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Water quality — Determination of nitrate —

Part 3 :
Spectrometric method using sulfosalicylic acid

Qualité de l'eau — Dosage des nitrates —

Partie 3 : Méthode spectrométrique avec l'acide sulfosalicylique

Reference number
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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. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 7890-3 was prepared by Technical Committee ISO/TC 147, *Water quality*.

ISO 7890 consists of the following parts, under the general title *Water quality — Determination of nitrate :*

— *Part 1 : 2,6-Dimethylphenol spectrometric method*

— *Part 2 : 4-Fluorophenol spectrometric method after distillation*

— *Part 3 : Spectrometric method using sulfosalicylic acid*

Annex A forms an integral part of this International Standard.

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Water quality — Determination of nitrate —

Part 3 :
Spectrometric method using sulfosalicylic acid

1 Scope

1.1 Substance determined

This part of ISO 7890 specifies a method for the determination of nitrate ion in water.

1.2 Type of sample

The method is suitable for application to raw and potable water samples.

1.3 Range

Up to a nitrate nitrogen concentration, ϱ_N of 0,2 mg/l using the maximum test portion volume of 25 ml. The range can be extended upwards by taking smaller test portions.

1.4 Limit of detection[1)]

Using cells of optical path length 40 mm and a 25 ml test portion volume the limit of detection lies within the range ϱ_N = 0,003 to 0,013 mg/l.

1.5 Sensitivity[1)]

A nitrate nitrogen concentration of ϱ_N = 0,2 mg/l gives an absorbance of about 0,68 unit, using a 25 ml test portion and cells of optical path length 40 mm.

1.6 Interferences

A range of substances often encountered in water samples has been tested for possible interference with this method. Full details are given in annex A. The main potential interferents are chloride, orthophosphate, magnesium and manganese(II), as shown in annex A.

Other tests have shown that this method will tolerate a sample colour of up to 150 mg/l Pt providing the test portion absorption correction procedure is followed. (See 6.5.)

2 Principle

Spectrometric measurement of the yellow compound formed by reaction of sulfosalicylic acid (formed by addition to the sample of sodium salicylate and sulfuric acid) with nitrate and subsequent treatment with alkali.

Disodium dihydrogen ethylenedinitrilotetraacetate ($EDTANa_2$) is added with the alkali to prevent precipitation of calcium and magnesium salts. Sodium azide is added to overcome interference from nitrite.

3 Reagents

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

3.1 Sulfuric acid, $c(H_2SO_4) \approx 18$ mol/l, $\varrho = 1{,}84$ g/ml.

WARNING — When using this reagent, eye protection and protective clothing are essential.

3.2 Glacial acetic acid, $c(CH_3COOH) \approx 17$ mol/l, $\varrho = 1{,}05$ g/ml.

WARNING — When using this reagent, eye protection and protective clothing are essential.

3.3 Alkali solution, $\varrho_{NaOH} = 200$ g/l, $\varrho_{[CH_2\text{-}N(CH_2COOH)CH_2\text{-}COONa]_2.2H_2O} = 50$ g/l.

Cautiously dissolve 200 g ± 2 g of sodium hydroxide pellets in about 800 ml of water. Add 50 g ± 0,5 g of disodium dihydrogen ethylenedinitrilotetraacetate dihydrate ($EDTANa_2$) $\{[CH_2\text{-}N(CH_2COOH)CH_2\text{-}COONa]_2.2H_2O\}$ and dissolve. Cool to room temperature and make up to 1 litre with water in a measuring cylinder. Store in a polyethylene bottle. This reagent is stable indefinitely.

WARNING — When using this reagent, eye protection and protective clothing are essential.

3.4 Sodium azide solution, $\varrho_{NaN_3} = 0{,}5$ g/l.

Carefully dissolve 0,05 g ± 0,005 g of sodium azide in about 90 ml of water and dilute to 100 ml with water in a measuring cylinder. Store in a glass bottle. This reagent is stable indefinitely.

1) Information derived from a United Kingdom interlaboratory test involving four participants. Limit of detection was taken as 4,65 times the within-batch standard deviation of the blank.

WARNING — This reagent is very toxic if swallowed. Contact between the solid reagent and acids liberates very toxic gas.

NOTE — Sulfamic acid solution, $\varrho_{NH_2 \cdot SO_3H}$ = 0,75 g/l, may be used as an alternative to sodium azide solution.

3.5 Sodium salicylate solution, $\varrho_{HO\text{-}C_6H_4\text{-}COONa}$ = 10 g/l.

Dissolve 1 g ± 0,1 g of sodium salicylate ($HO\text{-}C_6H_4\text{-}COONa$) in 100 ml ± 1 ml of water. Store in a glass or polyethylene bottle. Prepare this solution freshly on each day of operation.

3.6 Nitrate, stock standard solution, ϱ_N = 1 000 mg/l.

Dissolve 7,215 g ± 0,001 g of potassium nitrate (KNO_3) (previously dried at 105 °C for at least 2 h) in about 750 ml of water. Quantitatively transfer to a 1 litre one-mark volumetric flask and make up to volume with water.

Store the solution in a glass bottle for not more than 2 months.

3.7 Nitrate, standard solution, ϱ_N = 100 mg/l.

Pipette 50 ml of the stock standard solution (3.6) into a 500 ml one-mark volumetric flask and make up to the mark with water.

Store the solution in a glass bottle for not more than 1 month.

3.8 Nitrate, working standard solution, ϱ_N = 1 mg/l.

Into a 500 ml one-mark volumetric flask, pipette 5 ml of standard nitrate solution (3.7). Make up to volume with water. Prepare the solution freshly on each occasion of use.

4 Apparatus

Usual laboratory apparatus, and

4.1 Spectrometer, capable of operating at a wavelength of 415 nm and equipped with cells of optical path length 40 mm or 50 mm.

4.2 Evaporating dishes, about 50 ml capacity. If the dishes are new, or not in regular use, they shall first be thoroughly rinsed with water and taken through the procedure in the first two paragraphs of 6.3.2 to clean them.

4.3 Water bath, boiling, capable of accepting at least six of the evaporating dishes (4.2).

4.4 Water bath, capable of thermostatic regulation to 25 °C ± 0,5 °C.

5 Sampling and samples

Laboratory samples should be collected in glass bottles and should be analysed as soon as possible after collection. Storage of samples at between 2 °C and 5 °C may preserve many types of sample, but checks should be made to confirm this with each sample type.

6 Procedure

WARNING — This procedure involves the use of concentrated sulfuric acid, acetic acid, sodium hydroxide and sodium azide solutions. Eye protection and protective clothing are essential when using these reagents. They must never be pipetted by mouth.

6.1 Test portion

The maximum test portion volume which can be used for the determination of nitrate concentration up to ϱ_N = 0,2 mg/l is 25 ml. Use smaller test portions as appropriate in order to accommodate higher nitrate concentrations. Before taking the test portion, allow laboratory samples containing suspended matter to settle, centrifuge them or filter them through a washed glass fibre filter paper. Neutralize samples having a pH value greater than 8 with acetic acid (3.2) before taking the test portion.

6.2 Blank test

Carry out a blank test in parallel with the determination, using 5,00 ml ± 0,05 ml of water instead of the test portion. Let the absorbance measured be A_b units.

6.3 Calibration

6.3.1 Preparation of the set of calibration solutions

To a series of clean evaporating dishes (4.2), add, from a burette, 1; 2; 3; 4 and 5 ml respectively of the working standard nitrate solution (3.8), corresponding to nitrate amounts of m(N) = 1; 2; 3; 4 and 5 µg in the respective dishes.

6.3.2 Colour development

Add 0,5 ml ± 0,005 ml of sodium azide solution (3.4), and 0,2 ml ± 0,002 ml of acetic acid (3.2). Wait for at least 5 min, and then evaporate the mixture to dryness in the boiling water bath (4.3). Add 1 ml ± 0,01 ml of sodium salicylate solution (3.5), mix well and evaporate the mixture to dryness again. Remove the dish from the water bath and allow the dish to cool to room temperature.

Add 1 ml ± 0,01 ml of sulfuric acid (3.1) and dissolve the residue in the dish by gentle agitation. Allow the mixture to stand for about 10 min. Then add 10 ml ± 0,1 ml of water followed by 10 ml ± 0,1 ml of alkali solution (3.3).

Quantitatively transfer the mixture to a 25 ml one-mark volumetric flask, but do not make up to the mark. Place the flask in the water bath (4.4) at 25 °C ± 0,5 °C for 10 min ± 2 min. Then remove the flask and make up to the mark with water.

6.3.3 Spectrometric measurements

Measure the absorbance of the solution at 415 nm in cells of optical path length 40 mm or 50 mm against distilled water as a reference. Let the absorbance measured be A_s units.

NOTE — Tests have indicated that the absorbance of the coloured solutions remains constant for at least 24 h.

6.3.4 Plotting the calibration graph

Subtract the absorbance of the blank solution from the absorbances of each of the calibration solutions and plot a calibration graph of absorbance against mass of nitrate, m(N) µg. Check that the graph is linear and passes through the origin. If it is not, repeat the calibration.

6.4 Determination

Pipette the selected test portion (6.1), of volume V ml such that the aliquot contains a mass of nitrate nitrogen of between m(N) = 1 µg and 5 µg, into a small evaporating dish (4.2).

Then proceed as in 6.3.2 and 6.3.3.

6.5 Correction for test portion absorption

If absorption by the test portion at the analytical wavelength is known, or suspected, to interfere (as may arise with highly coloured samples), carry out the operations given in 6.3.2 and 6.3.3 on the duplicate test portion but omitting the addition of sodium salicylate solution. Let the absorbance measured be A_t units.

7 Expression of results

7.1 Method of calculation

Calculate the absorbance due to nitrate in the test portion, A_r, from the equation

$$A_r = A_s - A_b$$

or, when a correction for sample absorption has been made, from the equation

$$A_r = A_s - A_b - A_t$$

In both equations, A_s, A_b and A_t refer to the sample, blank and correction absorbances respectively (see 6.2, 6.3.3 and 6.5).

Read off from the calibration graph (6.3.4) the mass of nitrate, m(N), in micrograms corresponding to the absorbance value A_r.

The nitrate content in the sample, ϱ_N, in milligrams per litre, is given by the formula

$$\frac{m(N)}{V}$$

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

Table 1 — Conversion table

Nitrate	$c(NO_3)$	ϱ_{NO_3}	ϱ_N
	mmol/l	mg/l	mg/l
$c(NO_3)$ = 1 mmol/l	1	62	14,01
ϱ_{NO_3} = 1 mg/l	0,016 1	1	0,226
ϱ_N = 1 mg/l	0,071 4	4,427	1

Example :

ϱ_{NO_3} = 1 mg/l corresponds to ϱ_N = 0,226 mg/l.

7.2 Repeatability and reproducibility[1)]

Standard deviations of repeatability and reproducibility are shown in table 2.

8 Test report

The test report shall include the following information :

a) a reference to this part of ISO 7890;

b) precise identification of the sample;

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

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

e) the result, expressed as ϱ_N in milligrams per litre, or as ϱ_{NO_3} in milligrams per litre or as $c(NO_3)$ in millimoles per litre;

f) any deviation from the standard procedure or any other circumstances that may have affected the result.

Table 2 — Standard deviation of repeatability and reproducibility

Sample	Nitrate content ϱ_N	Test portion volume	Standard deviation*) Repeatability	ϱ_N Reproducibility
	mg/l	ml	mg/l	mg/l
Standard solution (blank)	0,00	25	0,001 to 0,005	———
Standard solution	0,20	25	0,003 to 0,011	0,005 to 0,011
River water	4,40	1,0	0,07 to 0,22	0,07 to 0,48
River water	9,18	0,5	0,13 to 0,54	0,16 to 0,98
River water	10,0	0,5	0,06 to 0,09	0,06 to 0,12

*) The highest and lowest values from the exercise. All values have 9 degrees of freedom.

1) Information derived from a United Kingdom interlaboratory test involving four participants.

Annex A
(normative)

The effect of other substances on this method[1)]

Other substance (expressed in terms of substance in brackets)	Amount of other substance in a 25 ml test portion	Effect in µg N of other substance in a 25 ml test portion	
	µg	m(N) = 0,00 µg µg	m(N) = 5,00 µg µg
Sodium chloride (Cl^-)	10 000	+0,03	−0,73
Sodium chloride (Cl^-)	2 000	+0,01	−0,16
Sodium hydrogen carbonate (HCO_3^-)	10 000	−0,02	−0,52
Sodium hydrogen carbonate (HCO_3^-)	2 000	−0,03	−0,18
Sodium sulfate (SO_4^{2-})	10 000	+0,04	+0,16
Sodium orthophosphate (PO_4^{3-})	1 000	+0,30	−0,73
Sodium orthophosphate (PO_4^{3-})	100	+0,11	+0,17
Sodium silicate (SiO_2)	250	+0,15	+0,30
Calcium chloride (Ca)	5 000	+0,23	+0,38
Calcium chloride (Ca)	2 500	+0,02	−0,14
Magnesium acetate (Mg)	5 000	+0,14	+0,29
Magnesium acetate (Mg)	2 500	−0,05	+0,12
Iron(III) sulfate (Fe)	20	+0,08	−0,02
Manganese(II) sulfate (Mn)	20	+0,92	+0,99
Manganese(II) sulfate (Mn)	5	+0,05	+0,13
Zinc sulfate (Zn)	20	−0,02	+0,07
Copper sulfate (Cu)	20	+0,03	+0,19
Lead acetate (Pb)	20	+0,02	+0,07
Aluminium sulfate (Al)	20	0,00	−0,02
Potassium fluoride (F^-)	20	−0,07	−0,06
Ammonium chloride (NH_3 as N)	500	−0,12	−0,17
Potassium cyanide (CN)	20	+0,15	+0,01
Urea [$CO(NH_2)_2$]	50	+0,04	+0,13

If the other substance did not interfere, the effects expected (95 %) would be

± 0,16 at m(N) = 0,00 µg

± 0,20 at m(N) = 5,00 µg

1) Data from the United Kingdom.