International Standard ISO 5664

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

Water quality — Determination of ammonium — Distillation and titration method

Qualité de l'eau — Dosage de l'ammonium — Méthode par distillation et titrimétrie

First edition — 1984-05-15

UDC 543.342 : 543.24 Ref. No. ISO 5664-1984 (E)

Descriptors : water, tests, determination of content, ammonium ion, distillation method, titration.

Price based on 3 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 5664 was developed by Technical Committee ISO/TC 147, *Water quality*, and was circulated to the member bodies in December 1982.

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

Australia	France	New Zealand
Austria	Hungary	Poland
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The member body of the following country expressed disapproval of the document on technical grounds:

Germany, F.R.

Printed in Switzerland

Water quality — Determination of ammonium — Distillation and titration method

1 Scope

This International Standard specifies a distillation and titration method for the determination of ammonium in raw, potable and waste water.

2 Field of application

2.1 Range

An ammonium nitrogen content 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.

2.2 Limit of detection

A practically determined (4 degrees of freedom) limit of detection, using a 250 ml test portion, is ϱ_N = 0,2 mg/l.

2.3 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.

2.4 Interferences

The main possible interference arises from urea which, under the conditions specified, will distil as ammonia thus causing high results. Interference will also arise from volatile amines which will distil and react with the acid during the titration, thus causing high results. Chloramines present in chlorinated water samples will be determined in this manner.

3 Principle

Adjustment of the pH of a test portion to within the range 6,0 to 7,4. Addition of magnesium oxide to produce mildly alkaline conditions, distillation of the liberated ammonia and collection in a receiving flask containing boric acid solution. Titration of the ammonium in the distillate with standard volumetric acid solution using boric acid/indicator solution.

4 Reagents

During the analysis, use only reagents of recognized analytical grade and only water prepared as described in 4.1.

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

4.1.1 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 eluate for storage purposes.

4.1.2 Distillation method

Add 0,10 ± 0,01 ml of sulfuric acid solution (ϱ = 1,84 g/ml) to 1 000 ± 10 ml of distilled water and redistil in an 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.

4.2 Hydrochloric acid, ϱ = 1,18 g/ml.

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

Prepare this solution by diluting the hydrochloric acid (4.2). Standardize it by normal analytical procedures. Alternatively, commercial solutions of guaranteed concentration may be used.

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

Prepare this solution by diluting the hydrochloric acid (4.2). Standardize it by normal analytical procedures. Alternatively, commercial solutions of guaranteed concentration, or a diluted solution of the standard volumetric hydrochloric acid (4.3), may be used.

4.5 Boric acid/indicator, solution.

4.5.1 Dissolve 0,5 ± 0,1 g of water-soluble methyl red in about 800 ml of water and dilute to 1 litre.

4.5.2 Dissolve 1,5 ± 0,1 g of methylene blue in about 800 ml of water and dilute to 1 litre.

4.5.3 Dissolve 20 ± 1 g of boric acid (H_3BO_3) in warm water. Cool to room temperature. Add 10 ± 0,5 ml of the methyl red indicator solution (4.5.1) and 2,0 ± 0,1 ml of the methylene blue solution (4.5.2) and dilute to 1 litre.

4.6 Bromothymol blue, 0,5 g/l indicator solution.

Dissolve 0,5 ± 0,02 g of bromothymol blue in water and dilute to 1 litre.

4.7 Hydrochloric acid, 1 % (*V*/*V*) solution.

Dilute 10 ± 1 ml of the hydrochloric acid (4.2) to 1 litre with water.

4.8 Sodium hydroxide solution, 1 mol/l.

Dissolve 40 ± 2 g of sodium hydroxide in about 500 ml of water. Cool to room temperature and dilute to 1 litre.

4.9 Light magnesium oxide, carbonate-free.

Heat the magnesium oxide at 500 °C to remove carbonate.

4.10 Anti-bumping granules.

4.11 Anti-foaming agent, for example paraffin wax chips.

5 Apparatus

Ordinary laboratory apparatus, and

Distillation apparatus, incorporating a distillation flask of capacity 800 to 1 000 ml attached to an anti-splash head and a vertical condenser arranged so that the outlet can be immersed in absorbent solution.

NOTE ON PRELIMINARY CLEANING OF THE DISTILLATION APPARATUS

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

Place about 350 ml of the ammonium-free water (4.1) in the distillation flask. Add a few anti-bumping granules (4.10), assemble the apparatus, and distil until at least 100 ml of the water has been collected. Discard the distillate and the residue in the distillation flask.

6 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 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.

7 Procedure

7.1 Selection of volume of test portion

If the approximate ammonium content of the sample is known, select the volume of the test portion according to table 1.

Table 1

Ammonium 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 standard volumetric hydrochloric acid (4.3) for the titration.

7.2 Determination

7.2.1 Transfer 50 ± 5 ml of the boric acid/indicator solution (4.5) into the receiving flask of the distillation apparatus. Ensure that the delivery tip of the condenser is below the surface of the boric acid solution. Measure the selected volume of test portion (see 7.1) into the distillation flask.

NOTE If chlorine is present in the test portion, a few small crystals of sodium thiosulfate should be added in order to remove it.

Add a few drops of the bromothymol blue indicator solution (4.6) and, if necessary, adjust the pH to within the range 6,0 (indicator yellow) to 7,4 (indicator blue) using the sodium hydroxide solution (4.8) or the hydrochloric acid (4.7), as appropriate. Then make up the total volume in distillation flask to about 350 ml with the ammonium-free water (4.1).

Add to the distillation flask 0,25 ± 0,05 g of the light magnesium oxide (4.9) and a few anti-bumping granules (4.10). [The addition of anti-foaming agent (4.11) may be necessary with some waste water samples.] Immediately attach the distillation flask to the apparatus.

7.2.2 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.

7.2.3 Titrate the distillate to the purple end-point using the standard volumetric hydrochloric acid (4.4) and record the volume used.

NOTES

1 The standard volumetric hydrochloric acid (4.3) may be used for titration of distillates from samples having high ammonium contents.

2 Ammonia can be titrated as it distils into the receiving flask. If protracted collection of ammonia is thus revealed, it may indicate the presence of interfering substances which are undergoing slow hydrolysis to yield ammonia.

7.3 Blank test

Carry out a blank test by proceeding as described in 7.2, but replacing the test portion with about 250 ml of the ammonium-free water (4.1).

8 Expression of results

8.1 Method of calculation

The ammonium nitrogen concentration, ϱ_N, expressed in milligrams per litre, is given by the equation

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

where

V_0 is the volume, in millilitres, of the test portion (see 7.1);

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

V_2 is the volume, in millilitres, of the standard volumetric hydrochloric acid used for the titration in the blank test (see 7.3);

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

14,01 is the atomic mass, in grams per mole, of nitrogen.

The result may be expressed as the mass concentration of nitrogen, ϱ_N, ammonia, ϱ_{NH_3}, or ammonium ion, $\varrho_{NH_4^+}$, in milligrams per litre, or as the amount of substance concentration of ammonium ion, $c(NH_4^+)$, in micromoles per litre. The appropriate conversion factors are given in table 2.

Table 2

	ϱ_N	ϱ_{NH_3}	$\varrho_{NH_4^+}$	$c(NH_4^+)$
	mg/l	mg/l	mg/l	µmol/l
ϱ_N = 1 mg/l	1	1,216	1,288	71,4
ϱ_{NH_3} = 1 mg/l	0,823	1	1,059	58,7
$\varrho_{NH_4^+}$ = 1 mg/l	0,777	0,944	1	55,4
$c(NH_4^+)$ = 1 µmol/l	0,014	0,017	0,018	1

Example:

An ammonium ion concentration $\varrho_{NH_4^+}$, of 1 mg/l corresponds to a nitrogen concentration of 0,777 mg/l.

8.2 Reproducibility

Reproducibility standard deviations have been determined as indicated in table 3.

Table 3*

Sample	Ammonium content, ϱ_N	Volume of test portion	Standard deviation	Degrees of freedom
	mg/l	ml	mg/l	
Standard solution	4,0	250	0,23	10
Standard solution	40	250	0,56	11
Settled sewage	35	100	0,70	16
Sewage effluent	1,8	25	0,16	11

* Information from the United Kingdom.

9 Test report

The test report shall include the following information:

a) reference to this International Standard;

b) all details required for the complete identification of the sample;

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

d) a statement of the repeatability achieved by the laboratory when using this method;

e) the result and the method of expression used;

f) details of any deviation from the procedure specified in this International Standard or any other circumstance that may have influenced the result.

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