International Standard ISO 4220

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Ambient air — Determination of a gaseous acid air pollution index — Titrimetric method with indicator or potentiometric end-point detection

Air ambiant — Détermination d'un indice de pollution gazeuse acide de l'air — Méthode titrimétrique avec indicateur ou détection potentiométrique du point final

First edition — 1983-12-01
Corrected and reprinted — 1984-08-15

UDC 614.71 : 543.27 : 543.257.1 **Ref. No. ISO 4220-1983 (E)**

Descriptors : air, air pollution, chemical analysis, determination of content, gases, acids, sulphur dioxide, volumetric analysis, potentiometric analysis.

Price based on 5 pages

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.

International Standard ISO 4220 was developed by Technical Committee ISO/TC 146, *Air quality*, and was circulated to the member bodies in October 1982.

It has been approved by the member bodies of the following countries:

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The member bodies of the following countries expressed disapproval of the document on technical grounds:

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Printed in Switzerland

INTERNATIONAL STANDARD ISO 4220-1983 (E)

Ambient air — Determination of a gaseous acid air pollution index — Titrimetric method with indicator or potentiometric end-point detection

1 Scope and field of application

This International Standard specifies a titrimetric method for the determination of a gaseous acid pollution index (see clause 3) of ambient air, using an indicator or a potentiometric procedure to detect the end-point.

The method is applicable to the determination of a gaseous acid pollution index of ambient air equivalent to mass concentrations of sulfur dioxide higher than $30\ \mu g/m^3$.

The results obtained following this method depend on the amounts of both acid and alkaline gaseous air pollutants which are likely to be determined under the specified sampling and analytical conditions.

The sampling period is 24 or 48 h.

The method is not specific for sulfur dioxide.

2 Reference

ISO 4219, *Air quality — Determination of gaseous sulphur compounds in ambient air — Sampling equipment.*

3 Definition

gaseous acid air pollution index: Concentration of water-soluble "acidic" gaseous components of the air sample expressed conventionally in terms of sulfur dioxide.

NOTE — The gaseous acid air pollution index is not a total acidity index as this would also include particulate acid air pollutants.

4 Principle

Absorption and oxidation of the soluble gaseous components of the air sample passing through an acidified solution of hydrogen peroxide of defined pH within a specified period, resulting in the formation of sulfuric acid, the main product of oxidation.

Titration (colorimetric or potentiometric end-point detection) of the resultant solution with sulfuric acid or sodium tetraborate to restore the original pH.

5 Reagents

During the analysis, use only reagents of recognized analytical grade and only double-distilled or deionized and distilled water.

5.1 Hydrogen peroxide, solution, 27 to 30 % (*m*/*m*).

5.2 Potassium chloride, solution, saturated at room temperature (potentiometric procedure only).

NOTE — This solution improves the conductivity and the stability of the pH reading.

5.3 Buffer solutions.

Use appropriate commercially available buffer solutions or prepare buffer solutions of equivalent quality from commercially available powders or tablets or by established laboratory procedures (potentiometric procedure only).

The pH of the solutions shall be accurately known at a given temperature.

5.4 Absorption solution, pH 4,5.

Place 10 ml of the hydrogen peroxide solution (5.1) (colorimetric procedure) or 10 ml of the hydrogen peroxide solution and 25 ml of the potassium chloride solution (5.2) (potentiometric procedure) into a 1 000 ml one-mark volumetric flask, make up to the mark with water and mix well. Titrate a 50 ml aliquot portion of the solution obtained to pH 4,5 with the standard volumetric sulfuric acid solution (5.5) after the addition of 1,0 ml of indicator solution (5.7) (colorimetric procedure) or using a pH meter (potentiometric procedure). Titrate likewise a second 50 ml aliquot portion of the diluted hydrogen peroxide solution. Record the mean of the volume, V_1, of the standard volumetric sulfuric acid solution used for titration and add 18 V_1 of the standard volumetric sulfuric acid solution to the remainder of the diluted hydrogen peroxide solution.

Mix this solution well and store in a borosilicate glass bottle in the dark.

Discard the solution after 1 month.

NOTE — A pH 4,5 has been used partly because of the availability of a suitable indicator and partly because of the need to avoid the interfering effect of carbon dioxide, which becomes serious at pH values greater than 5,5.

5.5 Sulfuric acid, standard volumetric solution, $c(H_2SO_4) = 0{,}002$ mol/l.

Prepare by dilution of a commercially available sulfuric acid solution of defined concentration, for example by dilution of a 0,05 mol/l standard volumetric sulfuric acid solution.

5.6 Sodium tetraborate, standard volumetric solution, $c(Na_2B_4O_7 \cdot 10H_2O) = 0{,}002$ mol/l.

Prepare by dilution of a commercially available sodium tetraborate solution of defined concentration or, if this is not possible, proceed as follows.

Prepare a stock solution of sodium tetraborate slightly stronger than 0,02 mol/l by dissolving 4,2 g of sodium tetraborate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$) in 500 ml of water. Dilute a sufficient aliquot part of the stock solution for example 25 ml, with nine parts of water. Record the volume V_2, in millilitres, of the approximately 0,002 mol/l sodium tetraborate solution obtained. Withdraw 100 ml of this solution and standardize it as follows.

Place 50 ml of the absorption solution (5.4) into a conical flask (colorimetric procedure) or beaker (potentiometric procedure) of suitable capacity and add, by pipette, 25 ml of the standard volumetric sulfuric acid solution (5.5). Titrate with the diluted sodium tetraborate solution after the addition of 1,0 ml of indicator solution (5.7) (colorimetric procedure only) until the indicator colour change indicates that the pH is 4,5 or the measured pH is 4,5 (potentiometric procedure). Carry out likewise a second titration. Record the mean of the volume, V_3, in millilitres, of the diluted sodium tetraborate solution used for titration, and add a volume of water calculated according to

$$\frac{(V_2 - 100)\,(25 - V_3)}{V_3}$$

to the remainder of the diluted sodium tetraborate solution.

After the addition of the requisite volume of water, repeat the previous titration to ensure that the concentration of the standardized sodium tetraborate is 0,002 mol/l.

NOTES

1 Because the determination is not made at the equivalence point, the titre of the standard volumetric sodium tetraborate solution depends on the volume V_1 of the standard volumetric sulfuric acid solution used in the preparation of the absorption solution (5.4).

It has been found experimentally that, for values of V_1 between 1 and 100 ml, using the same solution of sodium tetraborate (approximately 0,002 mol/l) to titrate to pH 4,5, the relative variation in V_3 and thus of the apparent titre (to pH 4,5) of this solution, is approximately 3 %. A similar variation is found in the final titre on dilution to obtain $V_3 = V_1$.

2 If an exactly 0,002 mol/l solution of sodium tetraborate is used for the titration, the addition of 25 ml of this solution does not restore the pH to 4,5 for the reason mentioned in note 1, which will result in a small error in the determination of the gaseous acid air pollution index.

3 The choice of 25 ml of standard volumetric sulfuric acid solution to be added is arbitrary. It allows

a) consistency with the methods of preparation of sodium tetraborate solutions used up to this time whilst simulating what happens at the time of determining the gaseous acid air pollution index;

b) minimal errors in the preparation of the standard volumetric tetraborate solution because of the relatively large volumes added.

5.7 Indicator solution (colorimetric procedure).

Any indicator having a precise colour change (that is, within 0,1 ml of titrant) at pH 4,5 and which does not react with the hydrogen peroxide solutions to be titrated may be used. The following mixture is suitable:

> **Solution A:** Dissolve 2 g of thymolsulfonephthalein (thymol blue) in 45 ml of 0,1 mol/l sodium hydroxide solution and make up to 1 000 ml with water.
>
> **Solution B:** Dissolve 2 g of 3′, 3″, 5′, 5″-tetrabromophenolsulfonephthalein (bromophenol blue) in 30 ml of 0,1 mol/l sodium hydroxide solution and make up to 1 000 ml with water.

These solutions keep well in the dark.

Before use, mix 20 ml of solution A with 20 ml of solution B and dilute to 250 ml with water.

The colours obtained with this indicator are yellow at pH $\leqslant$ 4, pale lilac at pH 4,5, and blue to violet at pH $\geqslant$ 5.

6 Apparatus

Ordinary laboratory apparatus and

6.1 Sampling equipment, as specified in ISO 4219, sub-clauses 5.1 to 5.7 and, in addition, as specified in 6.1.1.

6.1.1 Absorption bottles.

Borosilicate glass bottles of the Drechsel type equipped with interchangeable ground glass joints (see the figure) shall be used. A bottle having the cone of the ground glass joint on the bottle is preferable, because of the smaller risk of deposited matter dropping into the absorption solution when the sampling head is removed.

The capacity of the bottle shall be 125 ml for a 24 h sampling period and 250 ml for a 48 h sampling period. The external diameter of the entry and exit tubes of the absorption bottle shall be 10 to 12 mm. The tube leading the air into the absorption solution shall have an internal diameter of 6 to 8 mm and shall end 5 to 10 mm from the bottom of the absorption bottle.

NOTE — The glass of the absorption bottle shall not cause an alkaline reaction with the absorption solution (5.4).

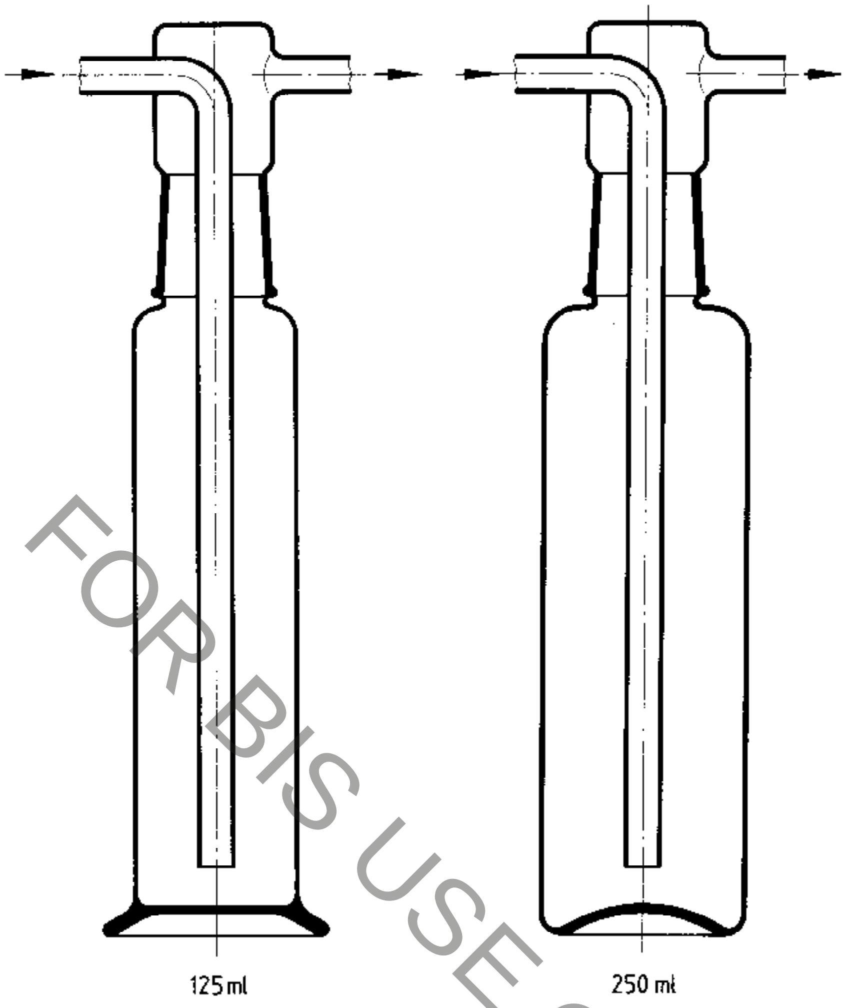

Figure — Examples of absorption bottle

Test all absorption bottles before use by rinsing and then filling with the absorption solution. Check the pH of the absorption solution after four days and after a further four days.

If the pH of the absorption solution has not changed by more than 0,02 pH units the absorption bottle is satisfactory. If the change is greater than 0,02 pH units the absorption bottle shall not be used because the alkalinity is too high.

6.2 Microburettes, capacity 2 ml, graduated in divisions of 0,01 ml.

Before use, rinse the microburettes thoroughly with water.

6.3 Burettes, capacity 10 ml, graduated in divisions of 0,02 ml.

Before use, rinse the burettes thoroughly with water.

6.4 Direct reading pH meter (potentiometric procedure), reading to 0,02 pH units, equipped with measuring and reference electrodes and, preferably, with temperature compensation.

Calibrate the pH meter using the buffer solutions (5.3) in accordance with the manufacturer's instructions. After calibration rinse the electrodes thoroughly before use.

6.5 Magnetic stirrer (potentiometric procedure), having a stirring bar covered with a material (for example PTFE), which does not react with any of the reagents used.

7 Sampling

Set up the equipment specified in ISO 4219 in accordance with the requirements of ISO 4219 and any special requirements for the particular atmosphere to be sampled.

Insert a particulate filter (5.3 of ISO 4219) into the filter holder (5.3.2 of ISO 4219).

In an absorption bottle (6.1.1) appropriately selected for the intended sampling period place a suitable volume of absorption solution (5.4) mark the level of the absorption solution and connect the absorption bottle to the sampling train.

Under normal conditions, the volume of absorption solution used shall be 50 ml for a sampling period of 24 h and 150 ml for a sampling period of 48 h.

NOTES

1 If the temperature of the air mass under investigation exceeds 25 °C, or if it is very dry, larger volumes of absorption solution may have to be used. The volume needed to obtain a sufficient retention efficiency should be ascertained by preliminary tests using, for example, absorption bottles in series.

2 Automatic equipment for changing the absorption bottles may be used.

At the time of placing the suitable volume of absorption solution into the absorption bottle used for sampling place a volume of absorption solution identical to that used for sampling into a second absorption bottle. Stopper the absorption bottle firmly with a ground glass stopper for use as a control and store it in the laboratory or preferably at the sampling site.

Adjust the air-flow regulator (5.6 of ISO 4219) to give an air volume flow rate of 100 l/h. Record the reading on the gas meter (5.6 of ISO 4219) and the time and start the sampling pump (5.7 of ISO 4219).

At the end of the sampling period (24 or 48 h selected), switch off the sampling pump, and note the reading on the gas meter and the time. Remove the absorption bottle from the sampling train and make up the level of exposed absorption solution to the original level with water.

Either stopper the absorption bottle firmly with a ground glass stopper or, if this is not feasible, transfer the sample solution to a clean, dry transfer bottle.

NOTE — Transfer bottles shall be inert with respect to the absorption solution (6.1.1).

Avoid using rubber stoppers as rubber may alter the pH of the sample solution.

Remove the particle filter and visually inspect it for the presence of moisture. Record the result of the inspection in the test report.

Replace the absorption bottle removed by an absorption bottle containing fresh absorption solution and renew the particle filter.

8 Procedure

8.1 Treatment of control solution

Transfer the control solution into a conical flask (colorimetric procedure) or beaker (potentiometric procedure) of suitable capacity and stir using the magnetic stirrer (6.4) (potentiometric procedure).

Add 1,0 ml of indicator solution (5.7) and note the pH as indicated by the colour of the control solution (colorimetric procedure) or measure the pH on the pH meter without addition of indicator solution (potentiometric procedure).

If the pH of the control solution differs from 4,5, titrate the control solution with sulfuric acid solution (pH > 4,5) or sodium tetraborate solution (pH < 4,5) using the microburettes (6.2) until the indicator colour change or the measured pH indicates that it is 4,5. Record the volume of titrant used.

NOTE — If the pH is markedly different from pH 4,5, the initial conditioning of the glassware may have been ineffective.

8.2 Determination

In cases where the volume of absorption solution exposed was 50 ml, transfer the whole of the sample solution into a conical flask (colorimetric procedure) or beaker (potentiometric procedure) of suitable capacity and stir using the magnetic stirrer (potentiometric procedure). In cases where the volume of absorption solution exposed was 150 ml, take a 50 ml aliquot portion and proceed as mentioned before. Add the volume of sulfuric acid solution or sodium tetraborate solution according to the volume found necessary in 8.1 to adjust the pH of the control solution.

Add 1,0 ml of indicator solution (5.7) and note the pH as indicated by the colour of the control solution (colorimetric procedure) or measure the pH on the pH meter without addition of indicator solution (potentiometric procedure).[1]

If the pH of the solution is less than 4,5, titrate with sodium tetraborate solution (5.6) until the pH is 4,5, using the microburettes (6.2) or, if necessary, the burettes (6.3). If the pH is greater than 4,5, titrate with sulfuric acid solution (5.5) until the pH is 4,5.

Record the volume of sulfuric acid solution or sodium tetraborate solution, V_4, in millilitres, used for the titration.

9 Expression of results

9.1 Method of calculation

The gaseous acid air pollution index, I_g, expressed in micrograms per cubic metre, is given by the equation

$$I_g = \frac{128\ V_4 V_5}{V_6\ V_7}$$

where

V_4 is the volume, in millilitres, of the sodium tetraborate solution (5.6) or of the sulfuric acid solution (5.5) used in the determination;

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[1] If the pH meter is not equipped with temperature compensation, apply appropriate temperature corrections to the pH readings.

V_5 is the volume, in millilitres, of the absorption solution exposed, i.e. 50 or 150 ml;

V_6 is the volume, in millilitres, of the sample solution titrated, i.e. 50 ml;

V_7 is the volume, in cubic metres, of the air sample;

128 is the mass equivalent, in micrograms, of sulfur dioxide corresponding to 1,0 ml of exactly 0,002 mol/l sodium tetraborate solution.

9.2 Method of expression

Express the gaseous acid air pollution index:

a) as a positive number when V_4 corresponds to an addition of the sodium tetraborate solution;

b) as a negative number when V_4 corresponds to an addition of the sulfuric acid solution.

10 Test report

The test report shall include at least the following information:

a) complete identification of the sample;

b) reference to this International Standard;

c) reference to ISO 4219;

d) the procedure used;

e) the results and the method of expression used;

f) any unusual features noted during the determination;

g) any operation not included in this International Standard or in the International Standard to which reference is made, or regarded as optional;

h) precision of the pH measurement.

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