Kinetic determination of hydroxylamine in soils by the initial rate method is based upon the reaction of neutral red with the nitrite ion, produced by oxidation of hydroxylamine with iodate in acidic media. The optimal conditions for determination are as follows: 0.3 mol L$^{-1}$ H$_2$SO$_4$, 0.024 mol L$^{-1}$ KIO$_3$, 6.92×10$^{-5}$ mol L$^{-1}$ neutral red. Hydroxylamine can also be determined in mixtures with nitrite ion, if the nitrite content has been found separately at the same conditions without iodate. The calibration graphs are linear in the range (3–27) μmol L$^{-1}$ of NH$_2$OH and (4–46) μmol L$^{-1}$ of NO$_2^-$.

Keywords: hydroxylamine, nitrite ion, kinetic analysis, initial rate method, neutral red, iodate ion, soil analysis.

Introduction

Both hydroxylamine (HA) and nitrite ion act as two important environmental pollutants [1]. Environmental pollution is causing serious health problems for humans, and their quantification is still a big challenge. Hydroxylamine and its derivatives lead to the formation of methemoglobin in man and animals. It induces point mutation by reaction with cytosine, but in the presence of trace metal ions and oxygen it also produces radicals which rapidly inactivate DNA [2]. Nitrite ion is able to react with secondary amines or amides to form nitrosamines which can act as carcinogenic reagents [3]. Hydroxylamine and nitrite recycle through the hydrosphere as a result of microbial processes. These compounds are important intermediates in the biological nitrogen cycle and are present in soils and surface waters [4]. In fact, both are formed during microbial nitrification, where ammonium (NH$_4^+$) is oxidized via NH$_2$OH to NO$_2^-$ and NO$_3^-$ [3].

Methods of separate determination of these substances are numerous. HA and its salts are usually determined by methods based on oxidation or reduction either in acid or in basic solution. Those most frequently employed are volumetric, electrochemical and spectrophotometric methods. A detailed review of literature is presented in [5]. Since then chromatographic methods have been added, both by cation-exchange chromatography [6] and gas chromatography, using the product of the redox reaction, N$_2$O [7]; this method has been successfully used for the determination of HA in soil samples [3]. Various modern methods have been suggested: electrochemical methods include determination of HA by capillary electrophoresis [8], electrocatalytic determination using HA with alizarin red S as a homogeneous mediator [9], voltammetric [10] and biamperometric determination [11].

Spectrophotometry is used as means of HA determination, drawing on redox reactions with various dyes [12]. Thus, various pharmaceutical formulations (after their hydrolysis into HA) have been determined by NH$_2$OH oxidation to nitrite with a known excess of bromine. Bromine in acidic medium bleaches the dye methyl red. A known excess of bromine when treated with HA is reduced to bromide and the unreacted bromine is determined using methyl red [13]. In this case nitrite ion is the product of HA oxidation, which makes it an interfering substance.

Several methods have been reported for determination of HA and nitrite in mixtures. For example, an electrochemical nanosensor using oxadiazole self-assembled on silver nanoparticle-modified glassy
carbon electrode; it has been applied to the determination of HA and nitrite in water samples with acceptable results [1]. In the paper [4] the analytical method is spectrophotometric. First, iodate ion oxidizes HA in acidic media to produce nitrite ions, then nitrite is determined with \(N,N\)-dimethylaniline and \(p\)-nitroaniline followed by micelle-mediated extraction of the produced azo dye (to increase its solubility). The proposed method was applied successfully to the determination of nitrite and HA in well water and urine samples with the relative error of measurement \(\leq 5\%\).

Among others the kinetic method was suggested, based on oxidation of a dye, for which HA is an inhibitor. A simple, precise and accurate method has been suggested by A. Afkhami et al. for rapid determination of trace amounts of HA, based on its oxidation by iodate in acidic media. The reaction of neutral red with the produced nitrite ion was used to monitor the reaction at 525 nm. The reaction rate is limited by nitrite formation from HA, which can be determined in the range of 0.040–1.20 \(\mu\)g mL\(^{-1}\). The developed method was applied to the determination of HA in water samples [14].

Though HA (after it has been oxidized into nitrite ion) and nitrite itself can be determined in mixtures spectrophotometrically, to the best of our knowledge, no kinetic method of their simultaneous determination has yet been suggested. There is a need in developing a simple, economical, reproducible, and accurate analytical method for the individual and simultaneous determination of the abovementioned compounds, which would be applicable in environmental researches. The present work deals with kinetic determination of HA, both individually and in mixtures with nitrite ion, in soil analysis.

**Experimental**

Absorption measurements at fixed wavelength were performed using a LEKI SS1207 spectrophotometer. A pH-meter millivoltmeter «EXPERT-pH», a centrifuge ELMI CM-6M, and a thermostat LOIP LT300 were used.

Reagents included the following:

A stock solution of HA 0.03028 mol L\(^{-1}\) was prepared by dissolving 0.0527 g of analytical grade reagent \(\text{NH}_2\text{OH}-\text{HCl}\) in distilled water and diluting to the mark in a 25-mL volumetric flask. Working solutions were prepared by precise diluting in distilled water.

A stock solution of nitrite ion 0.03623 mol L\(^{-1}\) was prepared by dissolving 0.0625 g of analytical grade reagent sodium nitrite \(\text{NaNO}_2\) in distilled water and diluting to the mark in a 25-mL volumetric flask. Working solutions were prepared by precise diluting in distilled water.

A standard solution of iodate ion 0.1000 mol L\(^{-1}\) was prepared by dissolving 2.1401 g of analytical grade reagent potassium iodate \(\text{KIO}_3\) in distilled water and diluting to the mark in a 100-mL volumetric flask.

A standard solution of bromate ion 0.1000 mol L\(^{-1}\) was prepared by dissolving 1.6700 g of analytical grade reagent potassium bromate \(\text{KBrO}_3\) in distilled water and diluting to the mark in a 100-mL volumetric flask.

A standard solution of persulfate ion 0.1000 mol L\(^{-1}\) was prepared by dissolving 2.7033 g of analytical grade reagent potassium persulfate \(\text{K}_2\text{S}_2\text{O}_8\) in distilled water and diluting to the mark in a 100-mL volumetric flask.

A solution of 3.46×10\(^{-4}\) mol L\(^{-1}\) neutral red was prepared by dissolving 0.01 g of neutral red in distilled water and diluting to the mark in a 100-mL volumetric flask.

A 3.0 mol L\(^{-1}\) sulfuric acid solution was prepared by appropriate dilution of concentrated sulfuric acid. This solution was standardized with a solution of sodium tetraborate from a standard titer 0.1000 N with the use of the methyl orange indicator.

The procedure of HA determination was as following. A suitable aliquot of a working solution was transferred into a 10-mL graduated test tube. Then 2.4 mL of 0.1 mol L\(^{-1}\) iodate ion solution was added followed by 1.0 mL of 3.0 mol L\(^{-1}\) sulfuric acid solution. Then 2 mL of 3.46×10\(^{-4}\) mol L\(^{-1}\) neutral red solution was added. The stop clock was started just after the addition of the last drop of neutral red. The solution was diluted with distilled water and a portion of it was transferred into a 1-cm glass cuvette. The absorbance measurement was begun in 1 min, necessary for diluting to the 10-mL mark and transferring the solution into the cuvette. The absorbance change in time was measured in reference to distilled water at wavelength 530 nm. The initial rate was calculated as follows: the linear part of a kinetic curve was identified (approximately 2.5 min), and the least square method was applied to experimental values in that range to get the slope coefficient (the tangent of the slope angle). As curves
showed the decreasing absorbance, tangents were negative. To represent them conveniently, the signs were changed.

The procedure of nitrite ion determination in the presence of iodate ion was the same as the above. The procedure of nitrite ion determination in the absence of iodate ion was as following: a suitable aliquot of a working solution was transferred into a 10-mL graduated test tube. Then 1 mL of 3.0 mol L\(^{-1}\) sulfuric acid solution was added and 2 mL of 3.46×10\(^{-5}\) mol L\(^{-1}\) neutral red solution. The initial rate measurement was the same as for HA determination.

The procedure of soil analysis included sampling: a soil sample was collected at the territory of Garin Park in Chelyabinsk. The sample was passed through a 2-mm sieve. The sample material for test development was put into closed plastic bags and stored in a refrigerator (4 ºC) until the beginning of the experiments. Sample preparation involved extraction according to the method in [3], namely, 4 g of fresh soil was added to a 100-mL conical flask, then 50 mL of distilled water was added. The solution was acidified with 2 mL of 1 mol L\(^{-1}\) hydrochloric acid to pH 2.7, the pH value was monitored by a pH-meter. The extraction was carried out by shaking the suspension for 10 min, then the solution was filtered, and the filtrate was centrifuged at 2000 rpm for 15 min in centrifuge tubes. Then the prepared solution was analyzed for both components by the standard addition method. Determination of nitrite ion was carried out without iodate ion. When iodate was added to the solution, the analytical signal related to the sum of nitrite and HA. The procedures conformed to those described above.

**Results and Discussion**

First of all, the properties of the neutral red have been investigated in order to separate the analytical effects of the analytes and the blank experiment. Neutral red is a diazine dye, a derivative of phenazine. Its structural formula is shown in Fig. 1.

Neutral red has the properties of an acid-base indicator, and it is used in analytical chemistry as such. At various acidic conditions its absorptivity and the maximal absorbance wavelength differ. Therefore, it is necessary to study the absorbance of the blank experiment. Its light absorption spectra in visual range (400–700 nm) at various acidity conditions are presented in Fig. 2a. As neutral red, like many organic dyes, can lose electrons and be oxidized, it is also of interest to study whether the oxidizing agent – potassium iodate that is present in the system – affects the absorption spectra of the neutral red indicator. The spectra are shown in Fig. 2b.

![Fig. 1. The structural formula of neutral red](image)

![Fig. 2. Light absorption spectra of neutral red](image)

\[
a: \text{C(NR) = } 3.46 \times 10^{-5} \text{ mol L}^{-1}; \text{C(H}_2\text{SO}_4) = 1 - 0; 2 - 0.30 \text{ mol L}^{-1}; 3 - 1.50 \text{ mol L}^{-1} \\
b: \text{C(NR) = } 3.46 \times 10^{-5} \text{ mol L}^{-1}; \text{C(H}_2\text{SO}_4) = 0.30 \text{ mol L}^{-1}; \text{C(KIO}_3) = 1 - 0.0025 \text{ mol L}^{-1}; 2 - 0.005 \text{ mol L}^{-1}; 3 - 0.03 \text{ mol L}^{-1}
\]
If the medium is too acidic (1.50 mol L\(^{-1}\) \(\text{H}_2\text{SO}_4\)), the region of the maximal absorbance is shifted from 530 nm to the interval 530–580 nm. However, if the acidity is near the optimum, neutral red remains in the same form as in pure water. The wavelength 530 nm has been taken to be optimal for absorbance measurement. At the chosen concentration of sulfuric acid within the studied range of iodate concentration the dissolved form of neutral red does not react with it, though the absolute absorbance values differ slightly. Actually, it is not of great importance, as the analytical signal in kinetic methods is not the absorbance itself, but the rate at which it changes during a reaction.

Determination of HA occurs in acidic conditions according to the reaction scheme, where iodate ion oxidizes hydroxylamine to form nitrite ion (neutral red then reacts with the produced nitrite [14]):

\[
2\text{IO}_3^- + 3\text{NH}_2\text{OH} \rightarrow 3\text{NO}_2^- + 3\text{H}^+ + 2\Gamma + 3\text{H}_2\text{O}.
\]

In other methods various oxidizing agents are used to oxidize HA, such as ferric salts, ceric salts, vanadate, potassium ferricyanide, bromine, bromate and bromine monochloride, iodine [5]. We studied the oxidizing agents of various nature to choose an optimal one. It appeared that the key process for efficient HA determination by the initial rate method was the stability of the dye itself. For example, we investigated the action of potassium persulfate and potassium bromate on HA and neutral red. Both are very strong oxidizing agents, but they proved not usable in the investigated method, as they both decomposed neutral red, therefore changing the blank experiment. We have chosen iodate ion for experimental study, as in its presence the absorbance of neutral red itself changes so very little that the slope tangent is statistically zero. The control of the blank experiment during our study has shown that its value remains equal to zero within the ranges of all conditions that varied.

Another oxidizing agent that can influence the analytical reaction is gaseous oxygen that diffuses from air to water, therefore it can affect the transformation of HA into nitrite, or perhaps neutral red itself. We compared 2 sets of experimental conditions: first, the solutions were kept in closed test tubes at all times except pipeting, absorbance measurements were taken in closed cuvettes (that is, at controlled conditions, when oxygen concentration was constant). In the second case the measurements were carried out without these precautions, as a consequence the reproducibility of the results suffered. To control the effect of oxygen, we routinely closed test tubes and cuvettes, to get a smoother dependence.

The authors of the paper [14] that used the same reaction of HA oxidation by iodate, preferred to stand the solution for 5 min before adding the neutral red solution, then the measurement began immediately after this. The interval of extra 5 min was used to allow for complete oxidation of HA into nitrite ion. Obviously, it slowed the determination. As we have chosen the initial rate method, we decided to check whether there is a need for additional time of 5 min for oxidation. We compared two sets of experimental conditions: first, according to [14]; second, measurement after mixing all the reactants at once (actually, the absorbance measurement was begun in 1 min, necessary for transferring the solution into the cuvette). The kinetic curves are presented in Fig. 3.

![Fig. 3. Absorbance-time plots for the reaction of neutral red with hydroxylamine](image)
The tangents, calculated by the least square method, are somewhat different: $|\tan \alpha| = 0.0545$ for curve 1, $|\tan \alpha| = 0.0608$ for curve 2. Obviously, the reaction of HA oxidation into nitrite ion runs quicker than the discoloration of neutral red by nitrite ion, which means that even in the initial stages of the process enough nitrite is accumulated to produce the colorless form of neutral red. We have come to the conclusion that it is unnecessary to wait for extra time. Even if HA is not oxidized for 100%, still, the loss of sensitivity is not so great, but the analysis is carried out faster.

Besides the time control, the authors of the paper [14] suggested equilibrating all the reagents in a thermostated water bath at 25 °C before beginning the reaction. Therefore it has been considered necessary to study the effect of temperature. We placed the reactants and the distilled water for diluting into a thermostat, investigating the temperature range (27–50) °C in two-degree steps. In other respects the preparation of solutions for absorbance measurement was the same. As a result, the absolute absorbance values gradually increased with temperature, while the slope coefficients fluctuated about more or less constant value. In Fig. 4 the bounding dependencies are presented. We continued to work at room temperature, without thermostating, because the initial rate method gives more stable results than the fixed time method.

As for nitrite ion, its behaviour is of peculiar interest to us here. Besides being one of the analytes, it is an intermediate product formed by oxidation of the other analyte. Actually, HA does not react with neutral red. It is nitrite ion resulting from the oxidation of HA by iodate ion that reacts with the indicator. However, N(III) can exhibit reducing properties. It has been necessary to examine whether the excess oxidizing agent will affect the analytical signal. The development of neutral red absorbance in the nitrite ion solution without HA, both in the absence and the presence of iodate, is shown in Fig. 5. The kinetic curves overlap, thus the influence of the oxidizing agent on nitrite has not been observed under the studied conditions.

Acidity influences the reaction of HA with iodate producing nitrite ion, and the initial rates of the colour reaction turn out to be somewhat lower than in similar experiments with the equimolar amount of pure nitrite, probably because not all of hydroxylamine turns into nitrite ion before it decolorizes neutral red (the same effect that was observed in Fig. 3). The initial rate values can be seen in Fig. 6.

The authors that previously investigated HA determination by kinetic method [14] suggested thermostating the HA–iodate solution at 25 °C for 5 min before adding neutral red, but we have come to the conclusion that at the same conditions of calibration and analyte measuring the initial rates reproduce well enough even in the case of partial oxidation.

The optimal conditions of determination have also been found for iodate and neutral red. The corresponding initial rates (tgα) dependencies are shown in Fig. 7 and 8, respectively. The concentration of iodate was changed in the range (0.003 – 0.04) mol L⁻¹; the neutral red concentration varied from 2.42×10⁻⁵ mol L⁻¹ to 2.77×10⁻⁴ mol L⁻¹. Blank experiments were studied within the concentration range (1.73×10⁻⁵ – 1.38×10⁻³) mol L⁻¹ of neutral red, the tangents are 0 – 0.003. The difference is within the random error of absorbance measurement.
At low concentrations of iodate the initial rates of the reaction are lower, its amount is obviously not enough to turn hydroxylamine into nitrite completely. At high concentration of iodate the reproducibility of the measuring method suffers. Therefore 0.024 mol L\(^{-1}\) potassium iodate was further used for determination, while the optimal concentration of neutral red solution equals 6.92×10\(^{-5}\) mol L\(^{-1}\), like in [14].

At optimal conditions the calibration graph for HA determination has been plotted. The initial rates of the indicator reaction adhere to linear law from 3×10\(^{-6}\) mol L\(^{-1}\) to 3×10\(^{-5}\) mol L\(^{-1}\) of the analyte. As the neutral red discoloration goes on because of nitrite ion formation from HA, and the study has been aimed at finding both forms of reduced nitrogen in a mixture, the calibration graphs for nitrite ion solution without HA have been plotted alongside this. These concentration dependencies have been graphed both in the absence and in the presence of iodate ion in the solution. The least square method has been used to get the characteristics of the linear plots, which are presented in Table 1.

### Table 1

| Analyte                    | Equation                              | Range (μmol L\(^{-1}\)) | \(r^2\) |
|----------------------------|---------------------------------------|--------------------------|---------|
| Hydroxylamine              | \(Y = (0.0009 \pm 0.0075) + (2040 \pm 440) \cdot X\) | 3.0–27                  | 0.9557  |
| Nitrite (with KIO\(_3\))   | \(Y = (-0.0093 \pm 0.0052) + (3700 \pm 220) \cdot X\) | 2.9–44                  | 0.9966  |
| Nitrite (without KIO\(_3\))| \(Y = (-0.002 \pm 0.014) + (3630 \pm 500) \cdot X\) | 4.3–46                  | 0.9954  |
In order to evaluate the metrological characteristics of HA and nitrite ion determination by the suggested method we analyzed the mixtures of the known amounts of diluted standard solutions. An aliquot of 1 mL of $1.5\times10^{-4}$ mol L$^{-1}$ HA solution was transferred into a 10-mL graduated test tube in 6 replicate aliquots and to each portion an aliquot of 1 mL of $1.45\times10^{-5}$ mol L$^{-1}$ sodium nitrite was added. For the determination of their combined concentration, 2.4 mL of 0.1 mol L$^{-1}$ iodate was added followed by 1 mL of 3.0 mol L$^{-1}$ sulfuric acid solution and 2 mL of $3.46\times10^{-4}$ mol L$^{-1}$ neutral red solution. The measurement of initial rates followed the procedure described in the Experimental section. To determine only the nitrite ion when it was present in the mixture with HA, potassium iodate was not added to test tubes. The procedure described above for analysis in the absence of potassium iodate was applied only the nitrite ion when it was present in the mixture with HA, potassium iodate was not added to test tubes. The procedure described above for analysis in the absence of potassium iodate was applied. Addion of HA was necessary to prove that it did not interfere with the determination of nitrite ion at those conditions. After calculating initial rates we found the concentrations in the analyzed solutions using the linear regression equations. The experiment in the absence of potassium iodate was considered to show the concentration of nitrite ion alone, which was used to calculate the HA concentration by subtracting it from the total amount. Evaluation of metrological characteristics has been carried out on the basis of conventional statistical criteria. The results are shown in Table 2.

Table 2

| $\Delta t_{0}\times10^2$ | $X_i\times10^2$, mol L$^{-1}$ | $X$ | $S$ | $\Delta X$ | $\left(\frac{\Delta X}{X}\right)$ 100% | $\delta$, % |
|-----------------------|-----------------------------|-----|-----|-----------|---------------------------------|--------|
| present in the solution: C(NaNO$_2$) = $1.45\times10^{-5}$ mol L$^{-1}$ | 1.36; 1.40; 1.39; 1.43 | 1.40$\times10^{-5}$ | 3.66$\times10^{-7}$ | 3.84$\times10^{-7}$ | 2.7 | 3.4 |
| present in the solution: C(NH$_3$OH) = $1.51\times10^{-7}$ mol L$^{-1}$ | 1.49; 1.63; 1.46; 1.50 | 1.53$\times10^{-5}$ | 7.86$\times10^{-7}$ | 8.25$\times10^{-7}$ | 5.4 | 1.3 |

It is not surprising that precision is somewhat worse for HA, as well as the characteristics of its calibration graph, as HA determination is indirect.

The studied method was applied for soil analysis, as in the environment both HA and nitrite ion are intermediates in bacterial reduction of nitrate that is present in soils, and both are in evidence when the conditions are reducing. The method of sampling and soil preparation was adapted from [3], which was basically the extraction into acidified water, as both substances are water soluble. The method of standard additions was used for analysis of a soil sample, that is, aliquots of the standard solutions of hydroxylamine and nitrite ion were mixed with the sample. Their specific amounts in the mixture and the results of calculation with the use of kinetic curves are represented in Table 3.

Table 3

| $\Delta t_{0}\times10^2$ | $X_i\times10^2$, mol L$^{-1}$ | $X$ | $S$ | $\Delta X$ | $\left(\frac{\Delta X}{X}\right)$ 100% | $\delta$, % |
|-----------------------|-----------------------------|-----|-----|-----------|---------------------------------|--------|
| added to the sample: C(NaNO$_2$) = $1.45\times10^{-5}$ mol L$^{-1}$ | 1.47; 1.49; 1.52; 1.49; 1.45; 1.46 | 1.48$\times10^{-5}$ | 2.50$\times10^{-7}$ | 2.62$\times10^{-7}$ | 1.8 | 2.1 |
| added to the sample: C(NH$_3$OH) = $1.51\times10^{-7}$ mol L$^{-1}$ | 1.57; 1.62; 1.50; 1.51; 1.59; 1.53 | 1.55$\times10^{-5}$ | 4.80$\times10^{-7}$ | 5.04$\times10^{-7}$ | 3.3 | 2.6 |

In the absence of the HA and nitrite mixture addition, the tangent is approximate to zero, so these components have not been detected in the studied soil sample. On the other hand, after preparation of the soil sample with added HA and nitrite ion, we determined the concentration of nitrite ion as $(1.48 \pm 0.03)\times10^{-5}$ mol L$^{-1}$; the added concentration $1.45\times10^{-5}$ mol L$^{-1}$ is within the confidence interval. The same is true about HA, the determined and added concentrations are $(1.55 \pm 0.05)\times10^{-5}$ mol L$^{-1}$ and $1.51\times10^{-5}$ mol L$^{-1}$, respectively. It means that the suggested method can be used for determination of...
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HA and nitrite ion simultaneously without a systematic error, though the investigated soil sample did not contain them in concentrations above the detection level.

Conclusions
1. The optimal conditions for HA determination by the initial rate method: concentration of neutral red is $6.92\times10^{-5}$ mol L$^{-1}$; iodate is 0.024 mol L$^{-1}$; sulfuric acid is 0.3 mol L$^{-1}$. The calibration curve is linear in the $(3.03\times10^{-5}–3.00\times10^{-5})$ mol L$^{-1}$ range.
2. Nitrite ion can be determined simultaneously with HA, if the described system absorbance is measured without iodate ion addition. The calibration curve is linear in $(4.3\times10^{-6}–4.64\times10^{-5})$ mol L$^{-1}$ range.
3. The method was applied to soil analysis for the content of HA and nitrite ion by the standard addition method. These substances were not found in the soil sample, but the determination of the mixture additions was carried out without a systematic error; the reproducibility error for nitrite ion determination is 1.8 %, while the relative error of accuracy proves to be 2.1%; the reproducibility of the results of HA determination is expressed by the relative error 3.3 %, while the relative error of determination was found to equal 2.6%.

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Кинетическое определение гидроксиламина в почвах методом тангенсов основано на реакции нейтрального красного с нитрит-ионом, получаемым при окислении гидроксиламина иодатом в кислых средах. Оптимальные условия определения: $\text{H}_2\text{SO}_4$ 0,3 М, $\text{KIO}_3$ 0,024 М, нейтральный красный $6.92\times10^{-5}$ М. Гидроксиламин можно также определять в смеси с нитрит-ионом, если найти содержание нитрита по отдельности в тех же условиях, без иодата. Градуировочные графики линейны в диапазоне (3–27) мкмоль/л $\text{NH}_2\text{OH}$ и (4–46) мкмоль/л $\text{NO}_2^-$.

Погрешности воспроизводимости 3,3 % и 1,8 %, относительные погрешности определения – 2,6 % и 2,1 %, для гидроксиламина и нитрит-иона, соответственно.

Ключевые слова: гидроксиламин, нитрит-ион, кинетический анализ, метод тангенсов, нейтральный красный, иодат-ион, анализ почв.

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