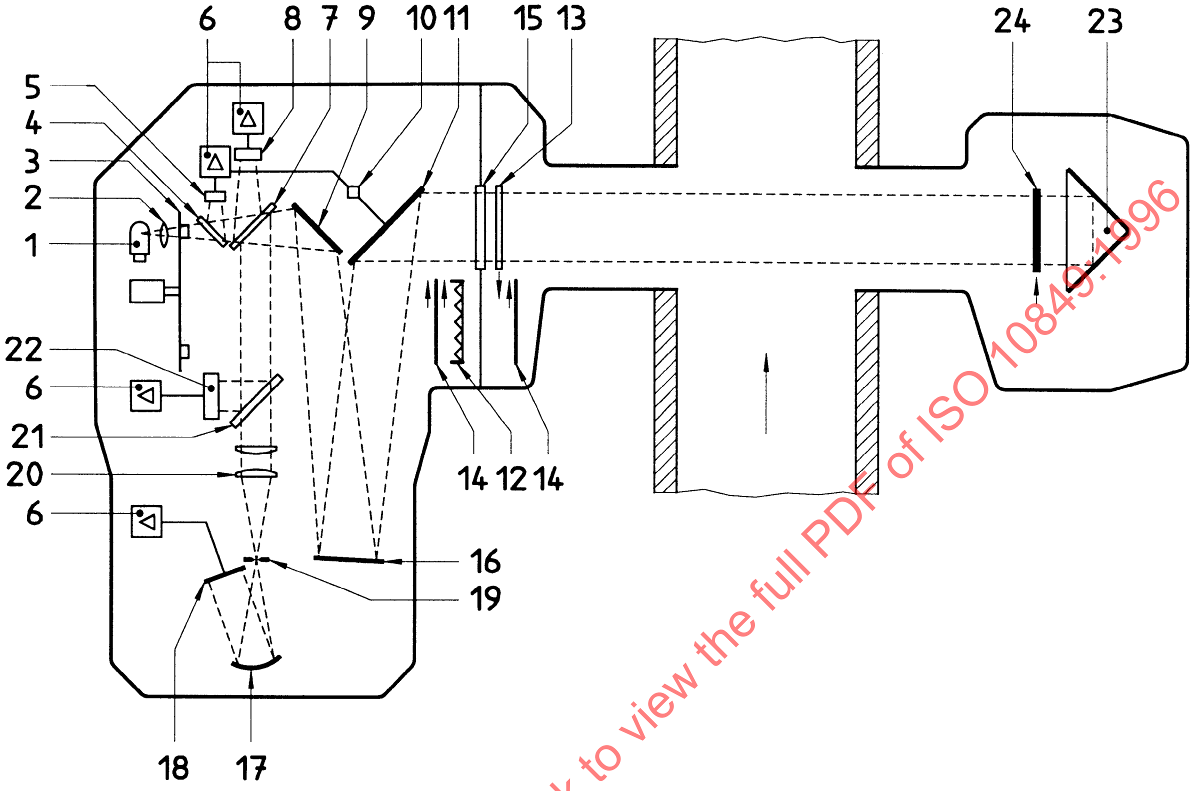
The system consists of the following major units: an optical head unit, a reflector unit, a control box and two purging units.

A deuterium lamp is used as a light source and radiates in the bandwidth from the ultraviolet to the visible range. By using a special grid, radiation in the wavelength range 218 nm to 233 nm is selected. The detector is an array of photodiodes. In addition, the intensity of the light emitted from the light beam which crosses the stack is measured with a reference detector.

The NO concentration is calculated from the intensity of the different signals, the stored NO spectrum and with reference to the stack gas temperature.

The range of application depends on the diameter of the stack; a minimum measuring range of 0 mg/m^3 to 150 mg/m^3 is possible.

Sulfur dioxide (SO_2) is a possible interferent and can also be measured with this method.



Key:

1	Deuterium lamp
2	Condenser
3	Filter wheel and control filters
4	Beam splitter
5	Position sensor
6	Pre-amplifiers
7	Beam splitter
8	Reference detector*)
9	Deflection mirror
10	Mirror-control motor
11	Correcting mirror
12	Zero-point reflector
13	Swivel window*)
14	Diaphragm*)
15	Front window
16	Objective mirror
17	Concave grid mirror
18	Detector row
19	Polychromators (entrance slot)
20	Condenser
21	Beam splitter
22	Photodiode (dust)*)
23	Triple reflector
24	Swivel window*)

*) The items are only in the version with dust.

Figure 6 — Example of an *in situ* monitor (path monitor)

5.2.4.1.2 Differential optical absorption spectroscopy (DOAS) is another UV-absorption principle.

The analyser measures the total absorption spectrum in the range of 200 nm to 2 000 nm. The obtained spectrum is mathematically compared with the stored spectrum of the light source. The differential absorption spectrum is calculated, this calculation being the basis for the calculation of the concentration of the compound(s).

The concentration of NO_2 and other gases can also be calculated with this method.

The minimum measuring ranges for NO and NO_2 are 0 mg/m^3 to 150 mg/m^3.

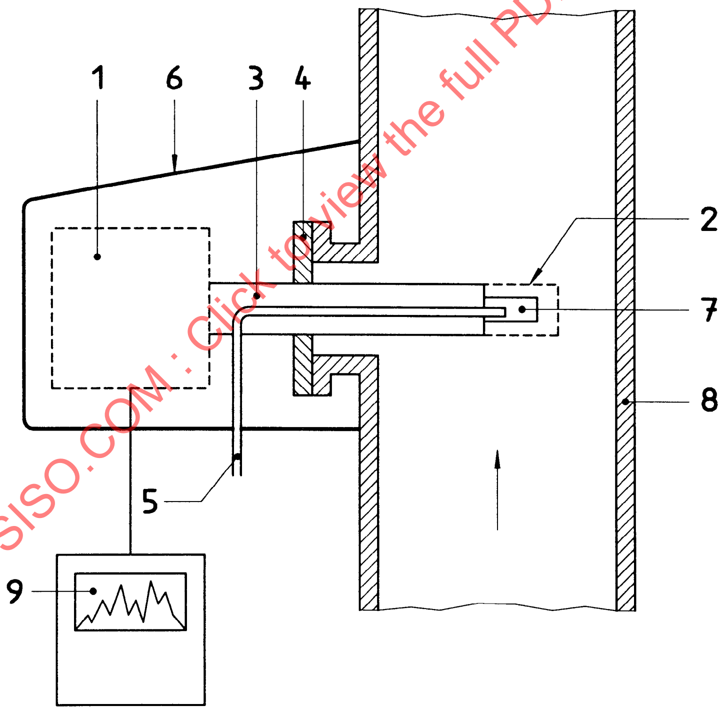
5.2.4.2 Point methods

In this type of monitor, the flue gas is also analysed directly in the gas stream. The measurement probe is inserted into the flue gas and the gas concentration is measured over a cell of small path length located at the end of the probe. This system is illustrated in figure 7.

The principle of the measurement is either a spectroscopic method (e.g. ultraviolet combined with a second derivative technique or infrared) or an electrochemical method.

The measuring cell is protected against dust by a sintered filter (ceramic or metal) and is connected to a transceiver unit via a probe. It is possible to introduce zero and span gases into the measuring cell via a calibration line.

The flue gas temperature can be up to about 350 °C (infrared method).



Key:

1	Instrument transceiver	6	Protective hood
2	Probe filter	7	Mesurement cell
3	Probe	8	Duct or stack
4	Probe mounting	9	Data recorder
5	Gas calibration line		

Figure 7 — Example of an *in situ* monitor (point monitor)

6 Numerical values of performance characteristics and their applicability

When measured in accordance with the respective methods given in annex A, the performance characteristics of automated measuring systems shall meet the requirements given in table 1.

Table 1 — Main performance characteristics of automated nitrogen oxides measuring systems

Performance characteristic 1)	Numerical value	Test method (see annex A)
Lower detection limit	⩽ 2 % 2)	A.4.2.1.1
Interference of the mixture	⩽ ± 4 % 2)3)	A.4.2.1.2
Response time	⩽ 200 s	A.4.2.1.3
Standard deviation, s_A (comparison with independent manual method or analyser with different principle of detection)	⩽ ± 5 % 2)4)	A.4.2.2.2

1) These performance characteristics were determined at plants where the NO/NO_2 ratio was high.

2) As a percentage of the full-scale deflection.

3) The main interfering substances in the flue gas from combustion plants are CO_2, CO, SO_2, H_2O and, in a smaller concentration, NH_3. If the water vapour is not removed (e.g. *in situ*) from the flue gas of coal or waste-fired incinerators, HCl and HF may also be present. In special cases, other interfering substances (e.g. cyanide or N_2O) may be of interest.

4) See 3.7.

Together with the measuring ranges from table 2, the values of table 1 show the state of the art of source emission measurement of nitrogen oxides.

The performance characteristics shall be determined with operative measuring equipment. The standard deviation, s_A, shall be determined during measurements under normal plant conditions, preferably at the type of plant of interest, the other characteristics can be determined both at a plant or in the laboratory.

NOTES

8 Table B.1 gives additional performance characteristics that serve as a guideline to facilitate meeting the performance characteristics given in table 1. Table 2 gives facilities at which the values of the performance characteristics given in table 1 have been applied and verified, as well as the applicable measuring range.

9 The result of a measurement (free from known systematic errors; test according to A.4.2.2.2) is presumed to lie within a range containing the true value of the measurement. The difference between the upper limit of this range and the measured value or the difference between the measured value and the lower limit of this range is termed the uncertainty of measurement.

Assuming that the measuring equipment complies with the performance characteristics given in table 1, an uncertainty of measurement of < ± 10 % can be found, in relation to the full scale (at 95 % statistical certainty).

The uncertainty of a measured value can be calculated by multiplying the uncertainty mentioned above with the full-scale value, divided by the measured value.

10 The performance characteristics shown in table 1 are based on the results of many measurements carried out with different extractive measuring systems and analysers using the chemiluminescence, NDIR or NDUV method and also with *in situ* analysers (traversal method).

The facilities at which the values of the performance characteristics given in table 1 have been verified according to this International Standard in the appropriate ranges are listed in table 2.

Table 2 — Facilities and measuring ranges

Facility	Measuring range 1) mg/m^3 of NO_2
Furnaces for hard coal	0 to 2 000
Furnaces for heavy fuel oil	0 to 1 000
Furnaces for natural gas	0 to 200
Furnaces for waste	0 to 650
Stack gas from a combined incinerator for waste and hard coal	0 to 3 000
Cement kiln	0 to 2 500
Diesel engine	0 to 5 000
Diesel engine in combination with DeNO$_x$-catalyst	0 to 600
Gas engine	0 to 3 000
Gas turbine	0 to 300

NOTE — When sufficient experience of new types of plant, new burners and/or different measuring ranges is available, the ranges and applications may be extended.

1) Related to 101,3 kPa, 273 K and dry gas.

Annex A
(normative)

Determination of main performance characteristics of automated measuring systems

A.1 Scope

This annex describes methods for determining the main performance characteristics of the AMS in the range between 0 mg/m^3 to 200 mg/m^3 and 0 mg/m^3 to 5 000 mg/m^3 of NO_2 for stack gases.

The calibration of the measuring system is the first step to be taken when determining the performance characteristics. Every calibration procedure has to begin with the use of calibration gases. The procedure using calibration gas is described in detail in A.4.1.

NOTE 11 The details of further calibration steps are often given by national regulations, which are not the subject of this International Standard.

Depending on the national regulations, comparative measurements can also be applied. The use of comparative measurements is time consuming and more costly than the method only employing calibration gases. Comparative methods are preferred when results of high integrity are required, for example, when installing continuous-monitoring equipment at large sources. This may be at the time of the installation of a system and again after several years of operation.

In the event of intermittent use of an AMS, only calibration gases are used.

Table 2 gives a list of verified applications of NO_x-measuring systems without reference to a defined AMS. For a new AMS or for an AMS where there is lack of information, the performance characteristics of the AMS must be evaluated for the desired new application. For a defined AMS, it is often possible to transfer the performance characteristics from one application to other applications.

A.2 Principle

The numerical values of performance characteristics of automated measuring systems are evaluated using the complete measuring device. Where there are exceptions, necessary attention is drawn.

Three of the main performance characteristics, namely lower detection limit, response time and effect of interfering substances, are determined either on-site or in the laboratory using gases of known concentration. In the case of an extractive system, these gases are introduced at the beginning of the sampling line of the AMS.

The standard deviation, s_A, of the AMS is then determined on-site, by comparison with measurements taken using a manual method or a verified AMS with a different principle of detection.

For determining the standard deviation, s_A, of the AMS, the AMS is installed on the duct or chimney in question, and its response to various processing conditions is compared with a number of manual samples (i.e. integrated sampling and analysis over at least 70 % of the range of the AMS, if the actual waste gas concentration is spread over this range), or with the output of another AMS with a different measuring principle.

Often the concentration of NO_x can only be changed within a small range. Therefore, s_A is mainly determined close to the concentration level of normal operating conditions. The data obtained are used to determine certain performance characteristics listed in table 1 and table B.1.

A.3 Reagents

A.3.1 Zero gas

The zero gas shall be a gas containing no nitrogen oxides, for example technically pure nitrogen or air that is free from nitrogen oxides.

A.3.2 Calibration gases

The primary calibration gas used shall have a certified concentration and be traceable to a national standard.

A.4 Test procedures

A.4.1 Calibration checks

Extractive automated measuring systems are provided with a basic calibration and a calibration curve of the analyser by the manufacturer. Non-extractive systems are precalibrated and have to be calibrated on-site.

A simple check that can be carried out by the user is the two-point setting (zero and span) of the analyser only. Information about the state of the AMS permits this check to be carried out on the AMS. More information is obtained by checking the entire scale of the analyser.

In the event of continuous use, the setting of the analyser (A.4.1.1) shall be checked at regular intervals given by the period of unattended operation (e.g. weekly) with calibration gases. The accurate full-scale deflection shall be checked at longer intervals (e.g. yearly) or after the analyser has been repaired.

In the case of brief intermittent measurements, the analyser shall be recalibrated before each use with calibration gases.

A.4.1.1 Setting of the analyser

Set up the analyser according to the manufacturer's instructions. Feed the zero gas (A.3.1) into the analyser and set the zero. Then feed in a calibration gas (A.3.2) that has a known concentration corresponding to approximately 70 % to 80 % of the full-scale deflection of the analyser and set the scale reading accordingly. Next, feed the zero gas into the analyser once more and check that the reading returns to zero; if not, re-adjust the zero and repeat.

NOTE 12 For non-extractive devices (path-monitors), the setting of the analyser does not apply as it is part of the AMS. Point monitors may feed zero and span gas into the measuring cell.

A.4.1.2 Checking of the setting of the AMS

Carry out the procedures described in A.4.1.1 again, but this time use the complete AMS. For extractive AMS, the zero gas and the calibration gas are fed into the measuring equipment as close as possible to the nozzle (if possible in front of the filter) at ambient pressure. In this way, the influence of the sampling system is taken into account.

For a non-extractive AMS, follow the manufacturer's instructions. These procedures involve the use of a tube of the same length as the measurement path used on-site and placed between the radiation source and the receiver or special absorption cells supplied by the manufacturer.

A.4.1.3 Checking the accuracy of the full-scale deflection of the analyser

In order to check the entire scale of measuring equipment with a linear calibration curve, carry out the procedure described in A.4.1.1 but use five uniformly distributed calibration gas concentrations (approximately 20 %, 40 %, 60 %, 80 % and 90 % of the full-scale deflection). To obtain these concentrations, gradually dilute the calibration gas (A.3.2) used for setting purposes (see A.4.1.1).

NOTE 13 ISO/TC 158, *Analysis of gases* is preparing standards for preparation of calibration gas mixtures. In this International Standard, ISO/CD 6145-2 has been used.

In the case of a non-linear calibration curve, a minimum of 10 concentrations is required.

An exact mathematical method to test the hypothesis of linearity is given in ISO 9169. However, this method gives only a "yes or no" result: it cannot be used to quantify the deviation of the calibration curve. (For common use, linearity is acceptable if the deviation of every measured value of the calibration curve is not greater than ± 2 % from full scale).

NOTE 14 The input of calibration gas to check the entire scale can take place directly in front of the analyser, because the calibration curve only depends on the analyser.

A.4.2 Determination of performance characteristics

A.4.2.1 Tests using calibration gases

Perform the tests with calibration gases on the complete AMS, either in the laboratory or on-site with the sampling line installed in a duct.

For an extractive system, feed zero gas (A.3.1) and calibration gas (A.3.2) directly into the sampling line, as near as practicable to the sampling head (see figure 1) and at such a pressure that the same sample flow is obtained through the analyser as in A.4.1.2. If the sampling head is installed in a duct, take measures to ensure that the calibration gases are not contaminated with the gas from the duct, for example by closing any valve adjacent to the sampling head.

For testing traversal measuring devices, special arrangements are necessary for the measurements with test gases. The test equipment shall include mechanical components to feed test gases into the measurement path at the appropriate temperature and pressure. A large optical cell is required, with windows transparent to the wavelengths used by the analyser. This optical cell shall be of sufficient diameter to accommodate the analyser beamwidth and of the same length as the optical path across the duct to simulate the highest test gas concentrations required. The temperature of the cell shall be the same as the duct temperature. The concentration of the gas in the cell shall vary under the same conditions as mentioned for extractive systems.

Calibration gases can be used for point monitors in the same way as for extractive systems. The manufacturers usually supply appropriate equipment to carry out this procedure.

A.4.2.1.1 Lower detection limit

Carry out a minimum of 30 determinations by feeding zero gas (A.3.1) into the AMS as described in A.4.2.1, and note the reading. Carry out these readings in the shortest time possible, in order to minimize the zero drift and the temperature-responsive zero deviation (see annex B).

Assuming a confidence level of 95 %, calculate the lower detection limit x, in milligrams per cubic metre, using the formula

$$x = \bar{x}_0 + 2s_{x0}$$

where

$\bar{x}_0$ is the mean, in milligrams per cubic metre, of the blank readings;

s_{x0} is the standard deviation, in milligrams per cubic metre, of the blank readings.

A.4.2.1.2 Measurement of the effect of interfering substances

Pass into the AMS, as described in A.4.2.1, test gases containing uniformly mixed known concentrations of the interfering gas, y_i, corresponding to typical values. Note the measured value, x_{si}, expressed as milligrams of NO_2 per cubic metre, as well as the mass concentration, ρ_{si}, of the interfering gas.

In cases where the change in measured value is linear with increasing mass concentration of a substance, the interfering effect of that substance may be given by x_{si}/ρ_{si}. If the change in measured value is not linear with increasing mass concentration of a substance, the interfering effect of that substance on mass concentration has to be determined separately.

Determine the effect of each interfering substance separately and also the combined effect of a mixture of all the interfering substances to determine the maximum likely interference.

Calculate the interfering effect, S, of a typical mixture of substances from the obtained individual effect, x_{si}/ρ_{si}, of the interfering substances, y_i, using the formula

$$S = \frac{1}{\rho_{FS}} \times \sum_{i=1}^{n} \frac{x_{si}}{\rho_{si}} \times \rho_{mi} \times 100$$

where

ρ_{mi} is the mass concentration of the interfering substance in the mixture, in milligrams per cubic metre;

ρ_{FS} is the measuring range, in milligrams of NO_2 per cubic metre;

n is the number of interfering substances.

Compare this calculated value with the measured value of the mixture. If these two values agree within 20 %, the effect of combination can be neglected and the interfering effects for other mixtures can be calculated.

Also determine the influence of the interfering substances at a concentration of the compound being measured at half-scale deflection (quenching effects, converter effects).

NOTES

15 If it is known that there are no synergistic effects with regard to gases or measuring principles, only the sum of the individual interferent effects can be calculated.

16 The maximum possible concentration of the tested interfering gases depends on the source and the measuring task. In general, valid maximum interfering substance concentrations cannot be given.

The following is an example of a typical mixture of interfering substances; the main components of the flue gas from a combustion plant fired with heavy oil are:

CO_2: 14 % (275 g/m^3)
CO: 100 mg/m^3
SO_2: 3 000 mg/m^3
NO_2: 30 mg/m^3

17 The value given in table 1 is the sum of interfering effects caused by the maximum interfering substance concentrations in the measuring sample.