

Water quality —

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

The European Standard EN ISO 13395:1996 has the status of a British Standard

ICS 13.060

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- British Agrochemicals Association Ltd.
- British Ceramic Research
- British Gas plc
- British Soft Drinks Association Ltd.
- Chemical Industries' Association
- Convention of Scottish Local Authorities
- Department of the Environment (Her Majesty's Inspectorate of Pollution)
- Department of the Environment (Water Directorate)
- Department of Trade and Industry (Laboratory of the Government Chemist)
- GAMBICA (BEAMA) Ltd.
- Industrial Water Society
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- Royal Society of Chemistry
- Soap and Detergent Industry Association
- Society of Chemical Industry
- Swimming Pool and Allied Trades Association Ltd.
- Water Companies Association
- Water Research Centre
- Water Services Association of England and Wales

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National foreword

This British Standard has been prepared by Subcommittee EH/3/2 and is the English language version of EN ISO 13395:1996 *Water quality — Determination of nitrite nitrogen and nitrate nitrogen and the sum of both by flow analysis (CFA and FIA) and spectrometric detection* published by the European Committee for Standardization (CEN). It is identical with ISO 13395:1996 published by the International Organization for Standardization (ISO).

NOTE The tests described in this British Standard should only be carried out by suitably qualified persons with an appropriate level of chemical expertise. Standard chemical procedures should be followed throughout.

Cross-references

Publication referred to	Corresponding British Standard
ISO 3696:1987	BS EN ISO 3696:1995 <i>Water for analytical laboratory use. Specification and test methods</i> BS EN 25667 <i>Water quality. Sampling</i>
ISO 5667-1:1980	Part 1:1994 <i>Guidance on the design of sampling programmes</i>
ISO 5667-2:1991	Part 2:1993 <i>Guidance on sampling techniques</i>
ISO 5667-3:1994	BS 6068 <i>Water quality</i> Part 6 <i>Sampling</i> Section 6.3:1996 <i>Guidance on the preservation and handling of samples</i>
ISO 6777:1984	BS EN 26777:1993 <i>Water quality. Physical, chemical and biochemical methods. Determination of nitrite: molecular absorption spectrometric method</i>

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Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, the EN title page, pages 2 to 18, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

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English version

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

(ISO 13395:1996)

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Foreword

The text of the International Standard ISO 13395:1996 has been prepared by Technical Committee ISO/TC 147, Water quality, in collaboration with Technical Committee CEN/TC 230, Water analysis, the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by January 1997 and conflicting national standards shall be withdrawn at the latest by January 1997.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.

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.

NOTE 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.

NOTE 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(N)/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 (H₃PO₄), $\rho = 1,71$ g/ml.

4.2 Sulfanilamide (4-aminobenzenesulfonamide, C₆H₈N₂O₂S).

4.3 *N*-(1-naphthyl)ethylenediaminedihydrochloride [*N*-(1-naphthyl)-1,2-diaminoethanedihydrochloride), C₁₂H₁₆N₂Cl₂].

4.4 Sodium nitrite (NaNO₂), dried to constant mass at, for example, 150 °C.

4.5 Potassium nitrate (KNO₃), dried to constant mass at, for example, 150 °C.

4.6 Imidazole (C₃H₄N₂), for synthesis, or alternatively **ammonium chloride** (NH₄Cl), 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 Figure A.1, Figure B.1 and Figure 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 solution C and B in Figure A.1, Figure B.1 and Figure C.1

Method	Parameter	Content of solution C (see Figure A.1, Figure B.1 and Figure C.1)	Contents of solution B (see Figure A.1, Figure B.1 and Figure C.1)
FIA	Nitrite	Water	Water ^a Buffer (4.14) ^a No solution B ^a
	Nitrite/nitrate	Buffer (4.14)	Buffer (4.14)
CFA	Nitrite	"C" is not necessary	Water ^{a,b} Buffer (4.14) ^{a,b} No solution B ^{a,b}
	Nitrite/nitrate	"C" is not necessary	Buffer (4.14) ^b

^a Three different alternatives.

^b 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 R₁ (4.17, see Figure A.1, Figure B.1 and Figure C.1).

4.16 Buffered copper sulphate 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 Figure A.1, Figure B.1 and Figure 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).