INTERNATIONAL STANDARD

ISO 11564

First edition
1998-04-01

Stationary source emissions — Determination of the mass concentration of nitrogen oxides — Naphthylethylenediamine photometric method

Émissions de sources fixes — Détermination de la concentration en masse des oxydes d'azote — Méthode photométrique à la naphtyléthylène diamine (NEDA)

Reference number
ISO 11564:1998(E)

Contents

International Organization for Standardization
Case postale 56 • CH-1211 Genève 20 • Switzerland
Internet central@iso.ch
X.400 c=ch; a=400net; p=iso; o=isocs; s=central

Printed in Switzerland

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 11564 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 1, *Stationary source emissions*.

Annexes A and B of this International Standard are for information only.

Stationary source emissions — Determination of the mass concentration of nitrogen oxides — Naphthylethylenediamine photometric method

1 Scope

This International Standard specifies a photometric method for the determination of the mass concentration of nitrogen oxides in exhaust gases from ducts or chimneys.

NOTE — Nitrogen oxides (NO_x) are practically 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.

The method is applicable to the determination of the mass concentration of nitrogen oxides in exhaust gases from combustion processes, processes for surface treatment of metals and from organic chemical reactions, if necessary after removal by washing, in-furnace reduction and/or catalytic denitration, prior to their dispersion into the atmosphere.

This International Standard is applicable to the concentration range 5 mg/m^3 to 1000 mg/m^3 as NO_2 for a sample gas volume of 1000 ml.

For gas concentrations greater than 1000 mg/m^3, the determination of sample gas concentrations up to 5000 mg/m^3 can be performed by diluting the sample solution or by taking an aliquot of the sample solution.

This International Standard is not applicable to the determination of dinitrogen monoxide (N_2O).

2 Principle

Nitrogen oxides in a gas sample are absorbed in an alkaline hydrogen peroxide solution (1,2 mol/l NaOH/ 0,6 % H_2O_2) in the presence of cupric ions (Cu^{2+}), which catalyse the oxidation reaction into nitrite ions.

At the above concentrations, nitrate ions are not produced in the absorption solution.

Hydrogen peroxide in the absorption solution interferes with the colour development. Therefore, hydrogen peroxide is catalytically decomposed with cupric ions by heating the solution for 30 min in a hot water bath at 80 °C.

Nitrite concentration is determined by measuring the absorbance of the coloured solution produced by the reaction with sulfanilamide and naphthylethylenediamine (NEDA) at a wavelength of 545 nm using a photometer.

The mass concentration of nitrogen dioxide is obtained by comparison of the absorbance obtained with a calibration graph prepared using a pure sodium nitrite standard solution.

The sampling time lies between 5 min and 12 min. The time required for the determination is about 60 min.

3 Reagents

Use only reagents of recognized analytical grade and distilled water free of nitrite during the analysis.

3.1 Absorption solution (1,2 mol/l NaOH, 0,6 % H_2O_2, 4,0 % Na_2CO_3, 0,0005 % HCOONa)

Dissolve 48 g of sodium hydroxide, 40,0 g of sodium carbonate and 5 mg sodium formate in about 800 ml of water, add 20 ml of hydrogen peroxide (30 %), and make up to 1000 ml with water.

NOTE — The absorption solution can be stored in a stoppered vessel in a cool dark place for a week. Shaking promotes the decomposition of hydrogen peroxide.

3.2 Cupric sulfate solution (4×10^{-4} mol/l)

Dissolve 1,0 g of cupric sulfate ($CuSO_4$ $5H_2O$) in water in a 1000 ml volumetric flask and make up to the mark. Then dilute 10 ml of this solution in a 100 ml volumetric flask with water and make up to the mark.

3.3 Sulfanilamide/ hydrochloric acid solution (sulfanilamide 0,5 %, hydrochloric acid 20 %)

Dissolve 1,0 g of sulfanilamide in about 50 ml water and add 112 ml of hydrochloric acid (37 %) in a 200 ml volumetric flask. Make up to the mark with water.

3.4 Naphthylethylenediamine (NEDA) solution (0,1 %)

Dissolve 0,1 g of NEDA dichloride in 100 ml water.

3.5 Nitrite solution (250 mg/l, expressed as NO_2^-)

Dissolve 375 mg of dried sodium nitrite ($NaNO_2$) and 0,2 g of sodium hydroxide (NaOH) in water in a 1000 ml volumetric flask. Make up to the mark with water and mix well.

NOTE — The solution is stable for at least three months if stored in a well-stoppered bottle.

3.6 Dilute nitrite solution (20 mg/l, expressed as NO_2^-)

Transfer 40,0 ml of the nitrite solution (3.5) to a 500 ml volumetric flask. Make up to the mark with water and mix well; 1 ml of this solution contains 20 µg of NO_2^-.

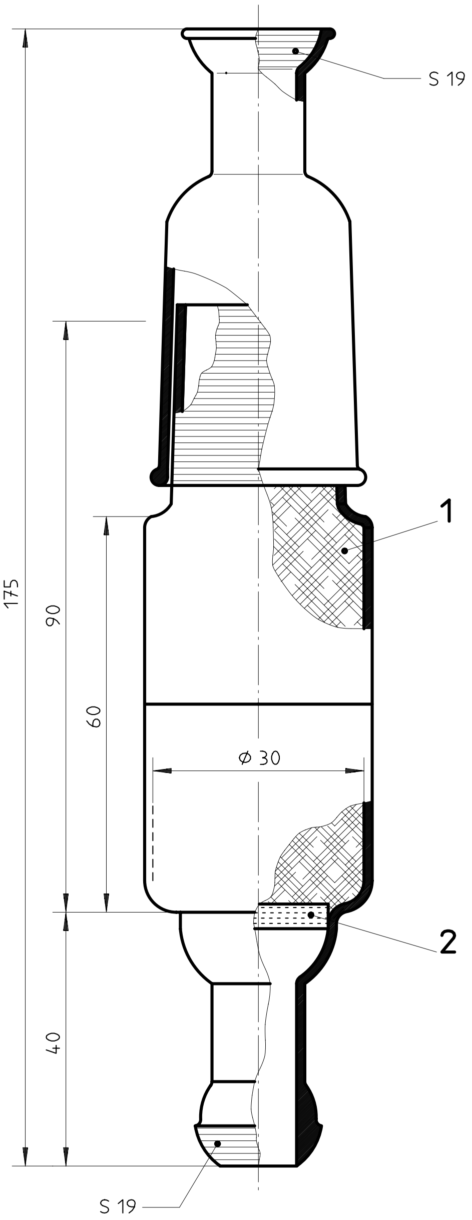
Prepare this solution immediately before use.

4 Apparatus

4.1 Sampling probe, made of corrosion-resistant material, e.g. borosilicate or quartz glass, internal diameter 6 mm to 10 mm; heated if necessary to a temperature above the dewpoint.

4.2 Particle filter, to remove particulate material from the gas, made e.g. from borosilicate or quartz glass. The filter may be integrated in the sampling probe or separate and may be located inside or outside the waste gas duct. An example of an outside filter is shown in figure 1. A suitable inert filter material is quartz wool; heated if necessary.

Dimensions in millimetres



Key

1 Quartz wool, about 0,5 g to 0,8 g, packed progressively

2 Perforated plate or sintered filter

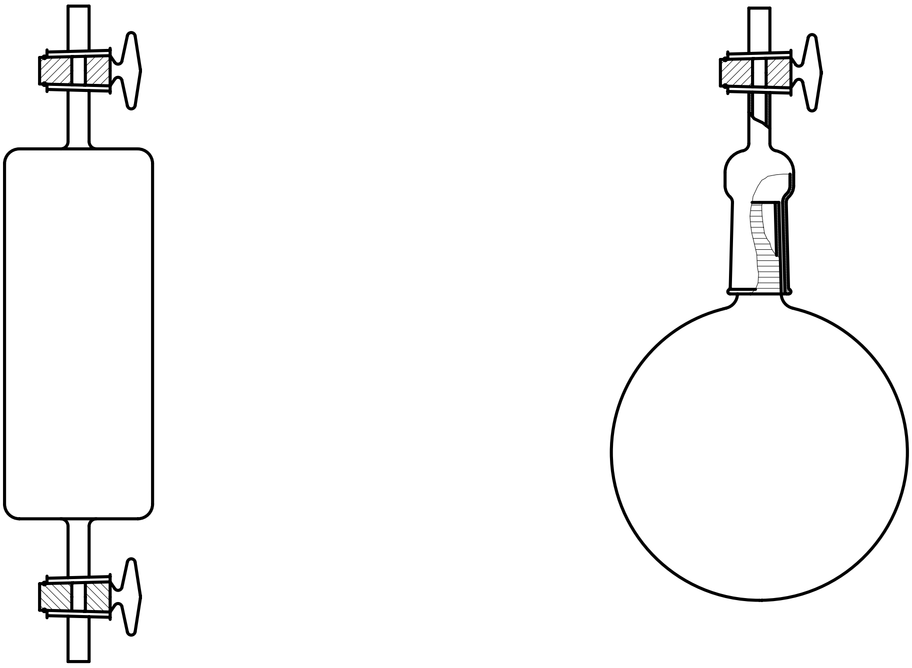
Figure 1 — Example of a particle filter used outside the waste gas duct

4.3 Heating element, e.g. thyristor-controlled heating tapes (for heating of sampling device outside the stack).

4.4 T-piece, e.g. borosilicate or quartz glass, heated if necessary.

4.5 Gas sampling flask, 1000 ml flask, having one or two taps [see figure 2 a) and b)]. The capacity of the flask shall be calibrated by the volumetric method using water.

NOTE — Instead of a gas sampling flask of exactly known volume, a syringe (volume 200 ml or 500 ml, see 4.13) may be used. In this case the given performance characteristics may not be reached.



a) with two one-way taps

b) with one one-way tap

Figure 2 — Examples of gas sampling flasks (approximately 1000 ml capacity)

4.6 Washing bottles, to remove acid gases (e.g. SO_2, HCl) to protect the suction pump. These are only necessary if a high amount of acid gases are present in the sample gas and the suction pump is not corrosion-resistant.

4.7 Drying tube, to protect the pump. Use granular silica gel or calcium chloride for the desiccant.

4.8 Vacuum pump, to evacuate the flask to a pressure below 20 hPa.

4.9 Pressure meter, to measure the pressure before and after gas sampling; a mercury or equivalent pressure meter; suitable to measure pressure in the range 1 hPa to 1000 hPa.

4.10 Critical nozzle, comprising a glass capillary with external diameter 6 mm, internal diameter 1 mm and length approximately 60 mm. In addition, the capillary shall be sharply narrowed at one end by melting.

Its throughput characteristics should be such that, in a gas sampling flask of approx. 1 l capacity, a linear rise in pressure from 10 hPa to about 500 hPa to 600 hPa occurs in a period of 5 min to 12 min.

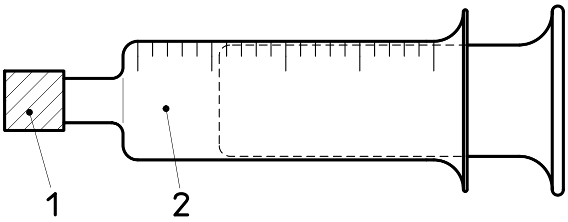
For the test, one tap of an evacuated gas sampling flask is connected to the pressure meter, the other to the capillary. Following opening of the taps, the pressure rise is noted.

4.11 Thermometer, to measure the ambient temperature when sampling gas.

4.12 Photoelectric spectrophotometer or photoelectric photometer, capable of measuring at a wavelength of 545 nm and of accepting cells with an optical pathlength of 1,0 cm to 5,0 cm.

NOTE — In order to protect finger skin from alkaline solution, the use of thin rubber gloves is recommended. Polyvinylchloride gloves are not recommended because they are apt to slip on a glass surface.

4.13 100 ml syringe (optional), as shown in figure 3. The syringe can be used to introduce the absorption solution into the sampling flask.



Key

1 Silicone rubber tube
2 Absorption solution

Figure 3 — Syringe for introducing the absorption solution

5 Sampling techniques

5.1 General

Depending on the measuring task and the available equipment, a sampling train in accordance with one of the examples in figure 4 shall be installed.

The sampling train shown in figure 4 b) can only be used if it is known that the amount of NO_2 is negligible. Generally in stack gases from incinerators, the amount of NO_2 compared with the amount of total nitrogen oxides (sum of $NO+NO_2 = NO_x$) is low; if the amount of NO_2 is lower than 10% NO_x the loss of NO_2 in the condensate in general is negligible.

Ensure that there are no leaks in the sampling train.

5.2 Gas sampling with flask with two taps

5.2.1 Sampling with evacuated flask

5.2.1.1 Connection of flask and measurement of pressure and temperature before gas sampling

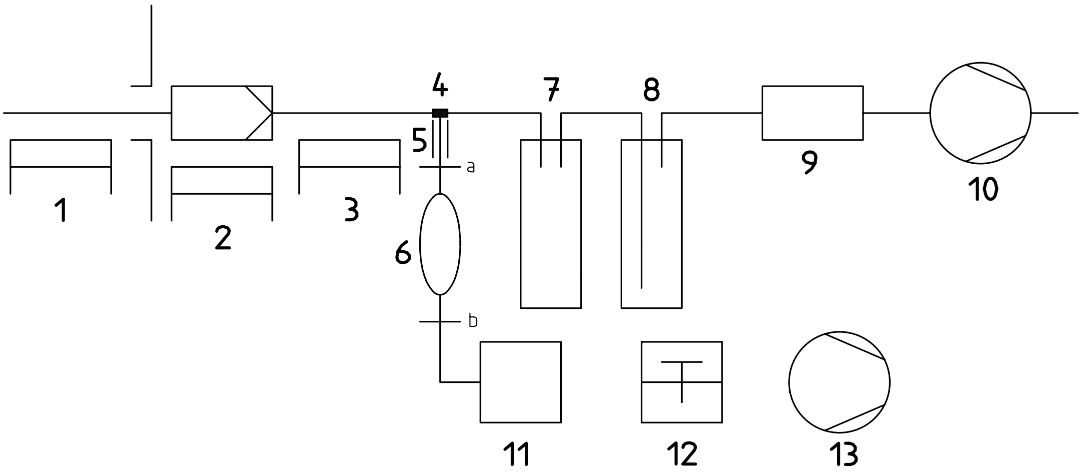
Connect the dried and evacuated sampling flask (6) to the sampling apparatus as shown in figure 4 a). Start the suction pump (10) and purge the sampling line for several minutes (minimum 3 min) with the flue gas. Then open the tap of the sampling flask (b) attached to the pressure meter and measure and record the pressure in the flask (p_o). Simultaneously measure and record the temperature (t_o) near the flask, which should be identical to the temperature in the flask.

5.2.1.2 Introduction of sample gas and measurement of pressure and temperature after gas sampling

Open the tap of the sampling flask (a) attached to the capillary. The gas sampling flask shall be filled with sample gas only up to a pressure of 100 hPa to 600 hPa (depending on the concentration of NO_x).

After closing the tap (a) from the flue, allow the sample to cool to ambient temperature, typically for 3 min but not longer than 5 min. After that time, the pressure indicated at the pressure meter should be stable. Measure and record the pressure in the flask (p_1). Verify the temperature near the flask again (t_1); normally $t_1 = t_o$.

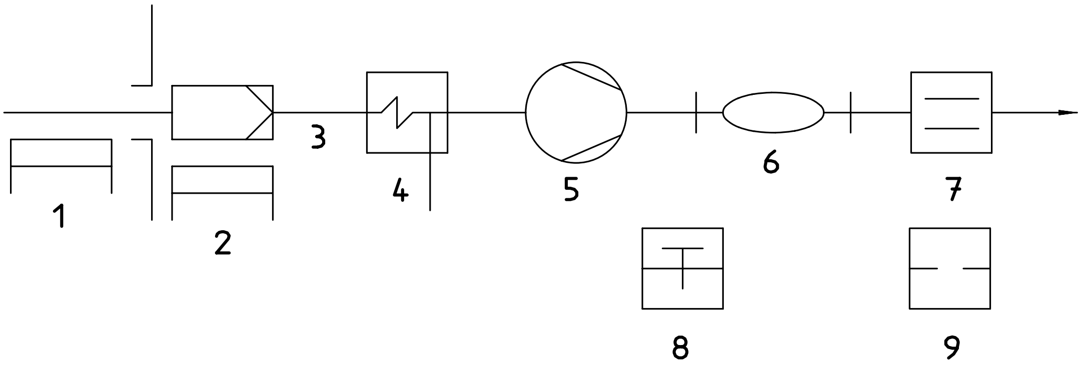
NOTE — Recommendations for choosing sampling pressure as a function of concentration of NO_2 and of the optical length of the cell are given in table 1.



Key

1 Sampling probe, heated when appropriate
2 Particle filter, heated when appropriate
3 Sampling line (as short as possible), heated when appropriate
4 T-piece
5 Capillary
6 Gas sampling flask [according to figure 2 a)]
7 Vacant bottle (to prevent back-flow), when appropriate
8 Washing bottle, containing sodium hydroxide solution, when appropriate
9 Drying tube
10 Suction pump
11 Pressure meter
12 Thermometer
13 Vacuum pump

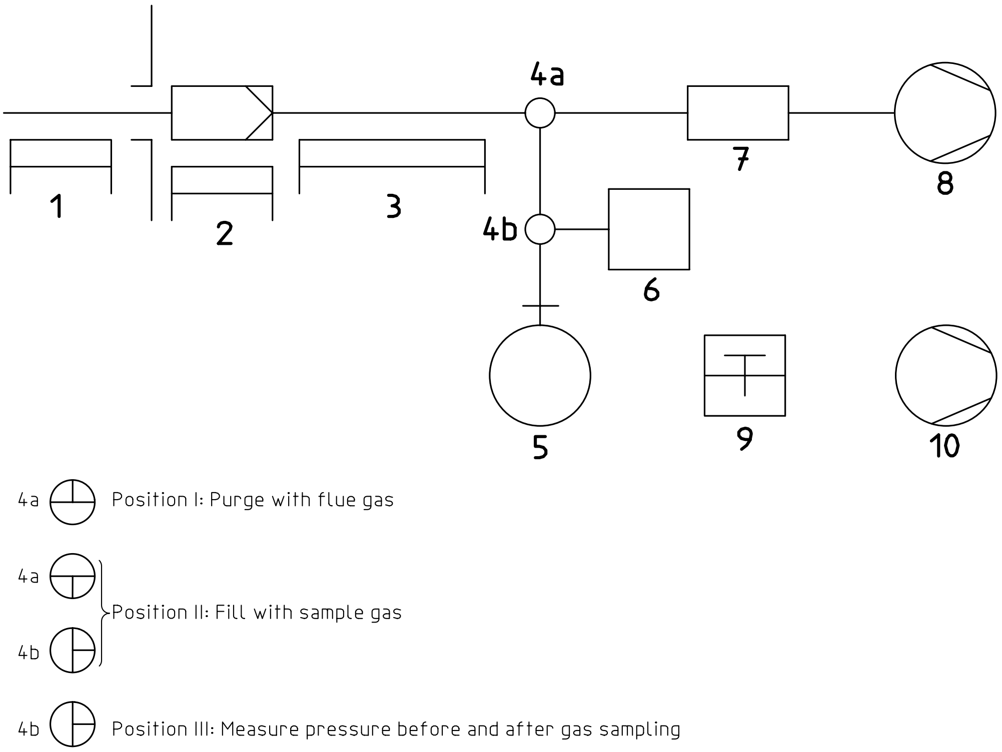
a) Heated sampling system, sampling flask with two taps



Key

1 Sampling probe, heated when appropriate
2 Particle filter, heated when appropriate
3 Sampling line (as short as possible), heated when appropriate
4 Condensate separator
5 Suction pump
6 Gas sampling flask
7 Gas flow meter
8 Thermometer
9 Barometer

b) Condensing sampling system, sampling flask with two taps



Key

1 Sampling probe, heated when appropriate
2 Particle filter, heated when appropriate
3 Sampling line (as short as possible), heated when appropriate
4 Three-way valve
5 Gas sampling flask [according to figure 2 b)]
6 Pressure meter
7 Drying tube
8 Suction pump
9 Thermometer
10 Vacuum pump

c) Heated sampling system, sampling flask with one tap

Figure 4 — Examples of a sampling train

Table 1

Concentration of NO_x mg/m^3 (expressed as NO_2)	**Length of optical cell** cm	**Pressure after sampling** kPa
100	5	40-60
200	5	20-40
500	1	40-60
500	5	10-20
1000	1	20-40
2000	1	10-20

5.2.1.3 Detaching the flask

Close the tap (b) of the gas sampling flask. Detach the flask (6) from the gas sampling apparatus.

NOTE — The absorption solution should be introduced after taking the gas sample in the sampling flask, because the pressure of the gas will drop due to absorption of carbon dioxide from the sample gas.

5.2.2 Sampling with purging the sampling flask

Connect the dried sampling flask (6) to the sampling apparatus as shown in figure 4 b). Start the suction pump (5) and purge the the sampling line and the flask until the volume of gas that has passed through it is about ten times the volume of the sampling flask. The two taps of the flask are then closed, so that a slight overpressure is produced in the flask. When the temperature has equalized (typically within 3 min) the flask is expanded against water, the ambient temperature and the atmospheric pressure are measured and the absorption solution is introduced by means of a syringe (see 4.13).

5.3 Gas sampling with flask with one tap

5.3.1 Connection of flask and measurement of pressure and temperature before gas sampling

Connect the dried and evacuated sampling flask (5) to the sampling apparatus as shown in figure 4 c). Start the suction pump (8) and purge the sampling line for several minutes (minimum of 3 min) with the flue gas [three-way valve (4a) in position I]. Bring three-way valve (4b) into measuring position III and open the tap of the sampling flask. Record the pressure in the flask (p_o). Simultaneously measure and record the temperature (t_o) near the flask, which should be identical to the temperature in the flask.

5.3.2 Introduction of sample gas and measurement of pressure and temperature after gas sampling

Bring three-way valve (4a) into position II to fill the flask with sample gas. The gas sampling flask shall be filled with sample gas only up to a pressure of 100 hPa to 600 hPa (depending on the concentration of NO_x).

Bring three-way valve (4a) back into position I. Wait until the pressure indicated at the pressure meter is stable (typically within 3 min) and measure and record the pressure of the flask (p_1). Measure the temperature near the flask again (t_1); normally $t_1 = t_o$.

5.3.3 Detaching the flask

Close the tap of the gas sampling flask. Detach the flask (5) from the gas sampling apparatus.

5.4 Introducing the absorption solution

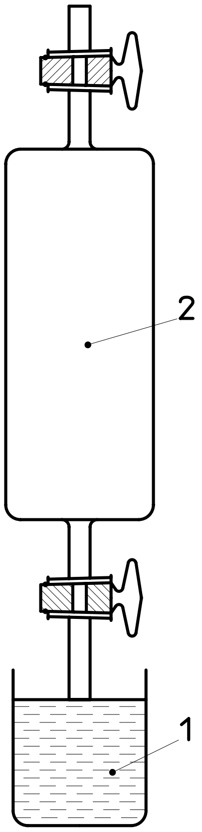
5.4.1 Method a

By means of a silicone rubber tube, connect the tap end of the sampling flask to the syringe (4.13; see figure 3) containing 50 ml of the absorption solution (3.1) and 5 ml of the cupric sulfate solution (3.2), which have been mixed together in advance. Then open the tap and introduce the mixed solution into the flask. Close the tap of the flask and detach the syringe from the flask.

5.4.2 Method b

Connect a silicone rubber tube (length about 5 cm) to the end of a tap of the sampling flask. Bring the other end of the silicone rubber tube to the bottom of a glass beaker or an Erlenmeyer flask (according to figure 5) containing 50 ml of the absorption solution (3.1) and 5 ml of the cupric sulfate solution (3.2), which have been mixed together in advance. Then open the tap and introduce the mixed solution by means of the remaining vacuum into the flask. Immediately close the tap of the flask and detach the silicone rubber tube.

The cupric sulfate solution shall be mixed with the absorption solution just before use, in order to minimize gas-phase reactions of SO_2 with NO and NO_2 in the sampling flask. The time interval from sampling the gas to start of shaking with the absorption solution shall be less than 5 min.



Key

1 Glass beaker or Erlenmeyer flask (containing the absorption solution)
2 Gas sampling flask

Figure 5 — Procedure for introducing the absorption solution

5.5 Shaking the flask

Either shake the flask vigorously with intermittent rests for a total of 3 min, or, after shaking vigorously for 1 min, fix the flask to a shaking machine and shake it mechanically for an additional 2 min.

5.6 Transferring the solution to a volumetric flask

Transfer the sample solution from the flask into a 100 ml volumetric flask (volume V_t). Wash the sampling flask with about 15 ml of water twice and add the washings to the sample solution in the volumetric flask.

NOTE — If the volumetric flask is well-stoppered, the solution can be stored for up to 36 h before the next step in the procedure (5.7).

5.7 Decomposition of hydrogen peroxide

Put the open volumetric flask into a water bath at 80 °C for 30 min. Remove and shake the flask. Cool the flask to room temperature with running water.

5.8 Preparing the sample solution for analysis

Add water to the 100 ml volumetric flask up to the mark and mix. This solution shall be used as the sample solution for analysis.

NOTE — If the volumetric flask is well-stoppered, the solution can be stored up to 48 h before the next step in the procedure (6.4).

6 Determination

6.1 Preparation of a set of calibration solutions

Prepare a set of calibration solutions having mass concentrations of nitrite ions of 0 mg/l (blank); 0,2 mg/l; 0,4 mg/l; 0,6 mg/l; 0,8 mg/l and 1,0 mg/l prepared by respectively pipetting, 0 ml (blank); 1 ml; 2 ml; 3ml; 4 ml and 5 ml of the dilute $NaNO_2$ solution (3.6) into a series of 100 ml volumetric flasks. Follow the procedure given in 5.4 to 5.8 [add 50 ml of the absorption solution (3.1) and 5 ml of the cupric sulfate solution (3.2) to a sampling flask (5.4), shake for 2 min (5.5), transfer the solution to a volumetric flask (5.6), decompose H_2O_2 (5.7) and prepare the calibration solutions for analysis (5.8)].

6.2 Preparation of the blank solution

Prepare the blank solution as follows:

a) Put 50 ml of the absorption solution (3.1) and 5 ml of the cupric sulfate solution (3.2) together into a 100 ml volumetric flask.

b) Decompose hydrogen peroxide as described in 5.7, then make up to the mark with water and mix well.

c) Follow procedure 6.3 a) to 6.3 c) and, after standing for 15 min at 15 °C to 30 °C, use this solution as a blank.

6.3 Procedure

a) Pipette 20,0 ml (*V*) of the sample solution into a 100 ml volumetric flask;

b) Add 10 ml of the sulfanilamide/hydrochloric acid solution (3.3);

c) Add 5 ml of the NEDA solution (3.4), make up to the mark with water and shake well;

d) Allow this solution to stand for about 15 min at 15 °C to 30 °C and measure the absorbance with a photoelectric photometer (4.12) at a wavelength near 545 nm, using the blank solution as a reference solution. The photometric analysis shall be performed within 2 h of preparation of the solutions.

NOTE — If the mass concentration of NO in the sample solution is more than 1,2 mg/l, the calibration graph will not be linear. In such a case, the sample solution should be diluted with blank solution to a concentration lower than this upper limit (1,2 mg/l).

6.4 Preparation of a set of calibration graphs

For the analysis of the calibration solutions, follow the procedure given in 6.3.

Plot a calibration graph with the absorbance of each calibration solution versus the mass concentration of nitrogen dioxide (see figure 6).

The slope of the straight line in the calibration graph is given by equation (1).

$$\frac{\Delta A}{\Delta c} = \frac{1}{f} \qquad (1)$$

where

A is the absorbance;
c is the mass concentration of nitrite ions, in milligrams per litre;
f is the calibration factor, in milligrams per litre, related to a 1 cm pathlength optical cell.

A typical value of *f* is about 0,9 mg/l (for a 1 cm pathlength cell).

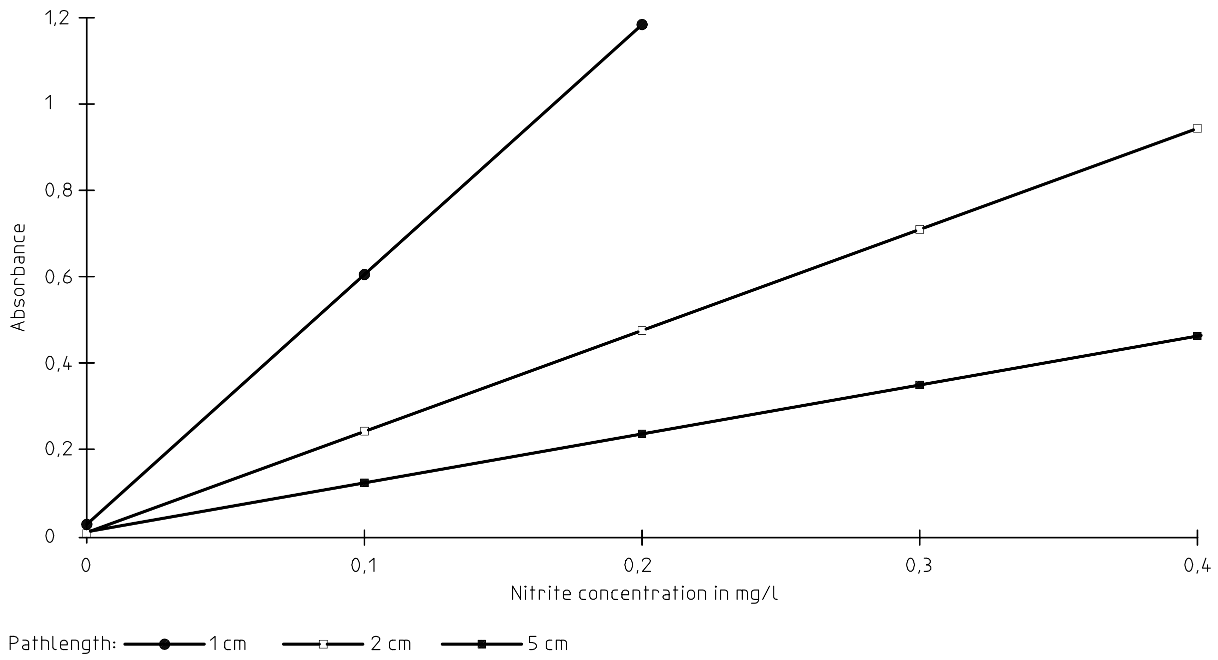


Figure 6 — Calibration curve for nitrogen oxides (example)

7 Calculation

7.1 Calculation of the amount of sample gas taken

Calculate the amount of sample gas taken, referred to standard atmospheric conditions (0 °C, 101,3 kPa), using equation (2):

$$V_s = V_a \times \frac{273}{101{,}3} \times \left(\frac{p_1 - p_{w1}}{273 + t_1} - \frac{p_0}{273 + t_0} \right) \tag{2}$$

where

V_s is the amount of sample gas taken, in litres;

V_a is capacity of gas sampling flask (4.5), in litres;

p_0 is the pressure in the flask before gas sampling, in kilopascals;

p_1 is the pressure in the flask after gas sampling, in kilopascals;

t_0 is the temperature in the flask before gas sampling, in degrees Celsius;

t_1 is the temperature in the flask after gas sampling, in degrees Celsius;

p_{w1} water vapour pressure at t_1 (zero if gas is dry) in kilopascals.

In general $t_1 = t_0$ and equation (2) is simplified to equation (3):

$$V_s = V_a \times \frac{273}{101{,}3} \times \frac{p_1 - p_{w1} - p_0}{273 + t_1} \tag{3}$$

Symbols are as in equation (2).

7.2 Calculation of mass concentration of nitrogen oxides

Calculate the mass concentration of nitrogen oxides in the sample gas as nitrogen dioxide using equation (4):

$$c = f \times A \times \frac{nV_t}{V_s} \times 10^3 \qquad (4)$$

where

c is the mass concentration of nitrogen oxides (expressed as NO_2) in the sample gas, in milligrams per cubic metre;

f is the calibration factor, in milligrams per litre solution (6.4);

NOTE — f is valid for the length of optical cell used. For cells with other pathlengths, separate calibration graphs must be prepared.

A is the absorbance;

n is the dilution ratio of the sample solution: (0,1/0,02 = 5);

V_t is the volume of the total sample solution, in litres: (0,1 l);

V_s is the volume, in litres, of the sample gas in standard conditions as calculated in 7.1.

8 Interferences

8.1 Reactions of SO_2 with NO and NO_2 in the gas phase before adding the absorption solution are evidently measured. But the absorption solution, as it contains H_2O_2, will quickly oxidize SO_2 into SO_4^{2-}, which does not react with NO and NO_2.

8.2 Hydrogen chloride does not affect the analysis if the amount of HCl in the flue gas is less than 365 mg/m^3 (higher concentrations not investigated but it is expected that higher concentrations likewise do not interfere). HCl does not interfere unless the amount of HCl in the sample gas reduces the pH of the absorption solution (pH 13) to less than pH 12. If the pH of the absorption solution decreases to less than pH 12 by adding acid, NO_3^-. will be produced.

8.3 Cupric ions (Cu^{2+}) reduce the formation of the azo dye when present in high concentrations. The amount of Cu^{2+} used should always be constant, including in the blank solution.

8.4 CO and CO_2 in exhaust gases do not interfere.

8.5 N_2O (up to 100 mg/m^3) is stable and does not interfere with the results (higher concentrations were not investigated).

8.6 NH_3 (up to 20 mg/m^3) does not interfere (higher concentrations were not investigated).

8.7 SO_3 (up to 100 mg/m^3) and HF (up to 10 mg/m^3) do not interfere (higher concentrations were not investigated).

9 Performance characteristics

9.1 Lower detection limit

The lower detection limit of the method may be expected to be 2 mg/m^3 (NO_2) when using a 5 cm pathlength optical cell.

9.2 Precision

The repeatability of the method is within 3 % at mass concentration levels of nitrogen oxides of about 50 mg/m^3 to about 1000 mg/m^3.

10 Test report

The test report shall include at least the following information.

a) complete identification of the sample gas;
b) the test results;
c) any unusual features noted during the determination;
d) all necessary data from the plant during measurements;
e) any operation not included in this International Standard or in the International Standards to which reference is made.

Annex A
(informative)

Experimental results

A.1 General

The photometric method described in this International Standard can be used as a reference method for the calibration of automated measurement systems (AMS) for nitrogen oxides as described in ISO 10849. For this use it is important to know the standard deviation of the photometric method.

The standard deviation is determined by comparative measurements of two identical sampling lines, which are installed at the same duct and which are supplied with identical sample gas. The standard deviation s_C is calculated from the results of comparative measurements (with two identical systems) according to the following formula:

$$s_C = \pm \frac{\sqrt{\Sigma(c_{1i} - c_{2i})^2}}{2n} \qquad \text{(A.1)}$$

where

s_C is the standard deviation of the method;

c_{1i}, c_{2i} is the mass concentration of nitrogen oxides determined by the two identical systems of the method, in milligrams per cubic metre;

n is the number of comparative measurements.

The standard deviation s_C of the manual method (in the case of verifying an AMS used as comparative method) is expressed in mg/m^3.

Experimental results of this manual method were obtained in Japan, Germany and the Netherlands. In all experiments some slight modifications on the original NEDA method were made. Also the NEDA method was compared to other systems for determination of nitrogen oxides, like the chemiluminescence method or the method using ionchromatography.

A.2 Japanese results

A.2.1 Modifications

- the absorption solution was constituted as follows: NaOH 1,5 mol/l, H_2O_2 0,6 %, Na_2CO_3 4 %; HCOONa 0,0002 %; (for the ore-sintering furnace)
- NaOH 2 mol/l, H_2O_2 0,6 %, Na_2CO_3 8 %; HCOONa 0,0002 %; (for the boiler)
- in some experiments a sampling syringe was used instead of a sampling flask.

A.2.2 Experiments

The method was tested in exhaust gases from a boiler and an ore-sintering furnace. The method was also compared to the chemiluminescence method.

Standard deviation of the method (boiler):
s_C = ± 1,5 mg/m^3; s_{rel} = ± 2,8 % (mean 54 mg/m^3)

Standard deviation of the method (ore-sintering furnace):
s_C = ± 6,1 mg/m^3; s_{rel} = ± 1,4 % (range 390 mg/m^3 to 420 mg/m^3)

Comparison to the chemiluminescence method (ore-sintering furnace):
s_{chem} = 8,6 mg/m^3; s_{rel} = 2,2 % (range 390 mg/m^3 to 420 mg/m^3)

A.3 German results

The NEDA-method was tested with span gases of a known NO_x-concentration. The method was also tested at a waste incineration plant (with DeNox). The method was also compared with an AMS, using an NDIR-analyser and with the ion chromatography method.
The standard deviation was calculated as described in A.1.

Standard deviation of the method:
s_C = ± 2,2 mg/m^3; s_{rel} = ± 3,5 % (range 40 mg/m^3 to 140 mg/m^3)

Comparison to the NDIR-analyser:
s_{NDIR} = 2,0 mg/m^3; s_{rel} = ± 3,1 % (range 40 mg/m^3 to 140 mg/m^3)

Comparison to the ion chromatography method:
s_{IC} = ± 2,4 mg/m^3; s_{rel} = 5,6 % (range 40 mg/m^3 to 140 mg/m^3)

A.4 Dutch results

The photometric NEDA method was investigated both in laboratory experiments (using a synthetic flue-gas composition with known concentration levels) and in field experiments (two different power plants). The method was compared to the Dutch standard NEN 2044 (sodium salicylate method), the same method using ion chromatography analysis and the chemiluminescence method.

Standard deviation of the method:
s_C = ± 2,7 % for the laboratory tests and ± 3,2 % for the field tests.

Comparison to NEN 2044:
$s_{So\text{-}Sal}$ = 6,2 %; Agreement within 3,5 % with NEDA method (95 % confidence limit)

Comparison to the chemiluminescence method:
Agreement within 3,8 % with NEDA method (95 % confidence limit)

Annex B
(informative)

Bibliography

[1] ISO 10849:1996, *Stationary source emissions — Determination of the mass concentration of nitrogen oxides — Performance characteristics of automated measuring systems.*

[2] M. Pourbaix, *Atlas d'equilibres électrochimiques*: Azote 493, Eau 97, Eau Oxygénée 106; (1963) CEBELCOR, Paris.

[3] K. Suzuki, T. Niimi, N. Yamamoto, M. Shibata, M. Saeki, A. Ono, T. Shirai, and S. Yanagisawa, Rapid photometric Method for the Determination of the Mass Concentration of Nitrogen Monoxide and Nitrogen Dioxide, *Anal. Chim. Acta*, **295** (1-2), 135-141, Sept. 1, 1994

ICS 13.040.40

Descriptors: air, quality, air pollution, exhaust emissions, gas emissions, chemical analysis, determination of content, concentration, nitrogen oxides, spectrometric method.

Price based on 16 pages