
**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)*



Contents	Page
1 Scope.....	1
2 Principle	1
3 Reagents	2
4 Apparatus.....	2
5 Sampling techniques	5
6 Determination	10
7 Calculation	11
8 Interferences	12
9 Performance characteristics	12
10 Test report.....	13
Annex A: Experimental results	14
Annex B: Bibliography.....	16

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 ($1,2 \text{ mol/l NaOH/0,6 \% H}_2\text{O}_2$) 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 % H₂O₂, 4,0 % Na₂CO₃, 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 (CuSO₄ · 5H₂O) 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 NO₂⁻)

Dissolve 375 mg of dried sodium nitrite (NaNO₂) 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 NO₂⁻)

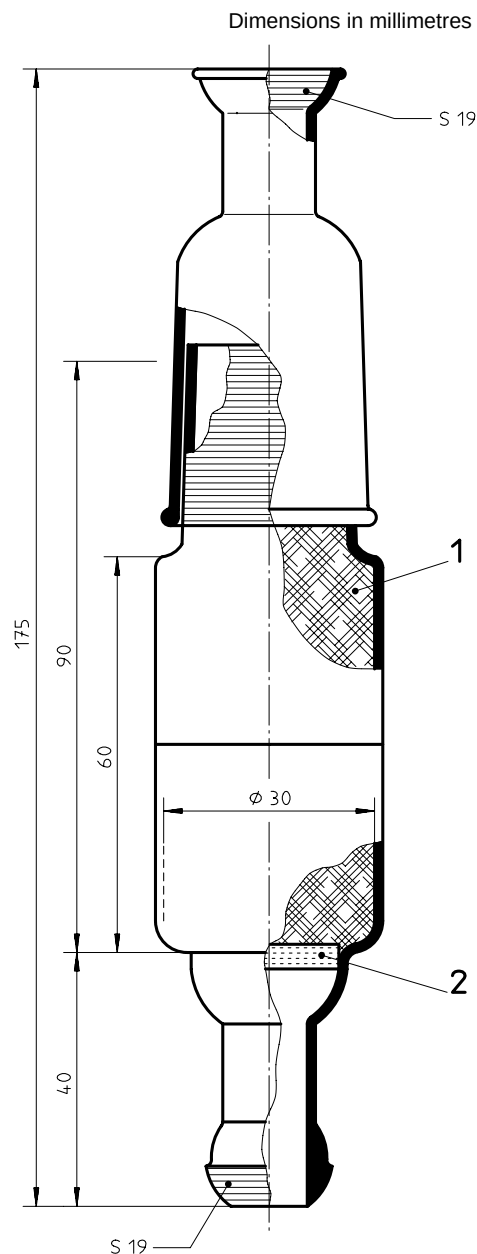
Transfer 40,0 ml of the nitrite solution (3.5) to a 500 ml volumetric flask. Make up to the mark with water and mix well; 1 ml of this solution contains 20 µg of NO₂⁻.

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.



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.