МИНИСТЕРСТВО ОБРАЗОВАНИЯ И НАУКИ РОССИЙСКОЙ ФЕДЕРАЦИИ

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Kinetic Determination of Hydroxylamine by Its Reaction with Iodate and Neutral Red

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ABSTRACT

BuskinaK.A. Kinetic Determination of Hydroxylamine by Its Reaction with Iodate and Neutral Red – Chelyabinsk: SUSU, ET-451, 2017. – 49pp., 32fig., 19tables, 18 references.

Hydroxylamine, initial rate method, neutral red, iodate ion, soil analysis.

The aim of the study is kinetic spectrophotometric determination of hydroxylamine based on its reaction with iodate and the consequent oxidation of neutral red.

In order to achieve the research aim the following objectives have been met:

- to compile the literature review in the research area;
- to findthe optimal conditions for determination of hydroxylamine;
- to determine nitrite ion simultaneously with hydroxylamine;
- to findthe metrological characteristics of hydroxylamine in the presence of nitrite ion determination;
- to applythe method to soil analysis for the content of hydroxylamine and nitrite ion by the standard addition method.

Kinetic determination of hydroxylamine by the initial rate method can be 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: 0.3 mol L^{-1} H_2SO_4, 0.024 mol L^{-1} KIO_3, 6.92×10^{-5} mol L^{-1} neutral red. Hydroxylamine can also be determined in the presence of nitrite ion, if the nitrite content is determined separately at the same conditions without iodate. The metrological characteristics are as follows: the reproducibility of the results of hydroxylamine determination is expressed by the relative error 5.4 %, while the relative error of accuracy proves to be 1.3 %; the corresponding values for nitrite determination are 2.7 % and 3.4 %. The method was applied to soil analysis for the content of hydroxylamine and nitrite ion.

CONTENT

INTRODUCTION

Environmentalpollutioniscausingseriushealthproblems for humans, and their quantification is still a big challenge. Hydroxylamine (HA) and nitrite ion act astwo important environmental pollutants [1].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].On the other hand hydroxylamine and its derivatives such as hydroxamic acid and oxime are widely used as anticholinesterase and antitumor agents [3].Hydroxylamine is a short-lived and reactive intermediate in the natural nitrogen cycle. It is formed during microbial nitrification, where ammonium (NH_4^+) is oxidized via HA to nitrite (NO_2^-) and nitrate (NO_3^-) [4].

Nitrite ion is one of the most active intermediary species in the nitrogen cycle and a useful indicator about the equilibrium state of the oxidative and reductive ways of this cycle. It is ubiquitous within environmental, food and physiological systems. Nitrite ion is able to react with secondary amines oramides to form nitrosamines which can act as carcinogenic reagents [4].Nitrite is also a versatile chemical agent that has found numerous applications ranging from dye manufacture to food preservation.

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 [5].

Methods of separate determination of these substances are numerous. Among other techniques the kinetic method was suggested, based on oxidation of a dye, for which hydroxylamine is an inhibitor [6].

In parallel to HA determination, sometimes nitrite ion was determined simultaneously, for example, spectrophotometrically [5], though to the best of our knowledge, no kinetic method of their simultaneously determination was suggested. There is a need in developing a simple, economical, reproducible, and accurate analytical method for the individual and simultaneous determination of the abovementionedcompounds, which would be applicable in environmentalresearches.The present work deals with kinetic determination of hydroxylamine,bothindividually and simultaneously with nitrite ion, in environmental analysis.

1 LITERATURE REVIEW

Quantitative determination of hydroxylamine

Hydroxylamine 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.

Volumetric methods

The most widely used of the classical titrimetric procedures for the determination of hydroxylamine and its salts are those based on redox reactions, generally involving the oxidation of hydroxylamine. The products depend on the oxidizing agent used, but can include nitrogen, nitrous oxide and nitric acid. Oxidation has also been made the basis of a complexometric method.Reducing methods have seldom been used. The volumetric methods are laborious but provide relatively accurate results if the analytical procedures are rigidly adhered to; the relative error isusually within ±1–2 %. They are particularly useful for fairly large (milligram) amounts of hydroxylamine.

The mixture is boiled, and the ferrous iron produced is titrated with standard potassium permanganate solution (Scheme 1.1). Another possibility is to use a mercuric salt in the presence of thiocyanate as titrant for unreacted iron(III).

$$2NH_2OH + 4Fe^{3+} \rightarrow 4Fe^{2+} + 4H^{+} + N_2O + H_2O.$$

Scheme 1.1

An advantage of the method ofoxidation with ceric salts is the good stability and high oxidation potential of ceric sulphate solution (Scheme 1.2). Nitrous oxide and nitrogen were produced, of which 69–73% was nitrous oxide in accordance with the followingreaction [7].

$$2NH_2OH + 4Ce^{4+} \rightarrow 4Fe^{3+} + 4H^{+} + N_2O + H_2O.$$

Scheme 1.2

Ammonium metavanadate acts on an alkaline solution of hydroxylamine to give amixture of NH_3, NO, $N_2O$and N_2. In neutral solution the reaction is slower and N_2O and NH_3 are produced. In acid solution, hydroxylamine is oxidized to N_2O and N_2 nearly quantitatively.

One of the most popular titrimetric methods is the methodthat consists in oxidation of the hydroxylamine with an excess of potassium ferricyanide in a borate buffer and subsequent iodometric titration of the excess of oxidant with a standard thiosulphate or arsenious acid solution (Scheme 1.3) [8].

The method of oxidation with bromine, bromate and bromine monochloride is applicable only to small amounts of hydroxylamine, because nitrogen oxide is also evolved from larger quantities (Scheme 1.4). Better results were obtained by using potassium bromate in hydrochloric acid medium to oxidize the hydroxylamine. This

procedure was employed to determine about 3–12 mg of hydroxylamine hydrochloride with an error of ±0.5 %.

$$2NH_2OH + 2[Fe(CN)_6]^{3-} + 2OH^- \rightarrow N_2 + 2[Fe(CN)_6]^{4-} + 4H_2O,$$
$$2[Fe(CN)_6]^{3-} + 2I^- \rightarrow 2[Fe(CN)_6]^{4-} + I_2,$$
$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-,$$
$$2H_3AsO_3 + 2I_2 + 2H_2O \rightarrow 2H_3AsO_4 + 4I^- + 4H^+.$$

Scheme 1.3

$$NH_2OH + 3BrCl + 2H_2O \rightarrow 3HBr + HNO_3 + 3HCl.$$

Scheme 1.4

A direct method was developed for the determination of hydroxylamine by titration with iodine (Scheme 1.5).

$$2NH_2OH + 2I_2 \rightarrow 4HI + N_2O + H_2O.$$

Scheme 1.5

Decomposition of hydroxylamine, which is unstable in strongly alkaline medium, is minimized by magnesium oxide, which gives only a weak alkaline reaction. The method is rapid and the results are fairly accurate and reproducible. It can be used for determining 5–30 mg of hydroxylamine hydrochloride.

The most widely used reductant for hydroxylamine is titanium(III) in acid solution, with exclusion of air, according to theScheme 1.6.

$$NH_2OH + 2Ti^{3+} + H_2O \rightarrow H^+ + NH_4^+ + 2TiO^{2+}.$$

Scheme 1.6

The excess is titrated with standard permanganate solution. The results from this method are comparable with those obtained by oxidation with ferric salts. It is however, somewhat laborious, as the reaction has to be carried out under an inert atmosphere, and the solution of titanium(III) must be prepared by prior reduction of a titanium(IV)[7].

Determination of hydroxylamine by the complexometric method, consists in oxidizing hydroxylamine with the mercury(II)-EDTA complex in basic medium according to the reaction (Scheme 1.7):

$$2NH_2OH + 2HgY^{2+} + 4OH^- \rightarrow N_2O + 2Y^{4-} + 2Hg + 5H_2O.$$

Scheme 1.7

The EDTA released is titrated with standard lead solution, Methylthymol Blue being used as indicator.This method can also be used for determining hydrazine andphenylhydrazine. Amounts of 10−30 mg may be determined with a relative error within ±1%.

Investigation of the hydroxylamine reaction with arsenic, antimony and bismuth salts has shown that these reagents cannot be utilized for the quantitative determination of hydroxylamine [7].

Electrochemical methods

The electrochemical methods utilize the oxidizing and reducing properties of hydroxylamine. Some are based on reactions exploited in classical volumetric methods.

Coulometricmethod consists in oxidizinghydroxylamine with coulometrically generated bromine. The determination is conducted in a silver coulometer, with potassium bromide solution as electrolyte. Bromine, which oxidizes hydroxylamine to nitric acid, is formed at the anode. The end-point of the reaction is indicated by the brown tint of free bromine, which can then be determined iodometrically.

This method is suitable for the determination of less than 8 mg of hydroxylamine, since larger amounts give rise to significant side-reactions.The relative error doesnot exceed ±1%.

Another method is based on the quantitative reduction of Fe^{3+} to $Fe^{2+}$by hydroxylamine(Scheme 1.8):

$$2NH_2OH + 4Fe^{3+} \rightarrow 4Fe^{2+} + 4H^{+} + N_2O + H_2O.$$

Scheme 1.8

The ferrous ions produced are titrated with electrogenerated ceric ion. The use of an electrolyte solution of ceric sulphate, ferric sulphate and hydrochloric acid at a constant current of suitable magnitude gives results within ±1%.

Chronopotentiometry can be used for determination of hydroxylaminein acidic medium at a platinum anode. A single anodic wave was observed when 1M sulphuric acid was used as the medium, and the transition time corresponded to a six-electron oxidation to nitrate. In any medium the oxidation is inhibited by an oxidized electrode. This method was employed to determine hydroxylamine with a precision of ±1% at concentrations over 1.4 mM. At lower concentrations, the error increased progressively owing to the fact that the electrode surfacebecame oxidized and charged.

Hydroxylamine wasdetermined by potentiometric methods in pyridine-ethyl alcohol medium (1:1), using cupric acetate as titrant at room temp. However, the break at the end-point is not very large, and very accurate results cannot be obtained. The mean relative error for 4−18 mg of hydroxylamine hydrochloride is ±0.5%. Moreover, the determination is inhibited by cyanide, thiocyanate and iodide[7].

Hydroxylamine can also be determined potentiometrically with potassium ferricyanide in 10−25% potassium hydroxide medium. A potential break of about 500mV is obtained at the end-point. For 14−26 mg of hydroxylamine, the error does not exceed 1.4%.

The fast reaction between hydroxylamine and titanium(III) has been the basis of an amperometric method for determining hydroxylamine. The reaction occurs according to the equation (Scheme 1.9).

$$Ti^{3+} + HONH_3^+ \rightarrow Ti^{4+} + NH_2 + (OH^- + H^+).$$

Scheme 1.9

An indirect procedurefor the polarographicdetermination of hydroxylamine is based on the reaction (Scheme 1.10) [7]:

$$NH_2OH + CH_2O \rightarrow H_2C{=}NOH + H_2O.$$

Scheme 1.10

Anodic oxidation of hydroxylamine by cyclic voltammetry showed that the catalytic current of the system dependson the hydroxylamine concentration. The anodic oxidation of hydroxylamine has been studied on a glassy carbon electrode by electrocatalytic effect of Alizarine red S (ARS) as a homogenous mediator in 0.1 M the phosphate buffer (pH 6). The magnitude of the peak current for ARS increased sharply in the presence of hydroxylamine and wasproportional to its concentration.The independency of the system from the interferences and itsability of easily removing the effect of most cationic interferences are the important features of the technique. This electrochemical method for the determination of hydroxylamine, is based on the following sequence of reactions (Scheme 1.11)[9]:

$$ARS_{(aq.red)} \rightarrow ARS_{(aq.ox)},$$

$$2ARS_{(aq.ox)} + 2NH_2OH \rightarrow 2ARS_{(aq.red)} + N_2O + H_2O.$$

Scheme 1.11

A highly dispersed ultramicro palladium-particle modified carbon fiber microdisk array electrode (Pd-CFE) was employed for capillary electrophoresis-electrochemical (CEEC) detection of hydroxylamine. The Pd particles obtained were in the nanometer scale, had a high electrocatalytic activity towards hydroxylamine and exhibited good reproducibility and stability.The applicability of the method for the determination of hydroxylaminein river water and waste water was investigated [10].

Indirect voltammetric determination using magnetic microspheresis based on the reduction of an electroactive derivative of hydroxylamine on the surface of a magnetic electrode.The electroactive derivative produced by hydroxylamine reacted with magnetic polymer microspheres containing carbonyl groupson the surface.The reaction path can be expressed as follows: the microspheres containing carbonyl groups on the surface can react with hydroxylamine to produce oxime compounds which are concentrated on a magnetic electrode. Oxime-groups can be reduced at a silver-based mercury film magnetic electrode. This determination is a highly sensitive and selective procedure [11].

Flow-injection biamperometry is used for the direct determination of hydroxylamine based on coupling two independent and irreversible electrode processes, the oxidation of hydroxylamine and the reduction of platinum oxide. In operation a potential difference of 0 V is imposed between two platinum wire electrodes pretreated by an

anodization step, and the resulting current is measured. Hydroxylamine can be determined in the range of (6×10^{-7}–4×10^{-5}) mol L^{-1} with the detection limit of 1×10^{-7} mol L^{-1}. Nitrogen-containing compounds such as nitrate, nitrite and ammonia that often accompany hydroxylamine in the process of nitrogen cycle do not cause significant interference. The stability of the detector is shown by a relative standard deviation of 1.4% for 50 replicate determinations of 1×10^{-5} mol L^{-1} hydroxylamine [12].

The report[13] describes a cation-exchange chromatographic method coupled with pulsed amperometric detection at a gold electrode for trace analysis of hydroxylamine.It has been successfully applied to waste streams for detection of hydroxylamine generated by a pharmaceutical reaction process.

A new and simple method for the determination of nanomolar NH_2OH by its oxidation to nitrous oxide using hypochlorite as an oxidizing agent was proposed. The N_2O produced in this manner was subsequently measured by using a gas chromatograph with an electron-capture detector (ECD).A glass vial filled with sample water was sealed by a butyl-rubber stopper and aluminum cap without head-space, and then sodium hypochlorite solution was injected into the vial through a syringe to convert hydroxylamine to nitrous oxide. The head-space in the glass vial was prepared with 99.9% grade N_2 using a gas-tight syringe. After the glass vial was shaken for a few minutes, nitrous oxide in the gas-phase was measured by a gas chromatograph with an electron-capture detector. The oxidation of NH_2OH to N_2O by hypochlorite was found to proceed stoichiometrically as Scheme 1.12.

$$2NH_2OH + 2NaClO \rightarrow N_2O + 2NaCl + 3H_2O.$$

Scheme 1.12

The proposed method was applied to the analysis of fresh-water samples[14].

This method also was used for the determination of hydroxylamine in a soil sample [4].To determine soil HA concentrations and to explore the correlation between soil HA concentrations and N_2O emission rates, the method based on fast extraction of HA from the soil, oxidation of HA to N_2O with Fe^{3+} and analysis of the N_2O with gas chromatography was developed.The method is extremely sensitive, being able to detect soil HA contents as low as 0.3 μg N kg^{-1} dry soil. Moreover, N_2O emission rates were significantly correlated with soil HA content ($r_2 = 0.80$), suggesting a key role of HA in N_2O formation under aerobic conditions [4].

Spectrophotometric methods

These methods are based on derivatives either of hydroxylamine itself, or of compounds obtained from it quantitatively, and can be classified into three groups.

1. Methods for the determination of nitrites previously obtained by quantitative oxidation of hydroxylamine.
2. Methods based on direct reaction with hydroxylamine.
3. Other methods.

The methods in the first group are based, for example, on reaction between nitrite and sulphanilic acid in acid solution, and subsequent coupling of the diazo-compound with *α*-naphthylamine to yield an intensely coloured dyestuff.

This reaction was used for the quantitative determination of hydroxylamine after prior oxidation with iodine to nitrite(Scheme 1.13):

$$2NH_2OH + 2I_2 + H_2O \rightarrow HNO_2 + 4HI.$$

Scheme 1.13

The accuracy of the determination depends on complete removal of nitrite from the sample, and on restriction of the concentration range to that where the Lambert-Beer law is obeyed. Method has many attractive features, including high sensitivity and rapidity of determination.

The nitrite wasconverted into diazosulphanilic acid, which was then decomposed by heating with sodium azide.This procedure was not very satisfactory and could cause an error of the order of 10% in the determination of hydroxylamine. Nitrite was therefore removed by conversion into diazosulphanilic acid and heating until this compound had completely decomposed. The error in the determination of hydroxylamine at concentrations of 10^{-8}−10^{-5} M did not exceed 2−3% [7].

The method isbased on the oxidation of hydroxylamine to nitrite using sodium arsenate under alkalinecondition. The formed nitrite is determined based on the diazo coupling reaction between *p*-nitroaniline and *N*-(1-naphthyl)ethylenediamine dihydrochloride [NEDA]according to Scheme 1.14 [15].

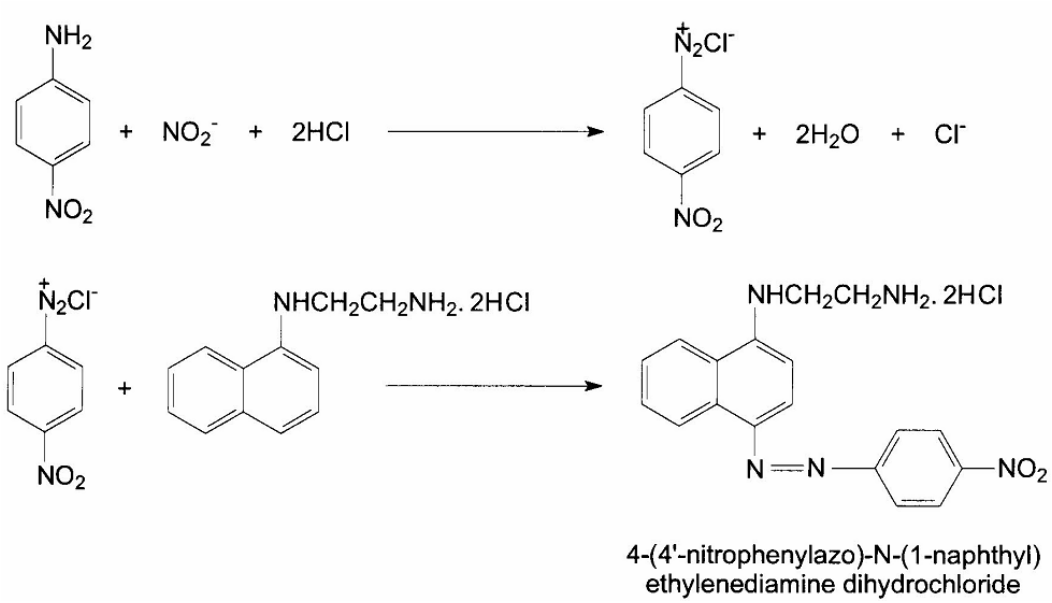
In the paper [2] this method has been applied to the determination of hydroxylamine and its derivatives used in pharmaceutical formulations after hydrolysis.

Hydroxylamine has been determined by its 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 hydroxylamine is reduced to bromide and the unreacted bromine is determined using methyl red.Thus with the increasing concentration of hydroxylamine, more of bromine is reduced and this is observed by a linear increase in the absorbance due to the unbleached methyl red under acidic condition (Scheme 1.15) [15].

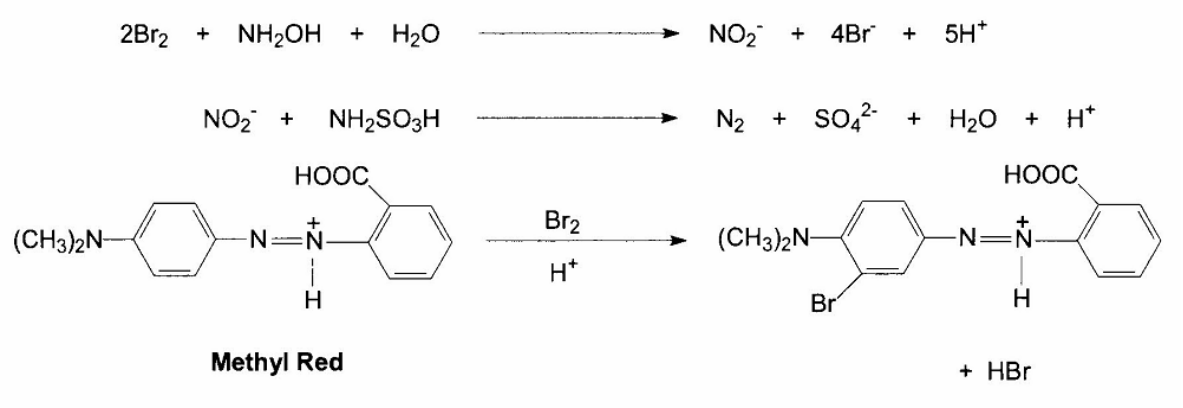
In the paper [3] this method has been also applied to the determination of hydroxylamine and its derivatives used in pharmaceutical formulations after hydrolysis.

The methods based on direct reaction with hydroxylamine involve a variety of reactions, and are not easily summarized. One of the methods is based on the reaction: hydroxylamine reacts with 8-hydroxyquinoline (**I**) in alkaline medium to yield 5-amino-8-hydroxyquinoline (**II**) which in the presence of aerial oxygen reacts with a second molecule of 8-hydroxyquinoline to produce an intensely green compound commonly called “indo-oxine” (**III**) (Scheme 1.16).

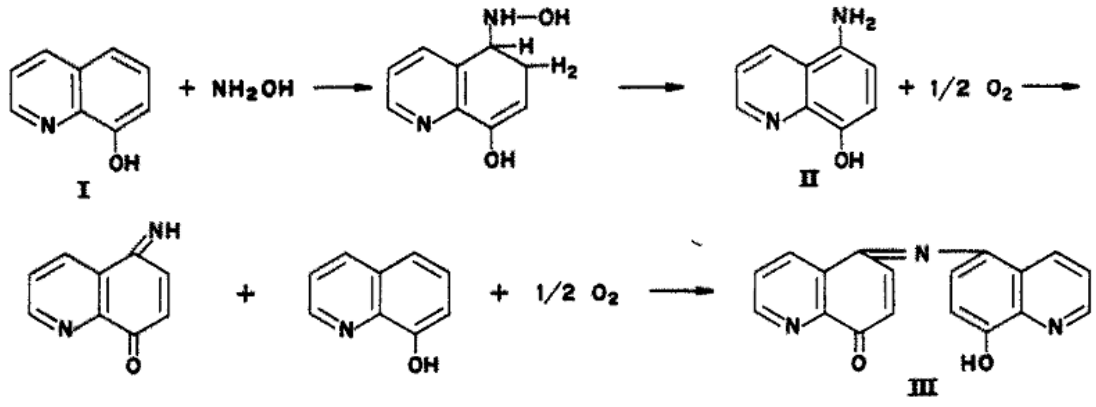
Hydroxylamine gives a colour reaction with ninhydrin, but in this case the molar absorptivities of the products from ammonia and hydroxylamine are identical, so the explanation that hydroxylamine is reduced to ammonia by stannous chloride present in the ninhydrin solution seems to be well-founded.



Scheme 1.14



Scheme 1.15



Scheme 1.16

Hydroxylamine was found to form a coloured complex with the Nessler reagent, the molar absorptivity of which is some five times that of the corresponding ammonia product.

The reactions of hydroxylamine and oximes with*p*-nitrobenzaldehyde to form *p*-nitrobenzaldoxime have been investigated.

In the third group are included the methods based on the reducing properties of hydroxylamine, and which are therefore indirect methods.

One of these is a method in which hydroxylamine reduces iron(III) to iron(II), which in turn isestimated photometrically as the 1,10-phenanthroline complex.The absolute error does not exceed 2%. In another method, potassium chromate is the oxidizing agent, and the excess of chromate is determined photometrically as the red oxidation product of*o*-dianisidine.

Summing up the spectrophotometric methods, it must be emphasized that they are sensitive and rapid but not one is universally applicable. They can also be used for determining hydroxylamine derivatives such as oximes, after quantitative hydrolysis [7].

Several methods have been reported for the spectrophotometric determination of hydroxylamine and nitrite.

For determination of hydroxylamine and nitrite a novel and highly sensitive electrochemical nanosensor was developed for the simultaneous determination of hydroxylamine and nitrite in the presence of nine interference moieties using oxadiazole self-assembled on silver nanoparticle-modified glassy carbon electrode (OAgNPs-GCE). The investigated method showed good stability, reproducibility, and repeatability and high recovery in real samples. Moreover, this modified electrode was found to be quite effective in simultaneous determination of hydroxylamine and nitrite in the presence of nine moieties. OAgNPsGCE has been applied to the determination of hydroxylamineand nitrite at water samples with acceptable results [1].

In the paper [5], a spectrophotometric determination method for resolving nitrite and HA mixtures after cloud point extraction (CPE) was presented. The method is based on the combination of two well-known reactions: oxidation of hydroxylamine to nitrite and nitrite determination with *N*,*N*-dimethylaniline and *p*-nitroaniline followed by micelle-mediated extraction of the produced azo dye. Iodate ion oxidizes hydroxylamine in acidic media to produce nitrite ions. In the presence of nitrite ions, the composite diazotization coupling reaction of *p*-nitroaniline (as a diazotizable aromatic amine) and *N*,*N*-dimethylaniline (as acoupling agent) proceeds in acidic media to produce an azo product. The produced azo compound is insoluble in water. However, it was observed that the azo compound becomes soluble in water on the addition of the neutral surfactant Triton X-114. The absorbance intensity of the solution is proportional to the nitrite concentration. Therefore, the system is suitable forspectrophotometric determination of nitrite and hydroxylamine. The relative errors of measurements were $\leq$5%. The method is applicable to the determination of mixtures having different concentration ratios of hydroxylamine and nitrite. The proposed method was applied successfully to the determination of nitrite and hydroxylamine in well water and urine samples.

Hydroxylamine can also be determined by kinetic methods. Kinetic methods of chemical analysis are attractive methods for rapid determination of trace amounts of inorganic species. These methods have some advantages including high sensitivity,

extremely low detection limit, good selectivity, rapid analysis and inexpensive instruments such as a spectrophotometer or spectrofluorometer.Kinetic methods of analysis are based on the fact that for most reactions the rate of the reaction and the analytical signalincrease with an increase ofthe analyte concentration. In kinetic methods, measurement of the analytical signal is made under dynamic conditions in which the concentrations of reactants and products are changing as a function of time.The application of kinetic spectrophotometric methods offers some specific advantages over classical spectrophotometry, such as improved selectivity due to the measurement of the evolution of the absorbance with the reaction time [16].The classification for chemical kinetic methods of analysis is shown in Figure 1.1 [17].

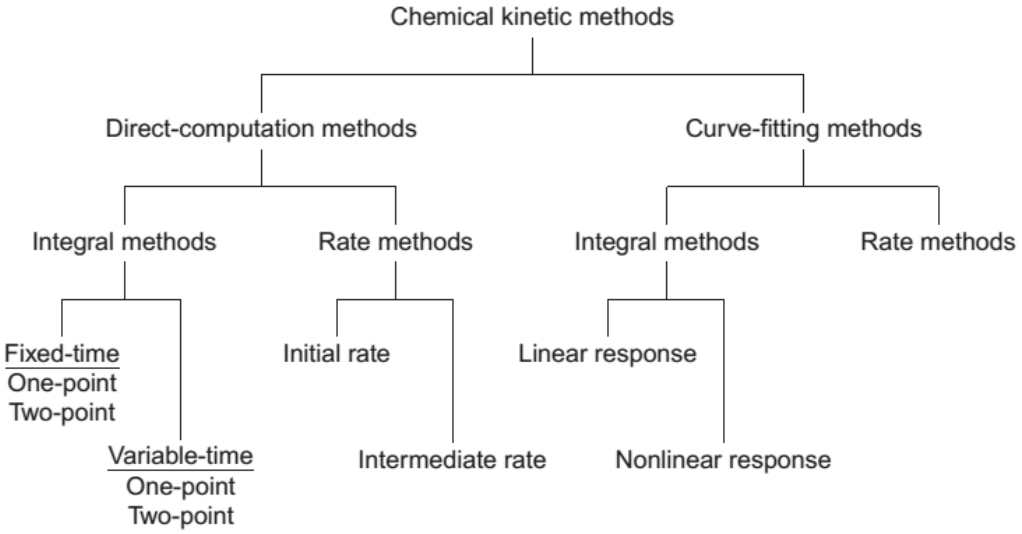


Figure 1.1 – Classification of chemical kinetic methods of analysis

The hydroxylamine determination by the kinetic method has not been studied enough, this method is described in only one paper [6]. The authors of this paper used the fixed-time method. The fixed-time integral method has the advantage of simplicity since only a single measurement is needed to determine the analyte's initial concentration. As with any method relying on a single determination, however, aone-point fixed-time integral method cannot compensate for constant sources ofdeterminate error.Fixed-time integral methods are advantageous for systems in which the signal is a linear function of concentration. In this case it is not necessary to determine the concentration of the analyte or product at times $t_1$or t_2, because the relevant concentration terms can be replaced by the appropriate signal [17].

A simple, precise and accurate method is proposed in paper [6] for rapid determination of trace amounts of hydroxylamine based on the reaction of hydroxylamine with iodate in acidic media. The reaction of neutral red by the produced nitrite ion was used to monitor the reaction spectrophotometrically at 525 nm by a fixed time method. Hydroxylamine in the range of 0.0400–1.200 μg mL^{-1} could be determined. The relative standard deviation for 10 determinations of 0.500 μg mL^{-1} hydroxylamine was 1.81% and the limit of detection was 0.010 μg mL^{-1}. The proposed method was applied to the determination of hydroxylamine in water samples [6].

2 EXPERIMENTAL

Instruments

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

Reagents

A stock solution of hydroxylamine 0.03028mol L^{-1} was prepared by dissolving 0.0527 g of analytical grade reagent hydroxylamine hydrochloride 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 0.03623mol L^{-1} was prepared by dissolving 0.0625 g of analytical grade reagent sodium nitrite 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 0.1000mol L^{-1} was prepared by dissolving 2.1401 g of analyticalgrade reagent potassium iodateKIO_3 in distilled water and diluting to the mark in a 100-mL volumetric flask.

A standard solution of bromate ion 0.1000mol L^{-1} was prepared by dissolving 1.6700 g of analyticalgrade reagent potassium bromate$KBrO_3$ in distilled water and diluting to the mark in a 100-mL volumetric flask.

A standard solution of persulfate ion 0.1000mol L^{-1} was prepared by dissolving 2.7033 g of analyticalgrade reagent potassium persulfate$K_2S_2O_8$ 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 redwas 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 standardized with a solution of sodium tetraborate from a standard titer 0.1000 N with the use of the methyl orange indicator.

Procedure

The procedure of hydroxylamine determination was as following: the reaction was followed spectrophotometrically by monitoring the change in the absorbance at 530 nm. A suitable aliquot of a working solution, in the range(3.03×10^{-6}–3.00×10^{-5}) mol L^{-1} hydroxylamine was transferred into a 10-mLgraduated 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 in a smartphone was started just after the addition of the last drop of neutral red. The solution was diluted to the mark withdistilled 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 procedure of nitrite ion determination in the presence of iodate ion was as following: a suitable aliquot of a working solution, in the range (2.90×10^{-6}– 4.35×10^{-5}) mol L^{-1}sodium nitrite was transferred into a 10-mLgraduated test tube. Then 2.4 mL of 0.1 mol L^{-1}potassium iodate was addedfollowed by 1 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 in a smartphone was started just after the addition of the last drop of neutral red. The solution was diluted to the mark withdistilled 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 procedure of nitrite ion determination in the absence of iodate ion was as following:a suitable aliquot of a working solution, in the range(4.3×10^{-6}–4.64×10^{-5}) mol L^{-1}sodium nitrite was transferred into a 10-mLgraduated test tube. Then 1 mL of 3.0 mol L^{-1}sulfuric acid solutionwas addedand 2 mL of 3.46×10^{-4} mol L^{-1}neutral red solution. The stop clock in a smartphone was started just after the addition of the last drop of neutral red. The solution was diluted to the mark withdistilled 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 procedure of soil analysis

Sampling:a soil sample was collected at the territory of Gagarin Park in Chelyabinsk. This 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: extraction was carried out according to the methods of the authors [4].4 g of fresh soil was added to a 100-mL conicalflask, 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, as in the paper [4], the pH value was monitored by a pH-meter. The extraction was carried out by shaking the suspension for 10 min, thenthe solution was filtered. After filtration, the filtrate was centrifuged at 2000 rpm for 15 min in centrifuge tubes.

Analytical determination: the soil sample was analyzed for several 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 hydroxylamine. The rest of determination is described above.

3 RESULT AND DISCUSSION

3.1 Absorption spectra

It is known that oxidation of hydroxylamine occurs in acidic conditions. Iodate ion oxidizes hydroxylamine to produce nitrite ion according to the following reaction (Scheme 3.1):

$$2IO_3^- + 3NH_2OH \rightarrow 3NO_2^- + 3H^+ + 2I^- + 3H_2O.$$

Scheme 3.1

The produced nitrite ion then reacts with neutral red [6].

Neutral redis an acid-base indicator. At various acidic conditions its absorptivity and the maximal absorbance wavelength differ. Therefore, it is necessary to study the absorption spectra of the blank experiment under various acidity.

Sulfuric acid solution was transferred into a 10-mL graduated test tube, then 1 mL of 3.46×10^{-4} molL^{-1} neutral red solution was added. The solution was diluted to the mark with distilled water and a portion of it was transferred into a 1-cm glass cuvette to measure the absorbance of the solution at wavelengths of 400−700 nm.The results are shown in Figure 3.1.

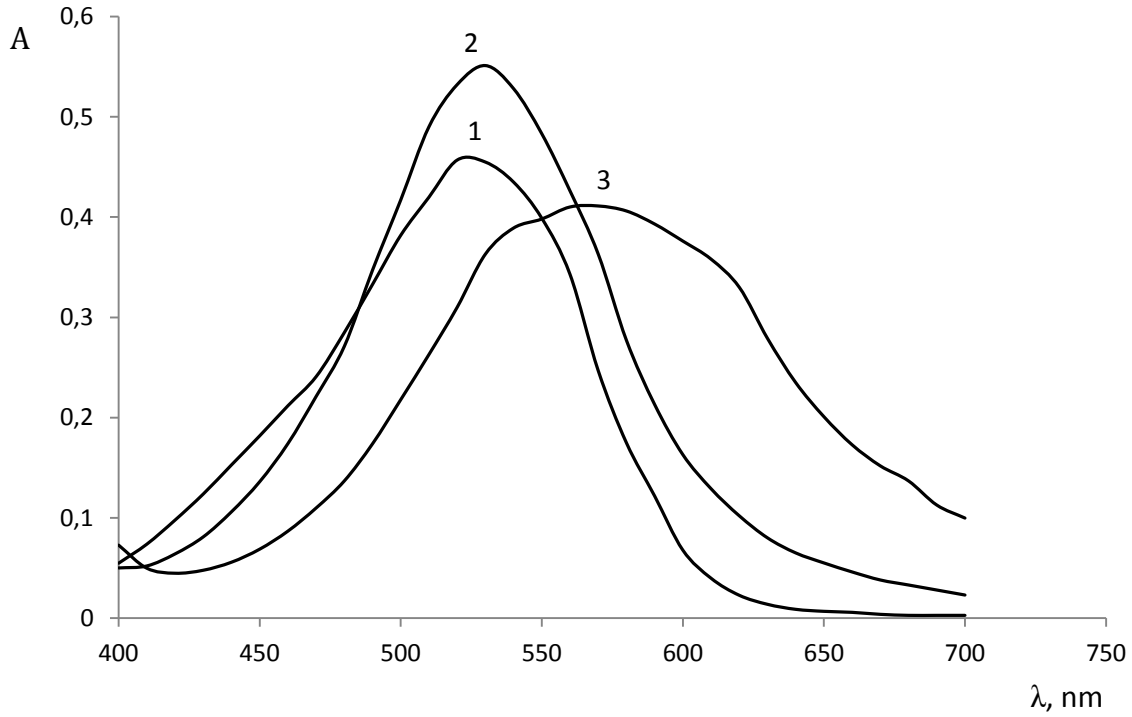
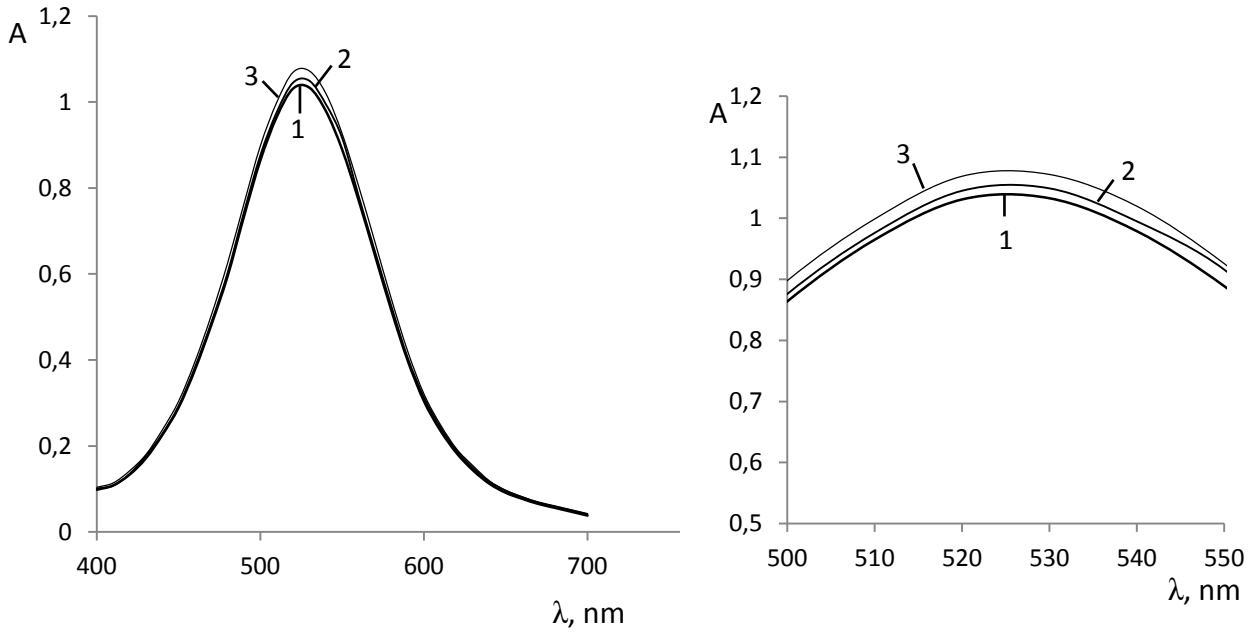


Figure 3.1 – Light absorption spectra of neutral red in the presence of sulfuric acid: C(NR) = 3.46×10^{-5} mol L^{-1}; C(H_2SO_4): **1** – 0; **2** – 0.30mol L^{-1}; **3** – 1.50 mol L^{-1}

At a sufficiently high acidity, region of the maximal absorbance is shifted from 530 nm to the interval 530–580 nm.However, if the acidity is near the optimum, the neutral red remains in the same form as in the neutral medium.

It was 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.

Potassium iodate solution was transferred into a 10-mL graduated test tube then 1 mL of 3.0molL^{-1} sulfuric acid solution was added. 2 mL of 3.46×10^{-4} molL^{-1} neutral red solution was added. The solution was diluted to the mark withdistilled water and a portion of it was transferred into a 1-cm glass cuvette to measure the absorbance of the solution at wavelengths of 400–700 nm.The results are shown in Figure 3.2 (a – the wavelength range is from 400 to 700 nm; b –a part of (a), to show the interval of maximum absorbance (500–550 nm)).



(a) (b)

Figure 3.2 – Light absorption spectra of neutral red in the presence of potassium iodate: C(NR) = 3.46×10^{-5} mol L^{-1}; C(H_2SO_4) = 0.30 mol L^{-1}; C(KIO_3): **1** – 0.0025 mol L^{-1}; **2** – 0.005 mol L^{-1}; **3** – 0.03 mol L^{-1}

Within thestudied iodate ion and acid concentrations ranges, neutral red does not change its form and remains in the same form as it is in neutral solution (Figure 3.3).

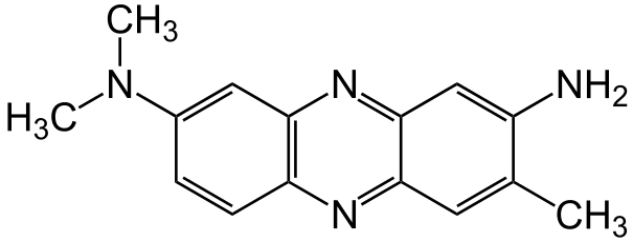


Figure 3.3 – The structural formula of neutral red

The wavelength 530 nm was taken to be optimal for absorbance measurement.

3.2 Kinetic curves

3.2.1 Development of neutral red absorbance

We need to find out whether time affects the development of the color of neutral red in order to compare the initial rate of the blank experiment with the initial rate of the analyzed hydroxylamine-containing solution.

The reaction was followed spectrophotometrically by monitoring the change in the absorbance at 530 nm. The concentration of potassium iodate was varied from 0.0025 to 0.05 molL^{-1}. A suitable aliquot of potassium iodate was transferred into a 10-mL graduated test tube. Then 1 mL of 3.0 mol L^{-1}sulfuric acid solution was added. Then 2 mL of 3.46×10^{-4} mol L^{-1}neutral red solution was added. The solution was diluted to the mark with distilled water and a portion of it was transferred into a 1-cm glass cuvette to measure the absorbance of the solution at 530 nm.Actually, the absorbance measurement was begun in 1 min, necessary for transferring the solution into the cuvette. The results are shown in Table 3.1.

Table 3.1 – Effect of potassium iodate concentration on the development of neutral red absorbance

t, min	Absorbance (A)				
	Molar concentration of iodate ($C(KIO_3)$), mol L^{-1}				
	0.0025	0.01	0.02	0.03	0.05
1	1.151	1.157	1.247	1.231	1.180
1.5	1.152	1.158	1.249	1.233	1.183
2	1.153	1.160	1.250	1.235	1.184
2.5	1.153	1.161	1.251	1.237	1.187
3	1.154	1.162	1.252	1.240	1.189
3.5	1.154	1.163	1.254	1.242	1.191
4	1.155	1.164	1.255	1.244	1.193
4.5	1.155	1.165	1.255	1.245	1.195
5	1.156	1.165	1.255	1.247	1.198

According to the table, we can conclude that the presence of various concentrations of the oxidizing agent affects the absolute values of the absorbance (they differ from 1.151 to 1.255), but not the tangent of the slope angle, nor the reaction rate. In other words, neutral red in the presence of iodateremains unchanged, the tangentapproximatelyequals zero.

The reaction was followed spectrophotometrically by monitoring the change in the absorbance at 530 nm. 1 mL of 0.05 mol L^{-1} potassium iodate was transferred into a 10-mL graduated test tube. The concentration of sulfuric acid was varied from 0.051 to 1.2 mol L^{-1}.A suitable aliquot of sulfuric acid solution was added. Then 2 mL of 3.46×10^{-4} mol L^{-1}neutral red solution was added. The solution was diluted to the mark with distilled water and a portion of it was transferred into a 1-cm glass cuvette to measure the absorbance of the solution at 530 nm. Actually, the absorbance

measurement was begun in 1 min, necessary for transferring the solution into the cuvette. The results are shown in Table 3.2.

Table 3.2–Effect of sulfuric acid concentration on the development of neutral red absorbance

t, min	Absorbance (A)			
	Molar concentration ($C(H_2SO_4)$), mol L^{-1}			
	0.051	0.3	0.6	1.2
1	1.253	1.153	1.141	0.942
1.5	1.256	1.155	1.141	0.940
2	1.259	1.158	1.142	0.940
2.5	1.263	1.161	1.144	0.940
3	1.266	1.164	1.146	0.940
3.5	1.269	1.166	1.147	0.940
4	1.272	1.167	1.148	0.940
4.5	1.274	1.170	1.150	0.940
5	1.276	1.171	1.150	0.940

The change in the conditions within the studied rangeaffects the absolute values of the absorbance (they differ from 0.940 to 1.276), but not the tangent of the slope angle, nor the reaction rate. In other words, neutral red in the presence of the studied range of sulfuric acidremains unchanged, the tangentapproximatelyequals to zero, and the initial rate remains at the level of zero value.

3.2.2 Development of neutral red absorbance in the presence of nitrite ion

According to the data of the authors [6] hydroxylamine does not react with neutral red.It is nitrite ionresulting from the oxidation of hydroxylamine by iodate ion reacts with the indicator (Equation 3.1). However, the nitrite ion can exhibit reducing properties. It is of interest to examine whether the excess oxidizing agentwill affect the analytical signal.

So we studied the effect of iodate ion on the development of neutral red absorbance in the presence of nitrite ion. We conducted an experiment in which nitrite ion was present, and hydroxylamine was absent.

We compared the results of 2 experiments. 1 mL of 3.62×10^{-4} sodium nitrite was transferred into a 10-mL graduated test tube.In the first case 1 mLof 0.05 mol $L^{-1}$of potassium iodate was added, and in the second case there was no iodate. Then 1 mL of 3.0 mol L^{-1}sulfuric acid solution was added.The mixture was allowed to stand for 5 min, similar to the procedure suggested by the previouslymentioned authors [6]. Then 2 mL of 3.46×10^{-4} mol L^{-1}neutral red solution was added. The stop clock in a smartphone was started just after the addition of the last drop of neutral red. The solution was diluted to the mark withdistilled water and a portion of it was transferred into a 1-cm glass cuvette to measure the absorbance of the solution at 530 nm for 1–5 min after initiation of the reaction.TheresultsareshowninFigure 3.4.

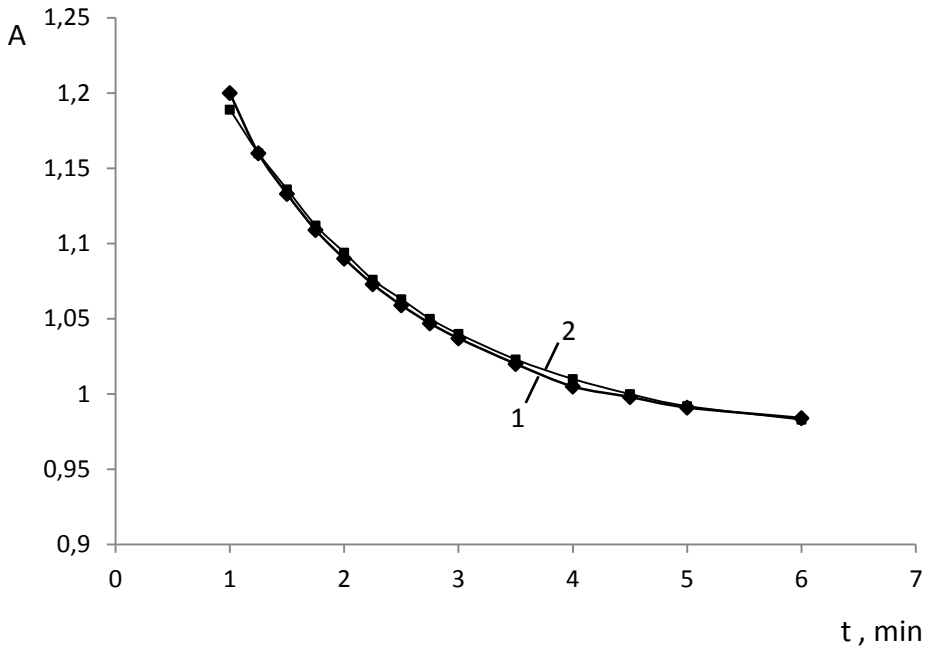


Figure 3.4 – Absorbance-time plots for the reaction of neutral red with nitrite ion: C(NR) = 6.92×10^{-5} mol L^{-1}; C(NO_2^-) = 3.62×10^{-5} mol L^{-1}; C(H_2SO_4) = 0.30 mol L^{-1}; C(KIO_3): **1** – 0; **2** – 0.005 mol L^{-1}

The influence of the oxidizing agenton nitrite ion under the studied conditions is not observed, and the kinetic curves overlap.

3.2.3 Development of neutral red absorbance in the presence of hydroxylamine

The aim of our work is to study the determination of hydroxylamine.The authors of the paper [6] used the fixed time method and stood the solution for 5 min before adding the neutral red solution, the measurement began immediately after this.The fixed time method requires great precision in time measurement (seconds), and, besides, the interval of extra 5 min that is allowed for the oxidation of hydroxylamine slows the determination. As we chose the initial ratemethod, we decided to check whether there is a need to stood the solution for additional time of 5 min for oxidation.We compared 2 sets of experimental conditions: first, according to [6], second, measuring after mixing all the reactants at once. Actually, the absorbance measurement was begun in 1 min, necessary for transferring the solution into the cuvette.

To control the development of absorbance, 1.2mL of 3.03×10^{-4} hydroxylamine was transferred into a 10-mL graduated test tube.Then 1 mLof 0.05 mol L^{-1}potassium iodate was added followed by 1 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 in a smartphone was started just after the addition of the last drop of neutral red. The solution was diluted to the mark withdistilled water and a portion of it was transferred into a 1-cm glass cuvette to measure the absorbance of the solution at 530 nm. TheresultsareshowninFigure3.5.

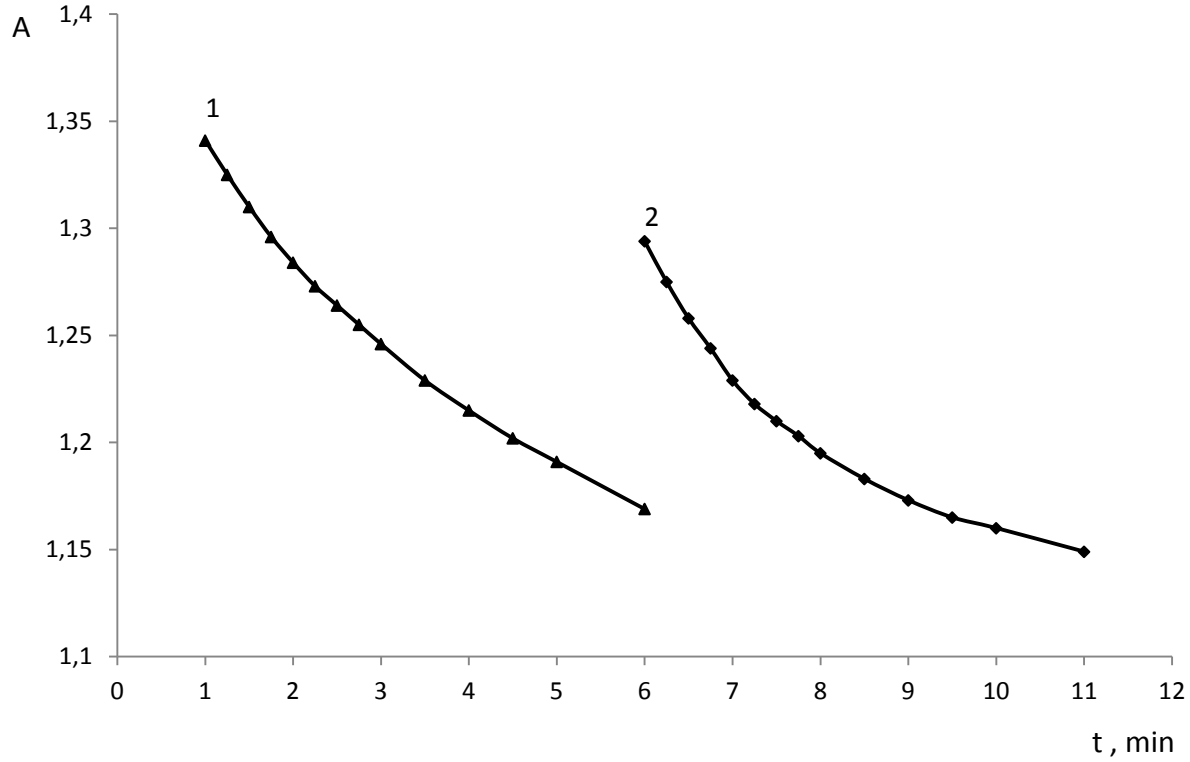


Figure 3.5 – Absorbance-time plots for the reaction of neutral red with hydroxylamine: C(NR) = 6.92×10^{-5} mol L^{-1}; C(NH_2OH) = 3.63×10^{-5} mol L^{-1}; C(H_2SO_4) = 0.30 mol L^{-1}; C(KIO_3) = 0.005 mol L^{-1}; **1** – measuring after mixing all the reactants; **2** –measuring after 5 min for oxidation

The tangents are somewhat different, tgα = 0.0545 for curve 1, tg α = 0.0608 for curve 2. Obviously, the reaction of hydroxylamine oxidation into nitrite ion runs quicker than the reaction of discoloration of neutral red by nitrite ion. Even if hydroxylamine does not oxidize for 100%, still, the loss of sensitivity is not so great, but the analysis is carried out faster.

3.2.4 Effect of the temperature

The solutions in [6]were equilibrated in 25 ℃ thermostated water bath before beginning the reaction.Therefore it is necessary to study the effect of temperature.

All the initial solutions in 10-mL portions were thermostated in water bath of a thermostate in the temperature range 27–50℃ for 15 min. 0.6mL of 3.03×10^{-4} hydroxylamine was transferred into a 10-mL graduated test tube.Then 2.4 mL of 0.1 mol $L^{-1}$of iodate was added followed by 1 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 in a smartphone was started just after the addition of the last drop of neutral red. The solution was diluted to the mark withdistilled water and a portion of it was transferred into a 1-cm glass cuvette to measure the absorbance of the solution at 530 nm.

TheresultsareshowninTable 3.3. The kinetic curves obtained at 27℃ and 50 ℃ are shown in Figure 3.6.

Table 3.3 – Effect of the temperature on the development of neutral red absorbance

t, min	Absorbance (A)							
	Temperature, ℃							
	27	29	31	33	35	40	45	50
1.25	1.069	1.063	1.134	1.138	1.122	1.154	1.080	1.120
1.5	1.059	1.052	1.123	1.123	1.116	1.145	1.071	1.109
1.75	1.050	1.043	1.113	1.113	1.109	1.133	1.064	1.100
2	1.044	1.035	1.106	1.104	1.104	1.122	1.057	1.095
2.25	1.039	1.027	1.093	1.094	1.096	1.117	1.051	1.088
2.5	1.032	1.019	1.087	1.090	1.092	1.113	1.045	1.082
2.75	1.026	1.010	1.084	1.086	1.089	1.108	1.042	1.078
3	1.021	1.007	1.080	1.081	1.087	1.104	1.038	1.072
3.25	1.018	1.000	1.076	1.078	1.081	1.099	1.036	1.069
3.5	1.014	0.996	1.072	1.072	1.080	1.096	1.030	1.065
3.75	1.010	0.993	1.069	1.067	1.078	1.094	1.028	1.062
4	1.006	0.989	1.065	1.064	1.076	1.092	1.026	1.060
4.5	1.002	0.983	1.061	1.059	1.070	1.085	1.022	1.054
5	0.999	0.976	1.056	1.055	1.068	1.087	1.020	1.052

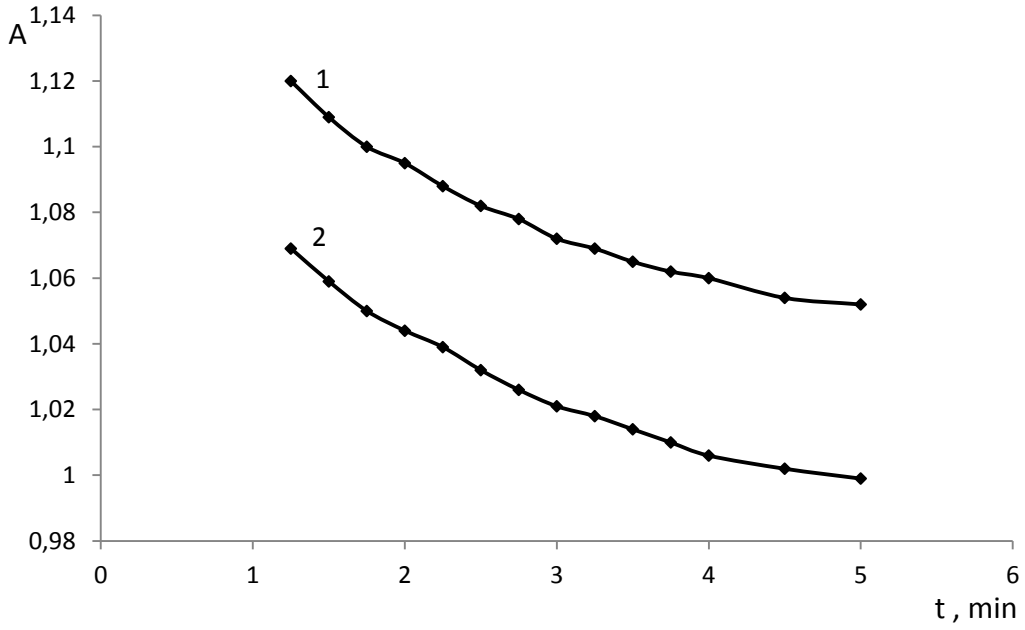


Figure 3.6 – Absorbance-time plots for thereactionat different temperatures: C(NR) = 6.92×10^{-5} mol L^{-1}; C(NH_2OH) = 1.82×10^{-5} mol L^{-1}; C(H_2SO_4) = 0.30 mol L^{-1}; C(KIO_3) = 0.024 mol L^{-1}; **1** – 50 ℃; **2** – 27 ℃

The influence of the temperature on the absolute value of absorbance is very strong and it is impossible to work with the fixed time method without thermostating.While its effect on the initialrate (on the kinetic curve itself) is not great, so we worked at room temperature, because the initial rate method gives more stable results than the fixed time method.

3.3 Choice of an oxidizing agent

3.3.1 Influence of different oxidizing agents

To oxidize hydroxylamine various oxidizing agents are used such as ferric salts, ceric salts, vanadate, potassium ferricyanide, bromine, bromate and bromine monochloride, iodine [7].We studied the oxidizing agents of various nature to choosean optimal one.

The aliquot 0.5mL of 3.62×10^{-4}mol L^{-1}sodium nitrite was transferred into a 10-mL graduated test tube.First, potassium bromate was used as the oxidizingagent, second, potassium persulfate. The oxidizingagent concentration was varied from 0.0005 mol L^{-1}to0.05 mol L^{-1} for bromate ion and from 0.005 mol L^{-1}to0.05 mol $L^{-1}$for persulfate ion.Then1 mL of 3.0 mol L^{-1}sulfuric acid solution was added and 2 mL of 3.46×10^{-4} mol L^{-1}neutral red solution. The stop clock in a smartphone was started just after the addition of the last drop of neutral red. The solution was diluted to the mark withdistilled water and a portion of it was transferred into a 1-cm glass cuvette to measure the absorbance of the solution at 530 nm. TheresultsareshowninTable 3.4.

Table3.4 –Effect of oxidizing agenton the development of neutral red absorbance

t, min	Absorbance (A)						
	Molar concentration of bromate ($C(KBrO_3)$), mol L^{-1}						
	0.0005	0.001	0.003	0.005	0.010	0.030	0.050
1	1.065	1.122	1.030	0.910	0.108	0.047	0.055
1.25	1.055	1.115	1.020	0.843	0.072	0.045	0.053
1.5	1.048	1.109	1.011	0.761	0.064	0.044	0.051
1.75	1.041	1.105	1.005	0.667	0.060	0.044	0.051
2	1.036	1.101	0.999	0.569	0.058	0.043	0.050
2.25	1.032	1.100	0.994	0.480	0.056	0.042	0.049
2.5	1.028	1.098	0.990	0.377	0.055	0.042	0.048
2.75	1.025	1.097	0.986	0.251	0.054	0.041	0.048
3	1.023	1.096	0.983	0.170	0.054	0.041	0.047
3.5	1.020	1.096	0.978	0.144	0.053	0.040	0.047
4	1.018	1.096	0.972	0.144	0.052	0.040	0.047
4.5	1.017	1.095	0.968	0.144	0.052	0.040	0.047
5	1.016	1.095	0.966	0.144	0.052	0.040	0.047

	Molar concentration of persulfate ($C(K_2S_2O_8)$), mol L^{-1}									
	0.005	0.008	0.01	0.012	0.014	0.015	0.02	0.03	0.04	0.05
1	1.045	1.020	0.993	0.844	0.969	1.024	0.627	0.604	0.487	0.493
1.25	1.026	0.998	0.970	0.820	0.945	0.998	0.610	0.585	0.476	0.483
1.5	1.010	0.978	0.948	0.797	0.923	0.971	0.594	0.570	0.469	0.475
1.75	0.994	0.958	0.929	0.776	0.901	0.946	0.580	0.557	0.462	0.468
2	0.980	0.940	0.910	0.756	0.881	0.923	0.569	0.546	0.457	0.463
2.25	0.966	0.922	0.892	0.737	0.861	0.902	0.559	0.536	0.452	0.458
2.5	0.954	0.910	0.876	0.720	0.842	0.882	0.551	0.527	0.447	0.454
2.75	0.942	0.895	0.861	0.706	0.825	0.863	0.543	0.520	0.444	0.451

Completed Table3.4

t, min	Absorbance (A)									
	Molar concentration of persulfate ($C(K_2S_2O_8)$), mol L^{-1}									
	0.005	0.008	0.01	0.012	0.014	0.015	0.02	0.03	0.04	0.05
3	0.932	0.883	0.847	0.691	0.808	0.844	0.537	0.513	0.440	0.447
3.5	0.914	0.859	0.820	0.666	0.777	0.811	0.525	0.501	0.435	0.442
4	0.897	0.838	0.797	0.645	0.749	0.780	0.516	0.492	0.430	0.436
4.5	0.883	0.819	0.775	0.628	0.724	0.752	0.509	0.484	0.425	0.431
5	0.870	0.801	0.757	0.614	0.702	0.728	0.503	0.477	0.421	0.426

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 show the decreasing absorbance, tangents are negative. To represent them conveniently, we changed the sign. All calculated initial rates are shown in Figure 3.7.

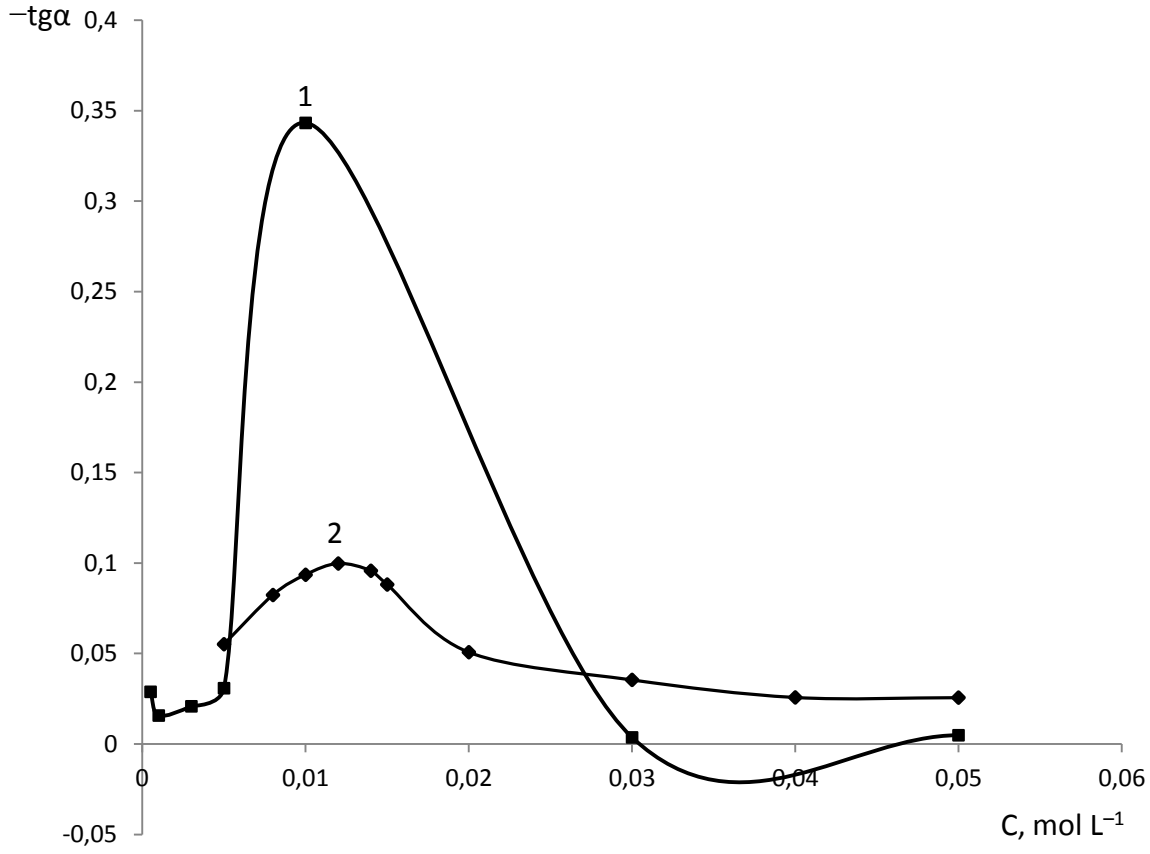


Figure 3.7 – Effect of an oxidizing agenton the initial rate: $C(NR) = 6.92\times10^{-5}$ mol L^{-1}; $C(NO_2^-) = 1.81\times10^{-5}$ mol L^{-1}; $C(H_2SO_4) = 0.30$ mol L^{-1}; **1** – $KBrO_3$; **2** – $K_2S_2O_8$

Potassium persulfate and potassium bromate are very strong oxidizing agents (E^0 = 1.96 V and 1.478 V [18]). The reaction proceeds so rapidly that the indicator very quickly decolorizes, and it is imposible to measure absorbance within this time (5 min).

Neutral red has reducing properties. Therefore, influence of oxidizing agents (other than nitrite ion produced from hydroxylamine) upon its absorbance is of great importance for accuracy of the method.

First, potassium iodate was used as the oxidizingagent, second, potassiumbromate, third, potassium persulfate. The oxidizingagents concentration was varied. A suitable aliquot of oxidizing agent solution was transferred into a 10-mL graduated test tube. Then1 mL of 3.0 mol L^{-1}sulfuric acid solution was added and 2 mL of 3.46×10^{-4} mol L^{-1}neutral red solution. The stop clock in a smartphone was started just after the addition of the last drop of neutral red. The solution was diluted to the mark withdistilled water and a portion of it was transferred into a 1-cm glass cuvette to measure the absorbance of the solution at 530 nm. TheresultsareshowninTable 3.5.

Table 3.5 –Development of neutral red absorbance in the presence of various oxidizing agents

t, min	Absorbance (A)				
	Molar concentration of iodate ($C(KIO_3)$), mol L^{-1}				
	0.0025	0.005	0.01	0.02	0.03
1	1.151	1.170	1.157	1.247	1.231
1.5	1.152	1.171	1.158	1.249	1.233
2	1.153	1.173	1.160	1.250	1.235
2.5	1.153	1.174	1.161	1.251	1.237
3	1.154	1.175	1.162	1.252	1.240
3.5	1.154	1.176	1.163	1.254	1.242
4	1.155	1.176	1.164	1.255	1.244
4.5	1.155	1.176	1.165	1.255	1.245
5	1.156	1.176	1.165	1.255	1.247
	Molar concentration of bromate($C(KBrO_3)$), mol L^{-1}				
	0.005	0.006	0.008	0.01	
1	1.120	1.136	1.118	1.136	
1.5	1.121	1.138	1.118	1.134	
2	1.122	1.140	1.117	1.130	
2.5	1.122	1.141	1.108	1.085	
3	1.121	1.141	1.061	0.719	
3.5	1.120	1.139	0.873	0.109	
4	1.117	1.132	0.382	0.074	
4.5	1.112	1.115	0.098	0.074	
5	1.105	1.078	0.074	0.074	
	Molar concentration of persulfate($C(K_2S_2O_8)$), mol L^{-1}				
	0.003	0.004	0.005	0.008	0.01
1	1.210	1.105	1.118	1.105	1.115
1.5	1.211	1.105	1.118	1.104	1.104
2	1.212	1.104	1.115	1.098	1.089
2.5	1.211	1.102	1.111	1.088	1.070
3	1.209	1.098	1.106	1.075	1.049
3.5	1.207	1.094	1.099	1.060	1.025

Completed Table3.5

t, min	Absorbance (A)				
	Molar concentration of persulfate($C(K_2S_2O_8)$), mol L^{-1}				
	0.003	0.004	0.005	0.008	0.01
4	1.202	1.087	1.091	1.044	1.001
4.5	1.198	1.079	1.082	1.025	0.975
5	1.193	1.072	1.071	1.008	0.951

The examples of kinetic curves for 0.005 mol L^{-1} of iodate ion, persulfate ion and bromate ion solutions are shown in Figure 3.8.

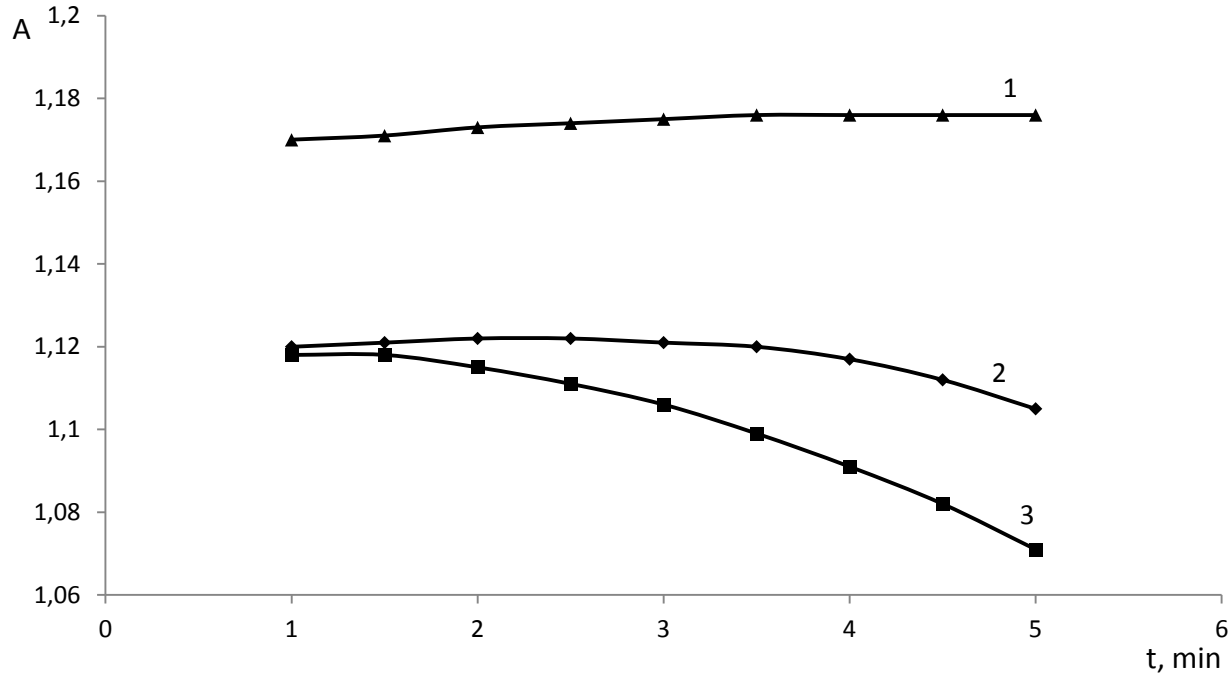


Figure 3.8 – Absorbance-time plots for thereaction of neutral red withdifferent oxidizing agents: $C(NR) = 6.92\times10^{-5}$ mol L^{-1}; $C(H_2SO_4) = 0.30$ mol L^{-1}; $C_{ox} = 0.005$mol L^{-1}; **1** – KIO_3; **2** – $KBrO_3$; **3** – $K_2S_2O_8$

Bromate ion and persulfate ion are not usable in the investigated method, as they both decompose neutral red, therefore changing the blank experiment. We have chosen iodate ion for experimental study ($E^0 = 1.195$ V [18]), like in [6].

3.3.2 Influence of air oxygen

Air oxygen is an oxidizing agent, besides, it dissolves in water, and therefore it can affect the neutral red. In order to ascertain its influence, we carried out the following experiment: 0.6mL of 3.03×10^{-4} hydroxylamine was transferred into a 10-mL graduated test tube. Potassium iodate concentration was varied. A suitable aliquot of iodate ion solution was added followed by 1 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 in a smartphone was started just after the addition of the last drop of neutral red. The solution was diluted to

the mark withdistilled water and a portion of it was transferred into a 1-cm glass cuvette to measure the absorbance of the solution at 530 nm. We compared 2 sets of experimental conditions: first, the solutions were kept in closed test tubeof all times except pipetting, measurements were taken in closed cuvettes (at controlled condition,when oxygen concentration is constant). Second, measurements were carriedout without these precautions. The absorbance measurement was begun in 1 min, necessary for transferring the solution into the cell. TheresultsareshowninTable 3.6

Table 3.6 – Development of neutral red absorbance in the presence of potassium iodate (in the close and the open cuvette)

t, min	Absorbance (A)					
	Molar concentration of iodate ($C(KIO_3)$), mol L^{-1} (close cuvette)					
	0.02	0.024	0.026	0.028	0.03	0.032
1	1.143	1.163	1.153	1.156	1.185	1.157
1.25	1.131	1.150	1.139	1.142	1.172	1.143
1.5	1.120	1.139	1.128	1.130	1.162	1.133
1.75	1.110	1.130	1.117	1.120	1.152	1.122
2	1.102	1.121	1.109	1.111	1.143	1.115
2.25	1.094	1.114	1.101	1.104	1.135	1.108
2.5	1.087	1.108	1.093	1.098	1.129	1.102
2.75	1.082	1.103	1.088	1.092	1.122	1.096
3	1.077	1.098	1.083	1.087	1.117	1.092
3.5	1.067	1.089	1.073	1.078	1.108	1.083
4	1.060	1.083	1.067	1.071	1.100	1.076
	Molar concentration of iodate ($C(KIO_3)$), mol L^{-1} (open cuvette)						
	0.02	0.024	0.026	0.028	0.03	0.032	0.035
1	1.178	1.146	1.158	1.169	1.181	1.166	1.160
1.25	1.165	1.136	1.145	1.155	1.169	1.153	1.147
1.5	1.153	1.126	1.133	1.145	1.156	1.141	1.138
1.75	1.143	1.118	1.123	1.135	1.146	1.131	1.129
2	1.135	1.11	1.115	1.126	1.137	1.123	1.121
2.25	1.128	1.104	1.108	1.118	1.130	1.117	1.114
2.5	1.122	1.099	1.101	1.111	1.123	1.110	1.108
2.75	1.116	1.094	1.096	1.106	1.118	1.105	1.102
3	1.111	1.090	1.09	1.100	1.112	1.099	1.098
3.5	1.103	1.082	1.082	1.091	1.104	1.091	1.089
4	1.096	1.076	1.074	1.085	1.098	1.085	1.082

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 show the decreasing absorbance, tangents are negative. To represent them conveniently, we changed the sign. All calculated initial rates are shown in Figure 3.9.

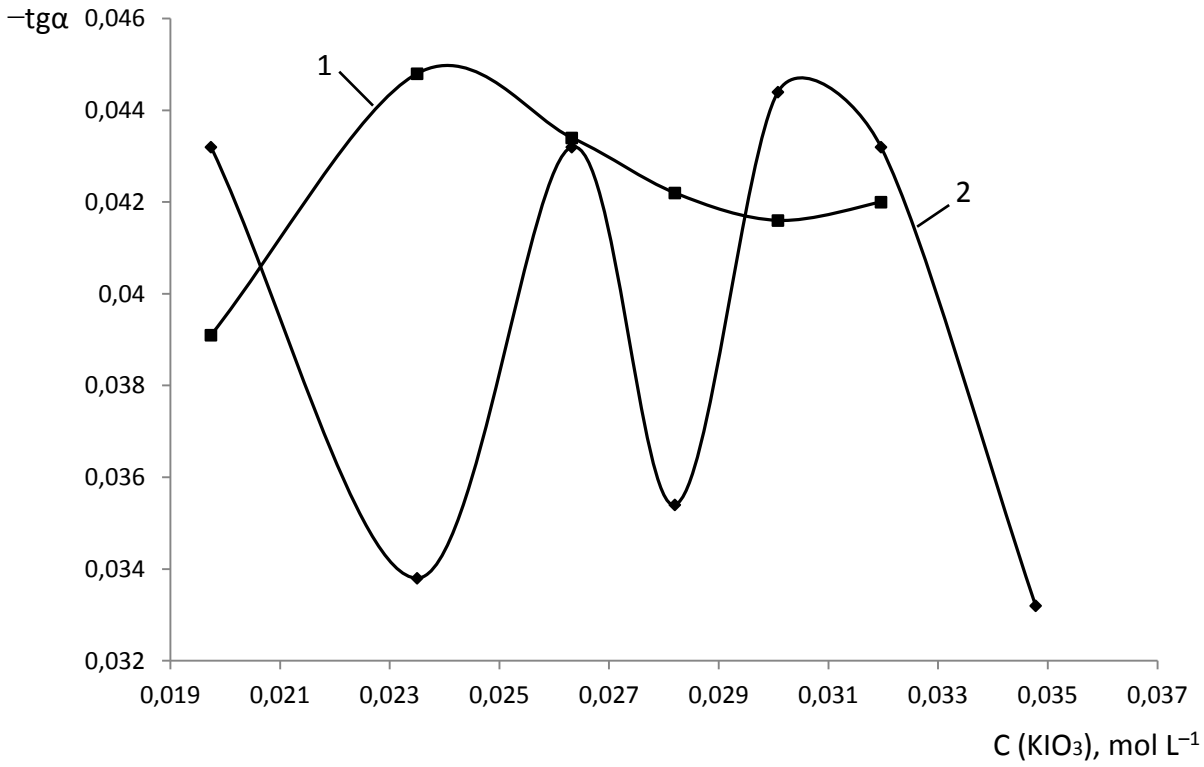


Figure 3.9 – Effect of potassium iodate concentration on the initial rate: C(NR) = 6.92×10^{-5} mol L^{-1}; C(NH_2OH) = 1.82×10^{-5} mol L^{-1}; C(H_2SO_4) = 0.30 mol L^{-1}; **1** – closed cuvette; **2** – open cuvette

To control the effect of oxygen, we began to close test tubes and cuvettes, we get a smoother dependence.

Then we measured the absorbance of the system in greater detail. 0.6mL of 3.03×10^{-4} hydroxylamine was transferred into a 10-mL graduated test tube. Potassium iodate concentration was varied from 0.003 mol L^{-1} to 0.04 mol L^{-1}. A suitable aliquot of iodate ion solution was added followed by 1 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 in a smartphone was started just after the addition of the last drop of neutral red. The solution was diluted to the mark withdistilled water and a portion of it was transferred into a 1-cm glass cuvette to measure the absorbance of the solution at 530 nm. The absorbance measurement was begun in 1 min, necessary for transferring the solution into the cuvette. TheresultsareshowninTable 3.7

Table 3.7–Development of neutral red absorbance in the presence of potassium iodate (in the close cuvette)

t, min	Absorbance (A)					
	Molar concentration of iodate (C(KIO_3)), mol L^{-1}					
	0.003	0.005	0.007	0.01	0.015	0.02
1	1.136	1.145	1.109	1.122	1.102	1.112
1.25	1.130	1.133	1.097	1.107	1.089	1.099
1.5	1.122	1.123	1.085	1.094	1.076	1.085

Completed Table3.7

t, min	Absorbance (A)					
	Molar concentration of iodate ($C(KIO_3)$), mol L^{-1}					
	0.003	0.005	0.007	0.01	0.015	0.02
1.75	1.114	1.112	1.074	1.081	1.065	1.073
2	1.106	1.103	1.064	1.070	1.055	1.062
2.25	1.099	1.094	1.056	1.060	1.046	1.053
2.5	1.092	1.087	1.047	1.051	1.038	1.045
2.75	1.085	1.078	1.040	1.043	1.030	1.037
3	1.078	1.071	1.033	1.034	1.024	1.029
3.5	1.067	1.059	1.021	1.022	1.011	1.017
4	1.056	1.049	1.010	1.011	1.003	1.007
4.5	1.045	1.040	1.001	1.002	0.997	1.000
5	1.036	1.031	0.994	0.994	0.990	0.993

	Molar concentration of iodate ($C(KIO_3)$), mol L^{-1}						
	0.024	0.028	0.03	0.032	0.035	0.038	0.04
1	1.097	1.092	1.079	1.104	1.092	1.089	1.087
1.25	1.079	1.079	1.065	1.087	1.079	1.078	1.072
1.5	1.066	1.068	1.053	1.076	1.068	1.067	1.059
1.75	1.054	1.057	1.043	1.066	1.058	1.058	1.048
2	1.045	1.048	1.034	1.056	1.049	1.050	1.038
2.25	1.036	1.041	1.026	1.048	1.041	1.042	1.029
2.5	1.028	1.033	1.019	1.040	1.034	1.035	1.021
2.75	1.021	1.026	1.012	1.033	1.028	1.029	1.014
3	1.014	1.021	1.007	1.026	1.023	1.024	1.008
3.5	1.003	1.011	0.997	1.017	1.014	1.014	0.998
4	0.993	1.002	0.989	1.009	1.005	1.007	0.989
4.5	0.986	0.996	0.983	1.002	0.999	1.000	0.982
5	0.980	0.991	0.978	0.997	0.995	0.994	0.976

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 show the decreasing absorbance, tangents are negative. To represent them conveniently, we changed the sign. All calculated initial rates are shown in Figure 3.10.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 used as the optimum concentration.

3.4 Influence of acidity

First, 0.5mL of 3.62×10^{-4} sodium nitrite was transferred into a 10-mL graduated test tube.Then 1 mL of 0.050 mol L^{-1}potassium iodate was added. Sulfuric acid concentration was varied from 0.03 mol L^{-1} to 1.50 mol L^{-1}. A suitable aliquot of

sulfuric acid solution was added. Then 2 mL of 3.46×10^{-4} mol L^{-1}neutral red solution was added. The stop clock in a smartphone was started just after the addition of the last drop of neutral red. The solution was diluted to the mark withdistilled water and a portion of it was transferred into a 1-cm glass cuvette to measure the absorbance of the solution at 530 nm. The absorbance measurement was begun in 1 min, necessary for transferring the solution into the cuvette. TheresultsareshowninTable 3.8. The experiment was repeated, but instead of nitrite 0.6mL of 3.03×10^{-4} hydroxylamine was added. TheresultsareshowninTable 3.9.

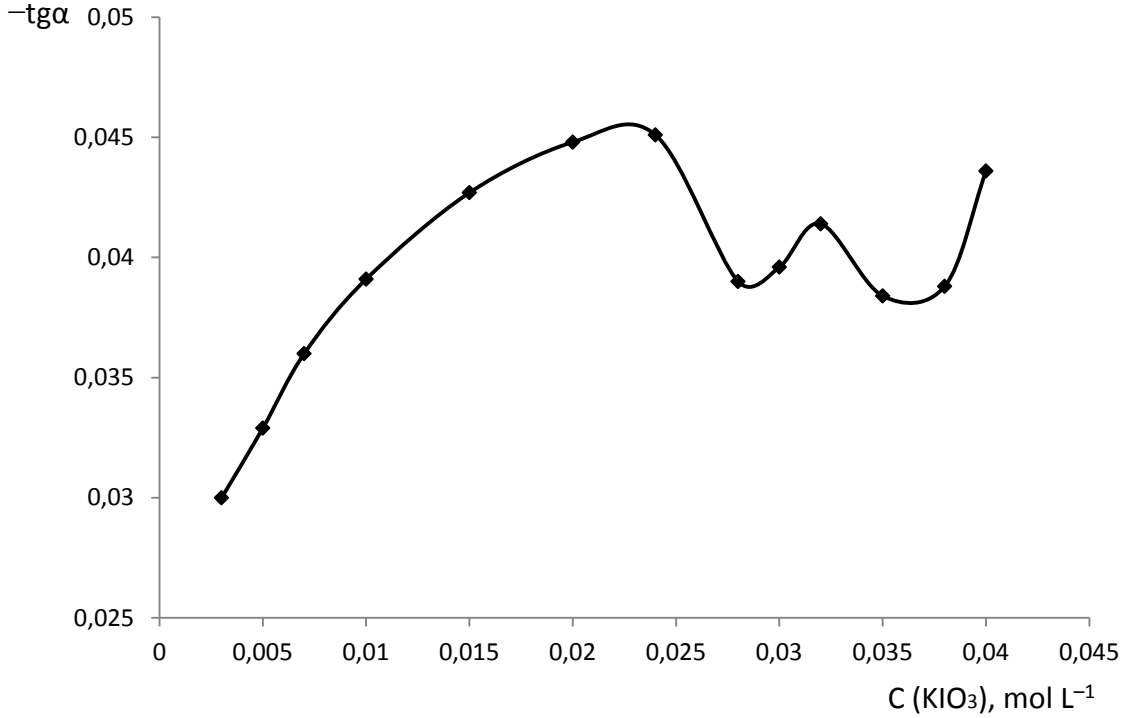


Figure 3.10 – Effect of potassium iodate on the initial rate: C(NR) = 6.92×10^{-5} mol L^{-1}; C(NH_2OH) = 1.82×10^{-5} mol L^{-1}; C(H_2SO_4) = 0.30 mol L^{-1}

Table 3.8 – Development of neutral red absorbance in the presence of sulfuric acid and nitrite ion

t, min	Absorbance (A)							
	Molar concentration of sulfuric acid (C(H_2SO_4)), mol L^{-1}							
	0.03	0.051	0.075	0.15	0.3	0.6	1.2	1.5
1	1.224	1.194	1.181	1.144	1.070	0.954	0.699	0.608
1.25	1.224	1.191	1.178	1.135	1.054	0.932	0.683	0.595
1.5	1.223	1.188	1.173	1.126	1.040	0.918	0.674	0.587
1.75	1.221	1.186	1.169	1.117	1.028	0.906	0.668	0.583
2	1.220	1.182	1.164	1.108	1.017	0.897	0.664	0.581
2.25	1.218	1.181	1.160	1.101	1.007	0.890	0.662	0.580
2.5	1.217	1.178	1.157	1.092	0.998	0.886	0.660	0.579
2.75	1.213	1.174	1.151	1.085	0.990	0.882	0.660	0.578
3	1.212	1.172	1.147	1.078	0.983	0.879	0.659	0.578

Completed Table3.8

t, min	Absorbance (A)							
	Molar concentration of sulfuric acid ($C(H_2SO_4)$), mol L^{-1}							
	0.03	0.051	0.075	0.15	0.3	0.6	1.2	1.5
3.5	1.208	1.165	1.139	1.065	0.972	0.875	0.658	0.577
4	1.205	1.16	1.13	1.054	0.963	0.873	0.657	0.577
4.5	1.201	1.153	1.122	1.045	0.957	0.871	0.657	0.577
5	1.197	1.147	1.115	1.036	0.951	0.871	0.657	0.577

Table 3.9 – Development of neutral red absorbance in the presence of sulfuric acid and hydroxylamine

t, min	Absorbance (A)							
	Molar concentration of sulfuric acid ($C(H_2SO_4)$), mol L^{-1}							
	0.03	0.051	0.075	0.15	0.3	0.6	1.2	1.5
1	1.272	1.239	1.257	1.21	1.168	1.034	0.906	0.82
1.25	1.272	1.238	1.252	1.200	1.157	1.023	0.898	0.814
1.5	1.272	1.236	1.247	1.193	1.146	1.013	0.891	0.808
1.75	1.270	1.235	1.243	1.185	1.137	1.004	0.886	0.804
2	1.268	1.233	1.238	1.178	1.129	0.996	0.882	0.800
2.25	1.267	1.231	1.233	1.172	1.122	0.990	0.878	0.797
2.5	1.266	1.228	1.229	1.164	1.115	0.984	0.875	0.795
2.75	1.265	1.226	1.225	1.157	1.109	0.979	0.873	0.792
3	1.264	1.224	1.220	1.153	1.103	0.974	0.870	0.790
3.5	1.260	1.217	1.210	1.141	1.092	0.966	0.866	0.786
4	1.257	1.212	1.202	1.132	1.083	0.959	0.864	0.783
4.5	1.252	1.207	1.194	1.123	1.075	0.954	0.862	0.782
5	1.248	1.201	1.186	1.115	1.067	0.950	0.860	0.780

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 show the decreasing absorbance, tangents are negative. To represent them conveniently, we changed the sign. All calculated initial rates are shown in Figure 3.11.

Concentration of nitrite ion, equimolar to hydroxylamine, shows somewhat higher reaction rate, probably because not all of hydroxylamine turns into nitrite ion before it decolorizes neutral red. Optimal concentration of sulfuric acid equals 0.3 mol L^{-1}.

3.5 Effect of neutral red on the color development

As the reaction is followed spectrophotometrically by monitoring the change in the absorbance of neutral red, its concentration is of important. 0.6mL of 3.03×10^{-4} mol L^{-1}hydroxylamine was transferred into a 10-mL graduated test tube.Then 2.4 mL of 0.1 mol L^{-1}iodate was addedfollowed by 1 mL of 3.0 mol L^{-1}sulfuric acid

solution.Neutral red solutionconcentration was varied from 2.42×10^{-5}mol L^{-1} to 2.77×10^{-4}mol L^{-1}.The stop clock in a smartphone was started just after the addition of the last drop of neutral red. The solution was diluted to the mark withdistilled water and a portion of it was transferred into a 1-cm glass cuvette to measure the absorbance of the solution at 530 nm. The absorbance measurement was begun in 1 min, necessary for transferring the solution into the cuvette. TheresultsareshowninTable 3.10.

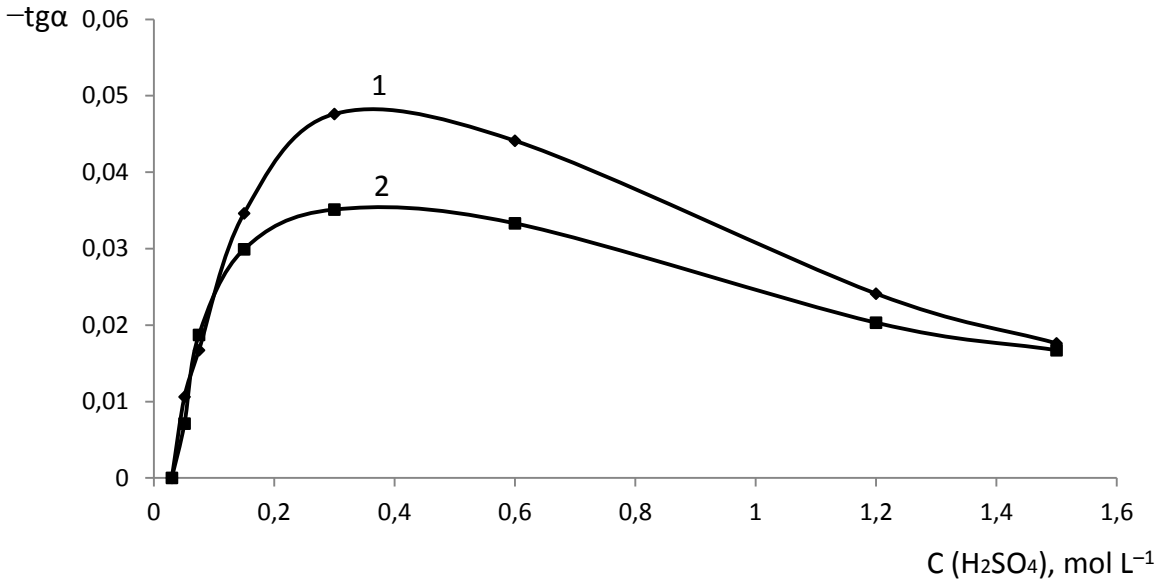


Figure 3.11 – Effect of sulfuric acid concentration on the initial rate:
$C(NR) = 6.92\times10^{-5}$ mol L^{-1}; $C(KIO_3) = 0.005$ mol L^{-1};
1 –$C(NaNO_2) = 1.81\times10^{-5}$ mol L^{-1}; **2** –$C(NH_2OH) = 1.82\times10^{-5}$ mol L^{-1}

Table 3.10 – Development of neutral red absorbance at various its concentrations

t, min	Absorbance (A)										
	Molar concentration of neutral red ($C(NR)\cdot10^5$), mol L^{-1}										
	2.422	3.46	4.844	6.228	6.92	6.12	8.996	10.38	12.11	13.84	27.7
1	0.107	0.444	0.606	0.834	1.030	1.146	1.233	1.396	1.507	1.624	1.703
1.25	0.094	0.439	0.599	0.821	1.017	1.132	1.220	1.384	1.497	1.618	1.701
1.5	0.084	0.434	0.592	0.810	1.006	1.121	1.207	1.373	1.490	1.613	1.699
1.75	0.074	0.432	0.586	0.799	0.994	1.110	1.197	1.365	1.484	1.609	1.697
2	0.067	0.430	0.580	0.790	0.986	1.100	1.187	1.360	1.480	1.607	1.695
2.25	0.060	0.428	0.575	0.782	0.977	1.092	1.180	1.352	1.476	1.605	1.693
2.5	0.055	0.427	0.571	0.774	0.969	1.084	1.173	1.346	1.475	1.604	1.690
2.75	0.051	0.426	0.566	0.767	0.961	1.078	1.166	1.343	1.471	1.602	1.690
3	0.048	0.425	0.562	0.760	0.955	1.072	1.162	1.339	1.470	1.600	1.690
3.5	0.043	0.424	0.555	0.749	0.943	1.061	1.152	1.334	1.466	1.599	1.690
4	0.041	0.423	0.548	0.739	0.934	1.053	1.145	1.330	1.463	1.599	1.690

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 show the decreasing absorbance, tangents are negative. To represent them conveniently, we changed the sign. All calculated initial rates are shown in Figure 3.12.

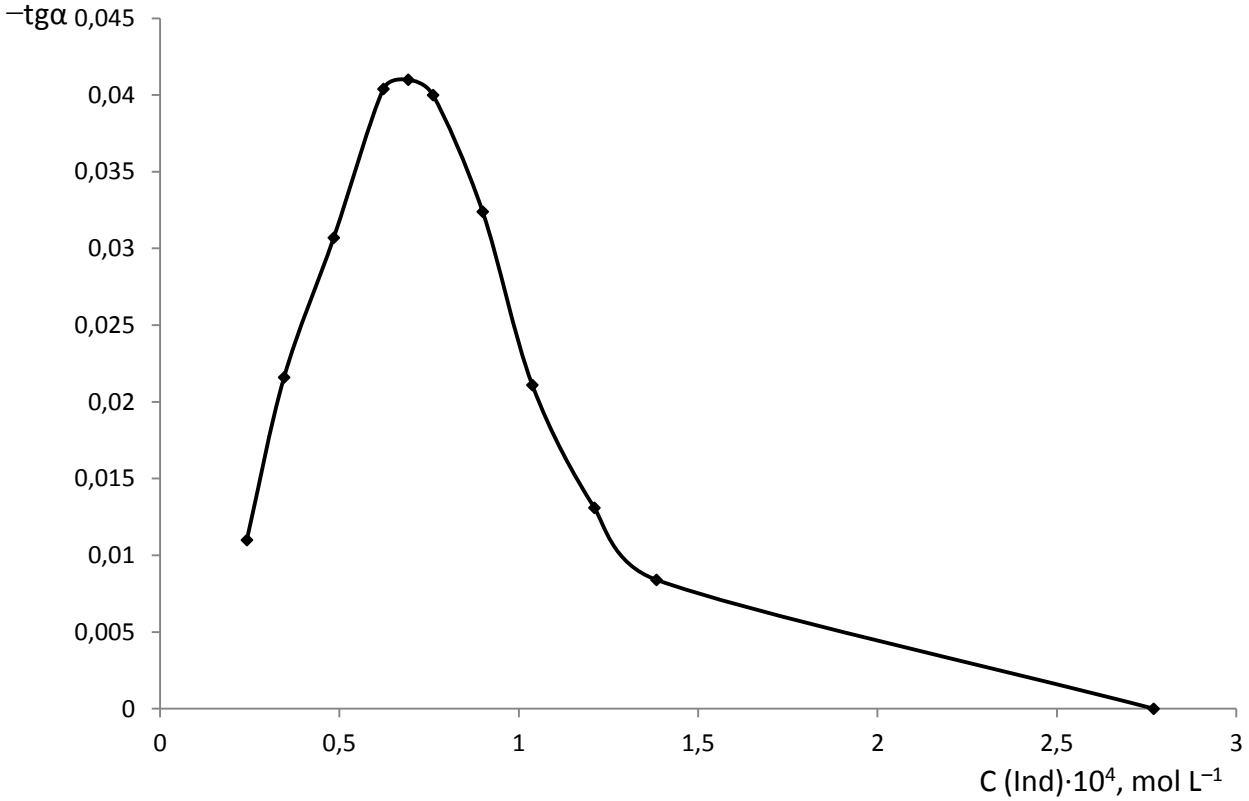


Figure 3.12 – Effect of neutral red concentration on the initial rate:
$C(H_2SO_4)$ = 0.30 mol L^{-1}; $C(KIO_3)$ = 0.024 mol L^{-1}; $C(NH_2OH) = 1.82\times10^{-5}$ mol L^{-1}

A blank experiment was 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. Optimal concentration of neutral red solution equals 6.92×10^{-5} mol L^{-1}, like in [6].

3.6 Calibration curves

3.6.1 Calibration curves for hydroxylamine

Kinetic method using neutral red and iodate works within (1.21×10^{-6}–3.63×10^{-5})mol L^{-1} hydroxylamine [6].

Hydroxylamine solutionconcentration was varied from 3.03×10^{-6}mol L^{-1} to 3.00×10^{-5}mol L^{-1}.A suitable aliquot of hydroxylamine solution was transferred into a 10-mL graduated test tube.Then 2.4 mL of 0.1 mol L^{-1}iodate was addedfollowed by 1 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 in a smartphone was started just after the addition of the last drop of neutral red. The solution was diluted to the mark withdistilled water and a portion of it was transferred into a 1-cm glass cuvette to measure the absorbance of the

solution at 530 nm. The absorbance measurement was begun in 1 min, necessary for transferring the solution into the cuvette. TheresultsareshowninTable 3.11

Table 3.11 – Development of neutral red absorbance in the presence of hydroxylamine with potassium iodate

t, min	Absorbance (A)							
	Molar concentration of hydroxylamine ($C(NH_2OH) \cdot 10^5$), mol L^{-1}							
	0.30	0.45	0.61	0.76	0.91	1.06	1.21	1.33
1	1.220	1.216	1.215	1.194	1.202	1.194	1.188	1.172
1.25	1.220	1.213	1.210	1.189	1.195	1.187	1.180	1.164
1.5	1.218	1.211	1.207	1.184	1.188	1.180	1.172	1.156
1.75	1.217	1.210	1.204	1.181	1.183	1.173	1.164	1.149
2	1.216	1.208	1.201	1.178	1.177	1.167	1.157	1.142
2.25	1.217	1.207	1.199	1.174	1.174	1.163	1.151	1.136
2.5	1.215	1.206	1.197	1.172	1.170	1.159	1.147	1.130
2.75	1.215	1.205	1.196	1.171	1.167	1.156	1.142	1.125
3	1.215	1.204	1.194	1.167	1.165	1.151	1.139	1.121
3.5	1.215	1.204	1.192	1.165	1.161	1.145	1.131	1.113
4	1.214	1.203	1.19	1.163	1.157	1.141	1.126	1.106
	Molar concentration of hydroxylamine ($C(NH_2OH) \cdot 10^5$), mol L^{-1}							
	1.51	1.64	1.82	1.94	2.12	2.24	2.42	2.66
1	1.175	1.167	1.165	1.160	1.166	1.150	1.151	1.150
1.25	1.164	1.155	1.152	1.146	1.152	1.136	1.135	1.131
1.5	1.155	1.144	1.14	1.135	1.139	1.123	1.120	1.114
1.75	1.146	1.136	1.129	1.123	1.126	1.110	1.107	1.099
2	1.138	1.128	1.119	1.113	1.115	1.099	1.094	1.087
2.25	1.131	1.119	1.110	1.104	1.106	1.089	1.083	1.076
2.5	1.125	1.112	1.102	1.094	1.097	1.079	1.072	1.065
2.75	1.118	1.105	1.094	1.087	1.088	1.069	1.062	1.056
3	1.113	1.099	1.087	1.079	1.079	1.061	1.053	1.046
3.5	1.103	1.089	1.074	1.066	1.066	1.046	1.036	1.030
4	1.096	1.081	1.064	1.055	1.055	1.033	1.023	1.017

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 show the decreasing absorbance, tangents are negative. To represent them conveniently, we changed the sign. All calculated initial rates are shown in Figure 3.13 (1 curve).

3.6.2 Calibration curves for nitrite ion

As the neutral red discoloration goes on because of nitrite ion, it is necessary to know how much of it is needed for the reaction.

Sodium nitrite solutionconcentration was varied from 2.90×10^{-6}mol L^{-1} to 4.35×10^{-5}mol L^{-1}.A suitable aliquot of nitrite solution was transferred into a 10-mL graduated test tube.Then 2.4 mL of 0.1 mol L^{-1}potassium iodate was addedfollowed by

1 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 in a smartphone was started just after the addition of the last drop of neutral red. The solution was diluted to the mark withdistilled water and a portion of it was transferred into a 1-cm glass cuvette to measure the absorbance of the solution at 530 nm. The absorbance measurement was begun in 1 min, necessary for transferring the solution into the cuvette. TheresultsareshowninTable 3.12.

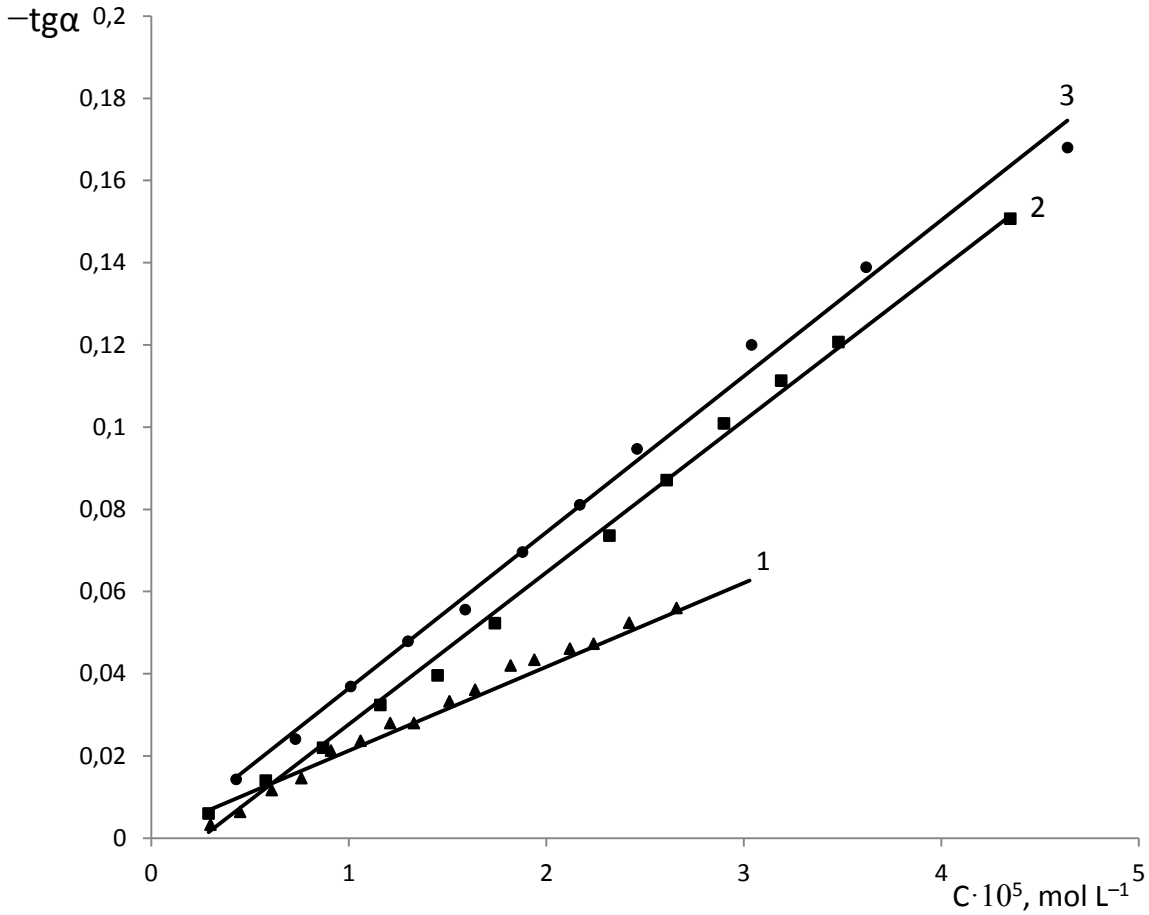


Figure 3.13 – Calibration curves: C(NR) = 6.92×10^{-5} mol L^{-1}; $C(H_2SO_4)$ = 0.30 mol L^{-1}; **1**– $C(KIO_3)$ = 0.024 mol L^{-1}, NH_2OH; **2** – $C(KIO_3)$ = 0.024 mol L^{-1},$NaNO_2$; **3** – $NaNO_2$

Table 3.12 – Development of neutral red absorbance in the presence of nitrite ion with potassium iodate

t, min	Absorbance (A)											
	Molar concentration of nitrite ($C(NaNO_2)\cdot10^5$), mol L^{-1}											
	0.29	0.58	0.87	1.16	1.45	1.74	2.32	2.61	2.9	3.19	3.48	4.35
1	1.203	1.179	1.155	1.114	1.096	1.066	1.017	0.987	1.016	0.950	0.922	0.971
1.25	1.200	1.174	1.146	1.102	1.082	1.047	0.992	0.956	0.980	0.911	0.882	0.920
1.5	1.198	1.170	1.139	1.092	1.069	1.031	0.969	0.928	0.950	0.878	0.845	0.874
1.75	1.196	1.165	1.133	1.083	1.059	1.017	0.950	0.906	0.923	0.848	0.813	0.834
2	1.195	1.163	1.128	1.076	1.050	1.006	0.932	0.886	0.900	0.823	0.785	0.800

Completed Table3.12

t, min	Absorbance (A)											
	Molar concentration of nitrite ($C(NaNO_2) \cdot 10^5$), mol L^{-1}											
	0.29	0.58	0.87	1.16	1.45	1.74	2.32	2.61	2.9	3.19	3.48	4.35
2.25	1.194	1.160	1.124	1.070	1.043	0.995	0.918	0.870	0.880	0.801	0.761	0.770
2.5	1.194	1.158	1.122	1.065	1.036	0.987	0.907	0.855	0.864	0.782	0.741	0.744
2.75	1.194	1.157	1.119	1.060	1.031	0.980	0.897	0.842	0.849	0.766	0.722	0.722
3	1.193	1.155	1.117	1.056	1.026	0.974	0.888	0.832	0.836	0.751	0.706	0.702
3.5	1.192	1.153	1.114	1.049	1.020	0.964	0.874	0.815	0.816	0.729	0.679	0.669
4	1.193	1.153	1.113	1.045	1.016	0.956	0.863	0.802	0.800	0.711	0.658	0.642

Repeat the experiment without added of potassium iodate. Sodium nitrite solutionconcentration was varied from 4.3×10^{-6}mol L^{-1} to 4.64×10^{-5}mol L^{-1}.A suitable aliquot of nitrite solution was transferred into a 10-mL graduated test tube.Then 1 mL of 3.0 mol L^{-1}sulfuric acid solution was addedfollowed by 2 mL of 3.46×10^{-4} mol L^{-1}neutral red solution. The stop clock in a smartphone was started just after the addition of the last drop of neutral red. The solution was diluted to the mark withdistilled water and a portion of it was transferred into a 1-cm glass cuvette to measure the absorbance of the solution at 530 nm. The absorbance measurement was begun in 1 min, necessary for transferring the solution into the cuvette. TheresultsareshowninTable 3.13.

Table 3.13 – Development of neutral red absorbance in the presence of nitrite ion without potassium iodate

t, min	Absorbance (A)										
	Molar concentration of nitrite ($C(NaNO_2) \cdot 10^5$), mol L^{-1}										
	0.43	0.73	1.01	1.3	1.59	1.88	2.17	2.46	3.04	3.62	4.64
1	1.219	1.199	1.174	1.156	1.125	1.114	1.094	1.076	1.041	1.007	0.905
1.25	1.213	1.188	1.160	1.139	1.105	1.089	1.066	1.044	1.001	0.962	0.845
1.5	1.209	1.181	1.148	1.124	1.088	1.068	1.041	1.015	0.966	0.922	0.794
1.75	1.204	1.174	1.138	1.111	1.073	1.050	1.020	0.991	0.933	0.885	0.750
2	1.201	1.169	1.130	1.101	1.061	1.034	1.002	0.969	0.907	0.853	0.713
2.25	1.200	1.165	1.124	1.091	1.050	1.020	0.986	0.950	0.882	0.824	0.680
2.5	1.197	1.162	1.118	1.084	1.041	1.009	0.971	0.933	0.860	0.798	0.650
2.75	1.196	1.158	1.113	1.078	1.033	0.999	0.959	0.919	0.840	0.775	0.625
3	1.194	1.157	1.109	1.073	1.026	0.989	0.949	0.906	0.823	0.755	0.601
3.5	1.193	1.153	1.104	1.064	1.015	0.976	0.932	0.884	0.795	0.720	0.564
4	1.192	1.151	1.100	1.059	1.008	0.965	0.920	0.869	0.773	0.692	0.533

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 show the decreasing absorbance, tangents are negative. To represent them conveniently, we changed the sign. All calculated initial ratesfor Table 3.12 and 3.13 are shown inFigure 3.13 (Curves 2 and 3).

Table 3.14 – Characteristics for the calibration graphs for the determination of hydroxylamine and nitrite ion

Analyte	Equation	Range (μmol L^{-1})	r^2
Hydroxylamine	$Y = (0.0009 \pm 0.0075) + (2040 \pm 440) \cdot X$	3.03 – 26.6	0.9557
Nitrite ion with KIO_3	$Y = (-0.0093 \pm 0.0052) + (3700 \pm 220) \cdot X$	2.90 – 43.5	0.9966
Nitrite ion without KIO_3	$Y = (-0.002 \pm 0.014) + (3630 \pm 500) \cdot X$	4.35 – 46.4	0.9954

3.7 Metrological characteristics

Evaluation of metrological characteristics has been carried out on the basis of conventional statistical criteria.

An aliquot of 1 mL of 1.5×10^{-4} mol L^{-1} hydroxylamine solution was transferred into a 10-mL graduated test tube in 6 replicate aliquotsand to each an aliquot of 1 mL of 1.45×10^{-4} mol L^{-1} sodium nitrite was added. For the determination of hydroxylamine with nitrite ion in mixture, 2.4 mL of 0.1 mol L^{-1}iodate was addedfollowed by 1 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 in a smartphone was started just after the addition of the last drop of neutral red. The solution was diluted to the mark withdistilled water and a portion of it was transferred into a 1-cm glass cuvette to measure the absorbance of the solution at 530 nm. The absorbance measurement was begun in 1 min, necessary for transferring the solution into the cuvette.

To determine only the nitrite ion in its mixture with hydroxylamine, potassium iodate was not added to an aliquot. The procedure described above was applied in the absence of potassium iodate.Hydroxylamine was added to prove that it does not interfere with the determination of nitrite ion.The results of measurements are shown in Table 3.15.

Decreasing absorbance was measured, the kinetic curve slope ratios was calculated, using the linear regression equation obtained in the similar conditions (both in the presence and in the absence of potassium iodate), nitrite ion and hydroxylamine concentrations in the analyzed solutions were determined. Theresultsof statistical determination of metrological characteristics areshowninTable 3.16.

Table 3.15 – Development of neutral red absorbance in the presence of nitrite ionand hydroxylamine

t, min	Absorbance (A)					
	In the presence of KIO_3					
1	1.042	1.042	1.038	1.036	1.036	1.055
1.25	1.010	1.012	1.008	1.006	1.006	1.025
1.5	0.982	0.986	0.982	0.979	0.982	0.998

Completed Table3.15

t, min	Absorbance (A)					
	In the presence of KIO_3					
1.75	0.959	0.962	0.959	0.956	0.959	0.976
2	0.939	0.943	0.939	0.936	0.939	0.955
2.25	0.921	0.925	0.921	0.918	0.921	0.937
2.5	0.906	0.910	0.906	0.903	0.906	0.921
2.75	0.891	0.896	0.891	0.889	0.891	0.907
3	0.879	0.883	0.879	0.876	0.879	0.894
3.5	0.857	0.862	0.857	0.855	0.857	0.873
4	0.840	0.845	0.840	0.836	0.840	0.855
	In the absence of KIO_3					
1	1.108	1.115	1.169	1.148	1.121	1.119
1.25	1.089	1.096	1.151	1.129	1.102	1.099
1.5	1.074	1.081	1.136	1.114	1.085	1.083
1.75	1.061	1.068	1.123	1.100	1.072	1.070
2	1.051	1.056	1.112	1.091	1.061	1.059
2.25	1.043	1.047	1.103	1.082	1.052	1.050
2.5	1.035	1.041	1.095	1.075	1.043	1.042
2.75	1.030	1.034	1.089	1.068	1.037	1.037
3	1.024	1.030	1.084	1.062	1.032	1.031
3.5	1.018	1.022	1.076	1.056	1.025	1.023
4	1.013	1.017	1.071	1.051	1.019	1.017

Table 3.16 – Evaluation of hydroxylamine and nitriteion determination errors (P =0.95; $t_{P, f}$ = 2.57)

$-tg\alpha \cdot 10^2$	$X_i \cdot 10^5$, mol L^{-1}	$\bar{X}$	S	ΔX	$(\Delta X/\bar{X})100\%$	δ, %
present in sample: $C(NaNO_2) = 1.45 \cdot 10^{-5}$ mol L^{-1}						
4.77; 4.93; 4.89; 4.80; 5.11; 5.04	1.36; 1.40; 1.39; 1.37; 1.45; 1.43	$1.40 \cdot 10^{-5}$	$3.66 \cdot 10^{-7}$	$3.84 \cdot 10^{-7}$	2.7	3.4
present in sample: $C(NH_2OH) = 1.51 \cdot 10^{-5}$ mol L^{-1}						
3.13; 3.42; 3.06; 3.07; 3.39; 3.15	1.49; 1.63; 1.46; 1.46; 1.62; 1.50	$1.53 \cdot 10^{-5}$	$7.86 \cdot 10^{-7}$	$8.25 \cdot 10^{-7}$	5.4	1.3

According to the table data, the reproducibility of the results of nitriteion determination is expressed by the relative error 2.7%, while the relative error of accuracy proves to be 3.4%; the reproducibility of the results of hydroxylamine determination is expressed by the relative error 5.4%, while the relative error of accuracy proves to be 1.3%.Nitrite ion was found $(1.40 \pm 0.04) \times 10^{-5}$mol L^{-1}compared to introduced amount 1.45×10^{-5} mol L^{-1}, and hydroxylamine was found $(1.53 \pm 0.08) \times 10^{-5}$mol L^{-1} compared to introduced amount 1.51×10^{-5} mol L^{-1}. There is no systematic error.

3.8 Analysis of a soil sample

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.

Sampling

A soil sample was collected at the territory of Gagarin Park in Chelyabinsk. This 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 [4].

Sample preparation

Extraction was carried out according to the methods of the authors [4].4 g of fresh soil was added to a 100-mL conicalflask, 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, as in the paper [4], the pH value was monitored by a pH-meter (марка). The extraction was carried out by shaking the suspension for 10 min, thenthe solution was filtered. After filtration, the filtrate was centrifuged at 2000 rpm for 15 min in centrifuge tubes.

The soil sample was analyzed for several components.

Soil analysis with addition in the presence of potassium iodate (the determination of the sum nitrite ion and hydroxylamine in mixture)

First,2 mL of the soil extract was transferred into a 10-mL graduated test tube. An aliquot of 1 mL of 1.51×10^{-4} mol L^{-1} hydroxylamine solution and an aliquot of 1 mL of 1.45×10^{-4} mol L^{-1} sodium nitrite were added. Then 2.4 mL of 0.1 mol L^{-1}iodate was addedfollowed by 1 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 in a smartphone was started just after the addition of the last drop of neutral red. The solution was diluted to the mark with distilled water and a portion of it was transferred into a 1-cm glass cuvette to measure the absorbance of the solution at 530 nm. The absorbance measurement was begun in 1 min, necessary for transferring the solution into the cuvette.We carried out 6 replicate measurements.The results are shown in Table 3.17. One of the kinetic curves is shown in Figure 3.14 (1).

Soil analysis with addition in the absence of potassium iodate (the determination of nitrite ion)

As described above, 2 mL of the soil extract was transferred into a 10-mL graduated test tube. An aliquot of 1 mL of 1.51×10^{-4} mol L^{-1} hydroxylamine solution and an aliquot of 1 mL of 1.45×10^{-4} mol L^{-1} sodium nitrite were added. Then 1 mL of 3.0 mol L^{-1} sulfuric acid solution was added and 2 mL of 3.46×10^{-4} mol L^{-1} neutral red solution. The stop clock in a smartphone was started just after the addition of the last drop of neutral red. The solution was diluted to the mark with distilled water and a portion of it was transferred into a 1-cm glass cuvette to measure the absorbance of the solution at 530 nm. The absorbance measurement was begun in 1 min, necessary for

transferring the solution into the cuvette.We carried out 6 replicate measurements. The results are shown in Table 3.17. One of the kinetic curves is shown in Figure 3.14 (2).

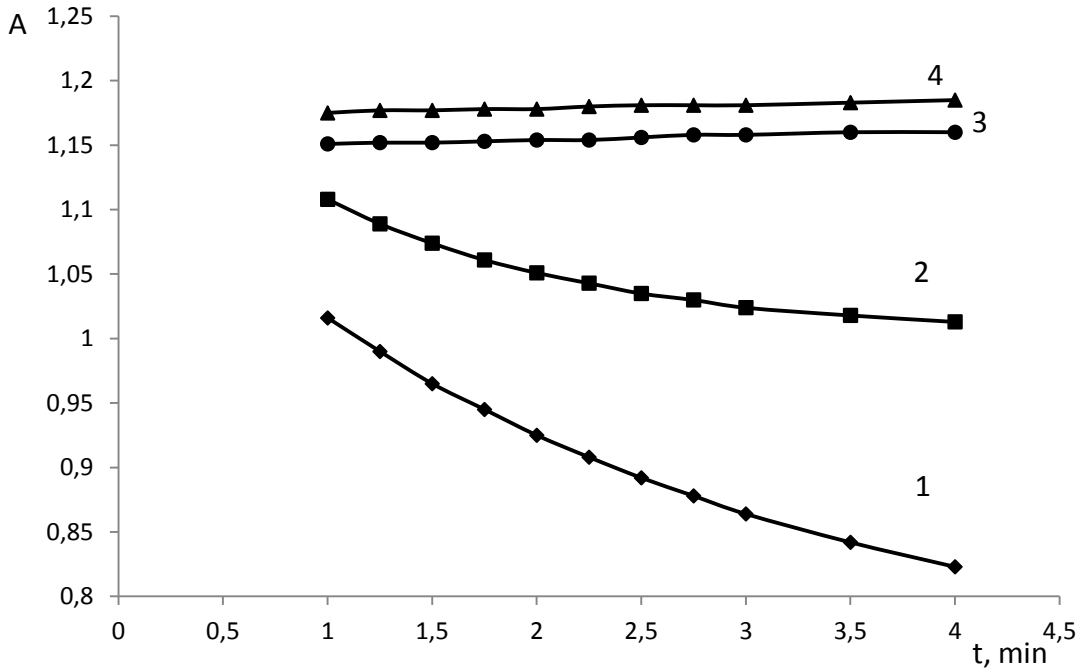


Figure 3.14 – Absorbance-time plots: C(NR) = 6.92×10^{-5} mol L^{-1}; C(H_2SO_4) = 0.30 mol L^{-1}; **1, 2** – C(NH_2OH) = 1.55×10^{-5} mol L^{-1}; C($NaNO_2$) = 1.45×10^{-5} mol L^{-1}; **1, 3** – C(KIO_3) = 0.024 mol L^{-1}

Table 3.17 – Development of neutral red absorbance in soil analysis with addition of nitrite ion and hydroxylamine

t, min	Absorbance (A)					
	In the presence of KIO_3					
1	1.016	1.032	1.024	1.030	1.036	1.036
1.25	0.990	1.005	0.999	1.003	1.006	1.006
1.5	0.965	0.983	0.978	0.980	0.979	0.982
1.75	0.945	0.963	0.958	0.960	0.956	0.959
2	0.925	0.944	0.940	0.941	0.936	0.939
2.25	0.908	0.927	0.923	0.923	0.918	0.921
2.5	0.892	0.912	0.908	0.908	0.903	0.906
2.75	0.878	0.898	0.894	0.894	0.889	0.891
3	0.864	0.886	0.881	0.881	0.876	0.879
3.5	0.842	0.865	0.859	0.859	0.855	0.857
4	0.823	0.847	0.841	0.841	0.836	0.84
	In the absence of KIO_3					
1	1.108	1.112	1.165	1.148	1.121	1.115
1.25	1.089	1.096	1.151	1.129	1.102	1.096
1.5	1.074	1.081	1.136	1.114	1.085	1.083
1.75	1.061	1.068	1.123	1.100	1.072	1.070

Completed Table3.17

t, min	Absorbance (A)					
	In the absence of KIO_3					
2	1.051	1.056	1.112	1.091	1.061	1.059
2.25	1.043	1.047	1.103	1.082	1.052	1.050
2.5	1.035	1.041	1.095	1.075	1.043	1.044
2.75	1.030	1.034	1.089	1.068	1.037	1.037
3	1.024	1.030	1.084	1.062	1.032	1.031
3.5	1.018	1.022	1.076	1.056	1.025	1.023
4	1.013	1.017	1.071	1.051	1.019	1.017

Soil analysis without addition

Besides,the experiment without the addition of nitrite ion and hydroxylamine was carried out. 2 mL of the soil extract was transferred into a 10-mL graduated test tube. In the first case 2.4 mL of 0.1 mol L^{-1}potassiumiodate was added, and in the second case there was no potassium iodate. Then 1 mL of 3.0 mol L^{-1} sulfuric acid solution was added and 2 mL of 3.46×10^{-4} mol L^{-1} neutral red solution. Measurements weremade according to the experimental procedure above. Wealso carried out 6 replicate measurements. The results are shown in Table 3.18. The kinetic curves are shown in Figure 3.14 (3and 4).

Table 3.18 – Development of neutral red absorbance in soil analysis without addition

t, min	A					
	In the presence of KIO_3					
1	1.151	1.155	1.148	1.160	1.156	1.150
1.25	1.152	1.156	1.149	1.160	1.156	1.152
1.5	1.152	1.156	1.150	1.162	1.158	1.152
1.75	1.153	1.158	1.150	1.162	1.158	1.152
2	1.154	1.158	1.151	1.162	1.160	1.154
2.25	1.154	1.158	1.151	1.162	1.160	1.154
2.5	1.156	1.160	1.151	1.164	1.160	1.155
2.75	1.158	1.160	1.152	1.164	1.162	1.156
3	1.158	1.160	1.152	1.165	1.162	1.158
3.5	1.160	1.162	1.154	1.166	1.164	1.158
4	1.160	1.162	1.155	1.168	1.164	1.160
	In the absence of KIO_3					
1	1.175	1.178	1.169	1.174	1.170	1.166
1.25	1.177	1.180	1.169	1.176	1.172	1.168
1.5	1.177	1.180	1.171	1.176	1.172	1.170
1.75	1.178	1.180	1.171	1.176	1.174	1.170
2	1.178	1.181	1.172	1.177	1.174	1.172
2.25	1.180	1.182	1.172	1.177	1.175	1.172
2.5	1.181	1.182	1.172	1.178	1.176	1.172
2.75	1.181	1.182	1.174	1.178	1.176	1.174

Completed Table3.18

t, min	A					
	In the absence of KIO_3					
3	1.181	1.183	1.174	1.178	1.178	1.176
3.5	1.183	1.183	1.176	1.180	1.178	1.178
4	1.185	1.185	1.176	1.180	1.180	1.178

In the absence of the addition, the tangent is approximate to zero, so in the studied soil sample hydroxylamine and nitrite ion has been not detected.

Evaluation of metrological characteristics have been carried out on the basis of conventional statistical criteria. The results are shown in Table 3.19.

Thus, after preparation of the soil sample with added hydroxylamine and nitrite ion, we determined the concentration of nitrite ion as $(1.48\pm0.03)\times10^{-5}$mol L^{-1}; the added concentration 1.45×10^{-5} mol L^{-1} is within the confidence interval. The same is true about hydroxylamine, the determined and added concentrations are $(1.55\pm0.05)\times10^{-5}$mol L^{-1} and 1.51×10^{-5} mol L^{-1}, respectively. It means that though the suggested method can be used for determination of hydroxylamine and nitrite ion simultaneously in principle, the investigated soil sample did not contain them in concentrations above the detection level.

Table 3.19 – Analysis of soil samples with the standard addition method

$-\mathrm{tg}\alpha\cdot10^2$	$X_i\cdot10^5$, mol L^{-1}	$\bar{X}$	S	ΔX	$(\Delta X/\bar{X})100\%$	δ, %
Added to sample: $C(NaNO_2) = 1.45\cdot10^{-5}$ mol L^{-1}						
5.17; 5.23; 5.36; 5.23; 5.11; 5.13	1.47; 1.49; 1.52; 1.49; 1.45; 1.46	$1.48\cdot10^{-5}$	$2.50\cdot10^{-7}$	$2.62\cdot10^{-7}$	1.8	2.1
Added to sample: $C(NH_2OH) = 1.51\cdot10^{-5}$ mol L^{-1}						
3.30; 3.39; 3.15; 3.16; 3.33; 3.21	1.57; 1.62; 1.50; 1.51; 1.59; 1.53	$1.55\cdot10^{-5}$	$4.80\cdot10^{-7}$	$5.04\cdot10^{-7}$	3.3	2.6

4 CONCLUSION

1.The optimal conditions for determination of hydroxylamine: concentration of neutral red is 6.92×10^{-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 (3.03×10^{-6}–3.00×10^{-5})mol L^{-1}range.

2. Nitrite ion can be determined simultaneously with hydroxylamine, if the described system absorbance is measured without iodate ion addition.The calibration curve is linear in (4.3×10^{-6}–4.64×10^{-5})mol L^{-1}range.

3. The metrological characteristics of hydroxylamine and nitrite ion determination are as follows:the reproducibility of the results of nitriteion determination is expressed by the relative error 2.7 %, while the relative error of accuracy proves to be 3.4%; the reproducibility of the results of hydroxylamine determination is expressed by the relative error 5.4 %, while the relative error of accuracy proves to be 1.3%.

4. The method was applied to soil analysis for the content of hydroxylamine and nitrite ion by the standard addition method.These substances were not found in the soil, but the determination of additions was carried out without a systematic error, namely: $(1.48\pm0.03)\times10^{-5}$mol $L^{-1}$for added 1.45×10^{-5} mol L^{-1} of nitrite ion and $(1.55\pm0.05)\times10^{-5}$mol $L^{-1}$for added 1.51×10^{-5} mol $L^{-1}$of hydroxylamine.

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РЕФЕРАТ

БускинаК.А.
Кинетическоеопределениегидроксиламинапоегореакциисиодатоминейтральнымкрасным – Челябинск: ЮУрГУ,
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Гидроксиламин, метод тангенсов, нейтральный красный, иодат ион, анализ почвы.

Цельработы – кинетическое спектрофотометрическое определение гидроксиламина на основе его реакции с иодатом и нейтральным красным.

Для достижения цели НИРрешены следующие задачи:

- проведен литературный обзор по проблеме исследования;
- найдены оптимальные условия для определения гидроксиламина;
- нитрит ион определенсовместно с гидроксиламином;
- найденыметрологические характеристики определения гидроксиламина и нитрита;
-метод применен к анализу почвы на содержание гидроксиламина в присутствии нитрита методом добавок.

Кинетическое определение гидроксиламина методом тангенсов может быть основано на реакции нейтрального красного с ионом нитрита, полученногопри окислении гидроксиламина йодатом в кислой среде. Оптимальные условия определения: 0,3 моль/л H_2SO_4, 0,024 моль/л KIO_3, 6.92×10^{-5}моль/лнейтрального красного. Гидроксиламин можно также определить в присутствии нитрита, при условии, что нитрит определяется отдельно при тех же условиях без иодата. Метрологические характеристики следующие: повторяемость результатов гидроксиламина 5,4%, погрешность определения 1,3%. Соответствующие значения определения нитрита составляют 2,7% и 3,4%. Метод был применен для анализа почвы на содержание гидроксиламина и нитрита.