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Water quality -- Determination of ammonium -- Part 2: Automated spectrometric method

Qualité de l'eau -- Dosage de l'ammonium -- Partie 2: Méthode spectrométrique automatique

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International Standard 7150/2

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Water quality — Determination of ammonium — Part 2: Automated spectrometric method

Qualité de l'eau — Dosage de l'ammonium — Partie 2: Méthode spectrométrique automatique

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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. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 7150/2 was prepared by Technical Committee ISO/TC 147, *Water quality*.

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

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Water quality — Determination of ammonium — Part 2: Automated spectrometric method

1 Scope and field of application

1.1 Substance determined

This part of ISO 7150 specifies an automated spectrometric method for the determination of ammonium in water.

NOTE — For a manual spectrometric method for the determination of ammonium, see ISO 7150/1.

1.2 Type of sample

The method is applicable to the analysis of raw, potable and most waste waters. Application to excessively coloured or saline waters shall be preceded by distillation (see clause 11).

For interferences, see clause 9.

1.3 Range

An ammonium nitrogen concentration, ϱ_N, of up to 50 mg/l can be determined using dialysis, or up to 0,5 mg/l without dialysis (see clause 5).

1.4 Limit of detection[1)]

With dialysis, the limit of detection is $\varrho_N \approx 0{,}03$ mg/l.

Without dialysis it is $\varrho_N \approx 0{,}01$ mg/l.

2 Reference

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

3 Principle

Spectrometric measurement at about 650 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 by the alkaline hydrolysis of 1,3-dichloro-5-sodio-1,3,5-triazinanetrione (sodium dichloroisocyanurate). Reaction of the resulting chloroamine with sodium salicylate takes place at pH 12,6 in the presence of nitroprusside. Any chloroamines present in the sample are quantitatively determined as a consequence. Sodium citrate is added to mask interference from cations, notably calcium and magnesium.

All reactions are carried out automatically using continuous flow techniques.[2)] The absorbance of the coloured compound is measured in a flow-through spectrometer.

Two distinct analytical manifold configurations are specified. One incorporates a dialyser block and is suitable for the determination of ammonium nitrogen concentrations up to 50 mg/l. The other omits the dialyser and is suitable for the determination of low level ammonium nitrogen concentrations up to 0,5 mg/l.

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.

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1) Limit of detection calculated from 3 $\hat{s}_w$, where $\hat{s}_w$ is an estimate, with at least 9 degrees of freedom, of the within-batch standard deviation of blank solution responses. Information from the United Kingdom.

2) HMSO. *Methods for Examination of Waters and Associated materials: Air Segmented Continuous Flow Automatic Analysis in the Laboratory.* London, Her Majesty's Stationery Office, 1979.

4.2 Citrate reagent.

4.2.1 Preparation

Dissolve 40,0 ± 0,5 g of trisodium citrate dihydrate ($C_6H_5O_7Na_3 \cdot 2H_2O$) in about 950 ml of water (4.1) in a 1 litre measuring cylinder. Dilute to 1 litre with water (4.1).

Store the solution in a glass or plastics bottle.

This reagent is stable for at least 3 weeks.

4.2.2 Wetting agent (optional)

The inclusion of a wetting agent in this reagent in order to promote smooth flow in the system is optional. If used, the wetting agent shall be a proprietary detergent of the alkyl benzenesulfonate type and shall be added to give a concentration of 1 ml/l.

4.3 Salicylate reagent.

Dissolve 34,0 ± 0,5 g of sodium salicylate ($C_7H_5O_3Na$) in water (4.1) in a 1 000 ml one-mark volumetric flask. Then add 0,400 ± 0,005 g of sodium nitrosopentacyanoferrate(III) dihydrate {sodium nitroprusside, $[Fe(CN)_5NO]Na_2 \cdot 2H_2O$}. Dissolve the solid and then make up to the mark with water (4.1).

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

4.4 Sodium dichloroisocyanurate, solution.

Dissolve 10,0 ± 0,1 g of sodium hydroxide in 500 ± 50 ml of water (4.1). Cool the solution to room temperature and then add 0,80 ± 0,02 g of 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. Make up to the mark with water (4.1) and mix well.

Stored in an amber glass bottle at 4 °C, this reagent is stable for at least 2 weeks.

4.5 Salicylate/citrate mixed reagent (for use in the determination of ammonium nitrogen concentrations up to 0,5 mg/l).

4.5.1 Preparation

Dissolve 34,0 ± 0,1 g of sodium salicylate ($C_7H_5O_3Na$) and 40,0 ± 0,5 g of trisodium citrate dihydrate ($C_6H_5O_7Na_3 \cdot 2H_2O$) in about 950 ml of water (4.1) in a 1 000 ml one-mark volumetric flask. Then add 0,400 ± 0,005 g of sodium nitrosopentacyanoferrate(III) dihydrate {sodium nitroprusside, $[Fe(CN)_5NO]Na_2 \cdot 2H_2O$}. Dissolve the solid and then make up to the mark with water (4.1).

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

4.5.2 Wetting agent (optional)

A wetting agent (see 4.2.2) may be incorporated in this reagent.

4.6 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. Make up to the mark with water (4.1).

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.

4.7 Ammonium nitrogen, standard solution, ϱ_N = 20 mg/l.

Pipette 10 ml of the ammonium nitrogen standard solution (4.6) into a 500 ml one-mark volumetric flask. Make up to the mark with water.

1 ml of this standard solution contains 0,02 mg of ammonium nitrogen.

Stored in a stoppered amber glass bottle and kept at 2 to 5 °C, this solution is stable for 1 week.

5 Apparatus

Apparatus for this continuous flow method consists basically of the following.

5.1 Sample presentation unit (sampler).

5.2 Multichannel peristaltic pump.

5.3 Analytical cartridge (manifold), including pump tubes, mixing coils and dialyser unit.

The design of the manifold depends on the intended range of application. Figure 1 shows that for the determination of ammonium nitrogen concentrations up to 50 mg/l. Figure 2 shows the manifold for the determination of ammonium nitrogen concentrations up to 0,5 mg/l. This is essentially a modification of figure 1 and permits greater sensitivity due to the larger sample flow rate. It is the preferred configuration for the analysis of potable waters.

For the analysis of low levels of ammonium the design of both systems can be improved by drawing air used for segmentation through dilute hydrochloric acid in order to scrub any atmospheric ammonia. Errors from the same source can also be reduced by capping the sample cups, once filled with samples, with thin aluminium foil which will be pierced as the sampling probe descends.

The manifold system shown in figure 2 is unsuitable for samples with a high suspended solids content unless the solids are first removed by settlement, centrifuging or filtration. Ensure that no ammonium is added or lost by any method of removal adopted. Alternatively, give consideration to using distillation (see clause 11).

5.4 Spectrometer capable of measuring absorbance at 650 nm, incorporating a flow cell with an optical path length of at least 15 mm.

5.5 Recorder.

6 Sampling and samples

Laboratory samples shall be collected in polyethylene or glass bottles. They shall 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 Starting operation

Connect the system as shown in figure 1 or figure 2 depending on the intended range of application. Follow the equipment manufacturer's general operating instructions where appropriate.

With the sample probe at rest in the blank water contained in the wash receptacle, place all the reagent lines in their respective reagents, start the pump and switch on the spectrometer and recorder. Allow the system to equilibrate for at least 20 min and during this period check that the bubble pattern and hydraulic behaviour of the system is satisfactory. If not, eliminate difficulties before proceeding.

7.2 Initial sensitivity setting

When an acceptably smooth baseline trace is given on the recorder, adjust the baseline response to about 5 % of full scale with the zero control and then transfer the sample probe into the $\varrho_{\mathrm{N,\ max}}$ calibration solution where $\varrho_{\mathrm{N,\ max}}$ is the greatest concentration that the calibration is intended to cover.

When there is a positive stable response at the measurement unit due to the colour produced from the $\varrho_{\mathrm{N,\ max}}$ calibration solution, adjust this response with the scale expansion control to about 95 % of full scale.

NOTE — The sample probe need remain in the $\varrho_{\mathrm{N,\ max}}$ calibration solution only for sufficient time to give a steady reading.

Then return the sample probe to rest in the wash position, first removing any traces of calibration solution from the outside of the probe.

7.3 Determination

Rinse each sample cup once with a portion of the laboratory sample, calibration standard or blank which it is to contain and then fill it to the top. Load the sample turntable with the filled cups in the order given in table 1.

Repeat the sequence 6 to 38 until all the samples have been loaded.

NOTE — When cross-contamination occurs between two samples (visible on the spectrometer and recorder trace as incomplete separation of consecutive sample responses) both samples should be reanalysed separated by a blank solution.

If necessary, readjust the baseline response to about 5 % of full scale deflection and start the sampling unit.

Table 1 — Order of loading of the turntable

Position No. on turntable	Solution
1 to 5	Calibration solutions* in ascending order (see 7.4)
6 and 7	Water blank (4.1)
8 to 17	Samples
18	Calibration solution*
19 and 20	Water blank (4.1)
21 to 30	Samples
31	Calibration solution*
32 and 33	Water blank (4.1)
34 to 38	Calibration solutions in ascending order

* "Calibration solution" indicates one of the calibration solutions (see 7.4) used in positions 1 to 5.

When all the system responses due to the processed solutions have appeared on the recorder and a final baseline has been obtained, the recorder can be switched off. Then transfer all reagent lines to water and pump for at least 15 min.

7.4 Calibration

Prepare calibration solutions from either of the standard solutions (4.6 or 4.7) as shown in table 2. Select the concentrations of the calibration solutions according to the expected sample ammonium concentrations and the manifold configuration in use.

Load the five selected calibration solutions in positions 1 to 5 of the sample turntable as indicated in table 1.

Table 2 — Volumes of standard solution for use in the preparation of the calibration solutions

Standard solution	Volume of standard solution for dilution to 1 litre	Ammonium nitrogen concentration, ϱ_N, of calibration solution
	ml	mg/l
4.6 (ϱ_N = 1 000 mg/l)	50 40 30 20 10 5 2,5	50 40 30 20 10 5 2,5
4.7 (ϱ_N = 20 mg/l)	50 40 30 25 20 10 5 2,5	1 0,8 0,6 0,5 0,4 0,2 0,1 0,05

At the end of the determination, measure the system response to the calibration solutions from the recorder trace, taking the baseline trace obtained during initial sensitivity setting (see 7.2) as the blank response value.

Plot a graph of response against ammonium nitrogen concentration, ϱ_N, expressed in milligrams per litre. This graph should be linear and should pass through the origin.

8 Expression of results

8.1 Method of calculation

Measure the system response to the samples from the recorder trace, taking the baseline trace obtained during initial sensitivity setting (see 7.2) as the blank response value. Read off the corresponding ammonium nitrogen concentration, ϱ_N, expressed in milligrams per litre, from the calibration graph.

If the responses from the blank or calibration solutions included on the turntable show any drift of the baseline and/or calibration response, apply a correction for the change in sensitivity thus revealed.

See table 3 for conversion of ϱ_N to ammonia and ammonium concentrations.

Table 3 — 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 Reproducibility

Reproducibility standard deviations have been determined as shown in table 4.

9 Interferences

A range of substances often encountered in water samples has been tested for possible interference with this method. Of these only iron and ethanolamine cause significant effects. Full details are given in the annex.

In saline samples, interference from magnesium precipitation arises when the complexing capacity of the citrate in the reagents is exceeded. In this case preliminary distillation is necessary (see clause 11).

10 Notes on procedure

10.1 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. A method for obtaining an indication of possible bias is given in 10.2.

10.2 Checking the accuracy of analytical results

When this method is first used, obtain an estimate of the total standard deviation (with at least 9 degrees of freedom) on the determination of a control ammonium nitrogen solution standard 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.

Table 4 — Reproducibility standard deviations*

Sample	Ammonium nitrogen concentration, ϱ_N	Calibration range as ϱ_N	Reproducibility standard deviation, s
	mg/l	mg/l	mg/l
Standard solution	0,1	0,5	0,007
Standard solution	0,4		0,038
Potable water	0,2		0,011
Standard solution	5,0	50	0,11
Standard solution	40,0		0,16
Polluted river water	11,2		0,13
Sewage effluent	20,2		0,40
Sewage effluent	29,1		0,26

* Data from the United Kingdom.

Analyse one portion of the control standard solution with every subsequent batch of determinations; perform the calibration with a series of calibration solutions (7.4). It is essential that the determined concentration of this controlled standard solution lie within the concentration range

$$\varrho_N \pm 3 s_1$$

where

ϱ_N 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 above criterion, use those values to recalculate the value of s_1 for subsequent use.

11 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.

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) which manifold configuration (figure 1 or 2) was used for the analysis;

e) a statement of the repeatability achieved;

f) the results and the method of expression used;

g) 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.