TC146

International Standard 6768

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

Air ambiant — Détermination de la concentration en masse du 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 approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

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Ambient air — Determination of the 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.

2 Field of application

The method is applicable to the determination of the mass concentration of nitrogen dioxide present in ambient and confined air within the range 0,010 to about 20 mg/m³. Sampling times can range from 10 min to 2 h.

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 should not exceed 8 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 8.5. Information on the performance characteristics is given in 9.2.

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

3 Reference

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

4 Principle

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

Determination of the absorbance of the sample solution at a wavelength of between 540 and 550 nm using an appropriate spectrophotometer (or colorimeter) and evaluation of the mass concentration of nitrogen dioxide by means of a calibration graph prepared using calibration gas mixtures obtained following the permeation technique.

According to the equipment available in the laboratory it may be convenient in certain cases to use, for routine tests, sodium nitrite solutions. However, this procedure shall only be used after a proper calibration by use of a permeation device.

5 Reagents

During the analysis, use only reagents of recognized analytical grade and only nitrite-free water (5.1).

5.1 Nitrite-free water.

Available distilled or deionized water may contain nitrite as impurity, and consequently may produce a distinct pink colour in solutions specified in 5.3, 5.4.3 and 8.3.1 when used for preparing these solutions. Therefore, redistill it, if necessary, in an all-glass still after adding a crystal of each of potassium permanganate ($KMnO_4$) and barium hydroxide [$Ba(OH)_2$], and check again.

5.2 *N*-(1-naphthyl)-ethylenediamine dihydrochloride, 0,9 g/l stock solution.

Dissolve 0,45 g of *N*-(1-naphthyl)-ethylenediamine dihydrochloride [$C_{10}H_7NH(CH_2)_2NH_2{\cdot}2HCl$] in 500 ml of nitrite-free water (5.1).

The solution is stable for several months if stored in a well-stoppered brown glass vessel in a refrigerator.

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

5.3 Absorption solution.

Dissolve 4,0 g of *p*-aminobenzenesulfonamide (sulfanilamide, $NH_2C_6H_4SO_2NH_2$), 10,0 g of tartaric acid [$HOOC(CHOH)_2COOH$], and 100 mg of disodium ethylenediaminetetraacetate dihydrate [$(HOOCCH_2)_2N(CH_2)_2N(CH_2COONa)_2{\cdot}2H_2O$] in about 100 ml of hot nitrite-free water (5.1) in a 1 000 ml one-mark volumetric flask. Cool the solution to room temperature, add 100 ml of *N*-(1-naphthyl)-ethylenediamine dihydrochloride solution (5.2) and 10,0 ml of acetone (CH_3COCH_3), mix and make up to the mark with nitrite-free water (5.1).

Store the absorption solution at a temperature below 25 °C. The absorption solution is stable for 3 months, if stored in a well-stoppered bottle in the dark.

5.4 Calibration gas mixtures.

Immediately before use, prepare, following the permeation technique specified in ISO 6349, zero gas and gas mixtures of at least four different concentration levels of nitrogen dioxide covering the whole desired working range.

5.5 Reagents for preparation of the routine test graph

5.5.1 Nitrite, 250 mg/l solution.

Dissolve 375 mg of sodium nitrite ($NaNO_2$) and 0,2 g of sodium hydroxide (NaOH) in nitrite-free water (5.1) in a 1 000 ml one-mark volumetric flask. Make up to the mark with nitrite-free water and mix well.

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

1 ml of this solution contains 250 µg of NO_2^-.

5.5.2 Nitrite, 2,5 mg/l solution.

Transfer 10,0 ml of nitrite solution (5.4.1) to a 1 000 ml one-mark volumetric flask. Make up to the mark with nitrite-free water (5.1) and mix well.

Prepare this solution immediately before use.

1 ml of this solution contains 2,5 µg of NO_2^-.

5.5.3 Colour test solution.

Dissolve 4,0 g of *p*-aminobenzenesulfonamide (sulfanilamide), 10,0 g of tartaric acid and 100 mg of disodium ethylenediaminetetraacetate dihydrate in 400 ml of hot nitrite-free water (5.1) in a 500 ml one-mark volumetric flask. Cool the solution to room temperature and dissolve in it 90 mg of *N*-(1-naphthyl)-ethylenediamine dihydrochloride. Add 10,0 ml of acetone, mix and make up to the mark with nitrite-free water.

Store the solution at a temperature below 25 °C. The solution is stable for 3 months, if stored in a well-stoppered bottle in the dark.

6 Apparatus

Ordinary laboratory apparatus and

6.1 Sampling equipment, as specified in 6.1.1 to 6.1.7.

6.1.1 Sampling probe.

Borosilicate glass, stainless steel or polytetrafluoroethylene tube the internal diameter of which 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 flow rate of about 2 m^3/h should be used (see figure 2).

6.1.2 Cotton wool filter.

Borosilicate glass tube, the internal diameter of which is at least 15 mm and which is about 80 mm long, loosely packed with bleached, not optically brightened, and non-finished cotton wool. It shall only be a component of the sampling train if it is considered necessary to remove ozone from the air before it enters the fritted bubbler (see also 8.5).

6.1.3 Absorber.

Borosilicate all-glass bubblers equipped with a frit, the porosity of which should 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 and 60 µm are suitable; the test factor as defined in 8.1.1 shall not be lower than 0,9. Three examples of fritted bubblers (types A to C) that have been found to be suitable are shown in figure 1.

The retention efficiency and the absorption efficiency of each individual fritted bubbler should be tested at least once a year using calibration gas mixtures prepared following the permeation technique specified in ISO 6349.

Coloured frits should 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 (5.1).

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

6.1.4 Trap.

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

6.1.5 Membrane filter.

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

6.1.7 Air metering device.

Use either a wet test meter, a calibrated all-glass variable area flowmeter or a calibrated critical orifice. In all cases, the air volume flow rate of about 0,4 l/min should be known to within ± 5 %.

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

6.2 Spectrophotometer (or **colorimeter**), capable of determining absorbance at a wavelength of between 540 and 550 nm, and capable of taking optical cells for spectrophotometric measurements of liquids as specified in 6.3.

6.3 Optical cells, plane, matched pairs, having an optical path length of 1,0 to 5,0 cm.

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

7 Sampling

Assemble a sampling train in accordance with the examples shown in figure 2 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 polyvinyl-chloride or polytetrafluoroethylene connections.

Transfer, by means of a pipette (6.4), a suitable volume of absorption solution (5.3) into the dry fritted bubbler (6.1.3), namely 10 ml for fritted bubblers of type A, 20 ml for fritted bubblers of type B and 50 ml for fritted bubblers of type C. Connect the fritted bubbler to the sampling train.

Record the reading on the wet test meter (6.1.7) and the time and start of the sampling pump (6.1.6). Adjust the air-volume flow regulator to give an air-volume flow rate of about 0,4 l/min.

The sampling period is 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 and mix the bulk of the sample solution outside the frit with the small quantity of the sample solution inside the frit. This mixing is carried out by sucking a sufficient portion through the frit and then releasing. This is repeated several times.

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

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.

8 Procedure

8.1 Test of fritted bubblers

8.1.1 Test of retention efficiency and of absorption efficiency

In accordance with the examples shown in figure 2 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 7.

Introduce the inlet of the sampling train into the outlet of a permeation device (see figure 3) capable of producing gas mixtures (see 5.4) at a volume flow rate higher than that expected to be present at the intake area of the sampling train. Prepare a gas mixture having a mass concentration of nitrogen dioxide of about 1 mg/m^3. Avoid mass concentrations of nitrogen dioxide higher than 2 mg/m^3, since above this mass concentration level the test factor f_T (see 9.1.2) may be up to 10 % lower depending on the mass concentration.

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 7.

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.

Calculate the test factor, f_T, by dividing the nitrite equivalent of the quantity of nitrogen dioxide absorbed in the absorption solution exposed in the first fritted bubbler by the quantity of nitrogen dioxide present in the volume of the calibration gas mixture passed through the sampling train.

The absorption efficiency shall be at least 0,95 and the test factor f_T at least 0,9. Fritted bubblers that do not fulfil these requirements should not be used.

8.1.2 Test of the porosity of frits

The porosity of the frits may be affected by repeated cleaning. Therefore, the frits should be checked, if such a change is believed to have occurred.

The porosity of the frits can be measured by a suitable surface tension method.

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

8.2 Calibration

8.2.1 Preparation of a set of calibration solutions

Assemble the sampling train in the same way as that used for sampling, and place into the fritted bubbler the appropriate volume of absorption solution, as specified in clause 7.

Introduce the inlet of the sampling train into the outlet of a permeation device (see figure 3) capable of producing gas mixtures (see 5.4) at a volume flow rate higher than that expected to be present at the intake area of the sampling train. Prepare a gas mixture in accordance with the requirements given in 5.4 and carry out a similar procedure to that specified in clause 7 for an interval of time approximately equal to that to be used for sampling. Proceed likewise at each of the mass concentration levels of nitrogen dioxide selected.

After switching off the sampling pump allow the respective solutions to stand for 15 min.

8.2.2 Zero member solution

Prepare a zero member solution from the zero gas (5.4). This preparation is carried out according to 8.2.1.

8.2.3 Spectrophotometric measurements

Test the spectrophotometer (or colorimeter) (6.2) in accordance with the manufacturer's instructions and after stabilization, set the wavelength to a fixed value in the range 540 to 550 nm.

Transfer a sufficient portion from each of the four or more calibration solutions (8.2.1) to optical cells (6.3) and read the absorbance of each against an optical cell containing a sufficient portion of the zero member solution (8.2.2).

8.2.4 Plotting the calibration graph

Prepare a calibration graph by plotting the absorbance, A, of each calibration solution with respect to the absorbance of the zero member solution (8.2.2), versus the mass of nitrogen dioxide contained in the volume of the calibration gas mixture passed through the sampling train divided by the volume of absorption solution placed into the fritted bubbler, ϱ_B (see figure 4).

The slope of the straight part of the calibration graph is given by the equation

$$\frac{\Delta A}{\Delta \varrho_B} = \frac{1}{f_G}$$

Take the reciprocal of the slope as the calibration factor f_G.

8.3 Routine test graph

8.3.1 Preparation of a set of calibration solutions

Prepare a set of calibration solutions having mass concentrations of nitrite ions of 0,25; 0,5; 0,75 and 1,0 µg/ml by pipetting 5; 10; 15; and 20 ml, respectively, of the nitrite solution (5.5.2) into a series of 50 ml one-mark volumetric flasks, adding 25 ml of the colour test solution (5.5.3), making up to the mark with nitrite-free water (5.1) and mixing.

Allow the solutions to stand for 15 min.

8.3.2 Zero member solution

Transfer, by means of a pipette (6.4), 25 ml of the colour test solution (5.5.3) into a 50 ml one-mark volumetric flask, make up to the mark with nitrite-free water and mix well.

Allow the solution to stand for 15 min.

8.3.3 Spectrophotometric measurements

Test the spectrophotometer (or colorimeter) (6.2) 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 to 550 nm.

Transfer a sufficient portion from each of the four calibration solutions (8.3.1) into optical cells (6.3) and read the absorbance of each against an optical cell containing a sufficient portion of the zero member solution (8.3.2).

8.3.4 Plotting the routine test graph

Prepare a routine test graph by plotting the absorbance, A', of each calibration solution (8.3.1) with respect to the absorbance of the zero member solution (8.3.2) versus the mass concentration of nitrite ions, ϱ_L, in the corresponding solution (see figure 5).

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

$$\frac{\Delta A'}{\Delta \varrho_L} = \frac{1}{f_L}$$

should be (0,992 ± 0,030) ml/µg. If it is not, test all reagents.

8.4 Determination

The measurement of the absorbance of the sample solution should be carried out as soon as possible, i.e. with a delay no longer than 8 h.

Transfer a sufficient portion of the sample solution into an optical cell and measure its absorbance as specified in 8.2.3 and 8.3.3, but using a matched optical cell containing a sufficient portion of absorption solution (5.3) 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 (8.2.4) or the mass concentration of nitrite ions in the sample solution by reference to the routine test graph (8.3.4).

NOTES

1 Use cells of long optical path length when high sensitivity is needed.

2 It is also possible to use a matched optical cell containing distilled water or air as reference; the absorbance of the absorption solution (5.3) is then deducted from the absorbance of the sample solution.

8.5 Interferents

The mass concentrations of nitrogen monoxide, sulfur dioxide, hydrogen sulfide, chlorine, 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 0,25 mg/m^3. This interfering effect can be avoided by the use of a cotton wool filter (see 6.1.2).

Peroxyacylnitrates (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 peroxyacylnitrates 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.

9 Expression of results

9.1 Calculation

9.1.1 Reference to the calibration graph

9.1.1.1 Absorbance in the linear part of the calibration graph

If the absorbance is in the linear part of the calibration graph, the mass concentration of nitrogen dioxide, $\varrho(NO_2)$, expressed in micrograms per cubic metre, in the air sample, is given by the equation

$$\varrho(NO_2) = f_G \times \frac{A_s - A_a}{b} \times \frac{V_1}{V_2}$$

where

f_G is the calibration factor, expressed in micrograms per millilitre, related to a 1 cm optical cell (see 8.2.4);

A_s is the absorbance of the sample solution;

A_a is the absorbance of the absorption solution (see note 2 to 8.4);

b is the optical path length, in centimetres, 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.

If there is any reason at all to suppose that the properties of the spectrophotometer (or colorimeter) used in the preparation of the calibration graph differ significantly from those of the one used in the determination of the absorbance of the sample solution, then use a corrected calibration factor, f'_G, expressed in micrograms per millilitre, given by the equation

$$f'_G = f_G \times \frac{f'_L}{f_L}$$

where

f_G is the calibration factor, expressed in micrograms per millilitre (see 8.2.4);

f'_L is the reciprocal of the slope, expressed in micrograms per millilitre, of the routine test graph (see 8.3.4) as evaluated by means of the spectrophotometer (or colorimeter) used in the determination of the absorbance of the sample solution;

f_L is the reciprocal of the slope, expressed in micrograms per millilitre, of the routine test graph as evaluated by means of the spectrophotometer (or colorimeter) used in the preparation of the calibration graph.

9.1.1.2 Absorbance in the non-linear part of the calibration graph

If the absorbance is in the non-linear part of the calibration graph, the mass concentration of nitrogen dioxide, $\varrho(NO_2)$, expressed in micrograms per cubic metre, in the air sample, is given by the equation

$$\varrho(NO_2) = \frac{1}{b} \times \varrho_B \times \frac{V_1}{V_2}$$

where

b is the optical path length, in centimetres, of the matched optical cells used;

ϱ_B is the mass concentration of nitrogen dioxide, expressed in micrograms per millilitre, related to a 1 cm optical cell, in the sample solution read from the calibration graph (see figure 4);

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.

9.1.2 Reference to the routine test graph

If, for convenience, the mass concentration of nitrite ions in the sample solution is evaluated by reference to the routine test graph, the mass concentration of nitrogen dioxide, $\varrho(NO_2)$, expressed in micrograms per cubic metre, in the air sample, is given by the equation

$$\varrho(NO_2) = \frac{1}{f_T} \times f_L \times \frac{A_s - A_a}{b} \times \frac{V_1}{V_2}$$

where

f_T is the test factor (see 8.1.1);

f_L is the reciprocal of the slope, expressed in micrograms per millilitre, of the routine test graph, related to a 1 cm optical cell;

A_s is the absorbance of the sample solution;

A_a is the absorbance of the absorption solution (see note 2 to 8.4);

b is the optical path length, in centimetres, 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.

NOTE — The mass concentration of nitrite ions, $\varrho(NO_2^-)$, expressed in micrograms per millilitre, in the sample solution, is given by the equation

$$\varrho(NO_2^-) = f_L \times \frac{A_s - A_a}{b}$$

9.2 Performance characteristics

9.2.1 Lower detection limit

The lower detection limit of the method may be expected to be at a mass concentration of nitrogen dioxide of 10 µg/m³.

9.2.2 Precision

9.2.2.1 Repeatability

The repeatability of the method is expected to be within 10 % at a mass concentration level of nitrogen dioxide of about 100 µg/m³.

9.2.2.2 Reproducibility

The reproducibility of the method may be expected to be within 10 % at a mass concentration level of nitrogen dioxide of about 100 µg/m³.

10 Test report

The test report shall include at least the following information :

a) a complete identification of the air sample;

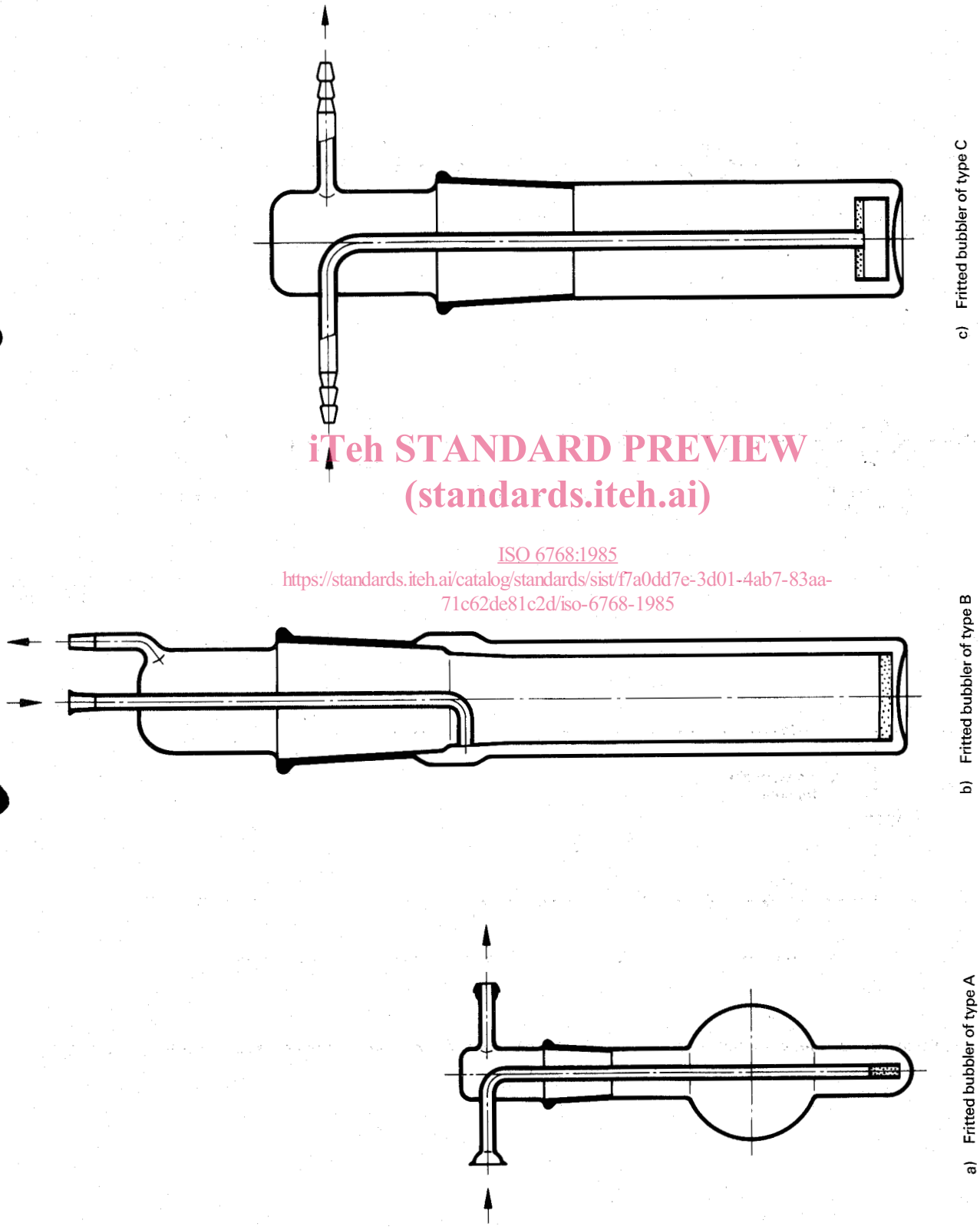
b) a reference to this International Standard;

c) a reference to ISO 6349;

d) the results obtained;

e) any unusual features noted during the determination;

f) any operation not specified in this International Standard or in the International Standard to which reference is made, or regarded as optional.



c) Fritted bubbler of type C

b) Fritted bubbler of type B

a) Fritted bubbler of type A

Figure 1 — 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.)