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Sulphuric acid and oleums for industrial use – Determination of oxides of nitrogen – 2,4-xylenol spectrophotometric method

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FOREWORD

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Austria
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Sulphuric acid and oleums for industrial use — Determination of oxides of nitrogen — 2,4-xylenol spectrophotometric method

1 SCOPE

This International Standard specifies a 2,4-xylenol spectrophotometric method for determining oxides of nitrogen in sulphuric acid and oleums for industrial use.

2 FIELD OF APPLICATION

The method is applicable to the determination of oxides of nitrogen contents, expressed as nitrogen (N), equal to or greater than 0.000 02 % (*m/m*).

3 REFERENCE

ISO/R 910, *Sulphuric acid and oleums for industrial use — Determination of total acidity and calculation of free* SO_3 *content of oleum — Volumetric method.*

4 PRINCIPLE

Oxidation of nitrous nitrogen to nitric nitrogen by potassium permanganate.

Reaction of nitric nitrogen with 2,4-xylenol under specified conditions to form a nitrate derivative. Distillation of the nitrate derivative and absorption in sodium hydroxide solution. Spectrophotometric measurement of the yellow coloured nitrophenol at a wavelength of about 445 nm.

5 REAGENTS

Distilled water, or water of equivalent purity, shall be used in the test.

5.1 Mercury(II) acetate $[Hg(CH_3COO)_2]$.

5.2 Sulphuric acid, ρ 1,84 g/ml approximately, 96 % (*m/m*) or 36 N approximately (free from nitrogen oxides).

To ensure complete elimination of nitrogen oxides, proceed as follows: cautiously add 80 ml of sulphuric acid, ρ 1,84 g/ml, to about 20 ml of water and heat until white fumes are liberated. Cool and repeat the dilution and heating twice.

5.3 2,4-xylenol, 10 g/l solution in acetic acid.

Dissolve 1 g of 2,4-xylenol in glacial acetic acid, ρ 1,05 g/ml, approximately 17,4 N solution, and dilute to 100 ml with the same acid.
Prepare the solution at the time of use.

5.4 Potassium permanganate, approximately 0,1 N solution.

Dissolve 3,16 g of potassium permanganate in water and dilute to 1 000 ml.

5.5 Sodium hydroxide, approximately 2 N solution.

Dissolve 80 g of sodium hydroxide in water and, after cooling, transfer the solution to a 1 000 ml one-mark volumetric flask. Dilute to the mark and mix.

5.6 Hydrogen peroxide, 1 g/l solution.

5.7 Potassium nitrate, standard solution with a nitrogen (N) content of 0,500 g/l.

Weigh, to the nearest 1 mg, 3,609 g of potassium nitrate, previously dried at 120 °C and cooled in a desiccator. Transfer to a 1 000 ml one-mark volumetric flask, dissolve in a little water, dilute to the mark and mix.

1 ml of this standard solution contains 500 μg of N.

5.8 Potassium nitrate, standard solution with a nitrogen (N) content of 0,050 g/l.

Take 50,0 ml of the standard potassium nitrate solution (5.7), transfer to a 500 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 50 μg of N.

6 APPARATUS

Ordinary laboratory apparatus and

6.1 Weighing pipette, approximately 50 ml, with ground glass stoppers.

6.2 Water bath, capable of being controlled at 35 ± 1 °C.

6.3 Distillation apparatus, with conical ground glass joints, comprising, for example, the following parts (see Figure):

6.3.1 *Distillation flask,* 250 ml (with female joint).

6.3.2 *Sloping recovery bend,* at 75° (with male joints).

6.3.3 *Liebig condenser,* water circulation, effective length approximately 450 mm (with female joint) connecting to the sloping recovery bend (6.3.2).

6.4 Spectrophotometer.

7 PROCEDURE

7.1 Test portion and preparation of the test solution

Fill the weighing pipettte (6.1) with the test sample and take a test portion of approximately 20 g, weighing by difference to the nearest 0,1 g.

If oleum[1] or sulphuric acid with a concentration greater than 75 % (*m/m*) is involved, place the test portion on crushed ice in the distillation flask (6 3.1) and calculate the quantity of ice so that the resulting concentration of the solution is approximately 75 % (*m/m*). If sulphuric acid with a concentration below 75 % (*m/m*) is involved, introduce the test portion into the distillation flask (6.3.1) and add the quantity of the sulphuric acid solution (5.2) necessary to bring the final concentration of the solution to approximately 75 % (m/m). During these operations maintain the temperature of the acid mixture below 35 °C.

NOTE — If the subsequent determination results in a content of oxides of nitrogen greater than 0,000 5 % (*m/m*) or if it is known *a priori* that the content will be greater than this limit, reduce the test portion accordingly and adjust the mass to approximately 20 g by adding sulphuric acid solution (5.2). Take account of this dilution in the final calculation.

7.2 Blank test

Carry out a blank test following the same procedure, with the same quantity of crushed ice and of all the reagents used for the analysis, replacing the test portion by a corresponding quantity of sulphuric acid solution (5.2).

7.3 Preparation of the calibration curve

Prepare the standard volumetric solutions by distillation for each point on the calibration curve (see 7.3.1.2).

7.3.1 *Preparation of standard volumetric solutions* for spectrophotometric measurements taken with an optical path length of 4 cm.

7.3.1.1 Preparation of diluted solutions

Into a series of ten 100 ml one-mark volumetric flasks, place respectively the following volumes of the standard nitrogen solution (5.8) :

Volume of the nitrogen standard solution (5.8)	Corresponding mass of N
ml	µg
0 *	0
2,0	100
4,0	200
6,0	300
8,0	400
10,0	500
12,0	600
14,0	700
16,0	800
20,0	1 000

* Compensating solution

Dilute each solution to the mark and mix.

7.3.1.2 Distillation for each dilution

Proceed as follows for each dilution (7.3.1.1). Place the distillation flask (6.3.1) in a bath of water and ice, and introduce into the flask 10,0 ml of one of the diluted solutions (7.3.1.1) and 0,200 g of the mercury(II) acetate (5.1)[2].

Then add very slowly, in small portions and with stirring, so that the temperature remains all the time below 35 °C, 20 ml of the sulphuric acid solution (5.2) Withdraw the flask from the water bath, add 1 ml of the 2,4-xylenol solution (5.3), stir and place the flask in the water bath (6.2) controlled at 35 ± 1 °C. After 30 min, add to the flask the quantity of water necessary to bring the volume to approximately 120 ml.

Connect the flask to the distillation apparatus, heat to boiling and collect, over a period of approximately 15 min, 60 ml of distillate in a 100 ml one-mark volumetric flask in which has already been placed 10 ml of the sodium hydroxide solution (5.5). When a volume of approximately 60 ml has been collected, stop the circulation of condenser water and distil a few more millilitres. Cool the flask containing the distillate to ambient temperature, dilute to the mark and mix.

The distillates collected and diluted to 100 ml will have the following nitrogen (N) contents : 0 – 10 – 20 – 30 – 40 – 50 – 60 – 70 – 80 and 100 µg.

7.3.2 *Spectrophotometric measurements*

Carry out the measurements with the spectrophotometer (6.4) at a wavelength of about 455 nm after having adjusted the apparatus to zero absorbance against the compensating solution.

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[1] Determine the total acidity of the sulphuric acid or oleum in accordance with ISO/R 910.

[2] The addition of mercury(II) acetate has been found necessary to avoid interference from chlorides.

7.3.3 *Preparation of the calibration chart*

Plot a graph having, for example, the quantities of nitrogen (N), expressed in micrograms, contained in 100 ml of the standard colorimetric solutions as abscissae, and the corresponding values of absorbance as ordinates.

7.4 Determination

7.4.1 *Distillation*

Add to the distillation flask containing the test solution (7.1) 0,200 g of the mercury(II) acetate (5.1) and the quantity of the potassium permanganate solution (5.4) necessary to give a stable pink coloration for a few minutes. Then decolorize the solution by adding a few drops of the hydrogen peroxide solution (5.6), add 1 ml of the 2,4-xylenol solution (5.3), stir and place the flask in the water bath (6.2) controlled at 35 ± 1 °C.

After 30 min dilute the contents of the flask with water to approximately 120 ml. Connect the flask to the distillation apparatus, heat to boiling and collect, over a period of approximately 15 min, 60 ml of distillate in a 100 ml one-mark volumetric flask in which has already been placed 10 ml of the sodium hydroxide solution (5.5). When a volume of approximately 60 ml has been collected, stop the circulation of condenser water and distil a few more millilitres.

Cool the flask containing the distillate to ambient temperature, dilute to the mark and mix.

7.4.2 *Spectrophotometric measurement*

Carry out the spectrophotometric measurement as described in 7.3.2, after having adjusted the apparatus to zero absorbance against the blank test solution (7.2).

8 EXPRESSION OF RESULTS

By means of the calibration chart (see 7.3.3), determine the quantity of nitrogen (N) corresponding to the values of the spectrophotometric measurement.

The content of oxides of nitrogen, expressed as nitrogen (N), is given, as a percentage by mass, by the formula :

$$\frac{m_1 \times 100}{m_0}$$

where

m_0 is the mass, in grams, of the test portion;

m_1 is the mass, in grams, of the nitrogen obtained.

9 TEST REPORT

The test report shall include the following particulars :

a) the reference of the method used;

b) the results and the method of expression used;

c) any unusual features noted during the determination;

d) any operation not included in this International Standard, or that document to which reference is made, or regarded as optional.

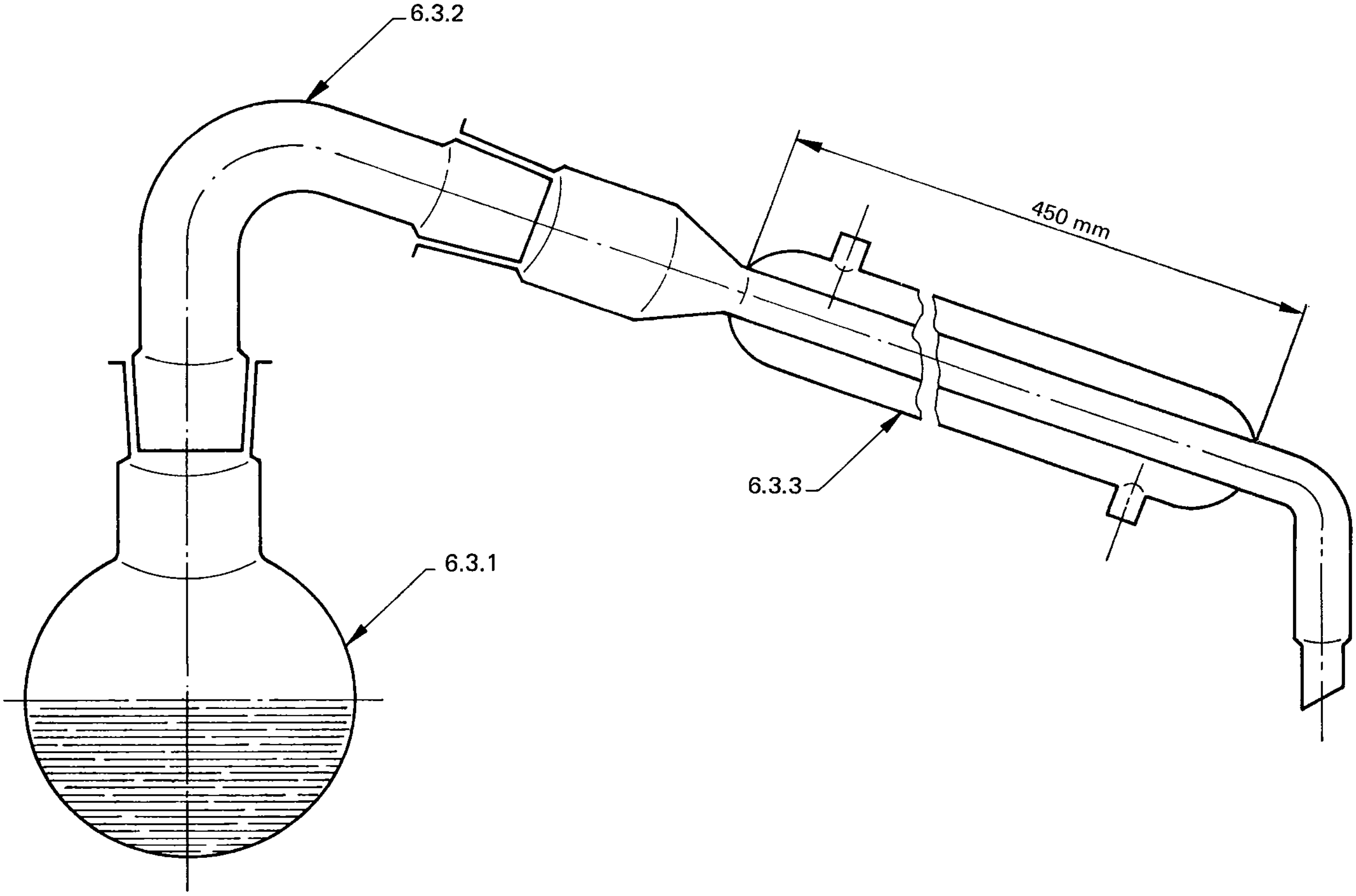

FIGURE – **Typical distillation apparatus**