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

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

Reference number
ISO 11732:1997(E)

Foreword

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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.

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

Annexes A to D of this International Standard are for information only.

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Introduction

Methods using flow analysis are automatized 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).

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

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

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

1.1 Scope

1.1.1 Field of application

This International Standard specifies a method 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 to 10 mg/l (in the undiluted sample). In particular cases, the range of application may be adapted by varying the operating conditions.

1.1.2 Interferences

Volatile amines will 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, erroneously high results may be expected [12]. In significant cases, prior to analysis an (online) distillation of the sample, adjusted to a pH of 5,8 may be necessary.

Interferences may occur in exceptional cases when the sample does not reach a pH at least 12 after the addition of the alkaline reagent, since then ammonium will not be converted quantitatively into ammonia. In particular, this may occur with strongly acidic or buffered samples. In such cases the pH of the sample should be adjusted to 3 to 5 by the addition of sodium hydroxide solution (1.4.1 or 1.4.2).

High concentrations of metal ions which may precipitate as hydroxides will give poorly reproducible results. The addition of a suitable complexing agent, such as (ethylenedinitrilo)tetraacetic acid, disodium salt, to the alkaline reaction solution (1.4.17) in a sufficiently large concentration will prevent interference by Cu, Zn, Fe, Ca, Mg and Al; up to individual metal concentrations of 0,2 mg/l, a concentration of 30 g/l of ethylenedinitrilotetraacetic acid, disodium salt, in solution R_1 (see 1.4.17) is adequate.

For samples containing particulate matter, see 1.6 (last paragraph).

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

1.2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

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

ISO 5667-1:1980, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes.*

ISO 5667-2:1991, *Water quality — Sampling — Part 2: Guidance on sampling techniques.*

ISO 5667-3:1994, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of samples.*

1.3 Principle

The test sample containing ammonium is injected into a continuous carrier stream by means of an injection valve, and is mixed with a continuous 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 colour; the colour change is monitored continuously in a flow spectrophotometer. Additional information concerning this analytical technique is given in [4], [5], [6], [7] and [8].

1.4 Reagents

Apart from the reagents listed in 1.4.4 to 1.4.6, use only reagents of analytical grade quality for the determination of nitrogen or, if not available, those of recognized analytical grade quality and water of grade 1 (in accordance with ISO 3696), freshly prepared. The ammonium content of the blank shall be checked regularly (see 1.7.3).

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

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

1.4.3 Ethylenedinitrilotetraacetic acid (EDTA), disodium salt, monohydrate, $Na_2C_{10}H_{14}N_2O_8 \cdot H_2O$.

1.4.4 Bromcresol purple, $C_{21}H_{16}Br_2O_5S$.

1.4.5 Bromthymol blue, $C_{27}H_{28}Br_2O_5S$.

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

1.4.7 Ammonium chloride, NH_4Cl, dried at 105 °C to constant weight.

1.4.8 Potassium chloride, KCl.

1.4.9 Boric acid, H_3BO_3.

1.4.10 Ethanol, C_2H_5OH, 95 % mass fraction.

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

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

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

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

1.4.15 Mixed indicator.

In a mortar prepare a dry mixture consisting of 10 g of Bromcresol purple (1.4.4), 5 g of Bromthymol blue (1.4.5), 2,5 g of Cresol red (1.4.6) and 45 g of potassium chloride (1.4.8).

The given quantities can be reduced (e.g. by one-tenth), maintaining the ratio.

1.4.16 Carrier solution, C (see figure 1).

Use grade 1 water (ISO 3696), degassed by reduced pressure.

1.4.17 Alkaline reaction solution, R_1 (see figure 1).

Dissolve in a graduated flask, nominal capacity 1 000 ml, 30 g of EDTA disodium salt (1.4.3) in approximately 800 ml of water, and add 12,4 g of boric acid (1.4.9).

Add dropwise to the suspension 100 ml of sodium hydroxide solution I (1.4.1), and make up to volume with water.

Degas the solution by filtering it through a membrane filter assembly (see 1.5.2).

The pH of the solution will be approximately 13. When stored in a polyethylene bottle at room temperature, it will be stable for 1 month.

1.4.18 Indicator solution

In a graduated flask, nominal capacity 200 ml, dissolve 1 g of the mixed indicator (1.4.15) in a mixture of 10 ml of sodium hydroxide solution II (1.4.2) and 10 ml of ethanol (1.4.10).

Add approximately 150 ml of water.

The solution should have a bright orange-red colour. If it has a blue colour, add hydrochloric acid III dropwise (1.4.13) until the colour changes.

Make up to volume with water.

Filter off any undissolved particles.

This solution can be stored without deterioration at room temperature for 3 months in a brown glass bottle.

1.4.19 Ammonia recipient solution, R_2 (see figure 1)

Dilute 10 ml of the indicator solution (1.4.18) with approximately 480 ml of water.

Add dropwise sodium hydroxide solution II (1.4.2) until an absorbance value of 0,45 to 0,6 (pathlength 10 mm, wavelength 590 nm) is obtained. Make up to a volume of 500 ml with water.

Degas and purify the solution using the membrane filter assembly (see 1.5.2), pour it into the reagent reservoir and let it stand for at least 2 h.

Immediately before starting the measurement (1.7), check the absorbance again and adjust, if need be, to the absorbance range specified above by adding sodium hydroxide solution II (1.4.2) or hydrochloric acid I, II or III (1.4.11 to 1.4.13).

This solution can be stored without deterioration at room temperature for 2 weeks in a glass bottle.

1.4.20 Ammonium stock solution, $\rho_B(N) = 1\ 000$ mg/l.

In a graduated flask, nominal capacity 1 000 ml, dissolve, 3,819 g of ammonium chloride (1.4.7) in approximately 900 ml water, acidify with sulfuric acid (1.4.14) to pH 2, and make up to volume with water.

This solution can be stored without deterioration in a refrigerator for at least 3 months.

1.4.21 Ammonium standard solution I, $\rho_B(N) = 100$ mg/l.

Pipette 10 ml of the ammonium stock solution (1.4.20) into a graduated flask, nominal capacity 100 ml, add approximately 80 ml water, acidify with sulfuric acid (1.4.14) to pH 2, and make up to volume with water.

This solution can be stored without deterioration in a refrigerator for at least 1 week.

1.4.22 Ammonium standard solution II, $\rho(N) = 10$ mg/l.

Pipette 1 ml of the ammonium stock solution (1.4.20) or 10 ml of the ammonium standard solution I (1.4.21) into a graduated flask, nominal capacity 100 ml, add approximately 80 ml water, acidify with sulfuric acid (1.4.14) to pH 2, and make up to volume with water.

This solution can be stored without deterioration in a refrigerator for at least 1 week.

1.4.23 Calibration solutions

Prepare the calibration solutions by diluting the ammonium standard solution I or II (1.4.21 or 1.4.22). At least five calibration standards per working range are recommended. Proceed for the working range I or II respectively, as follows:

a) Working range I [for mass concentrations $\rho_B(N)$ = 1 mg/l to 10 mg/l]:

Pipette into a series of graduated flasks, nominal capacity 100 ml each, 1 ml, 3 ml, 5 ml, 7 ml and 9 ml respectively of ammonium standard solution I (1.4.21), and make up to volume with water.

The mass concentrations of ammonium, expressed as nitrogen, in these calibration solutions are respectively 1 mg/l, 3 mg/l, 5 mg/l, 7 mg/l and 9 mg/l.

b) Working range II [for mass concentrations $\rho_B(N)$ = 0,1 mg/l to 1,0 mg/l]:

Pipette into a series of graduated flasks, nominal capacity 100 ml each, 1 ml, 3 ml, 5 ml, 7 ml and 9 ml respectively of the ammonium standard solution II (1.4.22), and make up to volume with water.

The mass concentrations of ammonium, expressed as nitrogen, in these calibration solutions are respectively 0,1 mg/l, 0,3 mg/l, 0,5 mg/l, 0,7 mg/l and 0,9 mg/l.

All calibration solutions shall freshly be prepared before use.

1.5 Apparatus

1.5.1 Flow injection system

In general, the flow injection system consists of the following components (see figure 1):

— reagent reservoirs;

— low pulsation pump;

— suitable pump tubes, if required;

— injection valve with a suitable injection volume;

— diffusion cell with hydrophobic semipermeable membrane [e.g. made from polytetrafluoroethylene (PTFE)].

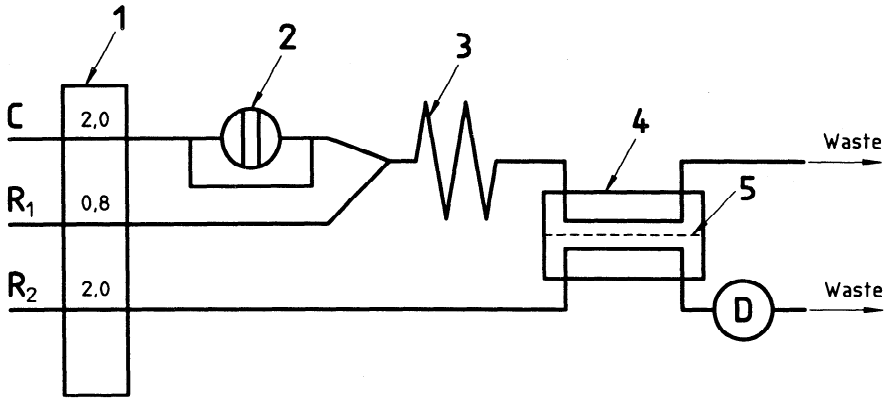
NOTE — Example of a typical membrane:
— thickness: 150 µm to 200 µm;
— pore size: 0,5 µm to 2,0 µm;
— porosity: 75 %.

— transport tubes and reaction coils, internal diameter 0,5 mm to 0,8 mm, tube connections and T-connections of inert plastic and with minimum dead volumes;

— spectrophotometric detector with flow cell, normal path length 10 mm to 50 mm, wavelength range 580 nm to 600 nm;

— recording unit (e.g. strip chart recorder, integrator or printer/plotter). In general peak height signals are evaluated;

— autosampler, if required.



Typical injection time: 20 s to 25 s
Typical residence time: approx. 45 s

Key

C Carrier solution
R_1 Alkaline reagent solution
R_2 Ammonia recipient solution
D Detector for 580 nm to 600 nm
1 Pump (ml/min)
2 Sample injection valve
400 µl [working range I: $\rho_B(N)$ = 1 mg/l to 10 mg/l]
40 µl [working range II: $\rho_B(N)$ = 0,1 mg/l to 1,0 mg/l]
3 Reaction coil
length: 30 cm/∅ int. 0,5 mm to 0,8 mm
4 Gas diffusion cell
5 PTFE membrane

Figure 1 — Example of a flow injection system for ammonium nitrogen concentrations for 0,1 mg/l to 10 mg/l

1.5.2 Additional apparatus

— graduated flasks, nominal capacity 100 ml, 200 ml and 1 000 ml;

— graduated pipettes, nominal capacity 1 ml to 10 ml;

— membrane filter assembly with membrane filters, pore size 0,45 µm.

1.6 Sampling

Containers of glass, polyalkylenes and polytetrafluoroethylene (PTFE) are suitable for sample collection. All containers coming in contact with the sample shall be cleaned thoroughly with hydrochloric acid I, II or III (1.4.11 to 1.4.13) and shall be rinsed several times with water.

Analyze the samples immediately after collection. Alternatively, add sulfuric acid (1.4.14) to adjust to a pH of approximately 2, store at 2 °C to 5 °C in the dark, and analyze within the next 24 h.

In exceptional cases, the sample may be stored up to 2 weeks provided it has been membrane-filtered after acidification. The applicability of this preservation procedure shall be checked for each individual case.

If there is a risk of clogging the injection system transport tubes, the samples shall be filtered before analysis.

1.7 Procedure

1.7.1 Preparation of the measurement

Prior to measurement, continuously run the reagent solutions C, R_1 and R_2 for approximately 10 min through the flow injection system, record and zero the baseline.

The system is ready when the baseline no longer shows any drift. A satisfactory signal-to-noise ratio should be obtained. Check the reagent blank and the operation of the membrane in accordance with 1.7.3. Calibrate the system as described in 1.7.4.

1.7.2 Quality requirements for the measuring system

In the measuring system being calibrated for working range I, a calibration solution (1.4.23) with mass concentration 0,5 mg/l shall give an absorbance of at least 0,040 per 10 mm pathlength.

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

1.7.3 Checking reagent blank

Wait for the baseline to stabilize.

Instead of the alkaline reagent solution R_1, 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 per 10 mm pathlength, 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.

Run the reagent solutions again.

1.7.4 Calibration

Select working range I or II and prepare the calibration solutions for the selected working range (1.4.23). Perform a separate calibration for each working range.

For working range I, use an injection volume of 40 µl, for working range II a volume of 400 µl.

Prior to the calibration, zero the system, in accordance with the manufacturer's instructions, if necessary.

Calibrate by alternately injecting calibration solutions and blank solution.

Determine the measurement values resulting from the respective calibration solutions. Follow the manufacturer's instructions as long as they do not contradict the specifications of this International Standard.

The test conditions for the calibration and the measurement of samples (1.7.5) are the same. The magnitude of the measured signal is proportional to the mass concentration of ammonium, expressed as nitrogen.

Establish the regression line obtained for the calibration series, using the following general equation (1):

$$y = b\rho + a \qquad \ldots (1)$$

where

- y is the measured value, in terms of instrument-related units;
- b is the slope of the calibration function, in instrument-related units × litres per milligram;
- ρ is the mass concentration of ammonium (expressed as nitrogen) in the calibration solutions, in milligrams per litre;
- a is the ordinate intercept of the calibration function, in instrument-related units.

Annex B shows examples of calibration lines.

Proceed as described in 1.7.5.

1.7.5 Sample measurement

Analyze the samples in the same manner as the calibration solutions using the flow injection system (1.5.1).

Dilute the sample or use the other working range if the mass concentrations exceed the validity 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 parts of the respective working range. Make a new calibration, if necessary.

1.8 Evaluation

Determine the mass concentration of the determinand in the measuring solution using the measured value obtained as described in 1.7.5, from the calibration function [equation (1), 1.7.4].

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

$$\rho_B = \frac{y - a}{b} \quad \ldots (2)$$

where

ρ_B is the mass concentration of ammonium, expressed as nitrogen, in the sample, in milligrams per litre.

For explanation of the other symbols, see equation (1).

All dilution steps shall be taken into account in the calculation.

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

2.1 Scope

2.1.1 Field of application

See 1.1.1.

2.1.2 Interferences

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

Interferences may occur if the reaction mixture, after addition of all reagent solutions, does not reach a pH of at least 12,6. This mainly happens with strongly acidic and buffered samples, which should be 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 an interfering organic matrix (compound with high molecular mass) the sample may be dialyzed, e.g. by an on-line procedure. Alternatively, the sample may be filtered through activated carbon, provided a change in ammonium concentration in the sample can be ruled out when this approach is chosen.

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

2.2 Normative references

See 1.2.

2.3 Principle

In a continuously flowing gas-segmented carrier stream, ammonium present in the sample reacts in alkaline solution with hypochlorite $\left(ClO^{-1}\right)$, which has previously been liberated from dichloroisocyanurate.