International Standard 6777

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Water quality — Determination of nitrite — Molecular absorption spectrometric method

Qualité de l'eau — Dosage des nitrites — Méthode par spectrométrie d'absorption moléculaire

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

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It has been approved by the member bodies of the following countries:

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No member body expressed disapproval of the document.

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INTERNATIONAL STANDARD ISO 6777-1984 (E)

Water quality — Determination of nitrite — Molecular absorption spectrometric method

1 Scope

This International Standard specifies a molecular absorption spectrometric method for the determination of nitrite in potable, raw and waste water.

2 Field of application

2.1 Range

A nitrite nitrogen concentration, ϱ_N, of up to 0,25 mg/l can be determined when using the maximum volume (40 ml) of test portion.

2.2 Limit of detection [1]

When using cells of optical path length 40 mm and a test portion of 40 ml, the limit of detection has been determined to lie within the range ϱ_N = 0,001 to 0,002 mg/l.

2.3 Sensitivity [1]

Using a 40 ml test portion and a cell of optical path length 40 mm, ϱ_N = 0,062 mg/l gives an absorbance of about 0,66 units.

Using a 40 ml test portion and a cell of optical path length 10 mm, ϱ_N = 0,25 mg/l gives an absorbance of about 0,67 units.

2.4 Interferences

If the alkalinity of the sample is high, some interference may be encountered (see clause 9).

A range of substances often encountered in water samples has been tested for possible interference. Full details are given in the annex. Of the substances tested, only chloramine, chlorine, thiosulfate, sodium polyphosphate and iron(III) interfere significantly.

3 Principle

Reaction of nitrite in the test portion with 4-aminobenzene sulfonamide reagent in the presence of orthophosphoric acid at pH 1,9 to form a diazonium salt which forms a pink-coloured dye with *N*-(1-naphthyl)-1,2-diaminoethane dihydrochloride (added with the 4-aminobenzene sulfonamide reagent). Measurement of the absorbance at 540 nm.

4 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Orthophosphoric acid, 15 mol/l solution, (ϱ = 1,70 g/ml).

4.2 Orthophosphoric acid, approximately 1,5 mol/l solution.

Add, by means of a pipette, 25 ml of the orthophosphoric acid (4.1) to 150 ± 25 ml of water. Mix and cool to room temperature. Transfer the solution to a 250 ml one-mark volumetric flask and dilute to the mark with water.

Store in an amber glass bottle. The solution is stable for at least 6 months.

4.3 Colour reagent.

WARNING — This reagent is hazardous. Skin contact or ingestion of it or its ingredients must be avoided.

Dissolve 40,0 ± 0,5 g of 4-aminobenzene sulfonamide ($NH_2C_6H_4SO_2NH_2$) in a mixture of 100 ± 1 ml of the orthophosphoric acid (4.1) and 500 ± 50 ml of water in a beaker.

Dissolve 2,00 ± 0,02 g of *N*-(1-naphthyl)-1,2-diaminoethane dihydrochloride ($C_{10}H_7\text{-NH-}CH_2\text{-}CH_2\text{-}NH_2 \cdot 2HCl$) in the resulting solution. Transfer to a 1 000 ml one-mark volumetric flask and dilute to the mark with water. Mix well.

Store in an amber glass bottle. The solution is stable for 1 month if stored at 2 to 5 °C.

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[1] Information derived from a United Kingdom interlaboratory trial involving five participants.

4.4 Nitrite, standard solution, $\varrho_N = 100$ mg/l.

Dissolve 0,492 2 ± 0,000 2 g of sodium nitrite (dried at 105 °C for at least 2 h) in about 750 ml of water. Transfer quantitatively to a 1 000 ml one-mark volumetric flask and dilute to the mark with water.

Store in a stoppered amber glass bottle at 2 to 5 °C. This solution is stable for at least 1 month. (See clause 10.)

4.5 Nitrite, standard solution, $\varrho_N = 1{,}00$ mg/l.

Transfer, by means of a pipette, 10 ml of the standard nitrite solution (4.4) to a 1 000 ml one-mark volumetric flask and dilute to the mark with water.

Prepare this solution each day as required, and discard after use.

5 Apparatus

All glassware shall be carefully cleaned using approximately 2 mol/l hydrochloric acid and then rinsed thoroughly with water.

Ordinary laboratory apparatus, and

Spectrometer, suitable for measurements at a wavelength of 540 nm, together with cells of optical path length between 10 and 50 mm.

6 Sampling and samples

Laboratory samples should be collected in glass bottles and should be analysed as soon as possible within 24 h of collection. Storage of the samples at 2 to 5 °C may preserve many types of sample, but this should be verified.

7 Procedure

7.1 Test portion

The maximum volume of test portion is 40 ml. This is suitable for the determination of nitrite concentrations of up to $\varrho_N = 0{,}25$ mg/l. Smaller test portions may be used as appropriate in order to accommodate much higher nitrite concentrations. If the laboratory sample contains suspended matter, this should be allowed to settle, or the sample should be filtered through a glass fibre paper before taking the test portion.

7.2 Determination

Transfer, by means of a pipette, the selected volume of test portion to a 50 ml one-mark volumetric flask, and, if necessary, dilute to 40 ± 2 ml with water.

NOTE — It is always essential to adjust the volume to 40 ± 2 ml to ensure that the correct pH is obtained (after addition of the reagent) for the reaction.

Add, by means of a pipette, 1,0 ml of the colour reagent (4.3). Mix immediately by swirling and dilute to the mark with water. Mix and allow to stand. The pH at this stage should be 1,9 ± 0,1. (See clause 9.)

At least 20 min after addition of the reagent, measure the absorbance of the solution at the wavelength of maximum absorbance, approximately 540 nm, in a cell of suitable optical path length, using water as the reference liquid.

NOTE — The wavelength of maximum absorbance should be checked when this method is first used, and should be used in all subsequent determinations.

7.3 Correction for colour

If the colour of the test portion is such that it may interfere with the measurement of absorbance, treat a duplicate test portion as described in 7.2, but replacing the colour reagent (4.3) with 1,0 ml of the orthophosphoric acid solution (4.2).

7.4 Blank test

Carry out a blank test by proceeding as described in 7.2, but replacing the test portion with 40 ± 2 ml of water.

7.5 Preparation of the calibration graph

Place, by means of a burette, into a series of nine 50 ml one-mark volumetric flasks, the volumes of the standard nitrite solution (4.5) shown in table 1.

Dilute the contents of each flask with water to give a volume of 40 ± 2 ml and proceed as described in 7.2, from the second paragraph to the end, using cells of optical path length specified in table 1.

Subtract the absorbance of the zero term from the absorbances obtained for the other standard solutions and plot a graph of absorbance against the mass of nitrite, as nitrogen, for each optical path length. The graph should be linear and should pass through the origin.

8 Expression of results

8.1 Method of calculation

The corrected absorbance, A_r, of the test solution is given by the equation

$$A_r = A_s - A_b$$

or, if correction for colour was made, by means of the equation

$$A_r = A_s - A_b - A_c$$

where

A_s is the absorbance, as measured, of the test solution;

A_b is the absorbance of the blank test solution;

A_c is the absorbance of the solution prepared for the correction for colour.

NOTE — It is essential that the values of A_s, A_b and A_c are measured in cells of the same optical path length for a particular sample.

From the corrected absorbance A_r, determine from the calibration graph (7.5), for the appropriate optical path length of the cell, the corresponding mass of nitrite, as nitrogen, in micrograms.

The nitrite content, expressed in milligrams of nitrogen per litre, is given by the formula

$$\frac{m_N}{V}$$

where

m_N is the mass, in micrograms, of nitrite nitrogen corresponding to the corrected absorbance (A_r);

V is the volume, in millilitres, of the test portion.

The result may be expressed as the mass concentration of nitrogen, ϱ_N, or nitrite, $\varrho_{NO_2^-}$, in milligrams per litre, or as the amount of substance concentration of nitrite ion, $c(NO_2^-)$, in micromoles per litre. The appropriate conversion factors are given in table 2.

Table 2

	ϱ_N mg/l	$\varrho_{NO_2^-}$ mg/l	$c(NO_2^-)$ µmol/l
ϱ_N = 1 mg/l	1	3,29	71,4
$\varrho_{NO_2^-}$ = 1 mg/l	0,304	1	21,7
$c(NO_2^-)$ = 1 µmol/l	0,014	0,046	1

Example:

A nitrogen concentration of 1 mg/l corresponds to a nitrite concentration of 3,29 mg/l.

8.2 Precision

Repeatability and reproducibility standard deviations have been determined as indicated in table 3.

Table 1

Volume of standard nitrite solution (4.5) ml	Mass of nitrite nitrogen, m_N µg	Optical path length of cell mm
0,00	0,00	10 and 40*
0,50	0,50	40
1,00	1,00	10 and 40
1,50	1,50	40
2,00	2,00	40
2,50	2,50	10 and 40
5,00	5,00	10
7,50	7,50	10
10,00	10,00	10

* 50 mm cells may also be used.

Table 3*

Sample	**Nitrite content, ϱ_N**	**Volume of test portion**	**Optical path length of cell**	**Standard deviation**** (mg/l)	
	mg/l	ml	mm	**Repeatability**	**Reproducibility**
Standard solution	0,000	40	40	0,000 1 to 0,000 3	—
Standard solution	0,040	40	40	0,000 2 to 0,000 8	0,000 2 to 0,001 8
Standard solution	0,40	40	10	0,001 1 to 0,005 4	0,003 to 0,009
Standard solution	1,60	5	10	0,002 to 0,026	0,007 to 0,040
Sewage effluent	1,01	5	10	0,002 to 0,020	0,004 to 0,021
Sea water	0,20	40	10	0,000 3 to 0,002 6	0,001 to 0,004
River water	0,30	25	10	0,000 8 to 0,011 6	0,002 to 0,012

* Information derived from a United Kingdom interlaboratory trial involving five participants.

** The highest and lowest values from the interlaboratory exercise. All values have 14 degrees of freedom.

9 Special cases

If the alkalinity of the sample is high, such that the pH is not 1,9 ±0,1 after treating test portion and diluting to 40 ml, additional orthophosphoric acid solution (4.2) should be added before dilution, so that the specified pH is attained. The method will, however, tolerate a hydrogen carbonate alkalinity of at least 300 mg/l in a test portion of 40 ml without deviation from the specified pH.

10 Notes on procedure

As standard nitrite solutions may become unstable, the concentration of the standard nitrite solution (4.4) used may be checked by the following method:

Place by means of a pipette, 50 ml of potassium permanganate standard volumetric solution, $c(1/5\ \mathrm{KMnO_4}) = 0{,}01$ mol/l, in a 250 ml conical flask. Add 10 ± 1 ml of 2,5 mol/l sulfuric acid solution and mix thoroughly. Fill a 50 ml burette with the standard nitrite solution (4.4) and arrange the apparatus so that the tip of the burette dips below the surface of the acid permanganate solution in the flask. Titrate to a colourless end-point. As the end-point approaches, warm the solution to about 40 °C and continue the titration slowly until the colour of the permanganate is just discharged. Note the volume of standard nitrite solution used in the titration.

50 ml of a potassium permanganate standard volumetric solution, $c(1/5\ \mathrm{KMnO_4}) = 0{,}01$ mol/l, is equivalent to 3,502 mg of nitrogen. Thus, for the standard nitrite solution (4.4), the volume used in the titration should be 35,02 ml. The standard nitrite solution is only suitable if the volume used in the titration lies within the range 35,02 ± 0,40 ml.

11 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) all details required for the complete identification of the sample;

c) details concerning the storage of the laboratory sample before analysis;

d) a statement of the repeatability achieved by the laboratory when using this method;

e) the results and the method of expression used;

f) details of any deviation from the procedure specified in this International Standard or any other circumstances that may have influenced the result.