International Standard 5663

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

Water quality — Determination of Kjeldahl nitrogen — Method after mineralization with selenium

Qualité de l'eau — Dosage de l'azote Kjeldahl — Méthode après minéralisation au sélénium

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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.

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

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Japan
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Water quality — Determination of Kjeldahl nitrogen — Method after mineralization with selenium

1 Scope and field of application

1.1 Substance determined

This International Standard specifies a method for the determination of nitrogen by a Kjeldahl-type method. Only trivalent negative nitrogen is determined. Organic nitrogen in the form of azide, azine, azo, hydrazone, nitrite, nitro, nitroso, oxime or semicarbazone is not determined quantitatively. Nitrogen may be incompletely recovered from heterocyclic nitrogen compounds.

1.2 Type of sample

This method is applicable to the analysis of raw, potable and waste waters.

1.3 Range

A Kjeldahl nitrogen content, ϱ_N, of up to 10 mg, in the test portion may be determined. Using a 10 ml test portion, this corresponds to a sample concentration of up to ϱ_N = 1 000 mg/l.

1.4 Limit of detection

A practically determined (4 degrees of freedom) limit of detection, using a 100 ml test portion, is ϱ_N = 1 mg/l.

1.5 Sensitivity

Using a 100 ml test portion, 1,0 ml of 0,02 mol/l hydrochloric acid is equivalent to ϱ_N = 2,8 mg/l.

2 Reference

ISO 7150/1, *Water quality — Determination of ammonium — Part 1: Manual spectrometric method.*

3 Definition

For the purpose of this International Standard, the following definition applies:

Kjeldahl nitrogen: The content of organic nitrogen and ammoniacal nitrogen in a sample determined after mineralization.

It does not include nitrate and nitrite nitrogen, and does not necessarily include all organically bound nitrogen.

4 Principle

Mineralization of the sample to form ammonium sulfate, from which ammonia is liberated and distilled for subsequent determination by titration.

Conversion of the nitrogen compounds responding to the test to ammonium sulfate by mineralization of the sample with sulfuric acid, containing a high concentration of potassium sulfate in order to raise the boiling point of the mixture, in the presence of selenium which acts as a catalyst.[1]

Liberation of ammonia from the ammonium sulfate by the addition of alkali and distillation into boric acid/indicator solution.

Determination of ammonium ion in the distillate by titration with standard acid.

Alternatively, direct determination of ammonium ion in the mineralizate by spectrometry at 655 nm. (See clause 11.)

5 Reagents

During the analysis, use only reagents of recognized analytical grade, and only distilled water prepared as described in 5.1.

5.1 Water, ammonium-free, prepared by one of the following methods.

5.1.1 Ion exchange method

Pass distilled water through a column of strongly acidic cation exchange resin (in the hydrogen form) and collect the eluate in a glass bottle provided with a well-fitting glass stopper. Add about 10 g of the same resin to each litre of collected eluate for storage purposes.

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[1] Selenium has been selected as the catalyst in preference to mercury because of concern in many countries about the toxicity of mercury. However, the toxicity of selenium must not be overlooked. See 11.2 for a suggested procedure for removal of selenium from mineralization residues.

5.1.2 Distillation method

Add 0,10 ± 0,01 ml of sulfuric acid (5.3) to 1 000 ± 10 ml of distilled water and redistil in all glass apparatus. Discard the first 50 ml of distillate, and then collect the distillate in a glass bottle provided with a well-fitting glass stopper. Add about 10 g of strongly acidic cation exchange resin (in the hydrogen form) to each litre of collected distillate.

5.2 Hydrochloric acid, ϱ = 1,18 g/ml.

5.3 Sulfuric acid, ϱ = 1,84 g/ml.

WARNING — This reagent causes severe burns.

The highest purity sulfuric acid shall always be used. Pay particular attention to the manufacturer's specification with respect to its nitrogen content.

5.4 Sodium hydroxide, approximately 500 g/l solution.

WARNING — This reagent causes severe burns.

Dissolve 500 ± 20 g of sodium hydroxide in about 800 ml of water. Cool to room temperature and dilute to 1 litre with water in a measuring cylinder.

5.5 Hydrochloric acid, standard volumetric solution, c(HCl) ≈ 0,10 mol/l.

This solution shall be prepared by dilution of hydrochloric acid (5.2) followed by standardization by normal analytical procedures. Alternatively, a commercial solution of guaranteed concentration may be used.

5.6 Hydrochloric acid, standard volumetric solution, c(HCl) ≈ 0,02 mol/l.

This solution shall be prepared by dilution of hydrochloric acid (5.2 or 5.5) followed by standardization by normal analytical procedures. Alternatively, a commercial solution of guaranteed concentration may be used.

5.7 Boric acid/indicator, solution.

5.7.1 Dissolve 0,5 ± 0,1 g of methyl red in about 800 ml of water and dilute to 1 litre with water in a measuring cylinder.

5.7.2 Dissolve 1,5 ± 0,1 g of methylene blue in about 800 ml of water and dilute to 1 litre with water in a measuring cylinder.

5.7.3 Dissolve 20 ± 1 g of boric acid (H_3BO_3) in warm water. Cool to room temperature. Add 10 ± 0,5 ml of methyl red solution (5.7.1) and 2,0 ± 0,1 ml of methylene blue solution (5.7.2) and dilute to 1 litre with water in a measuring cylinder.

5.8 Catalyst mixture.

WARNING — This mixture is toxic. Inhalation of any dust resulting from its preparation or use shall be avoided. All residues containing selenium shall be collected for selenium recovery (11.2) or controlled disposal.

Thoroughly mix 1 000 ± 20 g of potassium sulfate and 10,0 ± 0,2 g of selenium pellets.

5.9 Anti-bumping granules.

6 Apparatus

Ordinary laboratory apparatus and:

6.1 Kjeldahl mineralization flasks, specially designed, of sufficient capacity to accommodate the test portion volume to be used in the analysis, and in any event not exceeding 500 ml.

They should preferably be suitable for direct attachment to the distillation apparatus (6.2).

6.2 Distillation apparatus, incorporating an anti-splash distillation head and a vertical condenser whose outlet can be submerged in the absorbent solution.

If the Kjeldahl flasks (6.1) are not suitable for direct attachment to the distillation apparatus, separate distillation flasks are necessary.

NOTE ON PRELIMINARY CLEANING OF THE DISTILLATION APPARATUS

Carry out the following procedure whenever the apparatus has been out of use for more than a few days.

Add about 350 ml of water (5.1) to the distillation flask. Add a few anti-bumping granules (5.9), assemble the apparatus, and distil at least 100 ml. Discard the distillate and the residue in the distillation flask.

7 Sampling and samples

Laboratory samples shall be collected in polyethylene or glass bottles. They should be analysed as quickly as possible, or else stored at between 2 and 5 °C until analysed. Acidification with sulfuric acid (5.3) to < pH 2 may also be used as an aid to preservation, provided that possible contamination of the acidified sample by absorption of any atmospheric ammonia is avoided.

8 Procedure

8.1 Test portion

If the approximate nitrogen concentration of the sample is known, the test portion volume can be selected from table 1.

Table 1 — Selection of test portion

Kjeldahl nitrogen concentration, ϱ_N	Volume of the test portion*
mg/l	ml
up to 10	250
10 to 20	100
20 to 50	50
50 to 100	25

* When using the 0,02 mol/l hydrochloric acid standard volumetric solution (5.6) for titration.

8.2 Blank test

Proceed as described in 8.3, but using about 250 ml of water (5.1) instead of a test portion. Record the volume of hydrochloric acid (5.6) added.

8.3 Determination

WARNING — The mineralization procedure may evolve toxic sulfur dioxide gas. Hydrogen sulfide and/or hydrogen cyanide may also be liberated from polluted samples. The mineralization should therefore be carried out under an effective fume extraction system.

Place the test portion (8.1) in a Kjeldahl flask (6.1) and add, from a measuring cylinder, 10 ml of sulfuric acid (5.3) and 5,0 ± 0,5 g of the catalyst mixture (5.8). Add a few anti-bumping granules (5.9) and boil the flask contents rapidly, under a suitable fume extraction system. The volume of the contents will decrease as water is boiled away, then evolution of white fumes will begin.

After fume evolution has ended, periodically observe the mineralizate and, after it has become clear and either colourless or light brown in colour, continue heating for a further 60 min. (See note 1.)

After mineralization allow the flask to cool to room temperature. Meanwhile, measure 50 ± 5 ml of indicator (5.7) into the receiving flask of the distillation apparatus. Ensure that the delivery tip of the condenser is below the surface of the indicator solution.

Carefully add 250 ± 50 ml of water (5.1) to the mineralization flask, together with a few anti-bumping granules (5.9). Then add, from a measuring cylinder, 50 ml of sodium hydroxide solution (5.4) and immediately attach the flask to the distillation apparatus.(See note 2.)

Heat the distillation flask so that distillate collects at a rate of about 10 ml/min. Stop the distillation when about 200 ml have been collected. Titrate the distillate to a purple end-point with 0,02 mol/l hydrochloric acid (5.6) and record the volume added. (See note 3).

NOTES

1 After water has boiled away, the rate of heating should be sufficient to reflux the acid mixture half-way up the neck of the flask. This ensures the attainment of a sufficiently high mineralization temperature.

2 Where the flask is not compatible with the distillation apparatus, the contents must be transferred quantitatively to a suitable distillation flask. This may conveniently be done at the water addition stage.

3 0,10 mol/l hydrochloric acid (5.5) may be used for the titration of distillates from samples containing high concentrations of nitrogen.

9 Expression of results

9.1 Method of calculation

The Kjeldahl nitrogen concentration, ϱ_N, expressed in milligrams per litre, is given by the formula

$$\frac{V_1 - V_2}{V_0} \times c \times 14{,}01 \times 1\,000$$

where

V_0 is the volume, in millilitres, of the test portion (see 8.1);

V_1 is the volume, in millilitres, of the standard volumetric hydrochloric acid used for titration (see 8.3);

V_2 is the volume, in millilitres, of the standard volumetric hydrochloric acid used for the titration in the blank test (see 8.2);

c is the exact concentration, expressed in moles per litre, of the hydrochloric acid used for titration;

14,01 is the relative atomic mass of nitrogen.

The result may be expressed as the mass concentration of nitrogen, ϱ_N, in milligrams per litre, or as the amount of substance concentration of nitrogen, c_N, in micromoles per litre.

To convert ϱ_N to c_N, multiply ϱ_N by 71,4.

9.2 Repeatability

Repeatability standard deviations have been determined as shown in table 2.

10 Interferences

The presence of nitrate and/or nitrite may be a cause of both negative and positive errors. Nitrate and/or nitrite may be reduced under the test conditions to ammonium, leading to falsely high results. Nitrate and/or nitrite may also form ammonium salts with ammonium in the sample. These salts may be decomposed at the temperature of the mineralization, resulting in the loss of nitrogen in gaseous forms and consequently low results. If the concentration of nitrate and/or nitrite in the sample seems likely to cause unacceptable bias or loss of precision, separate reduction to ammonium should precede the mineralization process.

Falsely low results may also be obtained if the mineralization procedure is over-prolonged. The procedure given in clause 8 must be carefully observed.

11 Notes on procedure

11.1 Ammonium ion may be determined directly in the mineralizate by spectrometry at 655 nm. The following procedure should be used.

After allowing the flask to cool following mineralization, add 50 ± 10 ml of water (5.1) to the flask. Add 2 drops of a solution of 4-nitrophenol, 1 g/l. Then, very slowly, add sodium hydroxide solution (5.4) while thoroughly mixing and cooling the solution until a pale yellow persistent colour develops. Then add a few drops of sulfuric acid (5.3) until the yellow colour is discharged. Transfer the solution quantitatively to a 200 ml volumetric flask and dilute to volume with water (5.1). Determine ammonium ion in this solution using the spectrometric procedure (see ISO 7150/1). Calibration and blank solutions must be prepared by following the above procedure because the high concentration of sodium sulfate in the neutralized mineralizate solution will affect the calibration of the spectrometric procedure. The ammonium concentration, ϱ_N, expressed in milligrams per litre, determined by the spectrometric procedure must be multiplied by a factor $200/V_0$ where V_0 is the test portion volume in millilitres (8.1), to obtain the Kjeldahl nitrogen concentration, ϱ_N, expressed in milligrams per litre, of the sample.

11.2 Suggested procedure for removal of selenium from mineralization residues

The residues should be collected into a glass bottle labelled "Toxic". For removal of selenium, the bottle contents must be made acid (pH 2). Reduction of this acid solution with tin(II) chloride (added as a solid) will produce a precipitate of red selenium which can then be filtered off and disposed of in a controlled manner.

12 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) all information necessary for complete identification of the sample;

c) details of the storage and preservation of the laboratory sample before analysis;

d) a statement of the repeatability achieved;

e) the results and the method of expression used;

f) details of any operations not included in this International Standard, or regarded as optional, together with any circumstance that may have affected the results.

Table 2 — Repeatability standard deviations*

Sample	Nitrogen concentration, ϱ_N mg/l	Test portion volume ml	Standard deviation** mg/l	Degrees of freedom
Urea solution	2	500	0,027	19
Urea solution	50	100	0,31	19
Urea solution	150	100	2,69	19
Sewage	79***	50	0,68	19
Chemical waste	16***	200	0,19	15
Chemical waste	62***	100	0,48	15

* Data from France.

** 0,1 mol/l hydrochloric acid was used for all titrations, except those for the ϱ_N = 2 mg/l standard solution, for which 0,02 mol/l hydrochloric acid was used.

*** Mean value from the determinations.