INTERNATIONAL STANDARD ISO 2991

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Nitric acid for industrial use — Determination of ammoniacal nitrogen content — Spectrophotometric method

Acide nitrique à usage industriel — Dosage de l'azote ammoniacal — Méthode spectrophotométrique

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FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO Member Bodies). The work of developing International Standards is carried out through ISO Technical Committees. Every Member Body interested in a subject for which a Technical Committee has been set up 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.

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 2991 was drawn up by Technical Committee ISO/TC 47, *Chemistry*, and circulated to the Member Bodies in November 1972.

It has been approved by the Member Bodies of the following countries :

Australia
Austria
Belgium
Bulgaria
Czechoslovakia
Egypt, Arab Rep. of
France
Germany
Hungary
India
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Poland
Portugal
South Africa, Rep. of
Spain
Sweden
Switzerland
Thailand
Turkey
United Kingdom
U.S.S.R.

This International Standard has also been approved by the International Union of Pure and Applied Chemistry (IUPAC).

No Member Body expressed disapproval of the document.

Printed in Switzerland

INTERNATIONAL STANDARD **ISO 2991-1974 (E)**

Nitric acid for industrial use — Determination of ammoniacal nitrogen content — Spectrophotometric method

1 SCOPE

This International Standard specifies a spectrophotometric method using sodium phenate and sodium hypochlorite for the determination of the ammoniacal nitrogen content of nitric acid for industrial use.

2 FIELD OF APPLICATION

The method is applicable to products containing more than 0,000 1 % (*m/m*) of ammoniacal nitrogen. The procedure, as described, is suitable for contents between 0,000 1 and 0,000 5 % (*m/m*). If the acid analyzed contains more than 0,000 5 % (*m/m*) of ammoniacal nitrogen, the mass of the test portion should be decreased accordingly.

3 PRINCIPLE

Distillation, with entrainment by steam, of the ammonia in the presence of an excess of sodium hydroxide and collection of the distillate in an excess of acid solution.

Neutralization of the excess of acid and formation of the coloured complex by treatment with sodium phenate and sodium hypochlorite in the presence of acetone.

Spectrophotometric measurement of the indophenol obtained at a wavelength of about 630 nm.

4 REAGENTS

Distilled water, or water of equivalent purity, of which the ammoniacal nitrogen content is negligible, shall be used in the test.

NOTE — Verify the quality of this water by means of a mixture of sodium phenate and sodium hypochlorite. Proceed as described in 6.3.1 for the compensation solution; there should be no appreciable colour produced.

4.1 Sodium hydroxide, 350 g/l solution

Boil this solution for 20 min to remove traces of ammoniacal nitrogen and make up to the original volume.

4.2 Sulphuric acid, approximately 0,1 N solution.

4.3 Sodium hydroxide, approximately N solution.

4.4 Sodium hydroxide, approximately 0,1 N solution.

4.5 Phenolphthalein, 10 g/l ethanolic solution.

Dissolve 1 g of phenolphthalein in 95 % (*V/V*) ethanol and dilute to 100 ml with the same ethanol.

4.6 Acetone.

4.7 Sodium phenate (sodium phenolate), approximately 155 g/l solution.

Dissolve 12,5 g of phenol in 27 ml of approximately 5 N sodium hydroxide solution and dilute to 100 ml.

Immediately place the solution in the dark.

Prepare this solution immediately before it is required for use.

4.8 Sodium hypochlorite, solution containing 10 g of available chlorine per litre.

Dilute a concentrated solution of sodium hypochlorite (100 to 140 g of available chlorine per litre), previously standardized against a solution of sodium arsenite. Do not use concentrated solutions containing less than 80 g of available chlorine per litre.

Store the solution in a cool place and in the absence of light.

The solution is stable for about 4 weeks.

4.9 Ammonium chloride, standard solution corresponding to 1 g of ammoniacal nitrogen per litre.

Weigh, to the nearest 0,000 1 g, 3,819 g of ammonium chloride, previously dried at 100 °C and allowed to cool in a desiccator. Place in a beaker of suitable capacity and dissolve in water. Transfer quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this solution contains 1 mg of ammoniacal nitrogen.

Renew the solution at least once a month.

4.10 Ammonium chloride, standard solution corresponding to 0,1 g of ammoniacal nitrogen per litre.

Transfer 50,0 ml of the standard solution (4.9) to a 500 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this solution contains 0,1 mg of ammoniacal nitrogen.

Renew this solution at least once every 15 days.

4.11 Ammonium chloride, standard solution corresponding to 1 mg of ammoniacal nitrogen per litre.

Transfer 10,0 ml of the standard solution (4.10) to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this solution contains 1 µg of ammoniacal nitrogen.

Prepare this solution immediately before it is required for use.

5 APPARATUS

Ordinary laboratory apparatus and

5.1 Apparatus, with ground glass joints, for steam distillation (see the figure, which shows a typical example).

5.1.1 *Construction*

A) **Steam trap,** for the condensed water, fitted on one side to a steam generator and on the other side to the flask B;

B) **Distillation flask,** 500 ml capacity, fitted with an inlet for the introduction of the steam and with a dropping funnel with a PTFE[1] stopcock, closed by a tight bung and connected to the condenser, C, through a spray trap.

C) **Condenser,** fitted with a tapered extension dipping into the conical flask, D, and having on its base a glass collar to stop any external condensation running into the flask D;

D) **Conical flask** or **cylinder,** of about 250 ml capacity;

E) **Apparatus for heating the flask.**

5.1.2 *Precautions* to be taken before, during and after use

The apparatus should be tightly sealed; ensure that the ground glass joints are not too close to the source of heat. When the apparatus is exposed to the laboratory atmosphere, its walls can absorb traces of ammoniacal nitrogen which are not removed by rinsing with water. It is essential to wash the apparatus by carrying out one or two blank distillations in the presence of sodium hydroxide solution.

After this distillation, and between tests, keep the apparatus sealed from the laboratory atmosphere. Keep the dropping funnel sealed and the end of the delivery tube dipped in water or dilute acid.

5.2 pH meter, with glass electrode.

5.3 Spectrophotometer.

6 PROCEDURE

6.1 Test portion

Fill a weighing pipette with the test sample and take, weighing by difference to the nearest 0,010 g, a test portion of about 50 g. Place it in a beaker of convenient capacity (250 ml for example). Evaporate the nitric acid on a boiling water bath, in a fume cupboard, until the volume is reduced to about 1 ml.

6.2 Blank test

Carry out, at the same time as the determination, and following the same procedure, a blank test using the same quantities of all the reagents used for the test.

6.3 Preparation of calibration curve

6.3.1 *Preparation of standard matching solutions,* relating to measurements carried out with an optical path length of 1 cm.

Into a series of six 50 ml one-mark volumetric flasks, introduce the quantities of the standard ammonium chloride solution (4.11) shown in the following table :

Standard ammonium chloride solution (4.11)	Corresponding mass of ammoniacal nitrogen
ml	µg
0*	0
5,0	5
10,0	10
15,0	15
20,0	20
25,0	25

* Compensation solution

Add to each flask the quantity of water necessary to give a volume of 25 ml, then add 0,3 ml of the acetone (4.6) and stir.

Introduce into each flask, stirring in all cases and using a rapid delivery pipette, 10 ml of the sodium phenate solution (4.7) and, immediately afterwards, 5 ml of the sodium hypochlorite solution (4.8), using a rapid delivery pipette for this reagent also. Dilute to the mark and mix.

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[1] Polytetrafluoroethylene.

Allow each flask to stand, shielded from light, at ambient temperature for 60 ± 5 min.

6.3.2 *Spectrophotometric measurements*

Carry out the spectrophotometric measurements, using the spectrophotometer (5.3) at a wavelength of about 630 nm, after having adjusted the instrument to zero absorbance against the compensation solution.

6.3.3 *Preparation of calibration chart*

Plot a graph having, for example, the numbers of micrograms of ammoniacal nitrogen in 50 ml of the standard matching solutions as abscissae and the corresponding values of absorbance as ordinates.

6.4 Determination

6.4.1 *Preparation of the test solution*

Pour 30 ml of the sulphuric acid solution (4.2) into the conical flask (D).

Transfer the test portion (6.1) to the distillation flask (B), washing the beaker thoroughly with water and collecting the washings in the distillation flask. The final volume of the solution should be about 100 ml.

Add several drops of the phenolphthalein solution (4.5) and connect the flask to the distillation apparatus.

Neutralize the test solution, stirring continuously, with the sodium hydroxide solution (4.1) added through the dropping funnel.

Add 50 ml in excess of the sodium hydroxide solution (4.1) and the quantity of water necessary to attain a volume of about 300 ml. During these additions, ensure that several drops of solution remain above the stopcock as a seal.

Close the funnel with its bung. Warm the flask to the commencement of boiling and distil in a current of steam, controlled to give a drop-by-drop rate of delivery into the conical flask, until a volume of about 150 ml has collected. Thoroughly wash the end of the condenser with water, collecting the washings in the conical flask.

Adjust the pH of the solution to between 6 and 7, first by means of the sodium hydroxide solution (4.3) and then by means of the sodium hydroxide solution (4.4), checking the pH value with the pH meter (5.2).

Quantitatively transfer the solution to a 250 ml one-mark volumetric flask, dilute to the mark and mix.

6.4.2 *Colour development*

Take 25,0 ml of the solution (6.4.1) and transfer to a 50 ml one-mark volumetric flask. Stirring throughout each addition, introduce 0,3 ml of the acetone (4.6) and, by means of rapid delivery pipettes, 10 ml of the sodium phenate solution (4.7) and, immediately afterwards, 5 ml of the sodium hypochlorite solution (4.8).

Dilute to the mark, mix and allow to stand, shielded from light, at ambient temperature, for 60 ± 5 min.

6.4.3 Spectrophotometric measurements

Carry out the spectrophotometric measurements on the coloured solution (6.4.2) and on a corresponding aliquot portion of the blank test solution, according to the procedure described in 6.3.2, after having adjusted the instrument to zero absorbance against water.

7 EXPRESSION OF RESULTS

By means of the calibration chart (6.3.3), determine the quantities of ammoniacal nitrogen corresponding to the values of the spectrophotometric measurements.

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

$$\frac{(m_1 - m_2) \times D \times 100}{1\,000\,000 \times m_0} = \frac{(m_1 - m_2) \times D}{10\,000 \times m_0}$$

where

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

m_1 is the mass, in micrograms, of ammoniacal nitrogen found in the aliquot portion of the test solution taken for the colour development;

m_2 is the mass, in micrograms, of ammoniacal nitrogen found in the corresponding aliquot portion of the blank test solution;

D is the ratio between the volume of the test solution (6.4.1) and the aliquot portion taken for the colour development.

8 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 regarded as optional.

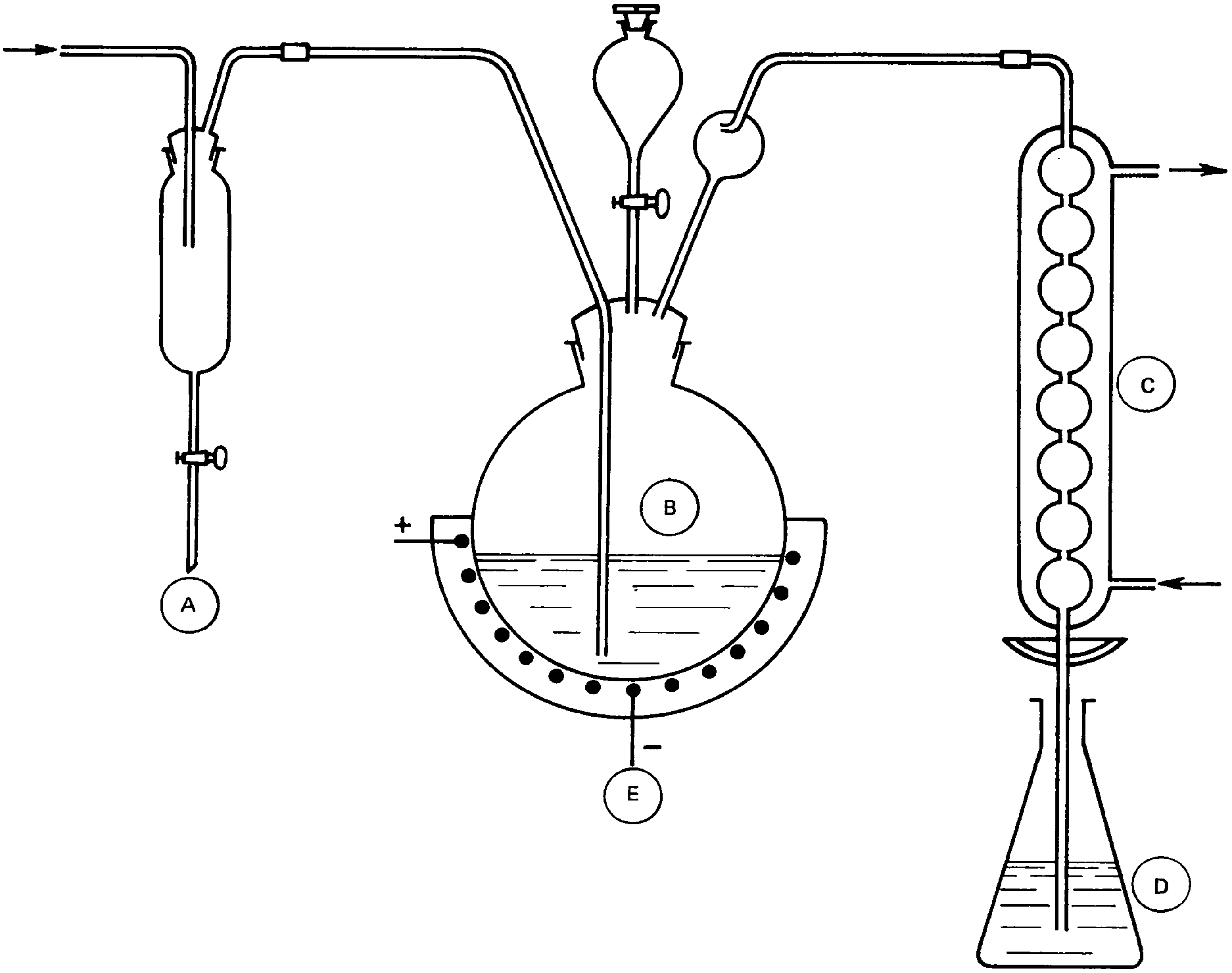

FIGURE – Typical apparatus for steam distillation

ANNEX

This document forms part of the following series on methods of test for nitric acid for industrial use :

ISO/R 1980 — *Determination of total acidity — Volumetric method.*

ISO/R 1981 — *Determination of nitrous compounds — Volumetric method.*

ISO/R 1982 — *Determination of iron content — 2,2'-bipyridyl photometric method.*

ISO/R 1983 — *Determination of sulphated residue on ignition — Gravimetric method.*

ISO 2990 — *Evaluation of the nitric acid concentration by measurement of density.*

ISO 2991 — *Determination of ammoniacal nitrogen content — Spectrophotometric method.*

ISO 3328 — *Determination of sulphate content — Titrimetric method after reduction.*[1]

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[1] At present at the stage of draft.