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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

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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, $c(\text{NaOH}) = 5$ mol/l.

3.3.3 Sodium hydroxide solution II, $c(\text{NaOH}) = 0{,}01$ 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 ± 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, $c(\text{HCl}) = 0{,}01$ mol/l.

3.3.12 Hydrochloric acid solution II, $c(\text{HCl}) = 0{,}1$ mol/l.

3.3.13 Hydrochloric acid solution III, $c(\text{HCl}) = 1{,}0$ 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.