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**Ambient air — Determination of mass  
concentration of nitrogen dioxide —  
Modified Griess-Saltzman method**

*Air ambiant — Détermination de la concentration en masse de dioxyde  
d'azote — Méthode de Griess-Saltzman modifiée*

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## Foreword

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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 6768 was prepared by Technical Committee ISO/TC 146, *Air quality*, Subcommittee SC 3, *Ambient atmospheres*.

This second edition cancels and replaces the first edition (ISO 6768:1985), which has been technically revised.

Annex A of this International Standard is for information only.

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# Ambient air — Determination of mass concentration of nitrogen dioxide — Modified Griess-Saltzman method

## 1 Scope

This International Standard specifies a modified Griess-Saltzman method for the determination of the mass concentration of nitrogen dioxide present in ambient air.

The method is applicable to the determination of the mass concentration of nitrogen dioxide present in ambient and confined air within the range 0,003 mg/m<sup>3</sup> to 2 mg/m<sup>3</sup> and for sampling times between 10 min and 2 h.

Substances present in the air mass under investigation, and thus in the air sample, and known to have an effect on the instrument reading, are given in 7.4. Information on the performance characteristics is given in 8.2.

The method is not suitable for personal breathing-zone sampling.

The Griess-Saltzman method is suitable for the analytical check of calibration gas mixtures which are used to calibrate chemiluminescence analysers (see ISO 7996).

## 2 Normative reference

The following standard contains provisions which, through reference to this text, constitute provisions of this International Standard. At the time of publication, the edition indicated was 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 edition of the standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 6349:1979, *Gas analysis — Preparation of calibration gas mixtures — Permeation method*.

## 3 Principle

The nitrogen dioxide present in an air sample is absorbed by passage through an azo-dye-forming reagent within a specified period, resulting in the formation of a pink colour within 15 min.

The absorbance of the sample solution is then determined at a wavelength between 540 nm and 550 nm using an appropriate spectrophotometer. The corresponding mass concentration of nitrogen dioxide is determined from a calibration graph of absorbance vs. concentration prepared using sodium nitrite solutions of known concentrations.

## 4 Reagents

During the analysis, use only reagents of recognized analytical grade and only nitrite-free water (4.1).

#### 4.1 Nitrite-free water.

If the water used to prepare the absorption and calibration solutions results in a pink coloration due to the presence of nitrite in the water, prepare nitrite-free water as follows. Add one crystal each of potassium permanganate ( $\text{KMnO}_4$ ) and barium hydroxide [ $\text{Ba}(\text{OH})_2$ ] to the water and redistill using an all-glass still.

#### 4.2 *N*-(1-naphthyl)ethylenediamine dihydrochloride, 0,5 g/l stock solution.

Dissolve 0,5 g of *N*-(1-naphthyl)ethylenediamine dihydrochloride [ $\text{C}_{10}\text{H}_7\text{NH}(\text{CH}_2)_2\text{NH}_2 \cdot 2\text{HCl}$ ] in 1000 ml of nitrite-free water (4.1).

Store in a stoppered brown glass bottle at a temperature below 5 °C. The solution is stable for several months.

NOTE It is also possible to store small weighed amounts of the solid reagent.

#### 4.3 Absorption solution.

Dissolve 5,0 g of sulfanilic acid ( $\text{C}_6\text{H}_4\text{SO}_3\text{H}_2\text{NH}_2$ ) in approx. 600 ml of nitrite-free water (4.1) and 50 ml of acetic acid by heating, if necessary, in a 1000 ml one-mark volumetric flask. Cool the solution to room temperature, add 100 ml of *N*-(1-naphthyl)ethylenediamine dihydrochloride solution (4.2), mix and make up to the mark with nitrite-free water (4.1).

Store in a well-stoppered brown glass bottle at a temperature below 5°C. The solution is stable for 2 weeks.

#### 4.4 Gas mixtures.

Prepare gas mixtures, which are used to test the absorption efficiency (7.1.1), following the permeation technique specified in ISO 6349 or by an equivalent method.

#### 4.5 Reagents for preparation of the calibration graph

##### 4.5.1 Nitrite solution, $\rho_{\text{NO}_2} = 250 \text{ mg/l}$ .

Dissolve 375 mg of sodium nitrite ( $\text{NaNO}_2$ ) in nitrite-free water (4.1) in a 1000 ml one-mark volumetric flask. Make up to the mark with nitrite-free water and mix well.

Store in a well-stoppered bottle. The solution is stable for at least 3 months.

1 ml of this solution contains 250  $\mu\text{g}$  of  $\text{NO}_2^-$ .

##### 4.5.2 Nitrite solution, $\rho_{\text{NO}_2} = 2,5 \text{ mg/l}$ .

Transfer 10,0 ml of nitrite solution (4.5.1) to a 1000 ml one-mark volumetric flask. Make up to the mark with nitrite-free water (4.1) and mix well.

Prepare this solution immediately before use.

1 ml of this solution contains 2,5  $\mu\text{g}$  of  $\text{NO}_2^-$ .

## 5 Apparatus

### 5.1 Ordinary laboratory apparatus and sampling equipment, as specified in 5.1.1 to 5.1.7.

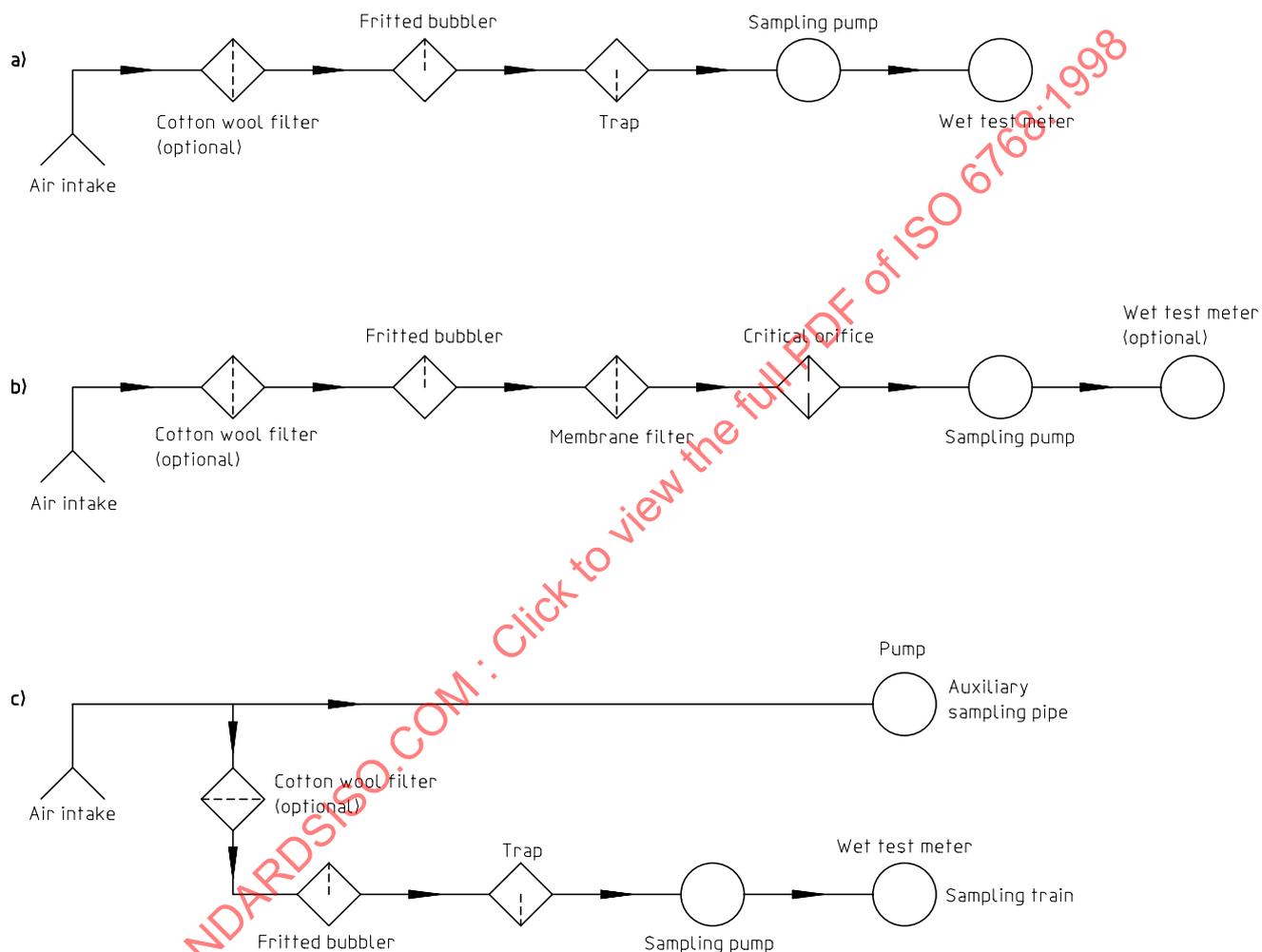
#### 5.1.1 Sampling probe.

Borosilicate glass, stainless steel or polytetrafluoroethylene tube whose internal diameter is approximately 6 mm and which is as short as possible, but in any case not longer than 2 m, provided with a downward-facing air intake.

If the use of such short sampling probes is not possible, an auxiliary sampling pipe consisting of a sampling probe of internal diameter about 50 mm, provided with a joint for attachment to the sampling train, and a pump drawing air at a volume flowrate of about 2 m<sup>3</sup>/h shall be used [see figure 1 c)].

### 5.1.2 Cotton wool filter.

Borosilicate glass tube, of internal diameter at least 15 mm and length approximately 80 mm, loosely packed with bleached, not optically brightened, and non-finished cotton wool. It shall be a component of the sampling train only if it is considered necessary to remove ozone from the air before it enters the fritted bubbler (see also 7.4).



**Figure 1 — Examples of sampling trains capable of the determination of the mass concentration of nitrogen dioxide in ambient air**

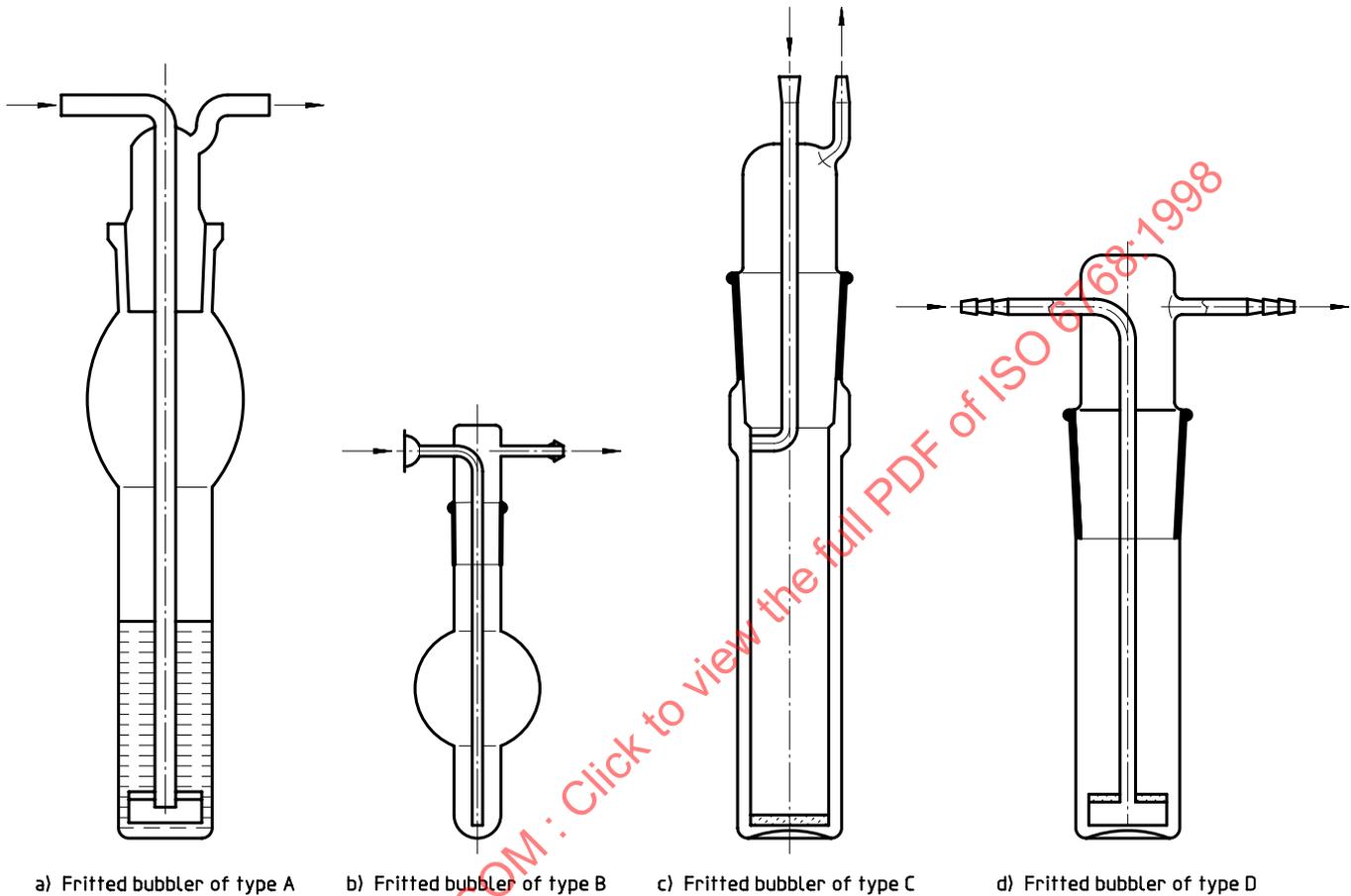
### 5.1.3 Fritted bubbler.

Borosilicate all-glass bubblers equipped with a frit whose porosity shall be fine enough to enable an absorption efficiency of at least 0,95 to be attained without providing too great a pressure drop in use. Frits having pore diameters between 40 µm and 60 µm are suitable. Four examples of fritted bubblers (types A to D) that have been found to be suitable are shown in figure 2.

The absorption efficiency of each individual fritted bubbler shall be tested at least once a year using calibration gas mixtures prepared following the permeation technique specified in ISO 6349 or by an equivalent method.

Coloured frits shall be cleaned with a mixture of a potassium dichromate solution and concentrated sulfuric acid or other appropriate cleaning agents. When a dichromate-sulfuric acid mixture is used, care shall be taken that the frits are thoroughly rinsed with nitrite-free water (4.1).

**WARNING** — Avoid physical contact with dichromate and reagents containing dichromate, in particular with a dichromate-sulfuric acid mixture.



**Figure 2 — Examples of absorbers suitable for sampling nitrogen dioxide**

(The ends of the glass tubes of each of these absorbers can be designed as spherical ground joints, conical ground joints or olives.)

#### 5.1.4 Trap.

Conical flask of capacity 100 ml, filled with glass-wool.

#### 5.1.5 Membrane filter.

**5.1.6 Sampling pump and control system**, capable of drawing air at a volume flow rate of about 0,4 l/min to 0,6 l/min during the sampling period.

#### 5.1.7 Air metering device.

Use either a wet test meter, a calibrated all-glass variable-area flowmeter, a calibrated critical orifice or a calibrated mass flowmeter. In all cases, the air volume flowrate should be known to within  $\pm 5\%$ .

A wet test meter or a soap bubble meter is convenient for testing the calibration of the variable-area flowmeter, the critical orifice or the mass flowmeter.

**5.2 Spectrophotometer**, capable of determining absorbance at a wavelength of between 540 nm and 550 nm, and capable of taking optical cells for spectrophotometric measurements of liquids as specified in 5.3.

**5.3 Optical cells**, plane, matched pairs, having an optical pathlength of 10 mm to 50 mm.

**5.4 One-mark pipettes**, of capacities 5 ml; 10 ml; 15 ml; 20 ml; 25 ml; 50 ml.

## 6 Sampling

Assemble a sampling train in accordance with the examples shown in figure 1 and any special requirements for the air mass under investigation. Use ground glass joints upstream from the fritted bubbler or butt-to-butt glass with polyvinylchloride or polytetrafluoroethylene connections.

Transfer, by means of a pipette (5.4), a suitable volume of absorption solution (4.3) into the dry fritted bubbler (5.1.3), namely 25 ml for fritted bubblers of type A, 20 ml for fritted bubblers of type B, 50 ml for fritted bubblers of type C and 10 ml for fritted bubblers of type D. Connect the fritted bubbler to the sampling train.

Record the reading on the wet test meter (5.1.7) and the time, and start the sampling pump (5.1.6). Adjust the air-volume flow regulator to give an air-volume flowrate of about 0,4 l/min to 0,6 l/min.

The sampling period shall be 10 min to 2 h as required. Protect the absorption solution from light during sampling.

At the end of the sampling period, switch off the sampling pump, note the reading on the wet test meter and the time. Remove the fritted bubbler from the sampling train. Mix the bulk of the sample solution outside the frit with the small quantity of the sample solution inside the frit by sucking a sufficient portion through the frit and then releasing. Repeat several times.

Stopper the fritted bubbler carefully and protect the sample solution from light. Allow the sample solution to stand for 15 min.

Due to the limited time stability of the sample solution, the interval of time between the end of sampling and the beginning of measurements to be carried out with the sample solution shall not exceed 20 h.

NOTE Generally, the influence of evaporation can be neglected for short sampling periods. However, with an extended sampling period, a small volume of absorption solution and dry air conditions, the influence of evaporation should be taken into account.

## 7 Procedure

### 7.1 Test of fritted bubblers

#### 7.1.1 Test of absorption efficiency

In accordance with the examples shown in figure 1, assemble a sampling train where two fritted bubblers of the same type are connected in series, each of them containing the appropriate volume of absorption solution, as specified in clause 6.

Introduce the inlet of the sampling train into the outlet of a permeation device (or use an equivalent method) capable of producing gas mixtures (see 4.4) at a volume flowrate higher than that expected at the intake area of the sampling train. Prepare a gas mixture having a mass concentration of nitrogen dioxide of about 1 mg/m<sup>3</sup>. Avoid mass concentrations of nitrogen dioxide higher than 2 mg/m<sup>3</sup>.

Choose a sampling period resulting in the absorption of a mass of nitrogen dioxide of about 0,5 µg per 1 ml of the absorption solution exposed in the first fritted bubbler, and carry out sampling as specified in clause 6.

Calculate the absorption efficiency by dividing the absorbance of the sample solution in the first fritted bubbler by the sum of the absorbances of the sample solution in the first and the second fritted bubbler.

The absorption efficiency shall be at least 0,95. Fritted bubblers that do not meet this requirement should not be used.

### 7.1.2 Test of frit porosity

The porosity of the frits may be affected by repeated cleaning. Therefore, the frits shall be checked, for example, using a suitable surface-tension method, if such a change is believed to have occurred.

NOTE Experienced and trained persons may judge the usefulness of a frit by observing the gas distribution obtained in a liquid.

## 7.2 Calibration

### 7.2.1 Preparation of a set of calibration solutions

Prepare a set of calibration solutions having mass concentrations of nitrite ions of 0,0 µg/ml; 0,25 µg/ml; 0,5 µg/ml; 0,75 µg/ml and 1,0 µg/ml by pipetting 0 ml; 5 ml; 10 ml; 15 ml and 20 ml, respectively, of the nitrite solution (4.5.2) into a series of 50 ml one-mark volumetric flasks, making up to the mark with absorption solution (4.3) and mixing.

Allow the solutions to stand for 15 min.

### 7.2.2 Spectrophotometric measurements

Test the spectrophotometer (5.2) in accordance with the manufacturer's instructions and after stabilization, carry out any necessary adjustments and set the wavelength to a fixed value in the range 540 nm to 550 nm.

Transfer a sufficient portion from each of the four calibration solutions (7.2.1) into optical cells (5.3) and read the absorbance of each against an optical cell containing a sufficient portion of the absorption solution (4.3).

### 7.2.3 Plotting the calibration graph

Prepare a calibration graph by plotting the absorbance,  $A$ , of each calibration solution (7.2.1) with respect to the absorbance of the absorption solution (4.3) versus the mass concentration of nitrite ions,  $\rho_{\text{NO}_2}$ , in the corresponding solution (see figure 3).

Note that the slope of the straight line, which is defined by the equation

$$\frac{\Delta A}{\Delta \rho_{\text{NO}_2}} = \frac{1}{f_{\text{NO}_2}}$$

should be  $(0,992 \pm 0,030)$  ml/µg with an optical range of 10 mm. If it is not, test all reagents.

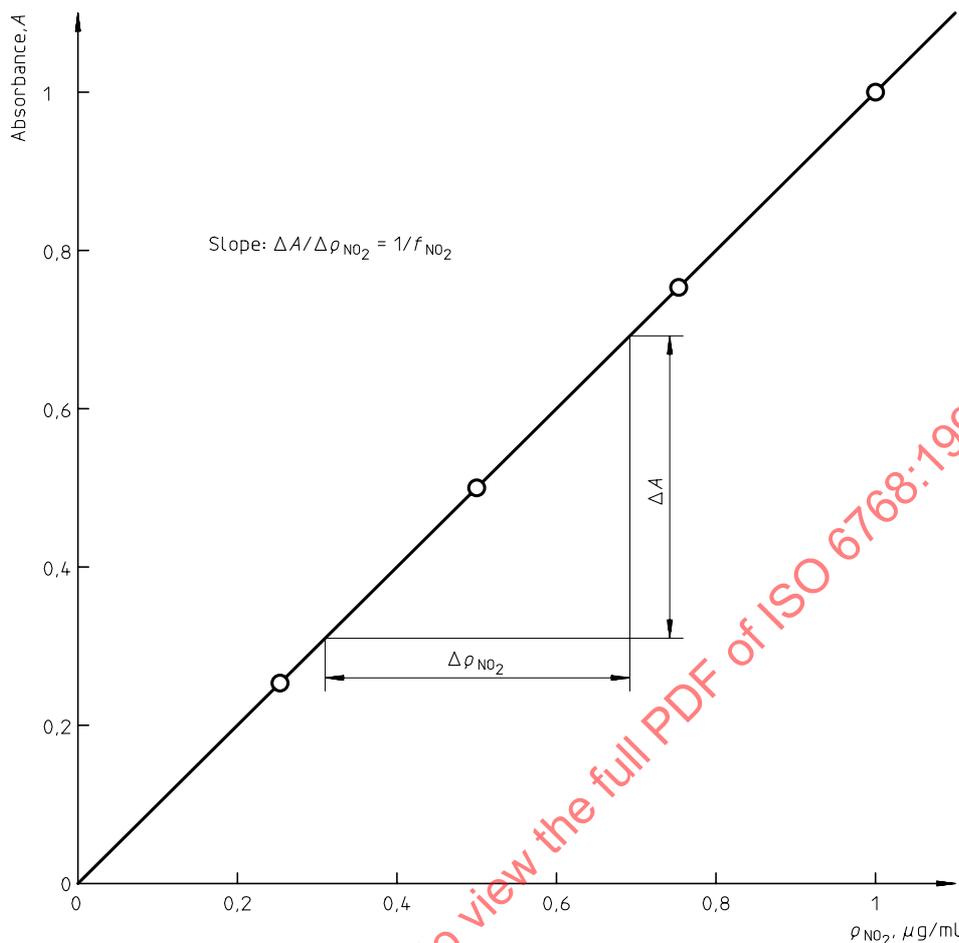


Figure 3 — Typical calibration graph

### 7.3 Determination

The measurement of the absorbance of the sample solution shall not be carried out earlier than 15 min or later than 20 h after completion of sampling.

Transfer a sufficient portion of the sample solution into an optical cell and measure its absorbance as specified in 7.2.2, but using a matched optical cell containing a sufficient portion of absorption solution (4.3) as reference. Evaluate the mass of nitrogen dioxide contained in the air sample divided by the volume of the sample solution by reference to the calibration graph (7.2.3).

NOTE 1 Cells of long optical pathlength may be used when high sensitivity is needed.

NOTE 2 It is also possible to use a matched optical cell containing distilled water or air as reference; the absorbance of the absorption solution (4.3) is then deducted from the absorbance of the sample solution.

### 7.4 Interferents

The mass concentrations of nitrogen monoxide, sulfur dioxide, hydrogen sulfide, hydrogen chloride and fluorine compounds generally present in ambient air have no effect on the determination of the mass concentration of nitrogen dioxide.

Ozone interferes slightly with the determination by increasing the instrument reading if the mass concentration of ozone in the air sample is higher than  $0,20 \text{ mg/m}^3$ . This interfering effect can be avoided by the use of a cotton wool filter (see 5.1.2).

Peroxyacynitrates (PAN) can give a response of approximately 15 % to 35 % of an equimolar concentration of nitrogen dioxide. In ambient air, however, the mass concentrations of peroxyacynitrates are usually too low to cause any significant error.

Nitrite and nitrous acid, which may be present in the air sample, produce a pink colour in the absorption solution like nitrogen dioxide.

## 8 Expression of results

### 8.1 Calculation

The mass concentration of nitrogen dioxide,  $\rho_{\text{NO}_2}$  expressed in micrograms per cubic metre, in the air sample, is given by the equation

$$\rho_{\text{NO}_2} = f_{\text{NO}_2} \times \frac{A_s - A_a}{b} \times \frac{V_1}{V_2} \times 10$$

where

$f_{\text{NO}_2}$  is the reciprocal of the slope, expressed in micrograms per millilitre, of the calibration graph, related to a 10 mm optical cell;

$A_s$  is the absorbance of the sample solution;

$A_a$  is the absorbance of the absorption solution (see note 2 to 7.3);

$b$  is the optical pathlength, in millimetres, of the matched optical cells used;

$V_1$  is the volume, in millilitres, of the absorption solution transferred to the fritted bubbler;

$V_2$  is the volume, in cubic metres, of the air sample.

### 8.2 Performance characteristics

#### 8.2.1 Lower detection limit

The lower detection limit of the method may be expected to lie at a mass concentration of nitrogen dioxide of  $3 \mu\text{g}/\text{m}^3$ .

#### 8.2.2 Precision

##### 8.2.2.1 Repeatability

The repeatability of the method is expected to be within 5 % at a mass concentration of nitrogen dioxide of about  $100 \mu\text{g}/\text{m}^3$ .

##### 8.2.2.2 Reproducibility

The reproducibility of the method is expected to be within 5 % at a mass concentration level of nitrogen dioxide of about  $100 \mu\text{g}/\text{m}^3$ .

## 9 Test report

The test report shall include at least the following information:

- a) a complete identification of the air sample;
- b) a reference to this International Standard;
- c) the results obtained;
- d) any unusual features noted during the determination;
- e) any operation not specified in this International Standard or in an International Standard to which reference is made, or regarded as optional.

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