International Standard 7150/1

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Water quality — Determination of ammonium — Part 1: Manual spectrometric method

Qualité de l'eau — Dosage de l'ammonium — Partie 1: Méthode spectrométrique manuelle

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Foreword

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

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The member body of the following country expressed disapproval of the document on technical grounds :

Japan

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Water quality — Determination of ammonium — Part 1: Manual spectrometric method

1 Scope and field of application

1.1 Substance determined

This part of ISO 7150 specifies a manual spectrometric method for the determination of ammonium in water.

NOTE — An automated spectrometric method for the determination of ammonium will form the subject of ISO 7150/2.

1.2 Type of sample

The method is applicable to the analysis of potable water, and most raw and waste waters. Application to excessively coloured or saline waters shall be preceded by distillation (see clause 10).

For interferences, see clause 9.

1.3 Range

An ammonium nitrogen concentration, ϱ_N of up to 1 mg/l, using the maximum test portion of 40 ml, can be determined. Much higher concentrations can be determined by taking smaller test portions.

1.4 Limit of detection [1)]

When using cells of optical path length 40 mm and a 40 ml test portion, the limit of detection lies within the range ϱ_N = 0,003 to 0,008 mg/l.

1.5 Sensitivity [1)]

Using a 40 ml test portion and a cell of optical path length 40 mm, ϱ_N = 0,200 mg/l gives an absorbance of about 0,69 units.

Using a 40 ml test portion and a cell of optical path length 10 mm, ϱ_N = 0,750 mg/l gives an absorbance of about 0,65 units.

2 Reference

ISO 5664, *Water quality — Determination of ammonium — Distillation and titration method.*

3 Principle

Spectrometric measurement at about 655 nm of the blue compound formed by reaction of ammonium with salicylate and hypochlorite ions in the presence of sodium nitrosopentacyanoferrate(III) (sodium nitroprusside).

Hypochlorite ions are generated *in situ* by the alkaline hydrolysis of *N*, *N'*-dichloro-1,3,5-triazine-2,4,6 (1H, 3H, 5H)-trione, sodium salt (sodium dichloroisocyanurate). Reaction of the chloramine with sodium salicylate takes place at pH 12,6 in the presence of sodium nitroprusside. Any chloramines present in the sample are quantitatively determined as a consequence. Sodium citrate is incorporated in the reagent to mask interference from cations, notably calcium and magnesium.

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 collected eluate for storage purposes.

4.1.2 Distillation method

Add 0,10 ± 0,01 ml of sulfuric acid (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.

1) Data from a United Kingdom interlaboratory exercise involving five participants.

4.2 Colour reagent.

Dissolve 130 ± 1 g of sodium salicylate ($C_7H_6O_3Na$) and 130 ± 1 g of trisodium citrate dihydrate ($C_6H_5O_7Na_3 \cdot 2H_2O$) in water (4.1) in a 1000 ml one-mark volumetric flask. Add sufficient water to give a total liquid volume of about 950 ml and then add 0,970 ± 0,005 g of sodium nitroso-pentacyanoferrate(III) dihydrate {sodium nitroprusside, $[Fe(CN)_5NO]Na_2 \cdot 2H_2O$}. Dissolve the solid and then dilute to the mark with water.

Stored in an amber glass bottle, this reagent is stable for at least 2 weeks.

4.3 Sodium dichloroisocyanurate, solution.

Dissolve 32,0 ± 0,1 g of sodium hydroxide in 500 ± 50 ml of water (4.1). Cool the solution to room temperature and add 2,00 ± 0,02 g sodium dichloroisocyanurate dihydrate ($C_3N_3O_3Cl_2Na \cdot 2H_2O$) to the solution. Dissolve the solid and transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask. Dilute to the mark with water.

Stored in an amber glass bottle, this reagent is stable for at least 2 weeks.

4.4 Ammonium nitrogen, standard solution, ϱ_N = 1 000 mg/l.

Dissolve 3,819 ± 0,004 g of ammonium chloride (dried at 105 °C for at least 2 h) in about 800 ml of water (4.1) in a 1 000 ml one-mark volumetric flask. Dilute to the mark with water.

1 ml of this standard solution contains 1 mg of ammonium nitrogen.

Stored in a stoppered glass bottle, this solution is stable for at least 1 month.

4.5 Ammonium nitrogen, standard solution, ϱ_N = 100 mg/l.

Pipette 100 ml of ammonium nitrogen standard solution (4.4) into a 1 000 ml one-mark volumetric flask. Dilute to the mark with water.

1 ml of this standard solution contains 0,1 mg of ammonium nitrogen.

Stored in a stoppered glass bottle, this solution is stable for 1 week.

4.6 Ammonium nitrogen, standard solution, ϱ_N = 1 mg/l.

Pipette 1 ml of ammonium nitrogen standard solution (4.5) into a 100 ml one-mark volumetric flask. Dilute to the mark with water.

1 ml of this standard solution contains 1 µg of ammonium nitrogen.

Prepare this solution immediately before use.

4.7 Cleaning solution.

Dissolve 100 ± 2 g of potassium hydroxide in 100 ± 2 ml of water. Cool the solution and add 900 ± 50 ml of 95 % (*V*/*V*) ethanol.

Store the solution in a polyethylene bottle.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Spectrometer, capable of operating at a wavelength of 655 nm with cells of optical path length between 10 and 50 mm.

5.2 Water-bath or **incubator,** capable of being maintained at 25 ± 1 °C.

NOTE ON CLEANING OF GLASSWARE

All glassware shall be carefully cleaned using the cleaning solution (4.7) followed by thorough rinsing with water (4.1).

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 Test portion

The maximum test portion volume is 40 ml, which can be used for the determination of ammonium nitrogen concentrations up to ϱ_N = 1 mg/l.

Smaller test portions may be used as appropriate in order to accommodate much higher ammonium nitrogen concentrations. Laboratory samples containing suspended matter should be allowed to settle, or filtered by gravity through a pre-rinsed glass fibre paper before taking the test portion. Alternatively, prior distillation of the sample may be used (see clause 10).

7.2 Preparation of test solution

Pipette the test portion (7.1) into a 50 ml one-mark volumetric flask, and, if necessary, dilute to 40 ± 1 ml with water (4.1).

7.3 Determination

7.3.1 Formation of the absorbing compound

Add 4,00 ± 0,05 ml of colour reagent (4.2) and mix well. Then add 4,00 ± 0,05 ml of sodium dichloroisocyanurate solution (4.3) and mix well.

NOTE — After this addition the pH of the solution should be 12,6 ± 0,1. Extremes of acidity or alkalinity in the sample may cause deviation.

Dilute to the mark with water (4.1). Shake the flask thoroughly and place it in the water-bath (5.2) maintained at 25 ± 1 °C.

NOTE — Other water-bath temperatures may be used, but all determinations and calibrations should be carried out at the same temperature (within ± 1 K).

7.3.2 Spectrometric measurements

After at least 60 min, remove the flask from the water-bath and measure the absorbance of the solution at the wavelength of maximum absorbance, approximately 655 nm, in a cell of suitable path length against water (4.1) in the reference cell.

NOTE — The wavelength of maximum absorbance should be checked when this method is first used, and should be used in all subsequent determinations.

7.4 Blank test

Proceed as described in 7.2 and 7.3, but using 40 ± 1 ml of water (4.1) in place of the test portion.

7.5 Calibration

7.5.1 Preparation of the set of calibration solutions

To a series of nine 50 ml one-mark volumetric flasks add, by means of a burette, the volumes of ammonium nitrogen standard solution (4.6) shown in table 1.

Add water (4.1) to give a volume of 40 ± 1 ml if necessary.

7.5.2 Formation of the absorbing compound

See 7.3.1.

7.5.3 Spectrometric measurements

Proceed according to 7.3.2 using the cell path length(s) specified in table 1 for absorbance measurements.

Table 1 — Volumes of standard solution for use in the calibration series

Volume of standard solution (4.6)	Mass of ammonium nitrogen, m_N	Cell path length
ml	µg	mm
0,00*	0	10 and 40**
2,00	2	40
4,00	4	40
6,00	6	40
8,00	8	40
10,00	10	10
20,00	20	10
30,00	30	10
40,00	40	10

* The zero member.

** 50 mm path length cells may be used.

7.5.4 Plotting the calibration graph

Subtract the absorbance of the zero member from the absorbances obtained from the other calibration solutions. Plot a graph of absorbance against mass of ammonium nitrogen, m_N, for each cell path length. This graph should be linear and should pass through the origin.

8 Expression of results

8.1 Method of calculation

The absorbance due to ammonium in the test portion, A_r, is given by the equation

$$A_r = A_s - A_b$$

where

A_s is the absorbance of the test solution (7.3.2);

A_b is the absorbance of the blank test solution (7.4).

NOTE — A_s and A_b must be measured in cells of the same path length for a particular sample.

The ammonium nitrogen content, ϱ_N, in milligrams per litre, is given by the formula

$$\frac{m_N}{V}$$

where

m_N is the mass, in micrograms, of ammonium nitrogen, determined from A_r and the calibration graph (7.5.4) for the appropriate cell path length;

V is the test portion volume, in millilitres.

See table 2 for conversion of ϱ_N to ammonia and ammonium concentrations.

Table 2 — Conversion table

	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 Precision

Repeatability and reproducibility standard deviations have been determined as shown in table 3.

9 Interferences

A range of substances often encountered in water samples has been tested for possible interference with this method. Full details are given in annex A. The only serious interferences which have been encountered are those from aniline and ethanolamine, and represent the interference to be expected from primary amines in general. However, such substances are seldom encountered at appreciable concentrations in water samples.

Extremes of acidity or alkalinity will interfere with the formation of the absorbing compound, as will the presence of any substance causing reduction of hypochlorite ions, although these circumstances are unlikely to arise in most water samples. The procedure referred to in clause 10 should be adopted in such circumstances.

In saline samples, interference from magnesium precipitation arises when the complexing capacity of the citrate in the reagents is exceeded. For this reason, preliminary distillation is necessary (see clause 10).

10 Special cases

If samples are excessively coloured or saline such that errors are likely in the absorbance measurements or such that interference from high concentrations of magnesium or chloride is likely, a test sample shall be prepared by distillation. The procedure given in ISO 5664 shall be followed, but note that collection of the distillate shall be made in 1 % (V/V) hydrochloric acid. The distillate shall then be neutralized and made up to a measured volume, V_2, in millilitres. The volume of sample taken for distillation, V_1, in millilitres, shall also be noted.

The test sample thus prepared can then be analysed as described in clause 7. However, the result will be the concentration of ammonium nitrogen in the test sample. The concentration in the original sample is given by the formula

$$\frac{\varrho_{N1}\, V_2}{V_1}$$

where

ϱ_{N1} is the result on the test sample;

V_1 and V_2 are as defined above.

11 Notes on procedure

11.1 General

The determination of low concentrations of ammonium is particularly susceptible to bias caused by the presence of traces of ammonium in the analytical environment. While careful attention to all the instructions given in this part of ISO 7150 should minimize this susceptibility, the possibility of biased results remains. Two methods for obtaining an indication of possible bias are now presented.

11.2 Monitoring of blank and calibration standard absorbance values

The actual absorbance values (measured against water in the reference cell) obtained for the blank test solution and the calibration series shall be recorded on each occasion the method is used. This record of values will enable any deviation to be recognized. Such deviation may be caused by contamination of the blank test solution or calibration series with ammonium, or by a deficiency in one or more of the reagents. In either case, remedial measures shall be taken. Annex B quotes typical values obtained in an interlaboratory exercise.

11.3 Checking the accuracy of analytical results

When this method is first used, an estimate of the total standard deviation (with at least 9 degrees of freedom) should be

Table 3 — Repeatability and reproducibility standard deviations*

Sample**	Ammonium nitrogen concentration ϱ_N	Cell path length	Standard deviation, s	
			Repeatability	Reproducibility
	mg/l	mm	mg/l	mg/l
Standard solution	0,150	40	0,002***	—
Standard solution	1,00	10	0,005 to 0,025†	0,015 to 0,038†
Standard solution	5,00	10	0,036***	—
Well water	0,217	40	0,002†	0,004 to 0,010†
Sewage effluent	0,877	10	0,007 to 0,027†	0,009 to 0,027†

* Data from the United Kingdom.

** All test portion volumes were 40 ml except for the 5,00 mg/l standard solution, for which it was 5 ml.

*** Result from one laboratory; 9 degrees of freedom.

† The lowest and highest values from an interlaboratory exercise involving five participants. All values have 9 degrees of freedom.

obtained on the determination of a control standard ammonium nitrogen solution with a concentration of approximately 50 % of that of the most concentrated calibration solution.

This control standard solution shall not be used for calibration purposes.

One portion of this control standard solution should be analysed with every subsequent batch of determinations; calibration shall be performed with the calibration series. The determined concentration of this control standard solution shall lie within the concentration range

$$\varrho_{N2} \pm 3 s_1$$

where

ϱ_{N2} is the concentration of the solution;

s_1 is the predetermined standard deviation for the control standard solution.

If this criterion is not attained in any batch of analyses, the reasons for the bias thus revealed shall be investigated, and the batch of analyses shall then be repeated.

After at least 20 more determinations of this control standard solution have been made, with all values complying with the criterion above, those values shall be used to recalculate the value of s_1 for subsequent use.

12 Test report

The test report shall include the following information :

a) a reference to this part of ISO 7150;

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 part of ISO 7150, or regarded as optional, together with any circumstance that may have affected the results.

Annex A

The effect of other substances on ϱ_N *

Substance	Concentration in a 40 ml test portion		Effect of substance on ϱ_N mg/l		
			Actual *** ϱ_N (mg/l)		
	ϱ_B **	mg/l	0,000	0,200	0,500
Sodium chloride	ϱ_{Cl}	1 000	+ 0,002	+ 0,013	+ 0,033
Sodium bicarbonate	ϱ_{HCO_3}	1 000	+ 0,002	+ 0,002	− 0,025
Sodium orthophosphate	ϱ_{PO_4}	100	0,000	− 0,001	− 0,015
Sodium sulfate	ϱ_{SO_4}	500	0,000	+ 0,001	—
Potassium fluoride	ϱ_F	5	+ 0,002	− 0,001	—
Potassium nitrate	ϱ_N	50	+ 0,006	+ 0,002	—
Sodium silicate	ϱ_{SiO_2}	50	+ 0,003	0,000	—
Sodium thiosulfate	$\varrho_{S_2O_3}$	10	− 0,001	+ 0,007	—
Potassium cyanide	ϱ_{CN}	5	+ 0,002	+ 0,019	+ 0,016
Calcium chloride	ϱ_{Ca}	500	0,000	+ 0,013	− 0,001
Magnesium acetate	ϱ_{Mg}	50	+ 0,004	− 0,009	+ 0,002
Iron(III) sulfate	ϱ_{Fe}	10	+ 0,001	+ 0,003	—
Aluminium sulfate	ϱ_{Al}	5	0,000	+ 0,008	—
Copper sulfate	ϱ_{Cu}	5	+ 0,003	+ 0,011	—
Zinc sulfate	ϱ_{Zn}	5	+ 0,003	+ 0,006	—
Lead acetate	ϱ_{Pb}	5	+ 0,001	+ 0,016	+ 0,011
Aniline	$\varrho_{C_6H_5NH_2}$	1	± 0,040	± 0,040	—
Ethanolamine	$\varrho_{NH_2C_2H_4OH}$	1	+ 0,164	+ 0,114	—

* Data from the United Kingdom.

** Ionic charges, if any, have been omitted.

*** If other substances do not interfere, the 95 % confidence limits would be

Nominal concentration, ϱ_N (mg/l)	0,000	0,200	0,500
95 % confidence limits (mg/l)	± 0,003	± 0,014	± 0,021

Annex B

Typical absorbance values* for blank and standard solutions

Solution of concentration ϱ_N	Cell path length	Absorbance**			
mg/l	mm	Lab. 1	Lab. 2	Lab. 3	Lab. 4
0,000	40	0,07	0,12	0,09	0,06
0,050	40	0,26	–	0,22	0,24
0,500	10	0,50	0,48	0,38	0,45

* Data from the United Kingdom.

** The absorbance values are averages obtained during an interlaboratory exercise lasting 5 days.