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Water quality — Determination of ammonium nitrogen — Method by flow analysis (CFA and FIA) and spectrometric detection

Qualité de l'eau — Dosage de l'azote ammoniacal — Méthode par analyse en flux (CFA et FIA) et détection spectrométrique

Reference number
ISO 11732:2005(E)

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established 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. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 11732 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

This second edition cancels and replaces the first edition (ISO 11732:1997), which has been technically revised.

Introduction

Methods using flow analysis are automating wet chemical procedures and are therefore particularly suitable for the processing of large sample series at a high analysis frequency (up to 100 samples per hour).

It is differentiated between flow injection analysis (FIA)[1],[2] and continuous flow analysis (CFA)[3]. Both methods consist of the automatic dosage of the sample introduced into a flow system (manifold) in which the sample analytes react with the reagent solutions on their way through the manifold. The sample preparation may be integrated into the manifold. The reaction product is measured in a flow detector.

The user should be aware that particular problems could require the specification of additional marginal conditions.

Water quality — Determination of ammonium nitrogen — Method by flow analysis (CFA and FIA) and spectrometric detection

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This International Standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted according to this standard be carried out by suitably trained staff.

1 Scope

This International Standard specifies methods suitable for the determination of ammonium nitrogen in various types of waters (such as ground, drinking, surface, and waste waters) in mass concentrations ranging from 0,1 mg/l to 10 mg/l (in the undiluted sample), applying either FIA (Clause 3) or CFA (Clause 4). In particular cases, the range of application may be adapted by varying the operating conditions.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods*

ISO 5667-1, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes*

ISO 5667-2, *Water quality — Sampling — Part 2: Guidance on sampling techniques*

ISO 5667-3, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of water samples*

ISO 8466-1, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

3 Determination of ammonium nitrogen by flow injection analysis (FIA) and spectrometric detection

3.1 Principle

The sample containing ammonium is injected into a continuous carrier stream by means of an injection valve and is mixed with a continuously streaming flow of an alkaline solution. The ammonia formed is separated in a diffusion cell from the solution over a hydrophobic semipermeable membrane and taken up by a streaming recipient flow containing a pH indicator. Due to the resulting pH shift, the indicator solution will change its colour which is measured continuously in the flow photometer. Additional information about this analytical technique is given in references [4], [5], [6], [7] and [8].

NOTE Equipment following this principle using CFA instead of FIA is commercially available, however it has not been validated.

3.2 Interferences

Volatile amines, if present, diffuse through the membrane and lead to a pH shift. If the concentrations of the volatile amines (e.g. methylamine or ethylamine) are equal to those of the ammonium, higher results may then be expected [12]. Significant concentrations of volatile amines can be reduced by distilling the sample adjusted to pH 5,8 prior to the analysis.

In rare cases, it may be possible that the sample does not reach a pH of 12 after the addition of the alkaline reagent solution, thus leading to a loss of ammonium because it will not be converted quantitatively into ammonia. This may particularly occur with strong acidic or buffered samples. In these cases, the pH of the sample shall be adjusted to the range of 3 to 5 by the addition of sodium hydroxide solution (3.3.2 or 3.3.3).

A high concentration of metal ions that can precipitate as hydroxides will give poorly reproducible results. The addition of a suitable complexing agent, such as ethylenedinitrilotetraacetic acid (EDTA), disodium salt, to the alkaline reaction solution (3.3.17) in sufficiently large concentration will prevent the interference by Cu, Zn, Fe, Ca, Mg, and Al. A concentration of 30 g/l of ethylenedinitrilotetraacetic acid, disodium salt (3.3.4), in solution R1 (3.3.17) is adequate for metal concentrations up to 0,2 mg/l each.

In the case of samples containing particulate matter, see 3.5 (last paragraph).

Samples with a total salt concentration of $>$ 10 g/l shall be diluted prior to the measurement.

3.3 Reagents

Apart from the reagents dealt with in the 3.3.6 and 3.3.7, use only reagents of “analytical grade quality for the determination of nitrogen”, or, if not available, those of recognized “analytical grade quality”. The ammonium content of the blank shall regularly be checked (3.6.3).

3.3.1 Water, of grade 1 as specified in ISO 3696:1987.

3.3.2 Sodium hydroxide solution I, c(NaOH) = 5 mol/l.

3.3.3 Sodium hydroxide solution II, c(NaOH) = 0,01 mol/l.

3.3.4 Ethylenedinitrilotetraacetic acid (EDTA)[1)], disodium salt, monohydrate, $C_{10}H_{14}N_2Na_2O_8 \cdot H_2O$.

3.3.5 Bromocresol purple, $C_{21}H_{16}Br_2O_5S$.

3.3.6 Bromothymol blue, $C_{27}H_{28}Br_2O_5S$.

3.3.7 Cresol red, $C_{21}H_{18}O_5S$.

3.3.8 Ammonium chloride, NH_4Cl, dried at 105 °C $\pm$ 2 °C to constant mass.

3.3.9 Potassium chloride, KCl.

3.3.10 Boric acid, H_3BO_3.

3.3.11 Hydrochloric acid solution I, c(HCl) = 0,01 mol/l.

3.3.12 Hydrochloric acid solution II, c(HCl) = 0,1 mol/l.

3.3.13 Hydrochloric acid solution III, c(HCl) = 1,0 mol/l.

3.3.14 Sulfuric acid, $\rho(H_2SO_4)$ = 1,84 g/ml.

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1) Commonly known as ethylenediaminetetraacetic acid.

3.3.15 Mixed indicator.

In a mortar prepare a dry mixture consisting of 10 g of bromocresol purple (3.3.5), 5 g of bromothymol blue (3.3.6), 2,5 g of cresol red (3.3.7), and 45 g of potassium chloride (3.3.9).

The given quantities can be reduced (e.g. by one tenth).

3.3.16 Carrier solution, C (see Figure A.1).

Use water according to 3.3.1, degassed e.g. by reduced pressure.

3.3.17 Alkaline reaction solution, R1 (see Figure A.1).

Dissolve in a graduated flask, nominal capacity 1 000 ml, 30 g of ethylenedinitrilotetraacetic acid, disodium salt (3.3.4) in approximately 800 ml of water (3.3.1), and add 12,4 g of boric acid (3.3.10).

Add 100 ml of sodium hydroxide solution I (3.3.2) dropwise to the suspension and make up to volume with water (3.3.1).

Degas the solution by filtering it through the membrane filter assembly (3.4.2).

The pH of the solution will be approximately 13. Being stored in a plastics bottle (polyethene) at room temperature, it will be stable for one month.

3.3.18 Indicator solution.

Dissolve in a 200 ml graduated flask 1 g of the mixed indicator (3.3.15) in a mixture of 50 ml of sodium hydroxide solution II (3.3.3). Make up to volume with water (3.3.1).

The solution should have a dark reddish colour.

Filter off any undissolved particles.

This solution may be stored at room temperature for three months in an amber glass bottle.

3.3.19 Ammonia recipient solution, R2 (see Figure A.1).

Dilute 10 ml of the indicator solution (3.3.18) with approximately 480 ml of water (3.3.1).

The absorbance of the solution should be 0,3 to 0,5. Otherwise, add dropwise sodium hydroxide solution II (3.3.3) or hydrochloric acid solution III (3.3.13) until an absorbance value of 0,3 to 0,5 (path length 10 mm, wavelength 590 nm) is obtained. Make up to 500 ml with water (3.3.1).

Degas and purify the solution by the membrane filter assembly (3.4.2), fill it into the reagent reservoir and let it stand for at least 2 h.

Immediately before starting the measurement (3.6), check the absorbance again and adjust, if need be, to the absorbance range specified above by adding sodium hydroxide solution II (3.3.3) or hydrochloric acid I, II or III (3.3.11 to 3.3.12) respectively.

This solution may be stored at room temperature for two weeks in a glass bottle.

3.3.20 Ammonium stock solution, ρ(N) = 1 000 mg/l.

Dissolve in a 1 000 ml graduated flask 3,819 g of ammonium chloride (3.3.8) in approximately 900 ml of water (3.3.1), acidify to pH 2 by dropwise addition of sulfuric acid (3.3.14), and make up to volume with water (3.3.1).

This solution may be stored in a refrigerator for at most three months.

3.3.21 Ammonium standard solution I, ρ(N) = 100 mg/l.

Pipette 10 ml of the ammonium stock solution (3.3.20) into a 100 ml graduated flask, add approximately 80 ml of water (3.3.1), acidify by dropwise addition of sulfuric acid (3.3.14), and make up to volume with water (3.3.1).

This solution may be stored in a refrigerator for at most one week.

3.3.22 Ammonium standard solution II, ρ(N) = 10 mg/l.

Pipette 1 ml of the ammonium stock solution (3.3.20) or 10 ml of the ammonium standard solution I (3.3.21) into a 100 ml graduated flask, add approximately 80 ml of water, acidify to pH 2 by dropwise addition of sulfuric acid (3.3.14), and make up to volume with water (3.3.1).

This solution may be stored in a refrigerator for at most one week.

3.3.23 Calibration solutions

Prepare calibration solutions by diluting the ammonium standard solutions I or II (3.3.21 or .3.3.22). At least five calibration standards per working range are recommended. As an example, if six standards are applied, proceed for the working ranges I or II respectively, as follows:

a) Working range I (1 mg/l to 10 mg/l):

— Pipette into a series of 100 ml graduated flasks, 1 ml, 2 ml, 4 ml, 6 ml, 8 ml and 10 ml respectively, of the ammonium standard solution I (3.3.21), and make up to volume with water (3.3.1).

— The mass concentrations of ammonium, expressed as nitrogen, in these calibration solutions are 1 mg/l, 2 mg/l, 4 mg/l, 6 mg/l, 8 mg/l and 10 mg/l.

b) Working range II (0,1 mg/l to 1,0 mg/l):

— Pipette into a series of 100 ml graduated flasks, 1 ml, 2 ml, 4 ml, 6 ml, 8 ml and 10 ml respectively, of the ammonium standard solution II (3.3.22), and make up to volume with water (3.3.1).

— The mass concentrations of ammonium, expressed as nitrogen, in these calibration solutions are 0,1 mg/l, 0,2 mg/l, 0,4 mg/l, 0,6 mg/l, 0,8 mg/l and 1,0 mg/l.

Prepare all calibration solutions freshly before use.

3.4 Apparatus

3.4.1 Flow injection system.

In general, the flow injection system consists of the following components (see Figure A.1).

3.4.1.1 Reagent reservoirs.

3.4.1.2 Low pulsation pump.

3.4.1.3 Suitable pump tubes, if required.

3.4.1.4 Injection valve with a suitable injection volume.

For working range I, an injection volume of 40 µl, for working range II, a volume of e.g. 360 µl or 400 µl is recommended.

3.4.1.5 Diffusion cell with hydrophobic semipermeable membrane (e.g. made from polytetrafluoroethene, PTFE).

EXAMPLES

thickness of membranes:	150 µm to 200 µm;
pore size:	0,5 µm to 2,0 µm;
porosity:	75 %.

3.4.1.6 Transport tubes and reaction coils, having an internal diameter of 0,5 mm to 0,8 mm, tube connections and T-connections of inert plastic and with minimum dead volumes.

3.4.1.7 Photometric detector with flow cell, having a normal path length of 10 mm to 50 mm and a wavelength range 580 nm to 600 nm.

3.4.1.8 Recording unit (e.g. strip chart recorder, integrator or printer/plotter), generally used for evaluation of peak height signals.

3.4.1.9 Autosampler, if required.

3.4.2 Additional apparatus.

Usual laboratory apparatus and the following.

3.4.2.1 Graduated flasks, of 100 ml, 200 ml and 1 000 ml capacities.

3.4.2.2 Graduated pipettes, of 1 ml to 10 ml capacities.

3.4.2.3 Membrane filter assembly with membrane filters, having a pore size of 0,45 µm.

3.5 Sampling and sample pretreatment

Take samples in accordance with ISO 5667-1, ISO 5667-2 and ISO 5667-3.

Containers of glass, polyalkenes and polytetrafluoroethene (PTFE) are suitable for sample collection. Clean all containers coming in contact with the sample thoroughly with hydrochloric acid solutions I, II or III (3.3.11 to 3.3.13) and rinse several times with water.

Analyse the samples immediately after collection. For preservation times up to 24 h, add sulfuric acid (3.3.14) to adjust to a pH of approximately 2 and store at 2 °C to 5 °C in the dark.

In exceptional cases, the sample may be stored up to two weeks, provided the sample has been membrane-filtered after acidification. The applicability of this preservation procedure shall be checked for each individual case of examination.

If there is a risk of clogging the transport tubes, filter the samples prior to measurement.

3.6 Procedure

3.6.1 Instrument set-up

Prior to measurement, continuously run the reagent solutions C, R1, and R2 for approximately 10 min through the flow injection system, record and zero the baseline.

The system is operational when the baseline does not show any drift. A satisfactory signal-to-noise relation should be obtained. Check the reagent blank and the operation of the membrane in accordance with 3.6.3. The system is calibrated as described in 3.6.4.

3.6.2 Instrument performance check

In the analytical system, prepared according to 3.6.1, a calibration solution (3.3.23) having a concentration of 0,5 mg/l in working range II (0,1 mg/l to 1,0 mg/l) or a concentration of 5,0 mg/l in working range I (1,0 mg/l to 10 mg/l) shall show an absorbance of at least 0,040 absorbance units per 10 mm path length. Otherwise, the flow system is not suitable and it shall be replaced by a system which fulfils this requirement.

If the photometric detector does not give any absorbance readings, the absorbance may be determined by comparing with an external absorbance-measuring spectrometer.

3.6.3 Reagent blank check

Wait for the baseline to stabilize.

In place of the alkaline reagent solution R1, run water through the system until a stable signal is obtained. Record the change in absorbance.

If the absorbance changes by more than 0,1 absorbance units per 10 mm path length, either the water being used or the alkaline reagent solution may be contaminated with ammonium, or the semipermeable membrane may be faulty. Appropriate measures shall then be taken to remedy the fault.

Then run reagent solutions again.

3.6.4 Calibration

Select working range I or II and prepare the calibration solutions for the selected working range (3.3.23). A separate calibration with at least five calibration solutions shall be used for each working range.

Before starting the analysis, set the baseline as recommended by the instrument manufacturer, or as appropriate.

Calibrate the analyser with the calibration solutions and a blank. The test conditions for the calibration and the measurement of samples (3.6.5) are the same. The magnitude of the measuring signal is proportional to the mass concentration of ammonium, expressed as nitrogen.

Determine the sample concentrations, using the procedure specified by the analyser manufacturer as long as it is not in contradiction with this International Standard.

The calibration curve is determined in accordance with ISO 8466-1.

The following Equation (1) is used:

$$y = b\rho + a \tag{1}$$

where

y is the measured value, in terms of instrument-related units;

b is the slope of the calibration function, expressed in instrument-related units $\times$ litres per milligrams (instrument-related units $\times$ l/mg);

ρ is the mass concentration, expressed in milligrams per litre (mg/l), of ammonium, expressed as nitrogen in the calibration solutions;

a is the ordinate intercept of the calibration function, in terms of instrument-related units.

Proceed as described in 3.6.5.

3.6.5 Measurement

Analyse the samples in the same way as the calibration solutions using the flow injection system (3.4.1).

Dilute the sample or use another working range, if the mass concentrations exceed the validity range of the selected working range.

Check the validity of the calibration function of the respective working range after each sample series, but at the latest after the measurement of 10 to 20 samples, using one calibration solution each for the lower and upper part of the respective working range. Perform a new calibration, if necessary.

4 Determination of ammonium nitrogen by continuous flow analysis (CFA) and spectrometric detection

4.1 Principle

In a continuously flowing, gas-segmented carrier stream, ammonium present in the sample reacts in alkaline solution with hypochlorite (ClO^-), which has previously been liberated from dichloroisocyanurate.

The chloroamine formed reacts under catalysis of nitroprusside with salicylate at a temperature of 37 °C to 50 °C to form a blue-green indophenol dye which is quantitatively measured in a flow photometer at 640 nm to 660 nm.

Additional information concerning this analytical technique may be obtained from references [9], [10], [11], and [13].

NOTE Equipment following this principle using FIA instead of CFA is commercially available, however it has not been validated.

4.2 Interferences

Low-molecular amines react similarly to ammonia and their presence will consequently lead to erroneously high results [12].

Interferences may occur if, after addition of all reagent solutions, the reaction mixture does not reach a pH of at least 12,6. This primarily happens with strong acidic and buffered samples, that are only approximately neutralized prior to analysis.

Metal ions in high concentrations, which tend to precipitate as hydroxides, cause poor reproducibility.

For a far-reaching removal of the interfering organic matrix (compounds with high molecular masses), the sample can be dialyzed, e.g. by an on-line procedure.

Alternatively, the sample can be filtered through activated carbon, provided a change of the ammonium concentration in the sample can be ruled out when this approach is chosen.

Particulate matter in the samples can clog the transport tubes and impede the spectrometric measurement. In the case of larger particles (> 0,1 mm), it is necessary to filter the sample by membrane filtration, whereas smaller particles can be removed by dialysis.

4.3 Reagents

In addition to the reagents listed in 3.3, with the exception of those described in 4.3.2 and 4.3.5, the following reagents of “analytical quality grade” and those of "analytical quality grade for the determination of nitrogen" shall be used.

4.3.1 **Trisodium citrate dihydrate**, $Na_3C_6H_5O_7 \cdot 2H_2O$.

4.3.2 Polyethylene glycol dodecyl ether, having a melting point of 33 °C to 41 °C, solution with mass fraction of w = 30 %.

The solution is stable for approximately four weeks.

4.3.3 Sodium salicylate, $NaC_7H_5O_3$.

4.3.4 Sodium nitroprusside dihydrate [sodium nitrosopentacyanoferrate(II)], $Na_2[Fe(CN)_5NO] \cdot 2H_2O$.

4.3.5 Sodium dichloroisocyanurate dihydrate (sodium 1,3-dichlorohexahydro-1,3,5-triazine-2,4,6-trione), $NaC_3Cl_2N_3O_3 \cdot 2H_2O$.

4.3.6 Citrate buffer solution, reagent solution R3 (see Figures A.2, A.3 and A.4).

In a 1 000 ml graduated flask, dissolve 40 g of trisodium citrate dihydrate (4.3.1) and 1 ml of polyethyleneglycol dodecyl ether (4.3.2) in water and make up to volume with water.

The solution is stable for one week, if stored in a refrigerator in a brown-glass bottle.

4.3.7 Diluting solution, consisting of a buffer solution, such as citrate buffer solution (4.3.6), required for the application with a dialyzer or a buffer solution or water may be used for the online dilution.

4.3.8 Sodium salicylate solution, reagent solution R4 (see Figures A.2, A.3 and A.4).

In a 1 000 ml graduated flask, dissolve 34 g of sodium salicylate (4.3.3), 0,4 g of sodium nitroprusside dihydrate (4.3.4), and 1 ml of polyethyleneglycol dodecyl ether (4.3.2) in water and make up to volume with water.

The solution may be stored in a refrigerator in a brown-glass bottle for one week.

4.3.9 Sodium dichloroisocyanurate solution, reagent solution R5 (see Figures A.2, A.3 and A.4).

In a 1 000 ml graduated flask, dissolve 0,8 g of sodium dichloroisocyanurate (4.3.5) and 50 ml of sodium hydroxide solution I (3.3.2) in water and make up to volume with water.

Prepare the solution fresh before use.

4.3.10 Segmentation gas (e.g. nitrogen), G (see Figures A.2, A.3 and A.4).

4.4 Apparatus

4.4.1 Continuous flow system

In general the system comprises the following components (see Figures A.2, A.3 and A.4).

NOTE Figures A.2 and A.3 show flow systems with internal diameters of 2,2 mm. For Figure A.3, a device with on-line dialysis is also applicable for the working range II (0,1 mg/l to 1 mg/l ammonium, expressed as nitrogen). Figure A.4 shows a corresponding system with internal diameters of 1 mm.

4.4.1.1 Sampler, or other appropriate devices which allow a reproducible sample introduction.

4.4.1.2 Reservoirs for carrier liquids and reagents.

4.4.1.3 Low pulsating pump and suitable chemically inert pump tubes.

4.4.1.4 Manifold with highly reproducible gas bubble feeding, sample and reagent feeding, with appropriate transport systems and connection assemblies of e.g. glass, chemically inert plastic or metal.

4.4.1.5 Dialysis cell, made of a material that depends on the sample matrix, e.g. cellophane membrane, if applicable.

In the lower part of Figure A.2, a device is shown with on-line dialysis that is also applicable for the working range II (0,1 mg/l to 1 mg/l ammonium, expressed as nitrogen).

Example of the separation size: maximum relative molecular mass for dialyzing molecules is between 5 000 to 14 000.

4.4.1.6 Continuous flow thermostat, controllable to about ± 1 °C, suitable for maintaining constant temperatures between 37 °C and 50 °C.

4.4.1.7 Spectrometric detector with continuous flow cell, having a path length maximum of 5 cm and a wavelength range of 640 nm to 660 nm.

4.4.1.8 Recording unit, such as a strip chart recorder or a printer/plotter, generally used for evaluation of peak height signals.

4.4.2 Additional apparatus.

See 3.4.2

4.4.3 Sampling and sample preparation.

See 3.5

4.5 Procedure

4.5.1 Instrument set-up

Continuously run the reagent solutions for approximately 10 min through the system, and record the baseline.

The system is ready when the baseline will no longer show any drift. A satisfactory signal-to-noise relation should be obtained.

4.5.2 Instrument performance check

In the analytical system, prepared according to 4.4.1, a 0,5 mg/l calibration solution (3.3.23) in working range II (0,1 mg/l to 1,0 mg/l) or a 5,0 mg/l calibration solution in working range I (1,0 mg/l to 10 mg/l) shall exhibit an absorbance of at least 0,10 per 10 mm path length. Otherwise, the flow system is not suitable and shall be replaced by a system that fulfils this requirement.

If the photometric detector does not give any absorbance readings, the absorbance may be determined by comparing with an external absorbance-measuring spectrometer.

4.5.3 Reagent blank check

Wait for a stable baseline.

Instead of reagent solutions, run water through the system until the signal is stable. Record the absorbance change.

If the absorbance changes by more than 0,015 absorbance units per 10 mm path length, either the water being used or the reagent solutions may be contaminated and shall be replaced.

Then run reagent solutions again.

4.5.4 Calibration

See 3.6.4.

In addition, dose the calibration solutions into the manifold during a reproducible time period of at least 20 s by means of an appropriate device (e.g. with the aid of a sampler).

Before and after each calibration solution and during a likewise reproducible time period, the so-called washing period, dose water.

Choose a sufficient washing time, so that the measured values of the calibration solutions do not show any cross contamination.

4.5.5 Measurement

See 3.3.5.

Analyse the samples, in the same way as the calibration solutions with the continuous flow system (4.4.1).

5 Calculation

5.1 Evaluation

Determine the mass concentration of the determinand in the measuring solution using the measured value obtained as described in 3.6.5, from the calibration function [Equation (1), 3.6.4].

For the evaluation, use the appropriate calibration function. Do not extrapolate beyond the working range selected. Calculate ρ using Equation (2):

$$\rho = \frac{y - a}{b} \tag{2}$$

where ρ is the mass concentration, expressed in milligrams per litre (mg/l), of ammonium expressed as nitrogen, in the sample.

See Equation (1) for the explanation of the other symbols.

In the calculation, take into account all dilution steps.

5.2 Expression of results

Report results to two significant figures at most.

EXAMPLE

Ammonium, expressed as nitrogen: $2{,}0 \times 10^{-1}$ mg/l

$9{,}2$ mg/l

$1{,}2 \times 10^{3}$ mg/l

6 Precision

Statistical performance data obtained by an interlaboratory trial are described in Annex B. It cannot be excluded that the data are unsuitable for other matrices or concentration ranges.

7 Test report

The test report shall include the following information:

a) reference to this International Standard (ISO 11732:2004);

b) identity of the water sample;

c) specification of the procedure applied, in accordance with Clause 3 or Clause 4, respectively;

d) description of the sample pretreatment;

e) description of the type of instrument or of the flow conditions;

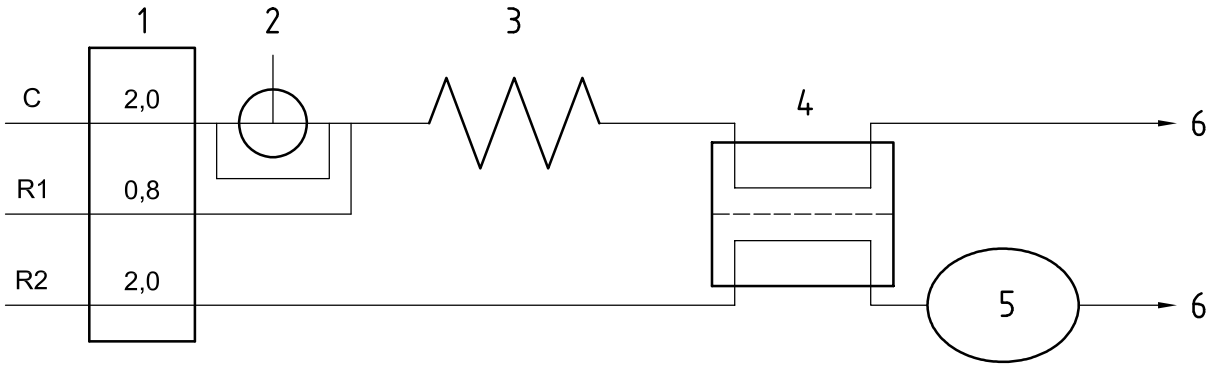
f) expression of results in accordance with 5.2;

g) precision and trueness of the results, if available;

h) any deviation from this method and all events which may have influenced the result.

Annex A
(informative)

Examples of flow analysis systems



Key

1 pump, flowrates in ml/min

2 injector for introducing samples; sample volume:

— 40 µl for working range I (1 mg/l to 10 mg/l)

— 360 µl for working range II (0,1 mg/l to 1,0 mg/l)

3 reaction coil, internal diameter 0,5 mm to 0,8 mm, length 30 cm

4 gas diffusion cell with PTFE membrane

5 detector, wavelength = 580 nm to 600 nm

6 waste

C carrier solution (3.3.16); flowrate: 2,0 ml/min

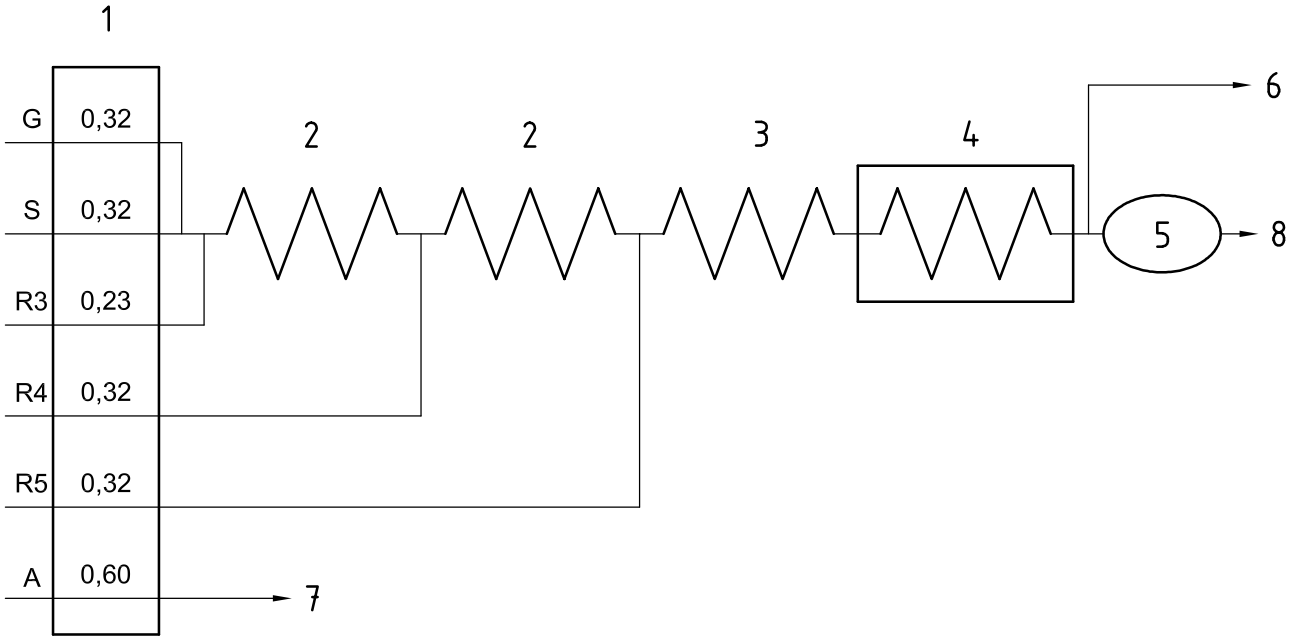
R1 alkaline reaction solution (3.3.17); flowrate: 0,8 ml/min

R2 ammonia recipient solution (3.3.19); flowrate: 2,0 ml/min

Typical injection time: 20 s to 25 s

Typical overall retention time: 45 s

Figure A.1 — Example of a flow injection system (FIA) for working ranges I and II [ρ(N): 0,1 mg/l NH_4–N to 10 mg/l NH_4–N]

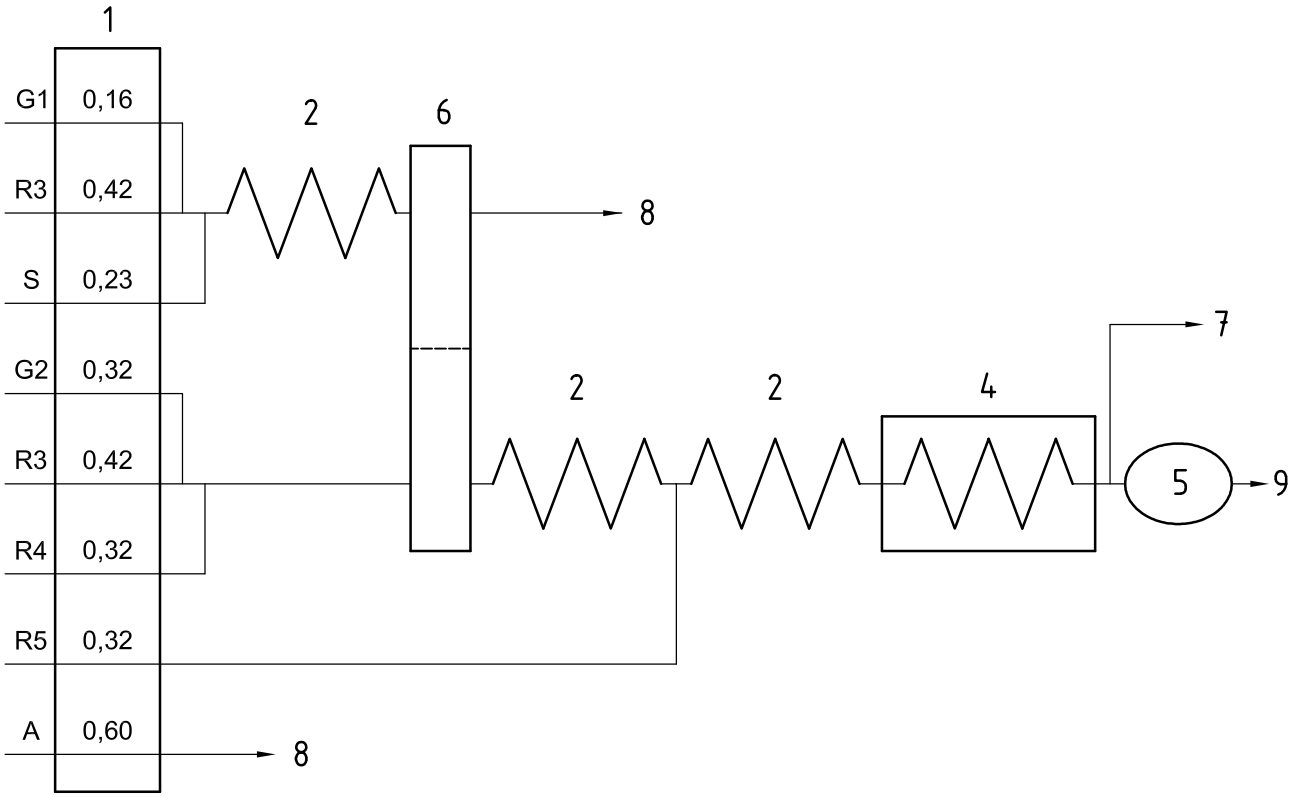


Key

1	pump, flowrates in ml/min
2	reaction coil, internal diameter 2,2 mm, length 25 cm
3	reaction coil, internal diameter 2,2 mm, length 50 cm
4	reaction coil, internal diameter 2,2 mm, length 100 cm, maintained at 37 °C to 50 °C
5	detector, wavelength = 640 nm to 660 nm
6	waste 1: gaseous waste (gas bubbles)
7	waste 2: aqueous (= debubbled) waste
8 = A	unsegmented reaction mixture, coming out of the detector; flowrate: 0,60 ml/min
G	segmentation gas (e.g. nitrogen); flowrate: 0,32 ml/min
S	sample; flowrate 0,32 ml/min
R3	citrate buffer solution (4.3.6); flowrate: 0,23 ml/min
R4	sodium salicylate solution (4.3.8); flowrate: 0,32 ml/min
R5	sodium dichloroisocyanurate solution (2.5.9); flowrate: 0,32 ml/min

Typical overall retention time: 6 min

Figure A.2 — Example of a continuous flow system (CFA, macroflow) for working range II [ρ(N): 0,1 mg/l NH_4–N to 1,0 mg/l NH_4–N]

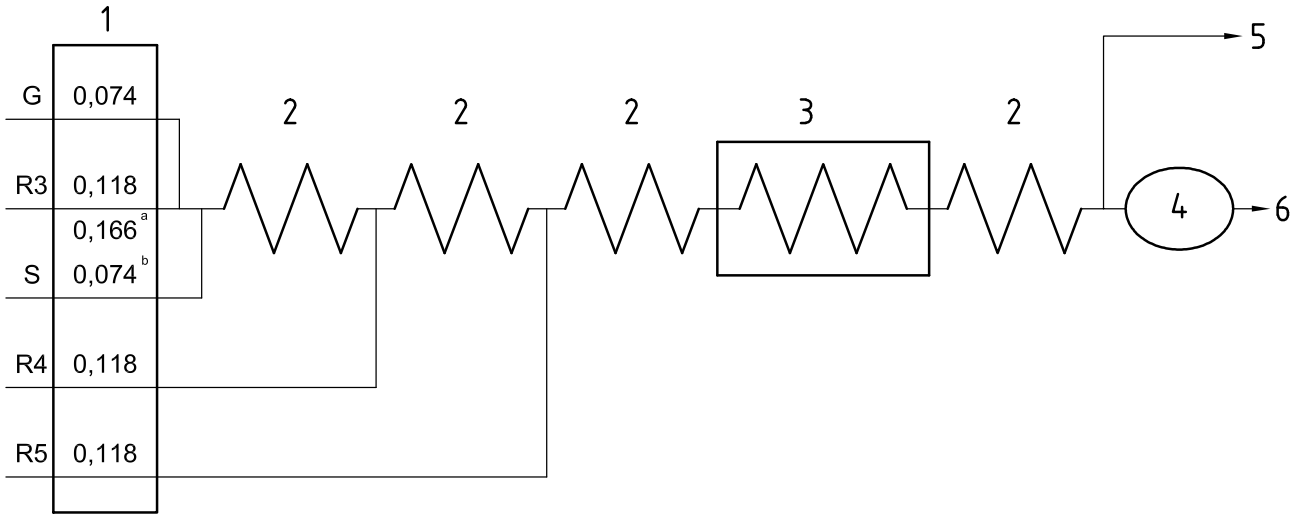


Key

1	pump, flowrates in ml/min
2	reaction coil, internal diameter 2,2 mm, length 25 cm
4	reaction coil, internal diameter 2,2 mm, length 100 cm, thermostatted at 37 °C to 50 °C
5	detector, wavelength = 640 nm to 660 nm
6	dialyzer
7	waste 1: gaseous waste (gas bubbles)
8	waste 2: aqueous (debubbled) waste
9 = A	unsegmented reaction mixture, coming out of the detector; flowrate: 0,60 ml/min
G1	segmentation gas (e.g. nitrogen); flowrate: 0,16 ml/min
G2	segmentation gas (e.g. nitrogen); flowrate: 0,32 ml/min
S	sample; flowrate: 0,23 ml/min
R3	citrate buffer solution (4.3.6); flowrate: 0,42 ml/min
R4	sodium salicylate solution (4.3.8); flowrate: 0,32 ml/min
R5	sodium dichloroisocyanurate solution (4.3.9); flowrate: 0,32 ml/min

Typical overall retention time: 6 min

Figure A.3 — Example of a continuous flow system (CFA, macroflow) for working range I [ρ(N): 1,0 mg/l NH_4–N to 10 mg/l NH_4–N]



Key

1 pump, flowrates in ml/min

2 reaction coil, internal diameter 1 mm, length 40 cm

3 reaction coil, internal diameter 1 mm, length 500 cm, thermostatted at 37 °C ± 1 °C

4 detector, wavelength = 640 nm to 660 nm

5 waste 1: gaseous waste (gas bubbles)

6 waste 2: aqueous (debubbled waste)

G segmentation gas (e.g. nitrogen); flowrate: 0,074 ml/min

S sample (pH = 2); flowrates:

a) for working range II [ρ(N) = 0,1 mg/l to 1,0 mg/l]: 0,166 ml/min

b) for working range I [ρ(N) = 1,0 mg/l to 10 mg/l]: 0,074 ml/min

R3 citrate buffer solution (2.5.6); flowrate: 0,118 ml/min

R4 sodium salicylate solution (4.3.8); flowrate: 0,118 ml/min

R5 sodium dichloroisocyanurate solution (4.3.9); flowrate: 0,118 ml/min

Typical gain factors:

— for working range II [ρ(N) = 0,1 mg/l to 1,0 mg/l]: 4

— for working range I [ρ(N) = 1,0 mg/l to 10 mg/l]: 0,6

Figure A.4 — Examples of a continuous flow system (CFA, microflow) for working ranges I and II [ρ(N): 0,1 mg/l NH_4–N to 10 mg/l NH_4–N]

Annex B
(informative)

Precision data

The precision data given in Tables B.1 and B.2 have been established in an interlaboratory trial, carried out in November 1990.

Table B.1 — Precision data for the determination of ammonium(N) with flow injection analysis (FIA) and spectrometric detection

Sample No	Matrix	l	n	o %	$\overline{x}$ mg/l	s_R mg/l	CV_R %	s_r mg/l	CV_r %
1	Drinking water [a]	15	56	6,67	0,284 1	0,027 9	9,81	0,011 4	4,01
2		15	54	10,0	0,901 9	0,038 2	4,24	0,017 6	1,95
3	Surface water [b]	15	55	8,33	0,531 8	0,026 1	4,91	0,016 5	3,10
4		15	60	0,00	0,916 0	0,073 7	8,05	0,020 4	2,22
5		15	54	10,0	2,460 0	0,095 8	3,90	0,052 6	2,14
6		14	52	7,14	8,033 3	0,287 5	3,58	0,128 8	1,60
7	Domestic water [c]	15	56	6,67	2,930 9	0,196 9	6,72	0,058 7	2,00
8		15	60	0,00	8,273 8	0,327 8	3,96	0,123 4	1,49
9	Industrial wastewater [d]	15	48	20,0	2,450 2	0,075 2	3,07	0,044 3	1,81
10		15	56	5,08	7,981 1	0,281 9	3,35	0,194 6	2,44

l is the number of laboratory sets (four values each per set);

n is the number of outlier-free individual analytical values;

o is the relative number of outliers;

$\overline{x}$ is the total mean;

s_R is the standard deviation of the reproducibility;

CV_R is the coefficient of variation of the reproducibility;

s_r is the standard deviation of the repeatability;

CV_r is the coefficient of variation of the repeatability.

Origin of samples:

[a] Drinking water, spiked with ammonium.

[b] River water (Rhine), spiked with ammonium.

[c] Effluent of a domestic water treatment plant:

Sample 7: Wastewater, diluted 1:10; not spiked;

Sample 8: Wastewater, diluted 1:4, spiked with ammonium.

[d] Effluent of an industrial water treatment plant, sample spiked with ammonium.

Table B.2 — Precision data for the determination of ammonium(N) with continuous flow analysis (CFA) and spectrometric detection

No.	Matrix	l	n	o %	$\overline{x}$ mg/l	s_R mg/l	CV_R %	s_r mg/l	CV_r %
1	Drinking water [a]	11	36	18,2	0,302 4	0,022 9	7,56	0,010 6	3,51
2		11	44	0,00	0,923 0	0,077 1	8,35	0,015 7	1,70
3	Surface water [b]	11	44	0,00	0,556 3	0,039 3	7,07	0,015 3	2,75
4		11	36	18,2	0,963 6	0,035 4	3,67	0,012 9	1,34
5		11	44	0,00	2,579 1	0,258 1	10,0	0,081 5	3,16
6		11	35	20,4	8,209 7	0,145 1	1,77	0,067 6	0,82
7	Domestic water [c]	11	32	27,3	2,984 7	0,038 4	1,28	0,032 9	1,10
8		11	44	0,00	8,466 1	0,221 7	2,62	0,075 2	0,89
9	Industrial wastewater [d]	11	44	0,00	2,711 8	0,126 4	4,66	0,043 6	1,61
10		11	40	9,09	8,316 5	0,204 0	2,45	0,059 3	0,71

For an explanation of the symbols, see Table B.1

Origin of samples:

[a] Drinking water, spiked with ammonium.

[b] River water (Rhine), spiked with ammonium.

[c] Effluent of a domestic water treatment plant:

Sample 7: Wastewater, diluted 1:10; not spiked;

Sample 8: Wastewater, diluted 1:4, spiked with ammonium.

[d] Effluent of an industrial water treatment plant, sample spiked with ammonium.

Bibliography

[1] R. RUZICKA and E. H. HANSEN, *Flow Injection Analysis*, Wiley & Sons, New York, 1981

[2] J. MÖLLER. *Flow Injection Analysis*, Analytiker Taschenbuch, Bd. 7, Springer Verlag, 1988, pp. 199-275, and B. KARLBERG, G.E. PACEY, *Flow Injection Analysis — A Practical Guide*, Elsevier, Amsterdam, 1989

[3] L. T. SKEGGS. *Anal. Chem*. **38** (6), 1966, p. 31 A

[4] W. E. VAN DER LINDEN. *Anal. Chim. Acta,* **151**, 1983, p. 359

[5] M. VAN SON and R.C. SCHOTHORTS. G. VAN DEN BOEF, *Anal.Chim.Acta*, **153**, 1983, p. 271

[6] W. WILLASON and K. S. JOHNSON. *Marine Biology*, **91**, 1986, p. 285

[7] G. SCHULZE, C. Y. LIU, M. BRODOWSKI, O. ELSHOLZ, W. FRENZEL and J. MÖLLER, *Anal. Chim. Acta*, **214**, 1988, p. 121

[8] R. NAKATA, T. KAWAMURA, H. SAKASHITA and A. NITTA, *Anal*. *Chim. Acta*, **208**, 1988, p. 81

[9] J. REARDON, J. A. FORMAN and R. L. SEARY. *Clin. Chim. Acta*, **14**, 1966, p. 403

[10] EPA-600/4-79-020, Method 350.1, *Nitrogen Ammonia*, March 1984

[11] EPA-600/4-79-020, Method 350.2, *Nitrogen, Kjeldahl, Total*, March 1984

[12] M. STADLER, B. NEIDHARDT, J. RÜTER, G. PAPKE and B. WINTER. *Laborpraxis*, **5**, 1993, p. 48

[13] ISO 7150-2, *Water quality — Determination of ammonium — Automated spectrometric method*

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