INTERNATIONAL STANDARD

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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)].

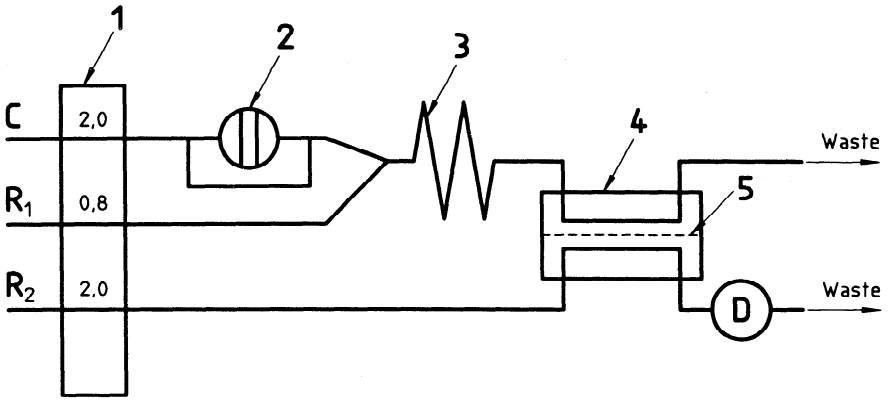
NOTE — Example of a typical membrane:
— thickness: 150 µm to 200 µm;
— pore size: 0,5 µm to 2,0 µm;
— porosity: 75 %.

— 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.

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

Additional information concerning this analytical technique is given in [9], [10], [11] and ISO 7150-2.

2.4 Reagents

In addition to the reagents listed in 1.4, with the exception of those described in 2.4.2 and 2.4.5, the following reagents of analytical quality grade and those of analytical quality grade for the determination of nitrogen shall be used:

2.4.1 Trisodium citrate dihydrate, $Na_3C_6H_5O_7 \cdot 2H_2O$.

2.4.2 Polyethylene glycol dodecyl ether, $F = 33$ °C to 41 °C; solution, mass fraction 30 %.

The solution is stable for approximately 4 weeks.

2.4.3 Sodium salicylate, $NaC_7H_5O_3$.

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

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

2.4.6 Citrate buffer solution, reagent solution R_3 (see figures 2 and 3).

Dissolve in a graduated flask, nominal capacity 1 000 ml, 40 g of trisodium citrate dihydrate (2.4.1) and 1 ml of polyethylene glycol dodecyl ether (2.4.2) in water and make up to volume with water.

The solution can be stored without deterioration, cooled in a brown-glass bottle, for 1 week.

2.4.7 Diluent.

For the application with dialyzer, a buffer solution, such as citrate buffer solution (2.4.6), is required. For online dilution, a buffer solution or water may be used.

2.4.8 Sodium salicylate solution, reagent solution R_4 (see figures 2 and 3).

Dissolve in a graduated flask, nominal capacity 1 000 ml, 34 g of sodium salicylate (2.4.3), 0,4 g of sodium nitroprusside dihydrate (2.4.4) and 1 ml of polyethylene glycol dodecyl ether (2.4.2) in water and make up to volume with water.

The solution can be stored without deterioration, cooled in a brown-glass bottle, for 1 week.

2.4.9 Sodium dichloroisocyanurate solution, reagent solution R_5 (see figures 2 and 3).

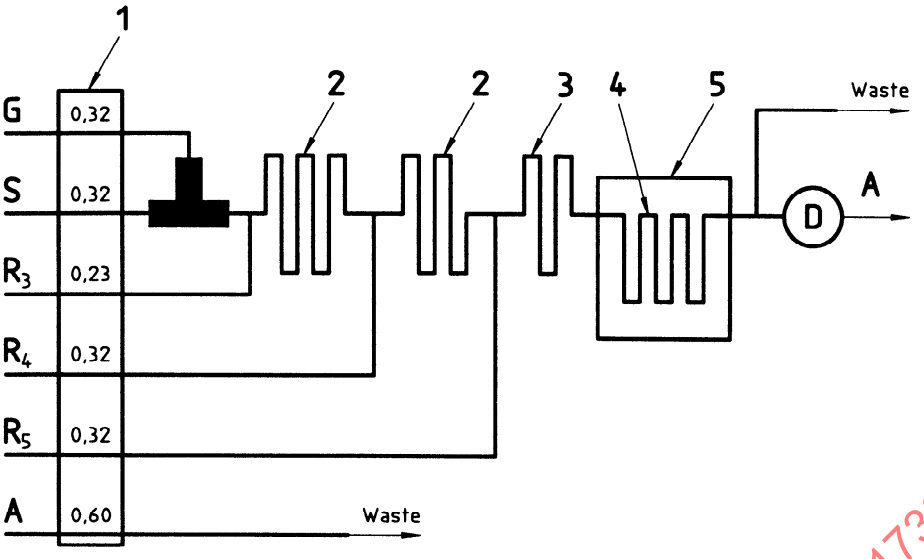
Dissolve in a graduated flask, nominal capacity 1 000 ml, 0,8 g of sodium dichloroisocyanurate (2.4.5) and 50 ml of sodium hydroxide solution I (1.4.1) in water and make up to volume with water.

Prepare the solution fresh before use.

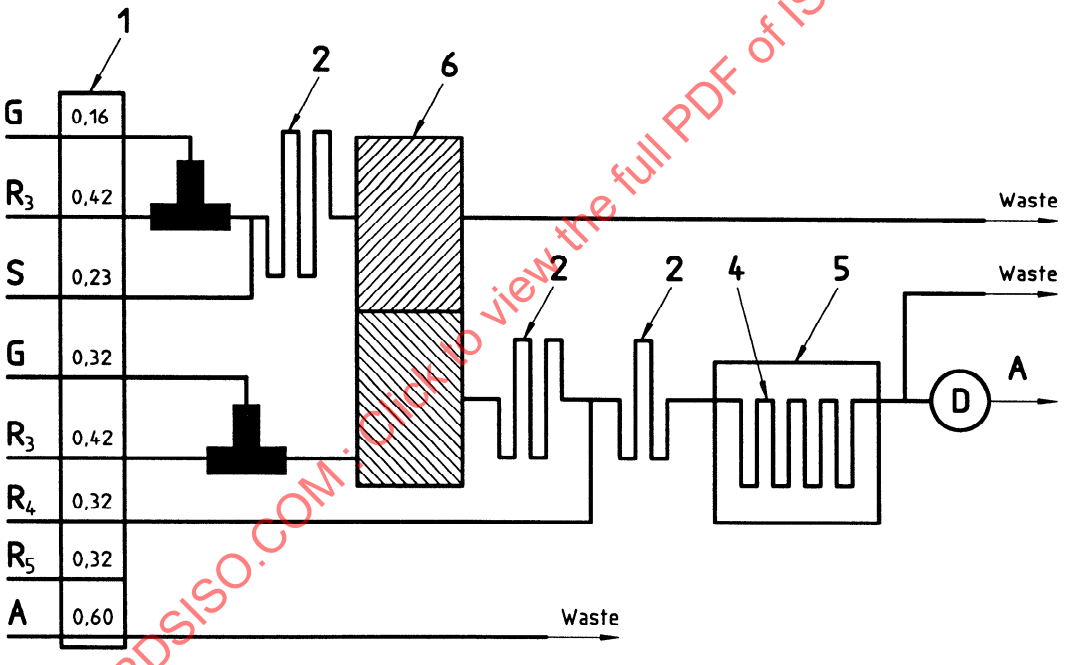
2.5 Apparatus

2.5.1 Continuous flow system

In general the system comprises the following components (see figures 2 and 3):



a) Working range II: ρ_B (N) = 0,1 mg/l to 1 mg/l



b) Working range I: ρ_B (N) = 1 mg/l to 10 mg/l

Residence time in thermostat ≥ 3 min
Total residence time: 6 min

Key

A Reaction mixture, nonsegmented, leaving the detector and returning to the pump
D Detector: 640 nm to 660 nm
G Segmentation gas (e.g. nitrogen)
R_3 Citrate buffer (2.4.6)
R_4 Sodium salicylate (2.4.8)
R_5 Sodium dichloroisocyanurate (2.4.9)
S Sample (pH = 2)

1 Pumps (ml/min)
2 Reaction coils
length: 25 cm/Ø int. 2,2 mm
3 Reaction coil
length: 50 cm/Ø int. 2,2 mm
4 Reaction coils
length: 100 cm/Ø int. 2,2 mm
5 Thermostats: 37 °C to 50 °C
6 Dialysis cell

Figure 2 — Examples of a continuous flow system (macroflow) for ammonium nitrogen concentrations 0,1 mg/l to 10 mg/l

— sampler or other appropriate devices which allow reproducible sample introduction;

— reservoirs for carrier liquids and reagents;

— low-pulsating pump and suitable chemically inert pump tubes;

— 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;

— dialysis cell, with e.g. cellophane membrane, if applicable. The membrane material depends on the sample matrix, e.g. cellophane may be applied.

NOTE — Example of separation size: maximum molecular mass for dialyzing molecules: 5 000 to 14 000.

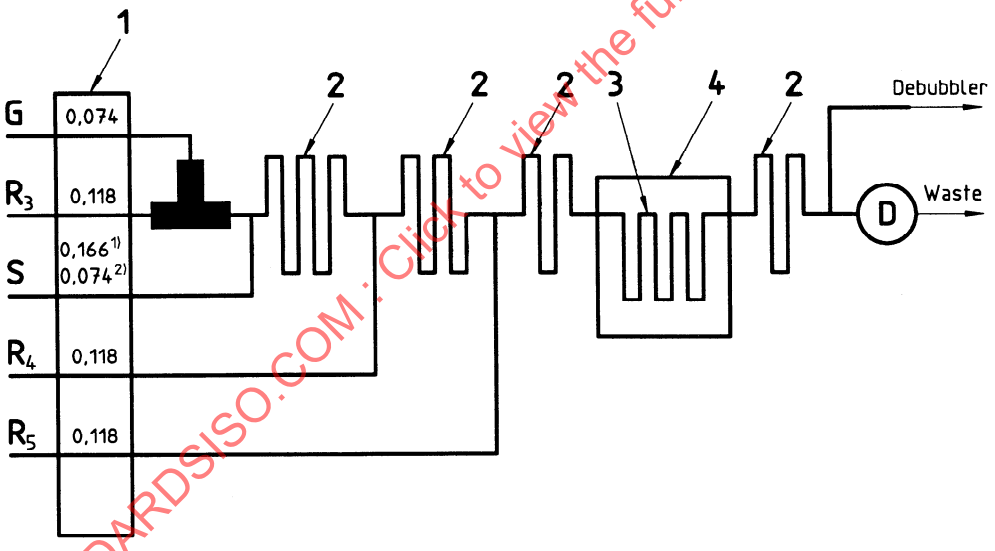
— continuous flow thermostat, controllable to about ± 1 °C, suitable for maintaining constant temperatures between 37 °C and 50 °C;

— spectrometric detector with continuous flow cell (pathlength maximum 5 cm), wavelength range 640 nm to 660 nm;

— recording unit, such as a strip chart recorder or a printer/plotter. In general peak height signals are evaluated.

NOTE — Figure 2 describes flow systems with internal diameters of 2,2 mm; a device with online dialysis is also shown for working range II [ρ_B(N) = 0,1 mg/l to 1 mg/l].

Figure 3 shows a corresponding system with internal diameters of 1 mm.



1) Working range II : ρ_B (N) = 0,1 mg/l to 1 mg/l; gain: 4
2) Working range I : ρ_B (N) = 1 mg/l to 10 mg/l; gain: 0,6

Key

D	Detector: 640 nm – 660 nm	1	Pump (ml/min)
G	Segmentation gas (e.g. N_2)	2	Reaction coils length: 40 cm/Ø int. 1 mm
S	Sample (pH = 2)	3	Reaction coils length: 500 cm/Ø int.1 mm
R_3	Citrate buffer (2.4.6)	4	Thermostat: 37 °C
R_4	Sodium salicylate (2.4.8)		
R_5	Sodium dichloroisocyanurate		

Figure 3 — Examples of a continuous flow system (microflow) for ammonium nitrogen concentrations 0,1 mg/l to 10 mg/l

2.5.2 Additional apparatus

See 1.5.2.

2.6 Sampling and sample preparation

See 1.6.

2.7 Procedure

2.7.1 Preparation of the measurement

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

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

2.7.2 Quality requirements for the measuring system

In the measuring system set up for working range I, a calibration solution (1.4.23) with mass concentration 0,5 mg/l shall give an absorbance of at least 0,1 per 10 mm pathlength (see the note in 1.7.2).

2.7.3 Checking reagent blank

Wait for the baseline to stabilize.

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

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

Run the reagent solutions again.

2.7.4 Calibration

Select working range I or II and prepare the calibration solutions for the selected working range (1.4.23). A minimum number of five calibration standards per working range is required. Perform a separate calibration for each working range.

Prior to calibrating, zero the system, following the manufacturer's instruction.

Calibrate by alternately introducing calibration solutions and blank solution.

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. a sampler).

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

Choose a washing time long enough so that the measured values of the calibration solutions do not show any cross-contamination.

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 paper.

The test conditions for the calibration and the measurement of samples (2.7.5) are the same. The magnitude of the measured signal is proportional to the mass concentration of ammonium, expressed as nitrogen.

Establish the regression line for the calibration series obtained according to equation (1). Annex C shows examples of calibration lines.

2.7.5 Sample measurement

Analyze the samples, in the same manner as the calibration solutions with the continuous flow system (2.5.1).

If the mass concentration to be determined exceeds the validity of the selected working range the sample must be diluted or analyzed using the other 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 or upper part of the respective working range. Make a new calibration, if necessary.

2.8 Evaluation

See 1.8.

3 Expression of results

Report results, in milligrams ammonium, expressed as nitrogen, per litre of test sample, to two significant figures at most.

EXAMPLE

$2{,}0 \times 10^{-1}$ mg/l;

9,2 mg/l;

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

4 Test report

The analysis report shall contain the following information:

a) reference to this International Standard;

b) identity of the water sample;

c) specification of the procedure applied, according to clause 1 or 2;

d) description of the sample pretreatment;

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

f) results obtained, expressed according to clause 3;

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

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

5 Statistical characteristics of the method

Statistical results of an interlaboratory trial are summarized in annex A. The values derived from this interlaboratory trial may not be applicable to concentration ranges and matrices other than those given.

Annex A
(informative)

Results of interlaboratory trial

The statistical characteristics of the method, given in tables A.1 and A.2, were established in an interlaboratory trial carried out in November 1990,

where

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, in percent;

$\bar{x}$ is the total mean value, in milligrams per litre;

s_R is the standard deviation of the reproducibility, in milligrams per litre;

CV_R is the coefficient of variation of the reproducibility, in percent;

s_r is the standard deviation of the repeatability, in milligrams per litre;

CV_r is the coefficient of variation of the repeatability, in percent;

Origin of the samples:

1) Drinking water, spiked with ammonium.

2) River water (Rhine), spiked with ammonium.

3) Effluent of a domestic water treatment plant;
Sample 7: waste water, diluted 1:10, not spiked;
Sample 8: waste water, diluted 1:4, spiked with ammonium.

4) Effluent of an industrial water treatment plant, sample spiked with ammonium.

Table A.1 — Statistical characteristics of the determination of ammonium(N) using flow injection analysis (FIA) and spectrometric detection

Sample No.	Matrix	L	N	O %	$\bar{x}$ mg/l	s_R mg/l	CV_R %	s_r mg/l	CV_r %
1	Drinking water[1)]	15	56	6,67	0,2841	0,0279	9,81	0,0114	4,01
2		15	54	10,0	0,9019	0,0382	4,24	0,0176	1,95
3	Surface water[2)]	15	55	8,33	0,5318	0,0261	4,91	0,0165	3,10
4		15	60	0,00	0,9160	0,0737	8,05	0,0204	2,22
5		15	54	10,0	2,4600	0,0958	3,90	0,0526	2,14
6		14	52	7,14	8,0333	0,2875	3,58	0,1288	1,60
7	Domestic water[3)]	15	56	6,67	2,9309	0,1969	6,72	0,0587	2,00
8		15	60	0,00	8,2738	0,3278	3,96	0,1234	1,49
9	Industrial waste water[4)]	15	48	20,0	2,4502	0,0752	3,07	0,0443	1,81
10		15	56	5,08	7,9811	0,2819	3,53	0,1946	2,44

Table A.2 — Statistical characteristics of the determination of ammonium(N) using continuous flow analysis (CFA) and spectrometric detection

Sample No.	Matrix	L	N	O %	$\bar{x}$ mg/l	s_R mg/l	CV_R %	s_r mg/l	CV_r %
1	Drinking water[1)]	11	36	18,2	0,3024	0,0229	7,56	0,0106	3,51
2		11	44	0,00	0,9230	0,0771	8,35	0,0157	1,70
3	Surface water[2)]	11	44	0,00	0,5563	0,0393	7,07	0,0153	2,75
4		11	36	18,2	0,9636	0,0354	3,67	0,0129	1,34
5		11	44	0,00	2,5791	0,2581	10,0	0,0815	3,16
6		11	35	20,4	8,2097	0,1451	1,77	0,0676	0,82
7	Domestic water[3)]	11	32	27,3	2,9847	0,0384	1,28	0,0329	1,10
8		11	44	0,00	8,4661	0,2217	2,62	0,0752	0,89
9	Industrial waste water[4)]	11	44	0,00	2,7118	0,1264	4,66	0,0436	1,61
10		11	40	9,09	8,3165	0,2040	2,45	0,0593	0,71

Annex B
(informative)

Ammonium calibration lines for FIA

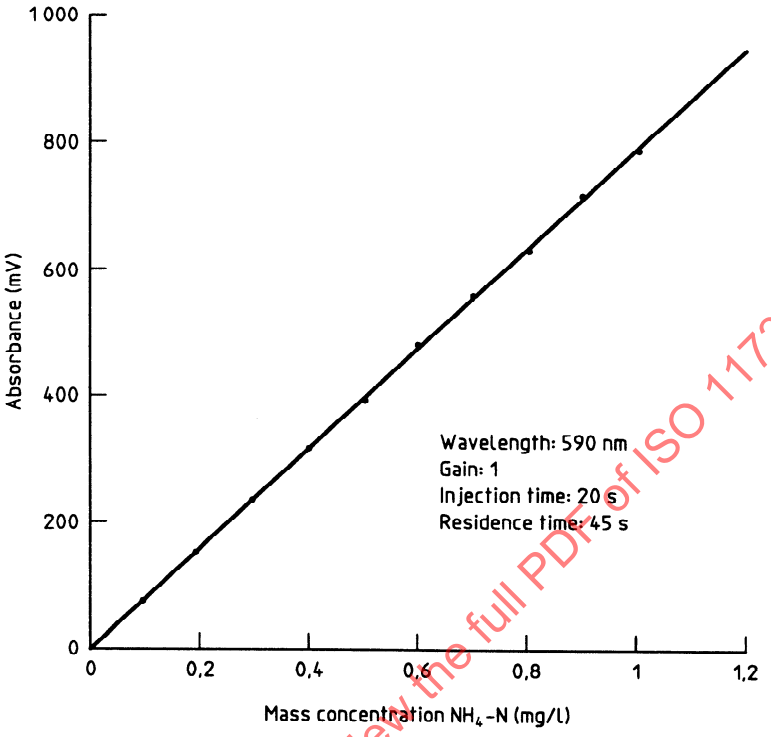


Figure B.1 — Ammonium calibration line — Flow Injection Analysis (FIA)
Working range NH_4 – N (0,1 – 1,0 mg/l)

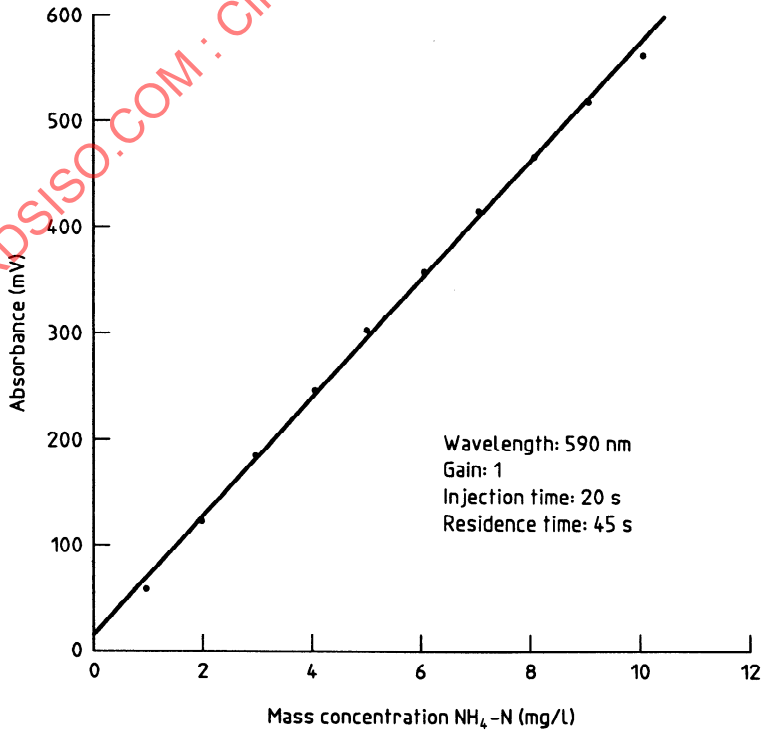


Figure B.2 — Ammonium calibration line — Flow Injection Analysis (FIA)
Working range NH_4 – N (1 – 10 mg/l)