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

Qualité de l'eau — Détermination de l'azote nitreux et de l'azote nitrique et de la somme des deux par analyse en flux (CFA et FIA) et détection spectrométrique



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Introduction

Methods using flow analysis enable wet chemistry procedures to be automatized 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) [1][2] and continuous flow analysis (CFA) [3]. Both methods share the feature of an automatic dosage of the sample into a flow system (manifold) where the analytes in the sample will react with the reagent solutions on their way through the manifold. The sample preparation may be integrated in the manifold. The reaction product is measured in a flow detector (e.g. flow photometer).

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

1 Scope

This International Standard specifies a method for the determination of nitrite(N) (see note 2), nitrate(N) or the sum of both [nitrite/nitrate(N)], in various types of waters (such as ground, drinking, surface, and waste waters) in mass concentrations ranging from 0,01 mg/l to 1 mg/l for nitrite(N) and from 0,2 mg/l to 20 mg/l for nitrite/nitrate(N), both in the undiluted sample. The range of application can be changed by varying the operating conditions.

NOTES

1 Seawater may be analysed with changes in respect to sensitivity and adaptation of the carrier solution and calibration solutions to the salinity of the samples.

2 The following concise terms are used in the text of this International Standard:

nitrite(N):	(mass concentration of) nitrite, expressed as nitrogen
nitrate(N):	(mass concentration of) nitrate, expressed as nitrogen
nitrite/nitrate(N):	(mass concentration of) the sum of nitrite(N) and nitrate(N)

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. 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 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*.

ISO 6777:1984, *Water quality — Determination of nitrite — Molecular absorption spectrometric method*.

3 Principle

3.1 Sum of nitrite(N) and nitrate(N), nitrite/nitrate(N)

With flow injection analysis (FIA), the sample is fed into a continuously flowing buffer solution (carrier stream) by means of an injection valve, or, with continuous flow analysis (CFA) being applied, it is continuously mixed with this buffer solution. Nitrate in the sample is reduced with metallic cadmium to nitrite[4]. Then, a phosphoric acid reagent solution that is also flowing continuously is admixed. Nitrite that is initially present and nitrite resulting from the reduction of nitrate will diazotize sulfanilamide in acid solution to the diazonium salt which is then coupled with *N*-(1-naphthyl)ethylenediamine to form a red dye [5] [6][7].

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

3.2 Nitrite(N)

Nitrite(N) is determined, omitting the cadmium reduction, directly by the above-mentioned diazotization and coupling reaction [8]. The chemical reactions of the nitrite are identical with those in the manual procedure (see ISO 6777).

3.3 Nitrate(N)

The mass concentration of nitrate(N) is given by the difference: nitrite/nitrate(N) – nitrite(N).

4 Reagents

If not stated otherwise, only reagents of recognized analytical grade and water according to grade 1 of ISO 3696 shall be used. The blank value of the reagents shall be checked regularly (see 9.3).

4.1 Phosphoric acid (H_3PO_4), $\rho = 1,71 \text{ g/ml}$.

4.2 Sulfanilamide (4-aminobenzenesulfonamide, $\text{C}_6\text{H}_8\text{N}_2\text{O}_2\text{S}$).

4.3 *N*-(1-naphthyl)ethylenediaminedihydrochloride [*N*-(1-naphthyl)-1,2-diaminoethanedihydrochloride], $\text{C}_{12}\text{H}_{16}\text{N}_2\text{Cl}_2$].

4.4 Sodium nitrite (NaNO_2), dried to constant mass at, for example, 150°C .

4.5 Potassium nitrate (KNO_3), dried to constant mass at, for example, 150°C .

4.6 Imidazole ($\text{C}_3\text{H}_4\text{N}_2$), for synthesis, or alternatively **ammonium chloride** (NH_4Cl), dried to constant mass at 105°C (see note 3).

4.7 Hydrochloric acid I (HCl) concentrated, $w = 37\%$.

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

4.9 Copper sulfate solution I, $\rho(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}) = 2,5 \text{ g/l}$; this solution is stable.

4.10 Copper sulfate solution II, $\rho(\text{CuSO}_4 \cdot 5\text{H}_2\text{O}) = 20 \text{ g/l}$; this solution is stable.

4.11 Polyethyleneglycol dodecyl ether

$[\text{HO} - (\text{CH}_2\text{CH}_2 - \text{O})_n - \text{C}_{12}\text{H}_{21}]$, surfactant, $\theta = 33^\circ\text{C}$ to 41°C , solution, $w = 30\%$.

The solution is stable for approximately 4 weeks.

4.12 Cadmium granulate (Cd), grain size, for example 0,3 mm to 1,5 mm (a minimum reduction capacity of 90 % shall be reached; see 5.1 and 5.2).

4.13 Imidazole stock solution, $c = 0,25 \text{ mol/l}$.

Dissolve, in a beaker of nominal capacity 1 litre, 17,0 g of imidazole (4.6) in approximately 900 ml of water.

While stirring with a magnetic stirrer, add hydrochloric acid I (4.7) and adjust, with the help of a pH electrode, the pH to 7.5.

Transfer to a volumetric flask, of nominal capacity 1 000 ml, and dilute to volume with water.

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

4.14 Buffer solution.

Mix 100 ml of the imidazole stock solution (4.13) with 100 μl of copper sulfate solution I (4.9).

Prepare the solution freshly before use.

NOTE 3 Alternatively an ammonium buffer solution can be used, for example:

85 g of ammonium chloride (NH_4Cl) should be dissolved in water and diluted to a volume of 1 000 ml, and the pH should be adjusted to approximately 7,5.

4.15 Carrier or dilution solutions, C and B in figures A.1, B.1 and C.1.

Table 1 shows some well-known options for preparing these solutions.

Prepare the solutions, containing the surfactant (4.11), freshly before use.

Prior to use, solutions C and B for FIA shall be degassed, for example by membrane filtration (vacuum).

Table 1 — Options for preparing the solutions C and B in figures A.1, B.1 and C.1

Method	Parameter	Content of solution C (see figures A.1, B.1 and C.1)	Content of solution B (see figures A.1, B.1 and C.1)
FIA	Nitrite	Water	Water ¹⁾ Buffer (4.14) ¹⁾ No solution B ¹⁾
	Nitrite/nitrate	Buffer (4.14)	Buffer (4.14)
CFA	Nitrite	"C" is not necessary	Water ^{1),2)} Buffer (4.14) ^{1),2)} No solution B ^{1),2)}
	Nitrite/nitrate	"C" is not necessary	Buffer (4.14) ²⁾
1) Three different alternatives. 2) If, in the case of CFA, water or buffer (4.14) is used as solution B and 1 ml of surfactant (4.11) per 1 litre of solution is added. If solution B is omitted, the surfactant (4.11) has to be added to the reagent solution R ₁ (4.17, see figures A.1, B.1 and C.1).			

4.16 Buffered copper sulfate solution.

Mix 20 ml of the copper sulfate solution II (4.10) and 20 ml of the imidazole stock solution (4.13) in a beaker of nominal capacity 50 ml.

Prepare the solution freshly before use.

4.17 Reagent solution, R₁ (in figures A.1, B.1 and C.1).

Dissolve, in a volumetric flask of nominal capacity 500 ml, 5 g of sulfanilamide (4.2), 0,5 g of *N*-(1-naphthyl)ethylenediaminedihydrochloride (4.3) in water, add 50 ml of phosphoric acid (4.1), and dilute to volume.

Stored in a brown glass bottle, the solution is stable for at least one week.

NOTE 4 For the preparation of this reagent solution, hydrochloric acid (4.7, 4.8) may be used instead of phosphoric acid, provided equivalent performance characteristics are obtained. The solutions of sulfanilamide (4.2) and *N*-(1-naphthyl)ethylenediaminedihydrochloride (4.3) can

also be made separately and dosed into the equipment by different lines.

Prior to use, solution R₁ for FIA shall be degassed, for example by membrane filtration (vacuum).

4.18 Nitrite(N) stock solution, $\rho_N = 100$ mg/l.

Dissolve 492,6 mg of sodium nitrite (4.4) in water, in a volumetric flask of nominal capacity 1 000 ml, and dilute to volume.

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

4.19 Nitrite(N) solution I, $\rho_N = 20$ mg/l.

Pipette 20 ml of the stock solution (4.18) into a volumetric flask of nominal capacity 100 ml, and dilute to volume with water.

Prepare the solution freshly before use.

4.20 Nitrite(N) solution II, $\rho_N = 1$ mg/l.

Pipette 1 ml of the stock solution (4.18) into a volumetric flask of nominal capacity 100 ml, and dilute to volume with water.

Prepare the solution freshly before use.

4.21 Nitrate(N) solution I, $\rho_N = 200$ mg/l.

Dissolve 144,4 mg of potassium nitrate (4.5) in water, in a volumetric flask of nominal capacity 100 ml, and dilute to volume.

The solution is stable for at least 1 month.

4.22 Nitrate(N) solution II, $\rho_N = 20$ mg/l.

Pipette 10 ml of the nitrate solution I (4.21) into a volumetric flask of nominal capacity 100 ml, and dilute to volume with water.

Prepare the solution freshly before use.

4.23 Calibration solutions

The calibration solutions are prepared by diluting the respective solutions described in 4.19 to 4.22. These solutions may be used in any combination for the preparation of calibration solutions for the determination of nitrite(N), nitrite/nitrate(N) or nitrate(N). At least five calibration standards per working range are recommended.

The following working ranges are provided:

For nitrite(N): Working range II:
0,01 mg/l to 0,1 mg/l
Working range I: 0,1 mg/l
to 1,0 mg/l

Proceed, for example, as recommended in tables 2 and 3 (if 10 standards are used).

All calibration solutions shall be prepared immediately before measurement.

For nitrite/nitrate(N): Working range II:
0,2 mg/l to 2 mg/l
Working range I: 2 mg/l to
20 mg/l

Table 2 — Preparation of the calibration solutions for nitrite(N)

Nitrite(N) concentration mg/l	Volume of nitrite(N) solution II (4.20) diluted with water to 100 ml ml	Nitrite(N) concentration mg/l	Volume of nitrite(N) solution I (4.19) diluted with water to 200 ml ml
0,01	1	0,1	1
0,02	2	0,2	2
0,03	3	0,3	3
0,04	4	0,4	4
0,05	5	0,5	5
0,06	6	0,6	6
0,07	7	0,7	7
0,08	8	0,8	8
0,09	9	0,9	9
0,10	10	1,0	10

Table 3 — Preparation of the calibration solutions for nitrite/nitrate(N)

Nitrate(N) concentration mg/l	Volume of nitrate(N) solution II (4.22) diluted with water to 100 ml ml	Nitrate(N) concentration mg/l	Volume of nitrate(N) solution I (4.21) diluted with water to 100 ml ml
0,2	1	2	1
0,4	2	4	2
0,6	3	6	3
0,8	4	8	4
1,0	5	10	5
1,2	6	12	6
1,4	7	14	7
1,6	8	16	8
1,8	9	18	9
2,0	10	20	10