

METHOD FOR NITRATE DETERMINATION IN WATER IN THE PRESENCE OF NITRITE

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Abstract. The study relates to determination of nitrate in presence of nitrite in water and can be used in the quality monitoring of natural water (surface and groundwater), drinking water, water from fish farms and public aquaria where autonomous filters is used. The nature and quantity of reagents used have insignificant impact on natural waters and sewages. According to the investigation, the method includes the removal of nitrite from the solution/water with sulfaminic acid, the nitrate ion reduction to nitrite using a reducing mixture that contains Na₂SO₄ and zinc dust in ratio of 100:5 and determining the nitrite with the Griess reagent.

Keywords: water, nitrate determination, nitrites, sulfaminic acid, Griess reagent, reducing mixture.

Introduction

Water quality in wells and often in centralized distribution systems, almost on all over the country territory don't correspond to the standard for drinking water even after nitrate content. Analysis of groundwater quality monitoring results conducted by the Agency for Geology and Mineral Resources of the Republic of Moldova (AGRM) shows that the most artesian water contains ammonium ions, nitrate and nitrite in considerable amounts, sometimes exceeding the maximum allowable concentration (MAC) for drinking purposes. In Ialoveni district, for example, about 32% of the wells contain 69-280 mg/dm³ NO₃⁻ [1].

The process of nitrification in natural waters has mandatory stage the appearance of nitrite content of which in surface waters in Moldova ranges from 0-0.4 mg/dm³ to tens of mg/dm³ in small rivers water downstream of sewage discharges, insufficiently treated in biological purification plants type. During of 2002-2004 years, in the river Bac downstream of Chisinau city it was registered 1.2 -16.8 mg/dm³ NO₂⁻; in river Lunga (village Lunga) - of 3.6 till 12.6 mg/dm³ NO₂⁻ and nitrates content ranged from 0.8 to 18.7 mg/dm³ [2].

Thus the assessment of nitrate and nitrite content (NO₃⁻ in the presence of NO₂⁻) in the aquatic medium, performed by analytical services for monitoring of natural, drinking, waste waters, food and soil is of real importance.

This highlights the necessity to develop the simple methods for determining nitrate in presence of nitrite in water and to identify those which are not presented in the normatives for drinking water.

Experimental

Apparatus

Visible spectrophotometer (Model HACH) with 2 cm matching cells was used for the absorbance measurements. A pH-ionometer I-120.1 was used for pH measure.

Reagents and Solutions

All chemicals used were of analytical reagent grade, and double distilled water was used in the preparation of all solutions for the experiments.

Nitrite solution (20 mg/cm³) was prepared by dissolving 3.0 g sodium nitrite in water and diluting to 100 cm³. Nitrate solution (1000 mg/dm³) was prepared by dissolving 1.371 g sodium nitrate in water and diluting to 1000 cm³. Working standard nitrate solutions were prepared by appropriate dilution. Sulfaminic acid solution was used of 3 mg/cm³ (0.3 g in 100 cm³) and Griess reactive – of 3% (3g in 100 cm³). To adjust the value of pH the solutions of HCl and NaOH (0.1 mol/dm³) were used.

Results and discussion

Allowable levels for drinking water, which are binding in the Republic of Moldova by Government Decision no. 934 of 15.08.2007 is of 50 mg/dm³ for nitrate and 0.5 mg/dm³ for nitrite. Thus the problem of nitrate and nitrite monitoring in waters intended for human consumption (drinking water, water for foods preparation etc.) is in attention of specialized institutions [3].

There are various methods for nitrate and nitrite determining, including spectrometric, fluorometric, luminescent, electrophoretic, electrochemical and chromatographic.

To determine nitrites it is widely used the photometric method with Griess reagent proposed in 1879 year [4] with sensitivity of 0.001 mmol/dm³. The sensitivity, simplicity of the method, the accessibility of Griess reagent permits to use them for nitrate determination after its reduction to nitrite, but it is necessary to remove nitrites present in the water/solution.

There is also the method for the determination of NO₃⁻ ions with sulfosalicylic acid, but the process is influenced by the presence of more than 2 mg/dm³ of nitrites and consists of several steps which hinder the analytical work (boiling, evaporation, dissolving the shift quantity of the solution in the other vessel, etc.) [5].

Determination of nitrates may be carried out also by reaction with diphenylamine, but in the presence of nitrite method can not be applied, since they formed with diphenylamine colour compound [6].

Widely for nitrate determination there are used methods based on the principle of nitrate to nitrite preventive reduction, those latter being determined by Griess reaction. The reduction NO₃⁻ → NO₂⁻ is carried out by cadmium column [7-9], vanadium compounds (+3 and +4) [10], zinc and manganese sulphate [11, 12]. In all cases nitrites influence the process. Since the determination of nitrate in the presence of nitrites has limitations [13], it has been proposed solution to remove preventative nitrite with sodium azide in the reduction system Zn-Fe (III)-Ferozin (sodium salt of p, p'-disulphonic hydrate, 3 - (2-pyridyl) -5,6-diphenyl-1,2,4-triazine acid) [14].

Determination of nitrate in presence of nitrite using the existing methods has the following disadvantages:

- For analysis of several samples of water, there are required simultaneously multiple columns with cadmium. A large amount of metallic Cd and cadmium column passes through several stages of preparation (Cd metal preparation, washing the column before and after the reduction of NO₃⁻ ions), that takes time. Cadmium is a relatively non-specific reductant and methods of its utilization are inefficient at lower concentrations of nitrate [15].

- Cadmium is a toxic element with a low limit of exhaust in wastewater treatment system and the environment (0.1 mg/dm³). In some countries, the production and cross-border movement of cadmium and its compounds are prohibited by law.

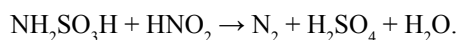
- In the case of vanadium, its compounds (+3 and +4 forms) are reduced by magnesium metal in an acid medium, and the solution is kept under argon, into the same flask.

- Vanadium is included in the families and groups of substances which have a deleterious effect on the aquatic medium [16].

- The disadvantage of the process of nitrite removal with sodium azide is that the reagent is toxic, including discharge into the natural water and sodium salt of p, p' - disulphonic acid hydrate 3 - (2- pyridyl) -5.6 – diphenyl - 1,2,4 - triazine acid is a shortage reagent and it is not known impact on the environment.

Pre-treatment of water with sulfaminic acid (ASA) allows the removal of the nitrite and nitrosating agents before nitrates determination after their reduction to nitrite [5, 17].

Sulfaminic acid reacts with nitrite and forms free nitrogen, water and sulphuric acid:



The advantage of sulfaminic acid using consists in economy, efficiency and ease of use.

In the passport of Security according Document 1907/2006/EC, art. 31(24/09/2013, version 3) it is mentioned that sulfaminic acid has insignificant effect in waste water canalization.

There are international standard methods taken by the Republic of Moldova for separate nitrates and nitrites determination in the water [18, 19]. But it is missing the standard for determining of nitrate in presence of nitrite.

The purpose of the present study is to develop a simple method for determination of nitrate in the presence of nitrite in aqueous solutions and natural waters using a reducing mixture Na₂SO₄:Zn, Griess reagent and sulfaminic acid.

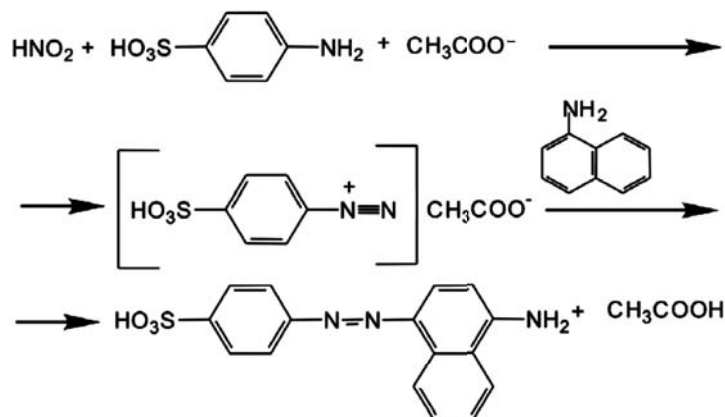
The most appropriate method to determine nitrates in the presence of nitrites is the process for removal of nitrite from the solution/water using sulfaminic acid [5] and the process of nitrate to nitrite reduction with a reducing mixture MnSO₄:Zn = 100:2 and determination of formed NO₂⁻ ions with Griess reagent [12]. The disadvantage of the method is the use of MnSO₄ (300 mg for a sample), which is more expensive, and Mn²⁺ has a low permissible content to discharge into canalization system (1 mg/dm³) and the environment.

Sodium sulphate, proposed as reducing mixture component Na₂SO₄:Zn = 100:5, is used in amounts of 2.5 times lower (120 mg for a sample) as MnSO₄, which is about two times cheaper and has a much higher discharge into waste water system or the environment (200 mg/dm³).

The process is characterised by simplicity, given the opportunity to perform simultaneous analysis of large numbers of samples, using efficient and accessible reagents that have a minimal negative effect on wastewater treatment technology and the environment to their discharge into drains and the environment. Zinc dust, which is not consumed in the reaction, is collected, washed with distilled water, dried and subsequently used for obtaining the reducing mixture Na₂SO₄: Zn.

The process consists in nitrite removal from natural waters and aqueous solutions to free nitrogen (N₂) by ASA (NH₂SO₃H + HNO₂ → H₂O + N₂ + H₂SO₄), reduction of nitrate to nitrite with a mixture consisting of sodium sulphate and zinc powder in ratio of components Na₂SO₄:Zn = 100:5. The chemistry of the reaction is in the process of reducing

of nitrates $Zn + NO_3^- = NO_2^- + Zn^{2+}$ (1 mg NO_3^- is reduced by 1.08 mg of metallic Zn). The reduction of nitrates from 10 cm³ water/solution with concentration of 0.2-10 mg/dm³ consumed about 0.005-0.1 mg of zinc. Nitrite formed in the reaction is determined by Griess reagent widely used in the present and enough sensitive for routine use:



To establish the conditions for removal of nitrite it was estimated the quantity of sulfaminic acid, the time and the value of pH necessary for nitrite transformation to free nitrogen. In order to elucidate the conditions for reduction of nitrates in water it was evaluated the quantity of reducing mixture, the time of there contact with nitrate ions and those for formed nitrite with Griess reagent.

The results indicate that the removal of nitrite from sulfaminic acid solution takes place during of 25-30 minutes (Figure 1).

Obtained data reveal that 3 mg of sulfaminic acid remove nitrite in solution containing of 20 mg/dm³ NO_2^- (Figure 2).

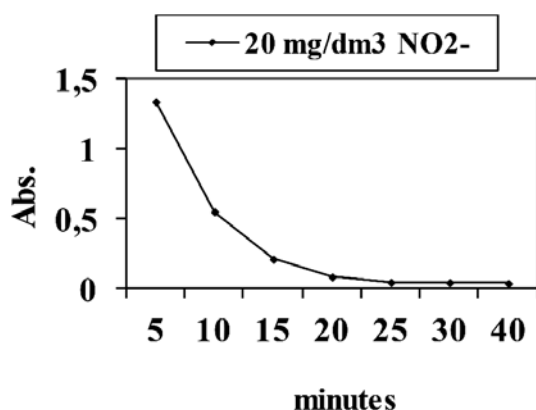


Figure 1. The amount of NO_2^- ion oxidation with sulfaminic acid by adding reduction mixture Na_2SO_4 ; Zn = 100:5.

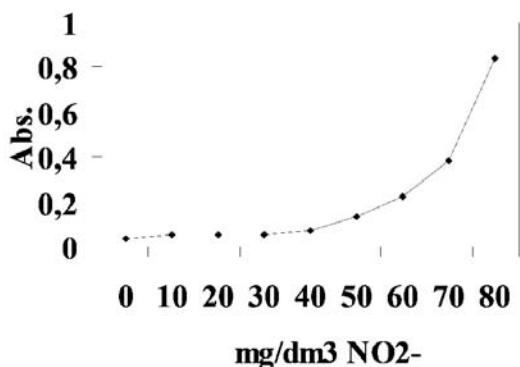


Figure 2. The absorbance of the solution containing 20 mg/dm³ of NO_2^- contacted with 3 mg of ASA in the conditions of NO_3^- ions determination.

Thus, by adding 3 mg of sulfaminic acid, to 10 cm³ of solution, it can be determined nitrate (less 10 mg/dm³) in the presence of nitrites (less 20 mg/dm³).

The effect of nitrate to nitrite reduction is optimal by using 120 mg of reduction mixture for one sample (Figure 3). The effect of nitrite removal from solution before nitrates determination is optimal at pH 1-2.5 (Figure 4). The results show that reduction mixture (120 mg) convert nitrate to nitrite in the solution during of 10 minutes (Figure 5).

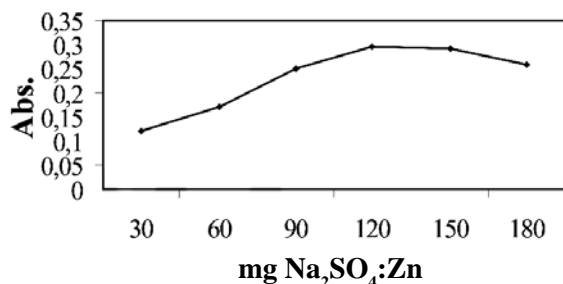


Figure 3. The absorbance of solutions containing 20 mg/dm³ of NO₂⁻ and 2 mg/dm³ of NO₃⁻ ions contacted with 3 mg of sulfaminic acid in function on the amount of reduction mixture.

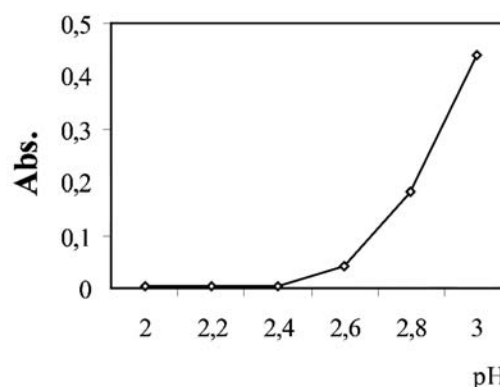


Figure 4. Solutions absorbance with contain nitrites (20 mg/dm³) and sulfaminic acid (3 mg) in dependence on the pH.

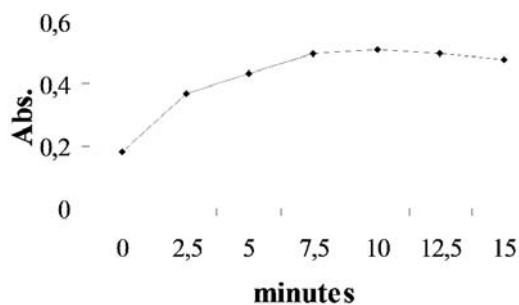


Figure 5. Time dependence of absorbance for NO₃⁻ ions reduction with mixture Na₂SO₄:Zn = 100:5 in the presence of nitrite and ASA.

So, it was obtained the following method for nitrate determination in presence of nitrite.

The method for nitrate determination in presence of nitrite

In the calibrated flask of 10 cm³, an aliquot of solution for analysis is used (0.1-10 mg/dm³ of NO₃⁻ and not more than 20 mg/dm³ of NO₂⁻), then 0.3 cm³ of sulfaminic acid solution with a concentration of 10000 mg/dm³ (3 mg/sample) is added. The volume is bringing up to 10 cm³ with distilled water, stirred after each 5 minutes during of 30 minutes (6 times). Then (after 30 minutes) 120 mg of reduction mixture Na₂SO₄:Zn = 100:5 is added and is stirred for 3 times during of 10 min. After the nitrate reduction period (10 min) in the solution is poured 1 cm³ of 3% solution of Griess reagent, 30 minutes later the absorbance of the red solutions is measured at the wavelength of 520 nm. As a comparison it is use a solution containing reagents used properly: to 9.7 cm³ of distilled water, 0.3 cm³ sulfaminic acid and 1 cm³ of 3% Griess reagent to meet stages and time mentioned.

The calibration curve is obtained using a standard solution of NaNO₃ with concentration of NO₃⁻ ions from 0.5 to 10 mg/dm³, adding reagents, and required time following the steps described in the method (Figure 6).

Nitrate and nitrite standard solutions are stored in a refrigerator at 4°C.

Result of the study and novelty criterion consists of the following:

1. In the process of nitrates determination in the presence of nitrites into aqueous solutions and natural waters the sulfaminic acid is used for removal of the nitrites and creation of appropriate pH of the reaction, reduction mixture consisting in chemical available substances (Na₂SO₄ and Zn powder in the ratio of 100:5) for the reduction of nitrates to nitrites and Griess reagents for the determination of formed nitrites.

2. The result of proposed method consists in minimizing of analysis cost and use of efficient reagents which have a minimal negative effect on wastewater treatment technology and the environment as a result of discharge into drains or the environment.

3. The procedure has a sensitivity of 0.1 mg/dm³ NO₃⁻ in the presence of 20 mg/dm³ of NO₂⁻ ions. Relative error of the method is from 0.21 to 1.5% and relative standard deviation - within the limits of 0.2 - 3.0%.

4. The removal of nitrite with ASA ensures the value of pH essential for process, the Na₂SO₄ - stable ionic strength in solutions with the effectiveness determination of nitrate in the presence of nitrite in ratio NO₂⁻ : NO₃⁻ = 20:(0.1-10), by using a reducing mixture Na₂SO₄: Zn = 100:5 and Griess reagent, reagents having a little impact on waste water sewage and the environment.

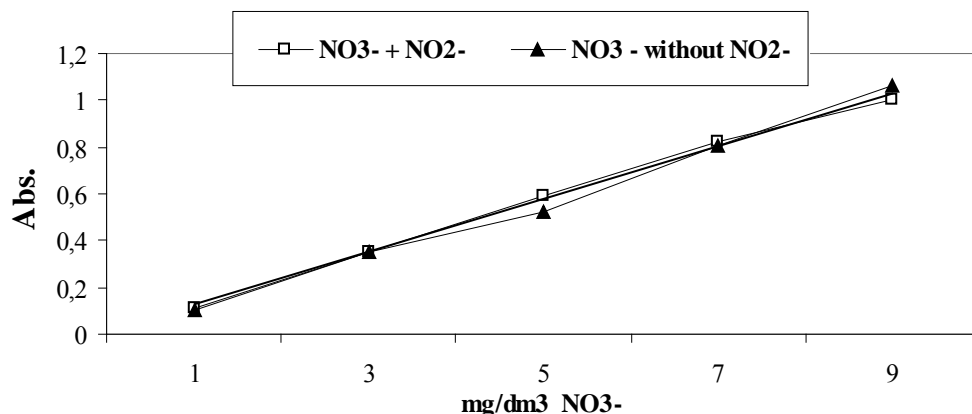


Figure 6. The calibration curve for nitrates determination in the absence ($y = 0.2362x - 0.3748$, $R^2 = 0.9955$) and presence ($y = 0.2249x - 0.3216$, $R^2 = 0.9975$) of nitrites.

The solution which contains 1 mg/dm³ (0.016 mol/dm³) in 2 cm cuvette has a media absorbance of 0.114±0.010 at 520 nm. So the molar extinction coefficient is of 3.56±0.09·10³ (cm⁻¹M⁻¹) and the sensibility of NO₃⁻ determination reaction - of 0.1 mg/dm³, relative standard deviation - within the limits of 0.2 - 3.0%.

A number of ions potentially present in natural, drinking waters, in public aquariums and fish farms do not affect the determination of nitrate in presence of nitrite under the conditions of the present method (Table 1).

Table 1

Ions that not affect nitrate determination in the presence of nitrite.

Ions	The tolerance (mg/dm ³)
Al ³⁺	150
Ba ²⁺	100
Ca ²⁺	300
Cd ²⁺	1000
Cu ²⁺	15
Fe ³⁺	15
K ⁺	2000
Mg ²⁺	350
Mn ²⁺	1000
Na ⁺	2000
Pb ²⁺	20
C ₂ O ₄ ²⁻ (oxalate)	300
CH ₃ COO ⁻ (acetate)	2000
C ₆ H ₅ O ₇ ³⁻ (citrate)	100
C ₄ H ₄ O ₆ ²⁻ (tartrate)	500

Conclusions

The procedure has a sensitivity of 0.1 mg/dm³ NO₃⁻ in the presence of 20 mg/dm³ of NO₂⁻ ions, and allows a large number of analyses simultaneously.

The removal of nitrite with sulfaminic acid is ensured of the value of pH essential for process, the Na₂SO₄ - stable ionic strength in solutions, all reagents having a little impact on waste water sewage and the environment.

Due to the use of zinc dust and Na_2SO_4 it is minimized the cost of the analysis, the level of water pollution from sewage system and the environment, compared to the use of cadmium metal, vanadium and manganese compounds, etc. for nitrates reduction.

The simplicity of the process steps allows of carrying out the analysis of a large number of samples simultaneously, including for evaluation of the error and the standard deviation of nitrate content in the presence of nitrite.

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