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Water quality — Determination of total nitrogen after UV digestion — Method using flow analysis (CFA and FIA) and spectrometric detection

Qualité de l'eau — Dosage de l'azote total après digestion UV — 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 29441 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

Introduction

Methods using flow analysis enable wet chemistry procedures to be automated and are particularly suitable for the processing of many analytes in water in large series of samples at a high analysis frequency (up to 100 samples per hour).

A differentiation is made between flow injection analysis (FIA, References [1][2]) and continuous flow analysis (CFA, Reference [3]). Both methods share the feature of an automatic dosage of the sample into a flow system (manifold) where the analytes in the sample react with the reagent solutions on their way through the manifold. The sample preparation can be integrated into the manifold. The reaction product is measured in a flow detector (e.g. a flow photometer).

Water quality — Determination of total nitrogen after UV digestion — Method using flow analysis (CFA and FIA) and spectrometric detection

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This 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.

Waste containing cadmium in liquid or solid form shall be disposed of appropriately.

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

1 Scope

This International Standard specifies a method for the determination of total nitrogen after inline UV digestion, in various types of waters, such as ground, drinking, surface, and waste waters, in mass concentrations ranging from 2 mg/l to 20 mg/l for total nitrogen, all in the undiluted sample.

Other mass concentration ranges are possible, provided the upper limit of the concentration range is exactly 10 times the lower limit (e.g. 0,2 mg/l to 2,0 mg/l). The range of application can be changed by varying the operating conditions.

NOTE Sea water can be analysed with changes in respect to sensitivity and adaptation of the carrier solution and calibration solutions to the salinity of the samples.

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 5667-3, *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*

ISO 8466-2, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 2: Calibration strategy for non-linear second-order calibration functions*

ISO 13395, *Water quality — Determination of nitrite nitrogen and nitrate nitrogen and the sum of both by flow analysis (CFA and FIA) and spectrometric detection*

3 Interferences

Samples with extreme pH values and samples with a high buffering capacity are prone to interferences. It is advisable to analyse several dilutions of the sample and to check the results for consistency.

High concentrations of organic substances can cause problems as the oxidation capacity may not be sufficient. For samples containing more than 100 mg/l of total organic carbon (TOC), reduced yields in the determination of nitrogen may arise. If the presence of more than 100 mg/l of TOC is suspected, the sample should be run with several dilutions in order to check for consistency, or standard addition techniques should be applied.

If the sample comprises larger particles (diameter, $d > 50$ µm), a homogenisation device (6.3.3) is necessary.

In sea water samples, high concentrations of calcium and magnesium may occur. In an alkaline medium, magnesium hydroxide or other hydroxides or calcium carbonate may be formed which interfere with the UV digestion.

4 Principle

The sample is pretreated with a buffered peroxodisulfate solution and thermal UV radiation. Nitrate is formed and determined either by flow injection analysis (FIA) or by continuous flow analysis (CFA). With FIA, the sample is fed into a continuously flowing buffer solution (carrier stream) by means of an injection valve, or, when applying CFA, it is continuously mixed with this buffer solution. Nitrate in the sample is reduced with metallic cadmium to nitrite (Reference [4]). Subsequently a phosphoric acid reagent solution also flowing continuously is admixed. Nitrite resulting from the reduction of nitrate diazotises sulfanilamide in acidic solution to the diazonium salt which is then coupled with *N*-(1-naphthyl)ethylenediamine to form a red soluble dye (see ISO 13395 and Reference [5]).

5 Reagents

During the analysis, unless otherwise stated, use only reagents of recognised analytical grade. Check the blank value of the reagents regularly (see 8.4).

5.1 General reagents

5.1.1 Water, complying with ISO 3696:1987, grade 1.

5.1.2 Phosphoric acid, $\rho(H_3PO_4)$ = 1,71 g/ml.

5.1.3 Potassium peroxodisulfate, $K_2S_2O_8$.

5.1.4 Sodium hydroxide, NaOH.

5.1.5 Titanium tetrachloride, $TiCl_4$, liquid, commercially available.

5.1.6 Sulfanilamide, 4-aminobenzenesulfonamide, $C_6H_8N_2O_2S$.

5.1.7 *N*-(1-Naphthyl)ethylenediamine dihydrochloride,
[*N*-(1–naphthyl)-1,2-diaminoethane dihydrochloride, $C_{12}H_{14}N_2 \cdot 2HCl$].

5.1.8 Sodium nitrite, $NaNO_2$, dried to constant mass at 150 °C.

5.1.9 Potassium nitrate, KNO_3, dried to constant mass at 150 °C.

5.1.10 Imidazole, $C_3H_4N_2$.

5.1.11 Hydrochloric acids.

5.1.11.1 Hydrochloric acid I, concentrated, w(HCl)= 37 %.

5.1.11.2 Hydrochloric acid II, c(HCl) = 4 mol/l.

5.1.11.3 Hydrochloric acid III, c(HCl) ≈ 0,1 mol/l.

5.1.12 Dichloromethane, CH_2Cl_2.

5.1.13 Copper(II) sulfate solution I, $\rho(CuSO_4 \cdot 5H_2O)$ = 2,5 g/l.

5.1.14 Copper(II) sulfate solution II, $\rho(CuSO_4 \cdot 5H_2O)$ = 20 g/l.

5.1.15 Boric acid, H_3BO_3.

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

5.1.17 Sulfuric acid II, $c(H_2SO_4)$ = 1 mol/l.

5.1.18 Urea, $CO(NH_2)_2$.

5.1.19 Cadmium (Cd) granulate, grain size e.g. 0,3 mm to 1,5 mm (for FIA preferably 0,3 mm to 0,8 mm). A minimum reduction capacity of 90 % shall be reached (see 6.1.4 and 6.2.4).

5.1.20 Imidazole stock solution, $c(C_3H_4N_2)$ = 1 mol/l (Figure A.1, R1).

Dissolve 68,1 g of imidazole (5.1.10) in approximately 800 ml of water (5.1.1) in a 1 l beaker.

While stirring with a magnetic stirrer, add hydrochloric acid I (5.1.11.1) and adjust the pH to 7,5 using a pH electrode (6.3.2).

Transfer to a 1 000 ml one-mark volumetric flask. Make up to the mark with water (5.1.1).

The solution is stable for 4 weeks if kept in a brown glass bottle at room temperature.

5.1.21 Urea stock solution, ρ(N) = 1 000 mg/l.

In a 500 ml one-mark volumetric flask, dissolve 1,071 7 g of urea (5.1.18) in water (5.1.1). Add 0,5 ml of dichloromethane (5.1.12) for preservation. Make up to the mark with water.

The solution is stable for 1 year if kept at (4 ± 2) °C.

5.1.22 Urea working solution, ρ(N) = 20 mg/l.

Dilute 5 ml of urea stock solution (5.1.21) in a 250 ml one-mark volumetric flask with water (5.1.1). Acidify the solution with sulfuric acid II (5.1.17) to pH ⩽ 2.

The solution is stable for 1 month if kept at (4 ± 2) °C.

5.1.23 Buffered copper(II) sulfate solution.

Mix 20 ml of the copper(II) sulfate solution II (5.1.14) and 20 ml of the imidazole stock solution (5.1.20) in a 50 ml beaker.

Prepare the solution freshly before use.

5.1.24 Reagent solution, (Figure A.1, R2 and Figure A.2, R1; see also ISO 13395).

In a 500 ml one-mark volumetric flask, dissolve 5 g of sulfanilamide (5.1.6) and 0,5 g of *N*-(1-naphthyl)ethylenediamine dihydrochloride (5.1.7) in water (5.1.1), add 75 ml of phosphoric acid (5.1.2). Make up to the mark with water (5.1.1).

Stored in a brown glass bottle, the solution is stable for 1 month.

NOTE The solutions of sulfanilamide (5.1.6) and *N*-(1-naphthyl)ethylenediamine dihydrochloride (5.1.7) can also be prepared separately and dosed into the manifold by different lines.

Prior to use, degas solution R2 for FIA, e.g. by membrane filtration (vacuum).

5.1.25 Nitrite(N) stock solution, ρ(N) = 100 mg/l.

In a 1 000 ml one-mark volumetric flask, dissolve 492,6 mg of sodium nitrite (5.1.8) in water (5.1.1). Make up to the mark with water (5.1.1).

This solution is stable for at least 2 weeks if kept in a stoppered glass bottle at (4 $\pm$ 2) °C.

5.1.26 Nitrite(N) solution, ρ(N) = 20 mg/l.

Pipette 20 ml of the nitrite stock solution (5.1.25) into a 100 ml one-mark volumetric flask. Make up to the mark with water (5.1.1).

Prepare the solution freshly before use.

5.1.27 Nitrate(N) solution, ρ(N) = 200 mg/l.

In a 100 ml one-mark volumetric flask, dissolve 144,4 mg of potassium nitrate (5.1.9) in water (5.1.1). Make up to the mark with water (5.1.1). Acidify the standard solutions with sulfuric acid II (5.1.17) to pH $<$ 2.

The solution is stable for at least 1 month.

5.1.28 Calibration solutions.

Prepare calibration solutions by diluting the nitrate(N) solution (5.1.27). At least five calibration solutions are recommended.

For example, proceed according to Table 1 for the preparation of 10 calibration solutions.

Prepare all calibration solutions immediately before measurement.

5.1.29 Blank solution, for diluting the samples and measuring the blanks (Clauses 7 and 8).

Acidify water to pH $\approx$ 2 with sulfuric acid II (5.1.17).

5.2 Additional reagents for FIA (see 6.1)

5.2.1 FIA oxidising reagent I (Figure A.1, R3).

In a 250 ml one-mark volumetric flask, dilute 6,8 ml of sulfuric acid II (5.1.17) in about 200 ml of water (5.1.1). Dissolve 7,2 g of boric acid (5.1.15) and 10,1 g of potassium peroxodisulfate (5.1.3) and make up to the mark with water (5.1.1).

The solution is stable for 1 day if kept at 2 °C to 8 °C. Do not hermetically close the reagent container.

Table 1 — Preparation of the calibration solutions for total nitrogen(N)

Nitrate(N) concentration mg/l	Volume of nitrate(N) solution (5.1.27) diluted with water (5.1.1) to 100 ml ml
2	1
4	2
6	3
8	4
10	5
12	6
14	7
16	8
18	9
20	10

5.2.2 FIA oxidising reagent II (Figure A.1, R4).

In a 250 ml one-mark volumetric flask, dissolve 6,0 g of sodium hydroxide (5.1.4) and 10,1 g of potassium peroxodisulfate (5.1.3) in about 200 ml of water (5.1.1). Make up to the mark with water (5.1.1).

The solution is stable for 1 week if kept at 2 °C to 8 °C. Do not hermetically close the reagent container.

5.2.3 FIA carrier solution (Figure A.1, C).

Mix 1 000 ml of water (5.1.1) with 100 µl of copper(II) sulfate solution I (5.1.13). Prepare the solution freshly before use.

Prior to use, degas the solution, e.g. by membrane filtration (vacuum).

5.3 Additional reagents for CFA (see 6.2)

5.3.1 Poly(ethylene glycol) dodecyl ether, $[HO(CH_2CH_2O)_nC_{12}H_{21}]$, surfactant, melting range 33 °C to 41 °C, aqueous solution with a mass fraction of 30 %.

5.3.2 CFA oxidising reagent (Figure A.2, R5).

Using a 1 000 ml volumetric flask, dissolve 45,0 g of potassium peroxodisulfate (5.1.3) in about 900 ml of water (5.1.1). Dissolve 12,0 g of sodium hydroxide (5.1.4) in this solution. Make up to the mark with water (5.1.1). Do not heat the solution, otherwise the peroxodisulfate spontaneously releases oxygen.

The solution is stable for 2 weeks if stored at room temperature.

A titanium catalyst can be used to improve digestion of nitrogen compounds. Prepare the catalyst by diluting 5 ml of titanium tetrachloride (5.1.5) with water (5.1.1) to 200 ml, and adding 0,25 ml of this solution to the CFA oxidising reagent.

5.3.3 CFA buffer solution I (Figure A.2, R4).

Dissolve 24,0 g of boric acid (5.1.15) in a 1 000 ml one-mark volumetric flask in water (5.1.1). Make up to the mark with water (5.1.1).

The solution is stable for 1 month if stored at room temperature.

5.3.4 CFA buffer solution II (Figure A.2, R3).

In a 1 000 ml one-mark volumetric flask, dissolve 5,0 g of Na_2EDTA (5.3.6) in 500 ml of the imidazole stock solution (5.1.20). Make up to the mark with water (5.1.1), add 1 ml of poly(ethylene glycol) dodecyl ether (5.3.1) and mix.

The solution is stable for 1 month if stored in a brown bottle at room temperature.

5.3.5 CFA buffer solution III (Figure A.2, R2).

Dilute 250 ml of the imidazole stock solution (5.1.20) to 1 000 ml with water (5.1.1). Add 1 ml of poly(ethylene glycol) dodecyl ether (5.3.1) solution and mix.

5.3.6 Ethylenedinitrilotetraacetic acid, disodium salt, dihydrate, Na_2EDTA, $C_{10}H_{14}N_2Na_2O_8 \cdot 2\ H_2O$.

6 Apparatus

Usual laboratory apparatus and in particular the following.

6.1 Flow injection analysis, usually comprising the components specified in 6.1.1 to 6.1.9 (see Figure A.1).

6.1.1 Reagent reservoirs.

6.1.2 Low pulsation pump, with suitable, chemically inert pump tubes.

6.1.3 Sample injector, injection volume 30 µl (or 400 µl for smaller concentrations).

6.1.4 Cadmium reductor, minimum reduction efficiency 90 %, e.g. cadmium tube (Reference [5]) of internal diameter 1,1 mm or cadmium column (5.1.19), e.g. with a length of 120 mm.

Other reductor types may be used as long as the reduction capacity exceeds 90 %. This is to encourage other techniques to be made available (e.g. enzymatic reductors).

6.1.5 Transport tubes and reaction coils, internal diameter 0,5 mm to 0,8 mm, with tube connections and T-connections of chemically inert plastics.

6.1.6 Photometric detector, with flow cell, wavelength range 520 nm to 560 nm.

6.1.7 Recording unit, e.g. strip chart recorder, integrator or printer/plotter. In general, peak height signals are evaluated.

6.1.8 Autosampler, if required.

6.1.9 UV reactor or digester.

6.2 Continuous flow analysis, usually comprising the components specified in 6.2.1 to 6.2.9 (see Figure A.2).

6.2.1 Autosampler, or any other device allowing a reproducible application of the sample.

6.2.2 Reagent reservoirs.

6.2.3 Low pulsation pump, with suitable, chemically inert pump tubes.

6.2.4 Cadmium reductor, with a minimum reduction efficiency of 90 %, e.g. packed cadmium column with granulate (5.1.19), of internal diameter 4,0 mm, and minimum length 50 mm (see 6.1.4).

See second paragraph of 6.1.4.

6.2.5 Manifold, with highly reproducible gas-bubble feeding (nitrogen is recommended), sample and reagent feeding, with appropriate transport systems and connection assemblies of chemically inert plastics or metal. The application of the cadmium reductor requires oxygen-free gas. Before entering the cadmium column, degas the flow stream, if air is used for segmenting the flow stream.

6.2.6 Dialysis cell, if required, with, for example, a cellulose membrane, suitable for the dilution of the sample (after digestion) or the elimination of interfering compounds.

6.2.7 Photometric detector, with flow cell, capable of operating in the wavelength range 520 nm to 560 nm.

6.2.8 Recording unit, e.g. strip chart recorder, integrator or printer and plotter. In general, peak height signals are evaluated.

6.2.9 UV reactor and digester.

NOTE Figure A.2 shows a flow system (CFA) with an internal diameter of approximately 2 mm. It is possible to use other diameters (e.g. 1 mm) as well.

6.3 Additional apparatus used for FIA and CFA.

6.3.1 Membrane filter assembly, for degassing FIA solutions, with membrane filters of pore size 0,45 µm. Cellulose acetate filters should be used.

6.3.2 pH electrode.

6.3.3 Homogenisation device [e.g. Ultra-Turrax[1)]], if needed.

6.3.4 Syringe, nominal capacity 25 ml.

7 Sampling and sample preparation

Before use, clean all containers coming into contact with the sample thoroughly with water (5.1.1) (see ISO 5667-3).

For total nitrogen, collect the sample in a glass or polyethene bottle. Acidify these samples with sulfuric acid II (5.1.17) to approximately pH 2. Store the samples for at least 12 h to dissolve and predigest particulate nitrogen.

The maximum storage time is 1 month at 2 °C to 8 °C.

The amount of suspended particulate matter shall not exceed 30 mg/l. If the concentration is higher, dilute the sample after homogenisation with blank solution (5.1.29).

As an exception, the samples may be stored in the freezer at approximately −20 °C for 8 days, provided the applicability of this preservation has been checked.

Prior to measurement, dilute samples containing a total salt concentration of greater than 30 g/l with blank solution (5.1.29).

1) Example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

8 Procedure

8.1 Preparation, activation and checking of the cadmium reductor

8.1.1 Cadmium column with granulate

Place a sufficient quantity of the cadmium granulate (5.1.19) to fill the column (see 6.1.4 or 6.2.4) in a 25 ml beaker. Stir with hydrochloric acid II (5.1.11.2) until the surface of the granulate shows a metallic shine.

NOTE Activated cadmium granules and columns are commercially available.

Remove the acid by rinsing several times with water (5.1.1).

Decant the water and stir the granulate twice for approximately 2 min with copper(II) sulfate solution II (5.1.14). The surface of the granulate turns black.

Decant and carefully rinse with water (5.1.1).

Fill the column with the granulate, avoiding air bubbles and large cavities, and stopper the ends of the column (e.g. with glass wool).

Assemble the column in the flow system and activate the reductor by applying the highest calibration solution (5.1.28) three times.

Repeatedly measure a calibration solution (5.1.28) with a nitrate(N) concentration of 20 mg/l, until stable results are obtained.

The cadmium column can be stored, free from air bubbles, in the imidazole stock solution (5.1.20). Prior to reuse, stabilise and activate the column as specified above.

8.1.2 Cadmium tube

Using the syringe (6.3.4), aspirate approximately 5 ml of the buffered copper(II) sulfate solution (5.1.23) into the cadmium tube (see 6.1.4) and allow to react for 5 min. Repeat the procedure, avoiding air bubbles.

Using the syringe, aspirate approximately 20 ml of imidazole stock solution (5.1.20) through the tube and allow to react, avoiding air bubbles.

Assemble the column in the flow system, activate and stabilise as specified in 8.1.1.

The cadmium tube can be stored, free from air bubbles, in the imidazole stock solution (5.1.20). Prior to measurement, stabilise or treat, if required (see 8.1.3), with buffered copper(II) sulfate solution (5.1.23).

8.1.3 Checking the reduction capacity of the cadmium reductor

By replacing the oxidising reagents (5.3.2 for CFA; 5.2.1 and 5.2.2 for FIA) with water (5.1.1) and with the UV reactor switched off, the reduction capacity of the cadmium reductor (6.1.4, 6.2.4) may be checked.

Sequentially analyse a nitrate calibration solution (5.1.28) and a nitrite solution (5.1.26) with a nitrogen mass concentration of 20 mg/l each, and compare the measured values obtained.

If the measured value for nitrate is less than 90 % of the measured nitrite value, take appropriate measures according to 8.1.1 and 8.1.2 in order to obtain a reduction capacity of at least 90 %.

Check the reduction capacity again, prior to the analysis of each series of samples.

8.2 Sensitivity, check of the digestion process

A calibration solution (5.1.28) with a nitrate(N) concentration of 10 mg/l, measured in the system (FIA or CFA respectively) should result in an absorbance of at least 0,04 for a pathlength of 10 mm.

NOTE If the photometric detector (see 6.1.6 or 6.2.7) does not allow any absorbance readings, the absorbance can be determined by comparing with an external absorbance-measuring photometer.

Sequentially analyse a nitrate calibration solution (5.1.28) and a urea working solution (5.1.22) with a nitrogen mass concentration of 20 mg/l each, and compare the measured values obtained.

If the measured value for urea is less than 85 % of the measured nitrate value, take appropriate measures by cleaning the system with hydrochloric acid III (5.1.11.3) or renew the UV lamp.

Check the UV digestion process weekly.

8.3 Preparation for measurement

Assemble the flow system according to the method of determination desired (CFA or FIA).

Prior to measurement of total nitrogen, continuously run the reagent solutions through the system for approximately 10 min without the cadmium reductor and subsequently for approximately 20 min with the cadmium reductor in operation. Record and zero the base absorbance.

The system is in operation condition when the baseline is stable. A satisfactory signal-to-noise ratio of at least 3:1 shall be obtained. Perform the reaction steps in the sequence specified in 8.4 to 8.6.

8.4 Monitoring the blank of the reagents

Allow the baseline to stabilise.

Instead of the buffer solution (R2) and the reagent solution (R1), transport water (5.1.1) for 2 min and record changes in the measuring signal.

If the absorbance changes by more than 0,030 per 10 mm pathlength, either the water being used or the reagent solutions may be contaminated. Take appropriate measures to eliminate the interference.

Then transport the reagent solutions again.

8.5 Calibration

Prepare the calibration solutions (5.1.28). Calibrate by sequentially adding the calibration solutions and the blank solution (5.1.29).

Prior to calibration, zero the instrument, if necessary, following the manufacturer's instructions.

Determine the measured values from the calibration solutions used while following 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 (8.6) are the same. The magnitude of the measuring signal is proportional to the mass concentration of nitrogen(N). Establish the regression line for the measuring series obtained.

Calculate the calibration curve as specified in ISO 8466-1.

Apply the following general Equation (1), in which y is the measured value, in instrument-related units:

$$y = b\rho_{(\mathrm{N})} + a \tag{1}$$

where

b is the slope of the calibration function, in instrument-related units times litres per milligram;

$\rho_{(N)}$ is the mass concentration, in milligrams per litre, of nitrogen(N);

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

If the linearity test specified in ISO 8466-1 shows that the calibration curve is not linear, calculate the calibration curve as specified in ISO 8466-2.

8.6 Sample measurement

Analyse the samples, pretreated according to Clause 7, in the same way as the calibration solutions (5.1.28), with the relevant flow system (for FIA, see 6.1 and Figure A.1; for CFA, see 6.2 and Figure A.2).

If the mass concentrations to be determined exceed the validity range of the selected working range, dilute the sample or analyse using another working range.

Check the validity of the calibration function after each sample series, but at latest after the measurement of 10 to 20 samples, using one calibration solution each for the lower and upper third of the respective working range. Set up a new calibration (8.5), if necessary.

After measurement, store the cadmium reductor in an oxygen-free imidazole solution (see the final paragraphs of 8.1.1 and 8.1.2).

9 Evaluation

Determine the mass concentration of the determinand in the measuring solution using the measured value obtained as specified in 8.6, from the calibration function in 8.5.

For the evaluation, use the appropriate function. Do not extrapolate beyond the working range selected.

Calculate the mass concentration, $\rho_{(N)}$, in milligrams per litre, of nitrogen(N) in the sample using Equation (2):

$$\rho_{(N)} = \frac{y - a}{b} \tag{2}$$

where the variables on the right-hand side are as defined in 8.5.

For the calculation of results in the case of a non-linear calibration curve, see ISO 8466-2.

10 Expression of results

Report the results to a maximum of two significant figures.

EXAMPLE

Total nitrogen(N): 2,9 mg/l

Total nitrogen(N): 13 mg/l

11 Test report

This test report shall contain at least the following information:

a) the test method used, with reference to this International Standard (ISO 29441:2010);

b) all information necessary for the complete identification of the water sample;

c) specification of the procedure applied (CFA or FIA);

d) description of the sample pretreatment;

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

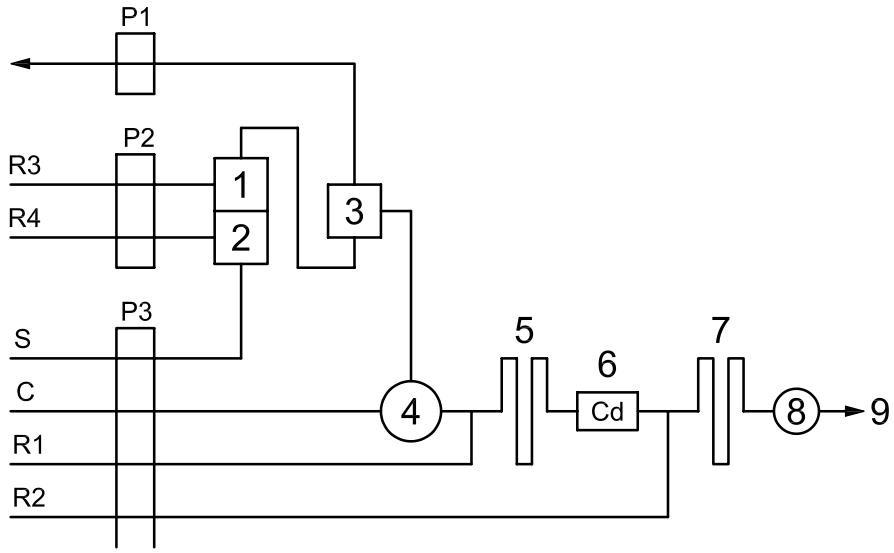
f) the test result(s) obtained, expressed in accordance with Clause 10;

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

h) all operating details not specified in this International Standard, or regarded as optional, together with details of any incidents which may have influenced the test result(s).

Annex A
(informative)

Examples of flow systems (6.1 or 6.2) for the determination of total nitrogen after inline UV digestion (2 mg/l to 20 mg/l)



Key

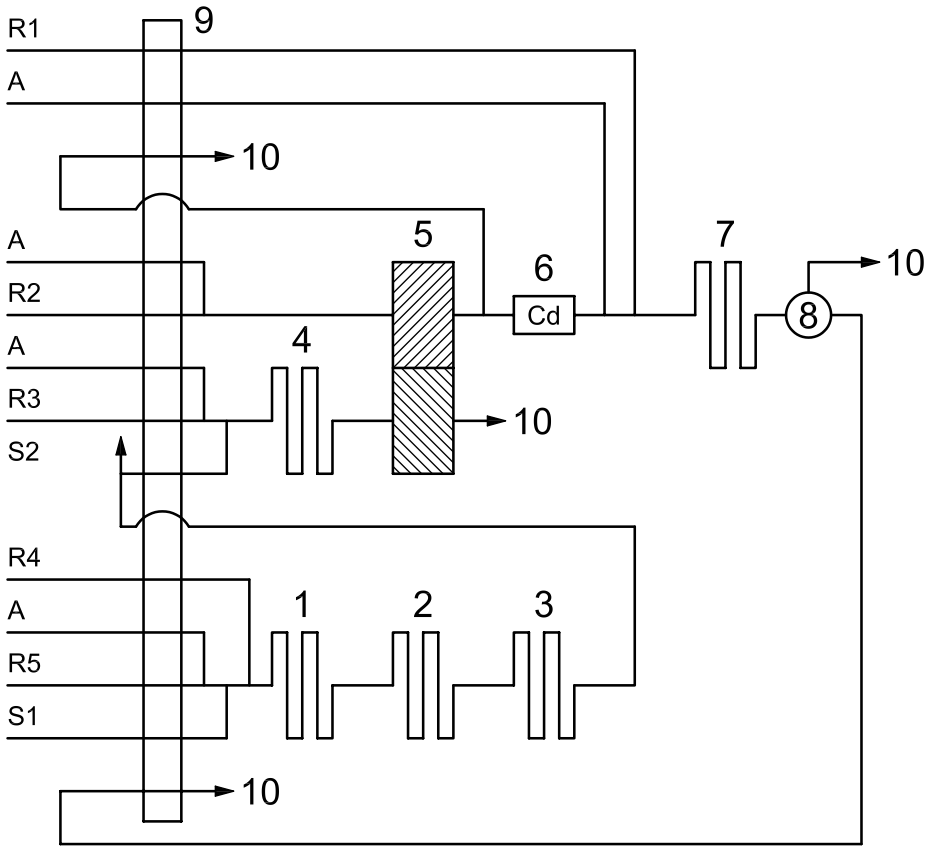
C carrier solution (5.2.3), 1,60 ml/min
P1 sample pump
P2 pump, showing flow rate in ml/min (6.1.2)
P3 pump, showing flow rate in ml/min (6.1.2)
R1 imidazole stock solution (5.1.20), 0,80 ml/min
R2 reagent solution (5.1.24), 1,20 ml/min
R3 FIA oxidising reagent I (5.2.1), 0,70 ml/min
R4 FIA oxidising reagent II (5.2.2), 0,70 ml/min
S sample, 1,20 ml/min

1 UV reactor (6.1.9), 254 nm, 9 W, with reaction coil, internal diameter 0,7 mm, length 5 000 mm
2 thermo reactor, 105 °C, with reaction coil, internal diameter 0,8 mm, length 8 000 mm
3 degassing station
4 injector, 30 µl
5 reaction coil, length 500 mm, internal diameter 0,5 mm
6 cadmium (Cd) reductor (6.1.4)
7 reaction coil, length 1 500 mm, internal diameter 0,5 mm
8 detector, optical pathlength 10 mm, operating in a wavelength range from 520 nm to 560 nm (6.1.6)
9 waste

Figure A.1 — Example of a flow injection system (FIA) for the determination of total nitrogen in the range 2 mg/l to 20 mg/l in accordance with 6.1

NOTE 1 An injector volume of 400 µl is suitable for the determination of total nitrogen in the range of 0,2 mg/l to 2 mg/l.

NOTE 2 A dialysis cell with, for example, a cellulose membrane, suitable for the dilution of the sample (after digestion) or the elimination of interfering compounds, can be introduced into the manifold (compare with 6.2.6).



Key

A air, flow rate 0,42 ml/min
R1 reagent solution (5.1.24), flow rate 0,23 ml/min
R2 CFA buffer solution III (5.3.5), flow rate 1,40 ml/min
R3 CFA buffer solution II (5.3.4), flow rate 0,80 ml/min
R4 CFA buffer solution I (5.3.3), flow rate 0,42 ml/min
R5 CFA oxidising reagent (5.3.2), flow rate 1,20 ml/min
S1 sample, flow rate 0,16 ml/min
S2 resample, flow rate 0,32 ml/min

1 reaction coil, length 680 mm, internal diameter 1,5 mm
2 UV digester with UV lamp (8 W) and quartz coil 3 320 mm, internal diameter 1,8 mm (6.2.9)
3 reaction coil, 90 °C, length 2 700 mm, internal diameter 2,0 mm
4 reaction coil, length 350 mm, internal diameter 1,5 mm
5 dialyser, 150 mm (6.2.6)
6 cadmium (Cd) reductor (6.2.4)
7 reaction coil, length 2 000 mm, internal diameter 1,5 mm
8 detector, wavelength range 520 nm to 560 nm, optical pathlength 10 mm (6.2.7)
9 pump (6.2.3)
10 waste

Figure A.2 — Example of a continuous flow system (CFA) for the determination of total nitrogen in the range 2 mg/l to 20 mg/l in accordance with 6.2

NOTE 3 The addition of a solution of titanium tetrachloride (for preparation, see the last paragraph of 5.3.2) to the destruction mixture to a final volume fraction of 0,001 % catalyses the decomposition.

Annex B
(informative)

Precision data

The results of an interlaboratory trial carried out in 2008-09/10 by the Netherlands are shown in Tables B.1 and B.2.

Table B.1 — Statistical data for the determination of nitrogen(N) with flow injection analysis

Sample	Matrix[a]	No. laboratories after outlier rejection	No. analytical results after outlier rejection	No. outliers	Assigned value	Overall mean of results (without outliers)	Recovery rate	Reproducibility standard deviation	Coefficient of variation of reproducibility	Repeatability standard deviation	Coefficient of variation of repeatability
		p	n	n_{OP}	ρ_{ass}	$\bar{\bar{\rho}}$	η	s_R	$C_{V,R}$	s_r	$C_{V,r}$
				%	mg/l	mg/l	%	mg/l	%	mg/l	%
1	spiked drinking water	11	57	1,7	3,29	3,32	100,9	0,097	2,9	0,080	2,4
2	spiked drinking water	11	57	3,4	16,79	16,6	99,0	0,39	2,4	0,36	2,2
3	spiked surface water	11	53	3,6	4,10	3,82	93,2	0,129	3,4	0,120	3,1
4	spiked surface water	11	57	0,0	15,02	14,6	97,4	0,36	2,5	0,33	2,2
5	original waste water	11	54	1,8	5,80	5,70	98,2	0,140	2,5	0,101	1,8
6	spiked waste water	11	56	3,4	17,95	17,5	97,7	0,37	2,1	0,31	1,7

[a] Origin of the samples:
drinking water from the city of Lelystad (Netherlands);
surface water from Ketelmeer/Markermeer (parts of IJsselmeer, Netherlands);
waste water from RWZI Dronten (waste water treatment plant, Netherlands).

Table B.2 — Statistical data for the determination of nitrogen(N) with continuous flow analysis

Sample	Matrix[a]	No. laboratories after outlier rejection p	No. analytical results after outlier rejection n	No. outliers n_{OP} %	Assigned value ρ_{ass} mg/l	Overall mean of results (without outliers) $\bar{\bar{\rho}}$ mg/l	Recovery rate η %	Reproducibility standard deviation s_R mg/l	Coefficient of variation of reproducibility $C_{V,R}$ %	Repeatability standard deviation s_r mg/l	Coefficient of variation of repeatability $C_{V,r}$ %
1	spiked drinking water	14	73	1,4	3,29	3,32	100,8	0,138	4,2	0,085	2,6
2	spiked drinking water	14	74	1,3	16,79	16,7	99,3	0,56	3,4	0,29	1,8
3	spiked surface water	13	68	8,1	4,10	4,00	97,7	0,117	2,9	0,067	1,7
4	spiked surface water	13	68	6,8	15,02	14,8	98,6	0,49	3,3	0,21	1,4
5	original waste water	14	76	0,0	5,80	5,72	98,6	0,279	4,9	0,145	2,5
6	spiked waste water	14	74	1,3	17,95	17,6	98,1	0,63	3,6	0,34	1,9

[a] Origin of samples: see Table B.1, footnote a.

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