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# International Standard



# 7890/2

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## Water quality — Determination of nitrate — Part 2: 4-Fluorophenol spectrometric method after distillation

*Qualité de l'eau — Dosage des nitrates — Partie 2: Méthode spectrométrique au fluoro-4 phénol après distillation*

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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.

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 7890/2 was prepared by Technical Committee ISO/TC 147, *Water quality*.

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

# Water quality — Determination of nitrate — Part 2: 4-Fluorophenol spectrometric method after distillation

## 1 Scope and field of application

### 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

This method is applicable to the analysis of all types of water, but is particularly intended for polluted waters and saline waters.

### 1.3 Range

Up to a nitrate nitrogen content of  $\varrho_N = 45$  mg/l using a 5 ml test portion, and a cell of path length 10 mm. This range may be modified by using different test portion volumes and cell path lengths. (See clause 8.)

### 1.4 Limit of detection

A nitrate nitrogen content of  $\varrho_N = 0,22$  mg/l.

### 1.5 Sensitivity

A nitrate nitrogen content of  $\varrho_N = 45$  mg/l gives an absorbance of about 1,4 units in a cell of path length 10 mm.

### 1.6 Interferences

Potential interferences from nitrite and chloride are removed by the addition of amidosulfonic acid and tin(IV) sulfate respectively. Certain substances, for example nitrophenols, may distil over and colour the distillate. No other interferences are known.

## 2 Principle

Reaction of nitrate with 4-fluorophenol in acid solution to produce 2-nitro-4-fluorophenol. Recovery of this compound from the reaction mixture by steam distillation into sodium hydroxide solution. Spectrometric measurement of the absorbance of this distillate at 430 nm and reading of the nitrate concentration in the test portion from a calibration graph. Alternatively, extraction of the compound into toluene and then back-extraction into sodium sulfite solution prior to measurement of the absorbance.

## 3 Reagents

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

### 3.1 Toluene ( $\text{CH}_3\text{C}_6\text{H}_5$ ).

**WARNING — Toluene is highly flammable and harmful by inhalation. Avoid breathing vapour, or contact with skin and eyes. Keep away from sources of ignition.**

### 3.2 Amidosulfonic acid mixture.

Using a mortar and pestle, grind together  $46 \pm 0,5$  g of sodium sulfate ( $\text{Na}_2\text{SO}_4$ ),  $1,5 \pm 0,1$  g of sodium chloride ( $\text{NaCl}$ ) and  $2,5 \pm 0,1$  g of amidosulfonic acid ( $\text{NH}_2\text{SO}_3\text{H}$ ). Mix thoroughly.

Store in a damp-proof container.

### 3.3 Sulfuric acid solution, $\varrho = 1,74$ g/ml.

**WARNING — When using this acid solution, eye protection and protective clothing are essential. The solution should never be pipetted by mouth.**

Place  $250 \pm 5$  ml of water in a 2 litre glass beaker. Gradually and cautiously add  $750 \pm 10$  ml of sulfuric acid ( $\varrho = 1,84$  g/ml) to the water, with continual stirring and cooling. Cool to room temperature.

Store in a glass-stoppered bottle.

### 3.4 Tin(IV) sulfate, stock solution.

Place  $70 \pm 2$  ml of water in a 500 ml glass beaker. Gradually and cautiously add  $300 \pm 5$  ml of sulfuric acid ( $\varrho = 1,84$  g/ml) to the water, with continual stirring and cooling. After cooling to room temperature, add  $60 \pm 0,5$  g of tin(II) sulfate ( $\text{SnSO}_4$ ) to the mixture, and dissolve. Then add, in small portions and with continual stirring,  $30 \pm 1$  ml of 300 g/l hydrogen peroxide solution. After all the hydrogen peroxide has been added, heat the mixture to the boiling point in order to destroy excess hydrogen peroxide. Cool the solution to room temperature.

Store in a glass-stoppered bottle.

Although complete dissolution may not be achieved, the presence of a small amount of sediment in this reagent can be tolerated. Filtration is not necessary.

### 3.5 Tin(IV) sulfate, solution P.

Dilute  $50 \pm 1$  ml of tin(IV) sulfate stock solution (3.4) to 1 litre with sulfuric acid (3.3) in a measuring cylinder.

### 3.6 Tin(IV) sulfate, solution Q.

Dilute  $100 \pm 1$  ml of tin(IV) sulfate stock solution (3.4) to 1 litre with sulfuric acid solution (3.3) in a measuring cylinder.

### 3.7 Tin(IV) sulfate, solution R.

Dilute  $200 \pm 2$  ml of tin(IV) sulfate stock solution (3.4) to 1 litre with sulfuric acid solution (3.3) in a measuring cylinder.

### 3.8 4-Fluorophenol, 112 g/l solution in 1,4-dioxacyclohexane.

**WARNING — 4-Fluorophenol is an irritant. Skin contact with it and solutions containing it shall be avoided. 1,4-Dioxacyclohexane is highly flammable, harmful by inhalation, and may form explosive peroxides. Avoid breathing its vapour.**

Dissolve  $11,2 \pm 0,1$  g of 4-fluorophenol ( $\text{FC}_6\text{H}_4\text{OH}$ ) in  $100 \pm 2$  ml of 1,4-dioxacyclohexane ( $\text{C}_4\text{H}_8\text{O}_2$ ) (peroxide-free).

Store in a glass-stoppered bottle.

### 3.9 Sodium hydroxide solution, about 8 mol/l.

Dissolve  $160 \pm 1$  g of sodium hydroxide in  $500 \pm 5$  ml of water. Cool the solution to room temperature.

Store in a polyethylene bottle.

### 3.10 Sodium sulfite solution, 160 g/l.

Dissolve  $40 \pm 0,5$  g of sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) in  $250 \pm 2$  ml of water.

Store in a glass-stoppered bottle.

### 3.11 Sodium sulfite, alkaline solution.

Mix  $250 \pm 2$  ml of sodium hydroxide solution (3.9) and  $125 \pm 2$  ml of sodium sulfite solution (3.10) and dilute to 500 ml with water in a measuring cylinder.

Store in a polyethylene bottle.

### 3.12 Sodium sulfite, diluted alkaline solution.

Dilute  $200 \pm 2$  ml alkaline sodium sulfite solution (3.11) to 1 litre with water in a measuring cylinder.

Store in a glass-stoppered bottle.

### 3.13 Sodium hydrogen sulfate solution, $c(\text{HSO}_4^-) \approx 0,5$ mol/l.

Dissolve  $69 \pm 0,5$  g of sodium hydrogen sulfate monohydrate ( $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ ) in  $1000 \pm 10$  ml of water.

Store in a glass-stoppered bottle.

### 3.14 Nitrate, stock solution, $\varrho_{\text{N}} = 1000$ mg/l.

Dissolve  $7,218 \pm 0,001$  g of potassium nitrate ( $\text{KNO}_3$ ) (previously dried at  $105^\circ\text{C}$  for at least 2 h) in about 750 ml of water in a 1000 ml one-mark volumetric flask. Make up to the mark with water.

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

### 3.15 Nitrate, standard solution, $\varrho_{\text{N}} = 100$ mg/l.

Pipette 50 ml of the nitrate stock solution (3.14) into a 500 ml one-mark volumetric flask. Make up to the mark with water.

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

## 4 Apparatus

**4.1 Spectrometer**, capable of operating at a wavelength of 430 nm and equipped with cells of path length 10 mm.

**4.2 Water-bath**, capable of accommodating 100 ml conical flasks.

**4.3 Apparatus for steam distillation.**

**4.4 Conical flasks**, capacity 100 ml, preferably suitable for direct connection to the steam distillation apparatus.

**4.5 Separating funnels**, capacity 250 ml.

## 5 Sampling and samples

Laboratory samples should be collected in glass or polyethylene bottles and should be analysed as soon as possible after collection. Storage of samples at between  $2$  and  $5^\circ\text{C}$  may preserve many types of sample, but checks should be made to confirm this with each sample type.

Laboratory samples containing suspended matter should be allowed to settle, or filtered through a glass fibre paper, before taking the test portion.

## 6 Procedure

### 6.1 Test portion

Pipette 5 ml of the laboratory sample (clause 5).

### 6.2 Blank test

Carry out a blank test in parallel with the determination, using 5 ml of water instead of the test portion.

### 6.3 Calibration

#### 6.3.1 Preparation of the set of calibration solutions

Into a series of six 100 ml one-mark volumetric flasks add, by pipette, 2; 10; 20; 30; 40; and 45 ml of nitrate standard solution (3.15). Make up to the mark with water. These solutions contain 2; 10; 20; 30; 40; and 45 mg of nitrate nitrogen per litre respectively.

Store these solutions in glass bottles for not more than 1 week.

#### 6.3.2 Colour development

Pipette 5 ml of each of the calibration solutions into a series of six dry 100 ml conical flasks. Add to each by pipette (using a safety filler) 1 ml of sulfuric acid (3.3). Then add  $1,0 \pm 0,1$  g of amidosulfonic acid mixture (3.2) and shake the flask until the mixture has dissolved. Heat the flask on a water-bath at  $70$  to  $80$  °C for  $15 \pm 2$  min.

Remove the flask from the water-bath and add  $40 \pm 1$  ml of tin(IV) sulfate solution P, Q or R (3.5, 3.6 or 3.7), as appropriate to the known or expected chloride concentration of the sample (see table 1). Shake the mixture and cool to room temperature.

Add by pipette (using a safety filler) 2 ml of 4-fluorophenol (3.8) and shake the flask vigorously. Allow the mixture to stand for at least 1 h and then quantitatively transfer the flask contents to the steam distillation apparatus, using two 5 ml portions of sulfuric acid (3.3) to rinse the flask.

NOTE — If the conical flask is suitable for direct connection to the steam distillation apparatus, it will not be necessary to transfer the flask contents.

Table 1

Tin(IV) sulfate solution	Known or expected chloride contents
	mg/l
P (3.5)	$\varrho_{\text{Cl}} < 7\,000$
Q (3.6)	$7\,000 \leq \varrho_{\text{Cl}} < 14\,000$
R (3.7)	$14\,000 \leq \varrho_{\text{Cl}} < 28\,000$

Place  $20 \pm 1$  ml of alkaline sodium sulfite solution (3.11) in a 100 ml graduated flask (receiver) and dip the discharging tube from the condenser of the distillation apparatus below the level of this solution. Admit steam to the apparatus and distil until

the volume of liquid in the receiver is about 90 ml. Then stop the steam supply. Remove the receiver from the discharging tube and rinse the outside of the tube with a little water into the receiver. Make the receiver contents up to the mark with water.

#### 6.3.3 Spectrometric measurements

Shake the flask vigorously and then measure the absorbance of the solution at 430 nm in a cell of path length 10 mm, against water as reference.

#### 6.3.4 Plotting the calibration graph

Subtract the absorbance of the blank test (6.2) from the absorbances of the calibration solutions and plot a graph of absorbance against concentration, expressed in milligrams per litre, of nitrate nitrogen. This graph should be linear and should pass through the origin.

### 6.4 Determination

Proceed as in 6.3.2 and 6.3.3, using one 100 ml conical flask and the test portion (6.1) instead of the calibration solutions.

## 7 Expression of results

### 7.1 Calculation

The absorbance,  $A_0$ , due to nitrate nitrogen in the test portion is given by the equation

$$A_0 = A_1 - A_2$$

where

$A_1$  is the absorbance of the test portion (6.4);

$A_2$  is the absorbance of the blank (6.2).

Read off from the calibration graph (6.3.4) the nitrate concentration,  $\varrho_{\text{N}}$ , expressed in milligrams per litre, corresponding to the absorbance,  $A_0$ .

The result may be expressed in various ways (see table 2).

Table 2

	$c(\text{NO}_3^-)$ mmol/l	$\varrho_{\text{NO}_3^-}$ mg/l	$\varrho_{\text{N}}$ mg/l
$c(\text{NO}_3^-) = 1$ mmol/l	1	62	14,01
$\varrho_{\text{NO}_3^-} = 1$ mg/l	0,016 1	1	0,226
$\varrho_{\text{N}} = 1$ mg/l	0,071 4	4,427	1

Example:

A nitrate ion concentration,  $\varrho_{\text{NO}_3^-}$ , of 1 mg/l corresponds to a nitrate nitrogen concentration,  $\varrho_{\text{N}}$ , of 0,226 mg/l.

## 7.2 Precision

### 7.2.1 Repeatability

The repeatability standard deviation for the determination<sup>1)</sup> of  $\varrho_N = 44,7$  mg/l was 0,26 (13 degrees of freedom).

### 7.2.2 Reproducibility

Reproducibility standard deviations have been determined<sup>1)</sup> in an interlaboratory exercise as shown in table 3.

Table 3

Sample	Nitrate content, $\varrho_N$	Total standard deviation	Degrees of freedom
	mg/l	mg/l	
Potable water	2,6	0,37	7
Ground water	5,8	0,39	5
Surface water	10,2	0,88	5
Sewage effluent	15,9	1,18	6

## 8 Special cases

The range of application of the method can be varied by use of different test portion volumes and spectrometric cell path lengths as shown in table 4.

Table 4

Modified range of application	Test portion volume	Cell path length
mg/l	ml	mm
$\varrho_N < 2$	10	40 or 50
$\varrho_N < 120$	2	10

In both cases, the procedure remains as specified in clause 6 except for the modification of the test portion volume and cell path length. Calibration should be carried out using at least six calibration solutions evenly spaced in the chosen range of application. These calibration solutions should be prepared from the nitrate standard solution (3.15) or the nitrate stock solution (3.14), as convenient.

## 9 Notes on procedure

As an alternative to steam distillation, the following extraction procedure can be used.

Follow the determination (6.4) to the addition of 4-fluorophenol solution. Shake the flask vigorously. Allow the mixture to stand for at least 1 h and then quantitatively transfer the flask contents to a 250 ml separating funnel, using two 5 ml portions of sulfuric acid (3.3) to rinse the flask. Add  $10 \pm 1$  ml of toluene (3.1) to the separating funnel and shake for  $5 \pm 1$  min. Allow the phases to separate and discard the lower aqueous layer.

Add  $20 \pm 1$  ml of sodium hydrogen sulfate solution (3.13) and shake gently for about 1 min. Discard the lower, aqueous, layer and add by pipette 100 ml of diluted alkaline sodium sulfite solution (3.12). Shake the separating funnel for  $5 \pm 1$  min and allow the phases to separate.

Measure the absorbance of the lower, aqueous, layer.

The blank test and calibration procedures are carried out in the same manner.

A fivefold increase in sensitivity of the method may be obtained by using 20 ml of diluted alkaline sodium sulfite solution for the final extraction.

## 10 Test report

The test report shall contain the following information:

- a reference to this part of ISO 7890;
- precise identification of the sample;
- details of the storage of the laboratory sample before analysis;
- a statement of the repeatability achieved by the laboratory when using this method;
- the result, in terms of  $\varrho_N$ , expressed in milligrams per litre, or  $\varrho_{NO_3^-}$ , expressed in milligrams per litre, or  $c(NO_3^-)$ , expressed in millimoles per litre;
- any deviation from the standard procedure or any other circumstance that may have affected the result.

1) Data from the Federal Republic of Germany.

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