Analytical application of the reaction system disulphonated hydroquinone-hydrogen peroxide for the kinetic spectrophotometric determination of iron traces in acidic media

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Abstract

A simple, rapid, sensitive and selective kinetic spectrophotometric method for determination of Fe(III) traces was elaborated in this paper. It is based on the catalytic effect of Fe(III) ions on oxidation of potassium salt of disulphonated hydroquinone (K_2S_2Hy) by hydrogen peroxide in acidic media, at a constant ionic strength. At the working temperature of 20 °C and the wavelength of 450.0 nm, optimal conditions for determination of iron were found so that iron (III) can be determined by the proposed method in the concentration range of 1.87 to 18.7 ng cm^{-3}. Corresponding RSD values were determined to be in the range 4.22 to 10.33 %. The limit of detection (LOD) calculated in two ways was found to be 1.07 ng cm^{-3} *i.e.* 1.11 ng cm^{-3} Fe(III). In order to assess the selectivity of the method effects of different ions on the reaction rate were also determined. It was found that presence of oxalates and citrates in the w/w ratio to Fe(III) 1:1 under selected experimental conditions interferes with determination of iron. Then the method was applied for determination of Fe(III) traces in white radish juice. The results agreed well with those obtained by atomic absorption spectrometry.

Keywords: Fe(III), catalyst, kinetic spectrophotometric method, white radish

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1. INTRODUCTION

It is well known that iron plays a significant biological role in different ecological systems. Also, iron has a central role in oxygen transport and energetic metabolism in animal and human organisms. In natural water systems, Fe(III) can precipitate rapidly by formation of hydrous iron oxide and hydroxides, which can absorb other trace metals, so that the presence of iron can control the bioavailability, toxicity and mobility of other trace metals. The total amount of iron in an adult human organism is about 3.5 to 4.0 g. Iron as a heavy metal becomes an essential one for humans and animals binding the proteins, which do contain heme (hemoglobin, myoglobin and enzymes like catalases and oxidases) or do not contain heme (ferritin and flavoproteins) [1]. Therefore, there is an increased need for iron determination in environmental and biomedical materials, as well as in food and drinks, which provide the source of iron in human organism. A variety of well-established methods for quantitative determination of iron have been developed: inductively coupled plasma mass and optical emission spectrometry (ICP-MS and ICP-OES), atomic absorption spectrometry (AAS), ion chromatography (IC), electrochemical methods, UV/Vis spectrophotometry, etc. Flow injection analysis (FIA) and kinetic methods based on catalytic reactions, equipped with an UV-Vis spectrophotometric detector or some other simple detecting system, are nowadays often applied as the best way for trace elemental analysis because of high sensitivity and low limits of detection [2-6].

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Many of the developed methods are based on the catalytic effect of the determined species on oxidation reactions of sulphonated products of phenols by hydrogen peroxide. Authors from Serbia have developed several kinetic spectrophotometric methods based on the catalytic effects of iodide ions, iron (III), copper (II), chromium (VI), arsenic (III) and nickel (II) on oxidation of sodium pyrogallol-5-sulphonate by hydrogen peroxide [7-12]. The catalytic effect of iron (III) on the oxidation reaction of sodium pyrogallol-5-sulphonate by hydrogen peroxide was followed spectrophotometrically by measuring the rate of change in absorbance of the colored product at 436.8 nm. Nanogram amounts of iron (III) (2.0-75.0 ng cm^{-3}) can be determined with good accuracy (7.2 to 0.5 %). The minimum concentration of iron that can be determined by this method is 0.16 ng cm^{-3}. Presence of Cu^{2+}, Cr^{6+} and I^- in the *w/w* ratio to Fe(III) 1:1 interferes with the reaction. The method was applied for determination of iron in tap water samples [8]. The catalytic effect of phosphates on oxidation of the same sulphonated product by dissolved oxygen was also described [13]. The monosulphonated product of hydroquinone can be also oxidized by hydrogen peroxide in acidic media at a constant ionic strength. Cu(II) ion has a catalytic effect on this reaction. The reaction was followed spectrophotometrically at 440 nm. Micro-amounts of Cu(II) (0.20-7.33 µg cm^{-3}) could be determined with a relative error ranging from 6.6 to 2.3 %. The method was applied for determination of copper concentration in strawberry juice [14]. The catalytic reaction of oxidation of chromotropic acid (disodium salt of 4,5-dihydroxynaphtalene-2,7-disulphonic acid) by hydrogen peroxide was used for determination of microamounts of Fe(III) in tap and sea water samples and in biological materials. The obtained calibration curve was linear in the concentration range from 11.2 to 167.6 ng cm^{-3} [15]. The oxidation reaction of dibromo-p-sulfonic acid-arsenazo by potassium bromate in sulfuric acid media was used for determination of Fe(III) as a catalyst over the range of 2.0-6.0 ng cm^{-3}. The method was used for determination of iron traces in potato samples [16]. Determination of Fe(III) by using kinetic thermometric methods were also published: a method based on the iron catalytic action on oxidation of sulphanilic acid by sodium periodate and a method based on the catalyzing effect of Fe(III)-EDTA complex on oxidation of hydroxylamine [17,18]. Kinetic spectrophotometric methods for simultaneous determination of Fe(II) and Fe(III) were also described and applied for iron determination in real environmental and synthetic samples [19,20]. Kinetic catalytic methods for iron determination by using a multipumping flow system, spectrophotometric flow - injection analysis, as well as simultaneous determination of Fe(II) and Fe(III) by a FIA method, were described in literature, too [21-25]. There is no doubt that new investigations of iron complexes form an excellent base for further method developments for Fe(III) determination in solutions [26].

The aim of this paper was to determine optimal conditions for the oxidation reaction of disulphonated hydroquinone by hydrogen peroxide in the presence of iron(III) as a catalyst; to establish rate equations; to calculate the rate constants and thermodynamic functions and to validate the new method for determination of iron(III) concentration in solutions.

2. EXPERIMENTAL

2. 1. Apparatus

Progress of the reaction was followed by using a Perkin-Elmer Lambda 15 UV/Vis spectrophotometer (PerkinElmer Inc., MA, USA, optical wave 10 cm), connected to a theromocirculating bath (Julabo MP-5A, Spain). Cylindrical cells were thermostated at 20.0 ± 0.1 °C, as well as all of the used work solutions. A 716 DMS Titrino titrator (Metrohm, Switzerland) was used to measure pH values of the solutions. Sigma buffers, pH 7.00±0.01 and pH 4.00±0.01 were used for calibration. Socorex automatic micropipettes (Socorex Isba SA, Switzerland) were used to measure the exact volume of solutions. AAS measurements were performed on a Perkin-Elmer spectrometer (model AA 300, PerkinElmer Inc., MA, USA).

2. 2. Reagents

All chemicals used (potassium salt of hydroquinone disulphonic acid, iron (III) chloride, sodium perchlorate and perchloric acid) were of p.a. quality provided by Merck (Germany). All solutions were prepared by dissolving the appropriate amount of the substance in deionized water (TKA MicroMed, TKA Wasseraufbereitungssysteme GmbH, Germany). The stock solution of Fe(III) (1 mmol dm^{-3}) was prepared in a 0.1 mol dm^{-3} perchloric acid. The ionic strength was kept constant at 0.1 by an $NaClO_4$ solution (1.5 mol dm^{-3}). pH of the solutions was adjusted by 0.1 mol dm^{-3} $HClO_4$

solution. All stock solutions (iron chloride, perchloric acid, sodium perchlorate) were stored in polyethylene containers. Working solutions (potassium salt of hydroquinone disulphonic acid, hydrogen peroxide) were prepared just before the use. All the polyethylene containers and the glassware were washed by diluted hydrochloric acid (1:1, v/v), followed by a solution of potassium hydroxide in ethanol and then repeatedly well rinsed by tap, distilled and deionized water. All of the concentrations described here are the initial concentrations in the reaction mixture at time zero after mixing. Each kinetic result is the average of three measurements.

2. 3. Procedure

In order to obtain good mechanical and thermal stability, the instruments were run for 10 min before the first measurement. Selected volumes of reactants and deionized water were poured separately in the reaction mixture vessel with four compartments (so-called Budarin's vessel) up to a predetermined total volume of 15 cm^3. An aliquot of the solution of Fe(III) was transferred into one compartments of the vessel for the catalyzed reaction while the same volume of deionized water was used for the non-catalyzed reaction. After thermostating for 10 min at 20.0 ± 0.1 °C, the reagents were mixed, and the stopwatch was simultaneously turned on. The solution was immediately added to the properly rinsed spectrophotometer cell with a path length of 10 cm, and absorbance was measured every 30 seconds over a period of 2-8 min after mixing. Spectrophotometric measurements were performed at the wavelength of 450.0 nm, and at the working temperature of 20.0 ± 0.1 °C. The tangents method was used to assess the reaction rate by determination of the slope of the linear section of the experimentally obtained dependence of absorbance *vs*. time (dA/dt) [27].

Influences of concentrations of each component of the reaction mixture on the reaction rate of the catalyzed and non-catalyzed reactions were investigated. Concentration of each component was changed consecutively, while the concentrations of other components, as well as the working temperature, were kept constant.

2. 4. White radish sample preparation

White radish was chopped up and the juice was squeezed out by a juice extractor device. The juice was treated by a dry mineralization procedure [28]. The juice sample (50 cm^3) was dried on a sand bath and the dry residue was burned during a 24-hour period at the temperature of 450 – 500 °C. The cold rest was moistened by a few drops of deionized water and an aliquot (1.0 cm^3) of concentrated nitric acid was added. After slow heating, the nitric acid addition procedure was repeated two more times. The obtained content was quantitatively transferred to a normal vessel through filter paper (due to a slight unmineralized residue) with 5 cm^3 of aqueous solution of HNO_3 (conc. $HNO_3 : H_2O = 1:2$, *v/v*). The sediment was rinsed by deionized water and the normal vessel was filled up to the 50 cm^3 volume by deionized water. The method of white radish sample preparation was repeated five times. The obtained samples were placed in PVC vessels and diluted up to 250 cm^3 volume before kinetic measurements. Aliquots (0.2 cm^3) of these solutions were transferred to the Budarin's vessel for catalytic reaction investigations. The method of calibration curve was applied.

3. RESULTS AND DISCUSSION

Aqueous solutions of the potassium salt of disulpfonated hydroquinone (K_2S_2Hy, pH 5.28) exhibit absorption spectra at which absorption maxima are observed at the following wavelengths: 196, 204, 224 and 309 nm. Positions and intensities of the absorption maxima did not change for a 5 h monitoring period, which indicated good stability of the salt over time. The salt is stable even at lower pH values, while in the basic medium it can be oxidized by air oxygen. In the acidic medium, this salt can be oxidized by some oxidizing agents resulting in appearance of a new absorption maximum at 450 nm and a shift of the existing absorption maxima towards longer wavelengths. Nano-amounts of Fe(III) catalyze the oxidation reaction of the potassium salt of disulphonated hydroquinone by hydrogen peroxide in an acidic medium. The formed colored oxidation product made it possible to follow the reaction progress spectrophotometrically. Changes in the absorbance as a function of time for the non-catalyzed and catalyzed reactions are shown in Figure 1.

Spectrophotometric measurements were performed at the wavelength of the absorption maximum for the reaction mixture (450.0 nm), for both the non-catalyzed (1, 2, 3) and the catalyzed (4, 5, 6) reactions (Fig.1).

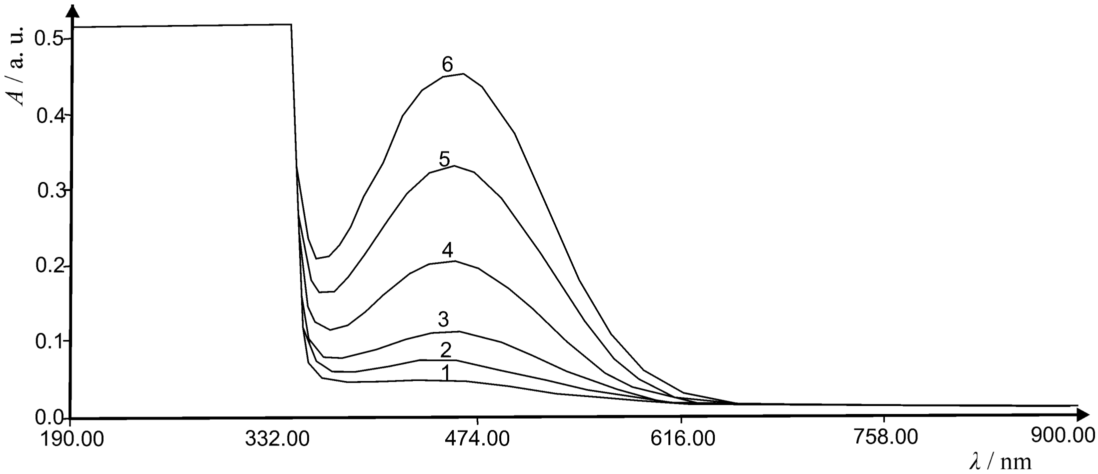

Figure 1. Absorption spectra of the non-catalyzed (1, 2, 3) and catalyzed (4, 5, 6) reaction monitored at time intervals of 0.5 min. Initial concentrations: 2 mmol dm^{-3} K_2S_2Hy, 60 mmol dm^{-3} H_2O_2, 0.24 mmol dm^{-3} $HClO_4$, 18.7 ng cm^{-3} Fe(III); temperature 20.0±0.1 °C

The absorbance-time dependences were linear during the first 8 min of the reaction for different Fe(III) concentrations (Fig. 2). The reaction rate was estimated from the slope (d*A/*d*t*) of the linear part of the kinetic curve *A* = *f*(*t*).

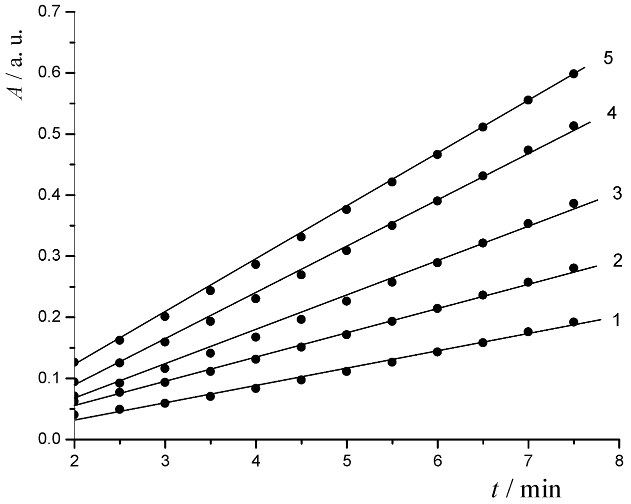

Figure 2. Absorbance as a function of the reaction time for different Fe(III) concentrations, ng cm^{-3}: 1) 3.7; 2) 11.2; 3) 18.7; 4) 37.3; 5) 44.8. Initial concentrations: 3 mmol dm^{-3} K_2S_2Hy; 66.7 mmol dm^{-3} H_2O_2; 0.133 mmol dm^{-3} $HClO_4$; λ = 450.0 nm; temperature 20.0±0.1 °C.

In order to determine the lowest possible quantifiable concentration of iron (III), the conditions needed to be optimized. Influences of the solution pH and concentrations of disulphonated hydroquinone and hydrogen peroxide were studied on both reactions. Keeping all other experimental parameters constant, the pH dependence of the system was studied in the range of 3.26-3.74 (Fig.3). The pH value of 3.39 was selected for subsequent investigations.

Orders of the non-catalyzed (-0.9) and catalyzed (-0.6) reactions were determined from the slopes of the function – log (d*A*/d*t*) = f(pH) (Fig.4).

Dependences of the non-catalyzed (1) and catalyzed (2) reaction rates on the hydrogen peroxide concentration in the reaction mixture is presented in Figure 5. There is an increase in the rate over almost the whole investigated concentration range for both reactions and the H_2O_2 concentration of 60 mmol dm^{-3} was chosen as the optimal for further work. The non-catalyzed reaction is of a +1 order while the catalyzed reaction is of a +1 order up to the concentration of 56 mmol dm^{-3} while with the further increase in H_2O_2 concentration is zero order.

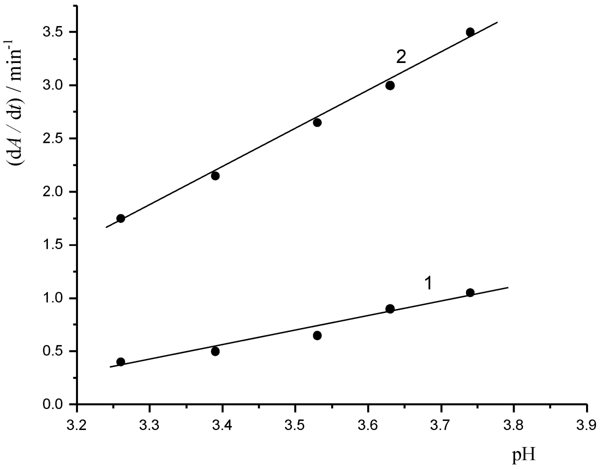

Figure 3. Reaction rate (dA/dt) dependence of the solution pH for the non-catalyzed (1) and catalyzed (2) reaction. Initial concentrations: 2.67 mmol dm^{-3} K_2S_2Hy; 26.7 mmol dm^{-3} H_2O_2; 18.7 ng cm^{-3} Fe(III); λ = 450.0 nm, temperature 20.0±0.1 °C

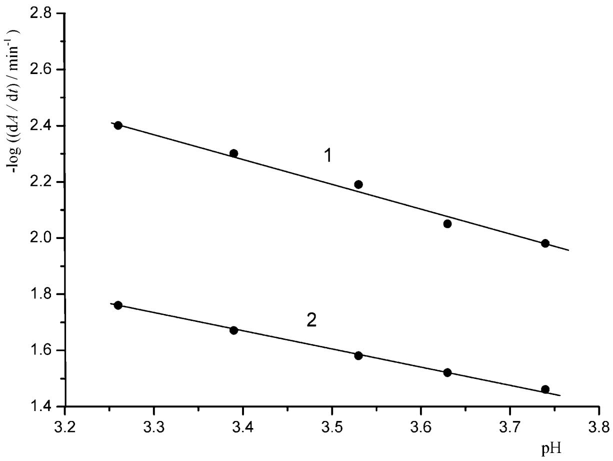

Figure 4. Logarithmic dependences of the reaction rate (-log (dA/dt) on the solution pH for the non-catalyzed (1) and catalyzed (2) reaction. Initial concentrations: 2.67 mmol dm^{-3} K_2S_2Hy; 26.7 mmol dm^{-3} H_2O_2; 18.7 ng cm^{-3} Fe(III); λ = 450.0 nm, temperature 20.0±0.1 °C

Figure 6 shows dependences of both reaction rates on the reducing agent concentration. It is evident that the non-catalyzed reaction (1) is the first order reaction in the concentration range of 0.267 to 2.67 mmol dm^{-3}. The catalyzed reaction (2) is of the first order reaction in the concentration range of 0.267 to 1.33 mmol dm^{-3} and zero order at higher concentrations. So, the K_2S_2Hy concentration of 2 mmol dm^{-3} was selected as optimal.

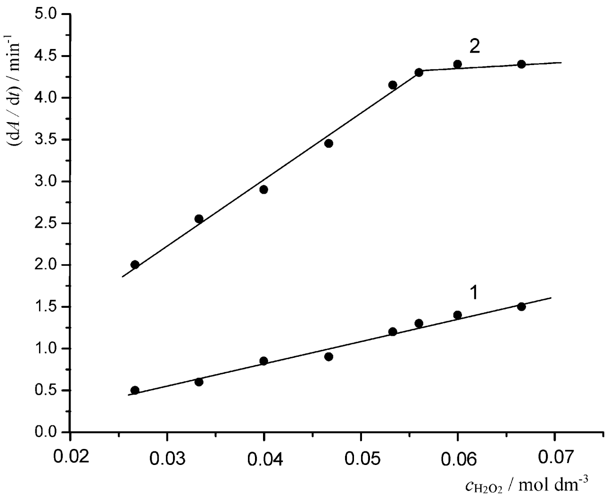

Figure 5. Reaction rate dependences on the H_2O_2 concentration for the non-catalyzed (1) and catalyzed (2) reaction. Initial concentrations: 2.67 mmol dm^{-3} K_2S_2Hy; 18.7 ng cm^{-3} Fe(III); pH 3.39; λ = 450.0 nm, temperature 20.0±0.1 °C.

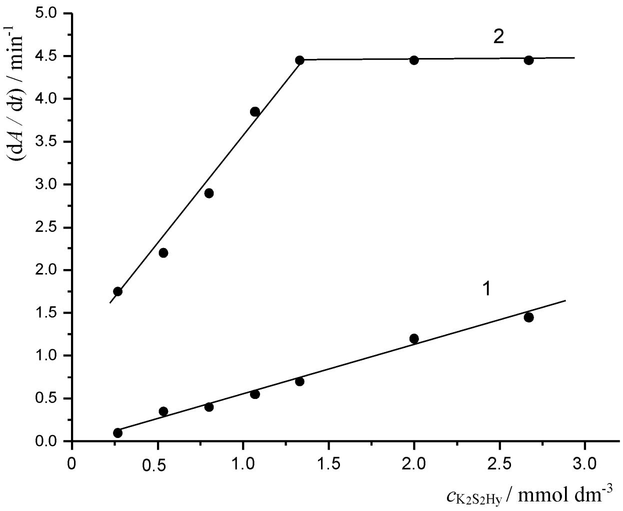

Figure 6. Reaction rate dependences on the K_2S_2Hy concentration for the non-catalyzed (1) and catalyzed (2) reaction. Initial concentrations: 60 mmol dm^{-3} H_2O_2, 18.7 ng cm^{-3} Fe(III); pH 3.39; λ = 450.0 nm, temperature 20.0±0.1 °C.

Thus, the optimal conditions for oxidation of K_2S_2Hy by hydrogen peroxide, in the presence of Fe(III) as the catalyst, at the working temperature of 20.0±0.1 °C, were found to be: $c_{K_2S_2Hy} = 2$; $c_{H_2O_2} = 60$; $c_{H_3O^+} = 0.407$ mmol dm^{-3}; $I = 0.1$.

At last, the concentration of iron was varied under the optimal conditions. The obtained calibration curve was linear in the Fe(III) concentration range of 1.87-18.7 ng cm^{-3} (Fig.7).

The calibration curve equation has a form:

$$dA/dT = (1.36449 \pm 0.04586)\ 10^{-2} + (0.16473 \pm 0.00405)\ 10^{-2}\ c_{Fe} / \text{ng cm}^{-3} \quad (1)$$

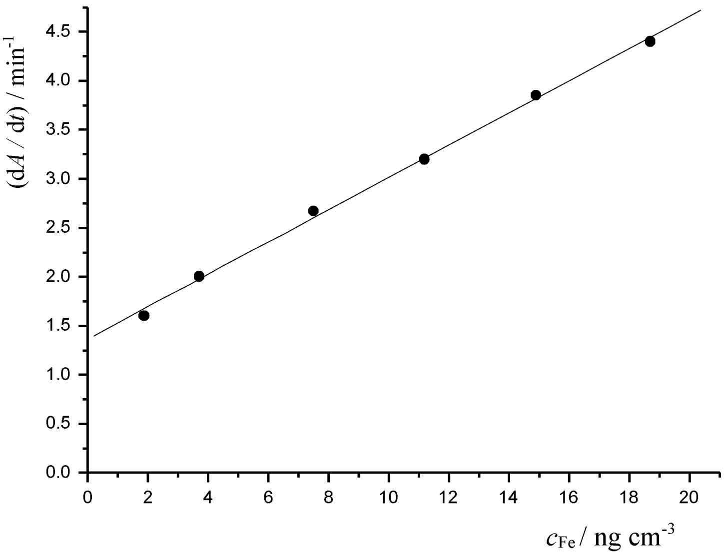

Figure 7. The catalyzed reaction rate dependence on the Fe(III) concentration. Initial concentrations: 2 mmol dm^{-3} K_2S_2Hy, 60 mmol dm^{-3} H_2O_2; pH 3.39; λ = 450.0 nm, temperature 20.0±0.1 °C.

The limit of detection (LOD) was calculated in two ways from next expressions:

$$LOD_1=3S_b/m = 1.11 \text{ ng cm}^{-3} \quad (2)$$

$$LOD_2=3S_{x/y}/m = 1.07 \text{ ng cm}^{-3} \quad (3)$$

where S_b is the standard deviation of the analytical signal (dA/dt) for the non-catalyzed reaction; $S_{x/y}$ is the standard deviation of the fitting of the calibration curve and m is the slope of the calibration curve [29-31].

In order to determine the accuracy and precision of the Fe(III) determination by the proposed kinetic method, the reaction rate was determined for three different Fe(III) concentrations in three repetitions. Using the equation of the calibration line and the statistical processing of data, the obtained results are presented in Table 1.

Table 1. The accuracy and the precision of iron(III) determinations

μ / ng cm^{-3}	$\overline{X}$ / ng cm^{-3}	$S(\overline{X})$ / ng cm^{-3}	RSD, %	Recovery, %
1.87	1.61	0.07	10.3	86.1
7.47	7.20	0.14	4.2	96.4
18.7	18.4	0.36	4.4	98.7

μ - real value; $\overline{X}$ - mean value; $S(\overline{X})$ - standard deviation of the mean value; RSD- relative standard deviation; Recovery, % = ($\overline{X}$ / μ) 100

Based on the presented results, kinetic equations for both the catalyzed and non-catalyzed reactions were formulated for the determined concentration intervals.

In concentration intervals: $c_{H_3O^+}$ = 0.182-0.549 mmol dm^{-3}, $c_{H_2O_2}$ = 26.7-66.6 mmol dm^{-3}, $c_{K_2S_2Hy}$ = 0.267-2.67 mmol dm^{-3}, the kinetic equation for the non-catalyzed reaction is:

$$dc/dt = k_0 \, (c_{H_3O^+})^{-0.9} \, c_{H_2O_2} \, c_{K_2S_2Hy} \quad (4)$$

In concentration intervals: $c_{H_3O^+}$ = 0.182-0.549 mmol dm^{-3}, $c_{H_2O_2}$ = 56.0-66.6 mmol dm^{-3}, $c_{K_2S_2Hy}$ = 1.33-2.67 mmol dm^{-3}, the kinetic equation for the catalyzed reaction is:

$$dc/dt=k \, (c_{H_3O^+})^{-0.6} \, c_{Fe(III)} \quad (5)$$

where: dc/dt is the concentration change of the reaction product over time; k_0 and k are the conditional rate constants for the non-catalyzed and catalyzed reaction, respectively.

Dependences of reaction rates of the catalyzed and non-catalyzed reactions on temperature were investigated in the temperature interval from 20 to 32 °C, although the rates of both reactions increased with the increase in temperature (Fig. 8).

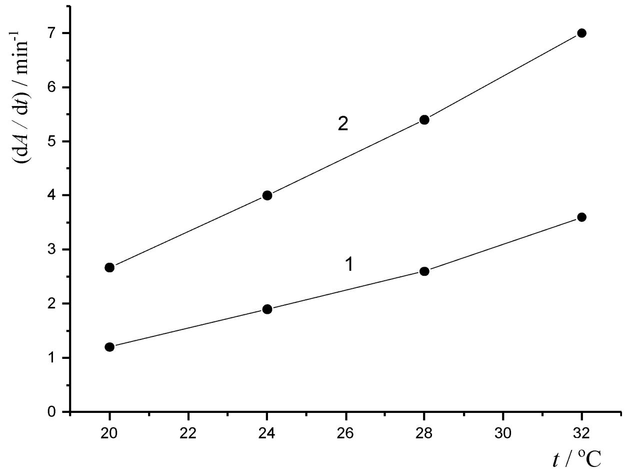

Figure 8. Reaction rate dependences on temperature for the non- catalyzed (1) and catalyzed (2) reaction. Initial concentrations: 2 mmol dm^{-3} K_2S_2Hy, 60 mmol dm^{-3} H_2O_2, 18.7 ng cm^{-3} Fe(III); pH 3.39; λ = 450.0 nm.

Conditional rate constants for the non-catalyzed (k_0) and catalyzed (k) reactions were calculated for three different temperatures (Table 2).

Table 2. Conditional rate constants for the non-catalyzed (k_0) and catalyzed (k) reactions at different temperatures

T / K	k_0 / (mmol dm^{-3})$^{1-n}$ s^{-1}	k / (mol dm^{-3})$^{1-n}$ s^{-1}
293	0.148±0.006	3.07±0.06
297	0.23±0.01	4.6±0.1
301	0.32±0.01	6.2±0.1

n is the total reaction order

Based on the Arrhenius equation, the plots are shown for the non-catalyzed (Fig. 9) and catalyzed (Fig. 10) reactions.

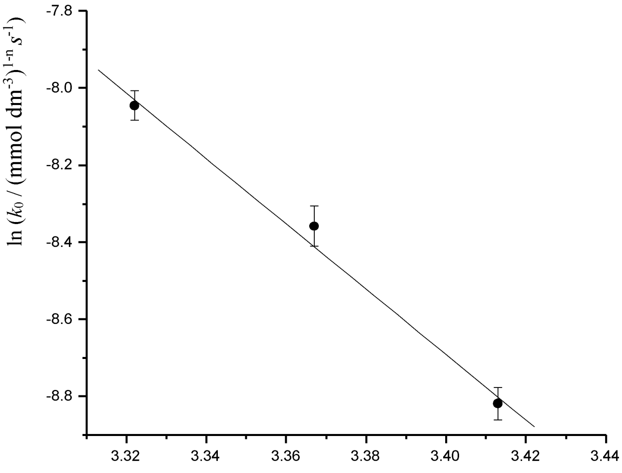

Figure 9. Arrhenius plot of ln k_0 vs. 1/T for the non-catalyzed reaction

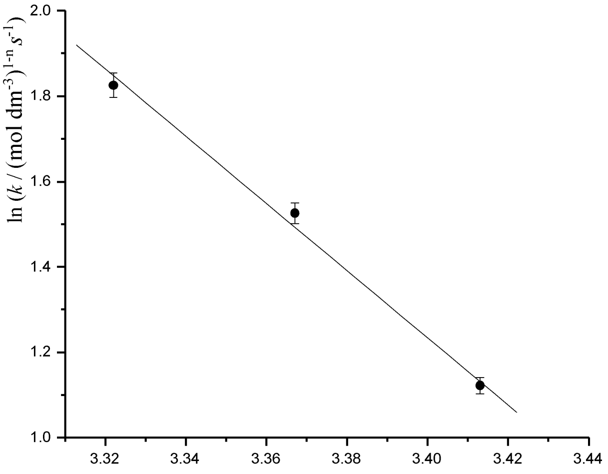

Figure 10. Arrhenius plot of ln k vs. 1/T for the catalyzed reaction

Slopes of the lines were used for calculation of the activation energy (E_a^*). The thermodynamic functions for the reaction of activated complex formation at 298 K are given in Table 3.

The obtained results show a decrease in the activation energy, enthalpy of activation, and free activation energy for the oxidation reaction in the presence of the catalyst and an increase in the entropy of the system. Mechanisms of the same reaction that proceeds without the catalyst and in its presence differ significantly. The comparison of these mechanisms cannot be achieved only by comparing their activation energies. Reduction of the activation energy of a reaction, although decisive, is not the only factor contributing to an increase in the reaction rate.

Table 3. Thermodynamic parameters for the reaction of activated complex formation at 298 K

reaction	E_a^* / kJ mol^{-1}	ΔH^* / kJ mol^{-1}	ΔS^* / J K^{-1} mol^{-1}	ΔG^* / kJ mol^{-1}	pK*
non-catalyzed	70.7	68.2	-85.2	93.6	16.4
catalyzed	64.4	61.9	-24.2	69.1	12.1

where E_a* is the activation energy, ΔH* is the enthalpy of activation, ΔS* is the entropy of activation, ΔG* is the free activation energy, pK* is the pK value of the activated complex

According to the activated complex theory, the pre-exponential factor *A* is determined by the magnitude of the entropy of activation. The magnitude of the activation entropy provides important information about the mechanism of catalytic reactions and the structure of the activated complex. A large negative value is characteristic for the reactions that are carried out *via* formation of an activated complex that simultaneously involves molecules of both reactants and the active center of the catalyst. In such an activated complex, formation of new bonds and breaking of existing bonds in reacting molecules take place simultaneously. These reactions proceed by an associative mechanism. In contrast, reactions where formation of the activated complex is preceded by the breakage of bonds in the reacting molecules are characterized by a positive entropy value. The mechanism of these reactions is termed dissociative [32].

Selectivity of the method was assessed by interference studies: the selected ions were separately added to the reaction mixture under the constant Fe(III) concentration of 7.47 ng cm^{-3}. The tolerance limit was estimated as the concentration of the added ion that produces a 3 % relative error in iron (III) determination. Cations were added as chlorides or nitrates and anions were added as sodium or potassium salts. The obtained results presented in Table 4 reveal that the presence of citrates and oxalates, in the w/w ratio 1:1 against the iron concentration in the reaction mixture, has the inhibitory effect on the reaction rate. The ions that interfere with the determination of iron can be easily removed by standard analytical methods like masking, precipitation, *etc.* depending on the samples nature. According to the obtained results, the proposed kinetic spectrophotometric method for Fe(III) determination has a very good selectivity.

Table 4. Results of interference studies for Fe(III) determination

q	Ion
100	CH_3COO^-, SO_4^{2-}, NO_3^-, Br^-, Mn^{2+}, Li^+, Ca^{2+}, Sr^{2+}, J^-, PO_4^{3-}, $Cr_2O_7^{2-}$
10	HPO_4^{2-}, HCO_3^-, Zn^{2+}, Cu^{2+}, NH_4^+, WO_4^{2-}, SCN^-, Al^{3+}, Cd^{2+}, F^-, Co^{2+}
1	Ni^{2+}, Hg^{2+}
interfere	oxalates, citrates

where *q* is the *w/w* ratio: added ion/Fe(III) when the added ion does not interfere with iron (III) determination

The proposed kinetic-spectrophotometric method for iron (III) determination as one of the methods in which sulfonated phenol products are used as an indicator substance is characterized by sensitivity of the same order of magnitude (ng cm^{-3}) as in the methods mentioned above. Also, the proposed method exhibits lower least quantifiable concentration than in some of the other methods (chromotropic acid and sulphanilic acid as indicator substances) [15,17], a greater range of linearity of the calibration line than in some other methods (dibromo-p-sulfonic acid-arsenazo as indicator substance) [16], and good selectivity. The fact that the reducing agent in the oxidoreduction reaction is very stable at acidic conditions at a constant ionic strength of the solution provides good reproducibility and repeatability of the developed method. Also, this kinetic-spectrophotometric method has better sensitivity than some methods based on the complex formation between iron and some ligands such as hydroxylamine, gallic acid and methylthymol blue with the least determinable concentration at the level of µg cm^{-3} [18-20].

In the next step, the presented method was applied for Fe(III) determination in white radish juice and AAS method was used as the referent one. A very good agreement of the results was achieved, and a little more iron was found by the kinetic method (Table 5).

Table 5. Determination of Fe(III) in white radish juice

Sample	Kinetic method: $\overline{X}$ / μg cm^{-3}	AAS method: $\overline{X}$ / μg cm^{-3}	Recovery*, %
1	2.74±0.06	2.60±0.01	105.4
2	2.70±0.05	2.59±0.02	104.2
3	2.69±0.03	2.62±0.02	102.7
4	2.79±0.06	2.70±0.04	103.3
5	2.77±0.04	2.69±0.03	103.0

*(Recovery-mean value (kinetic method)/mean value (AAS method)) 100

CONCLUSIONS

The proposed kinetic method is recommended for determination of Fe(III) in the concentration range of 1.87 to 18.7 ng cm^{-3}. It has shown a very good selectivity and provided a rapid and easy performance, by using the available equipment and low-cost chemicals. The obtained results are precise and reproducible. The RSD value was found to be in the range of 4.2 to 10.3 % for the investigated Fe(III) concentration range. The method was successfully applied for iron determination in white radish juice. AAS method was used as a reference method. Recovery range from 102.7 % to 105.4 %. Based on the obtained results, the new spectrophotometric kinetic method can be recommended for determination of Fe(III) content in environmental natural products, spring and tap water, food and drink samples as well as in different samples from the industrial processes. The results suggest that it could be also a good basis for further investigation in the area of the development of kinetic methods.

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SAŽETAK

Analitička primena reakcionog sistema disulfonovani hidrohinon-vodonik-peroksid za kinetičko spektrofotometrijsko određivanje tragova gvožđa u kiseloj sredini

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U ovom radu je predstavljena jednostavna, brza, osetljiva i selektivna kinetička spektrofotometrijska metoda za određivanje tragova Fe(III). Zasnovana je na katalitičkom dejstvu gvožđe (III) jona na oksidaciju kalijumove soli disulfonovanog hidrohinona (K_2S_2Hy) vodonik-peroksidom u kiseloj sredini, pri konstantnoj jonskoj sili rastvora. Na temperaturi od 20 °C i na talasnoj dužini od 450,0 nm, određeni su optimalni uslovi za određivanje gvožđa. U ispitivanom intervalu koncentracija Fe(III) (1,87 do 18,7 ng cm^{-3}), relativna standardna devijacija (RSD) je iznosila od 4,2 do 10,3 %. Granica detekcije (eng. limit of detection, LOD) računata na dva načina je 1,07 ng cm-3 tj. 1,11 ng cm^{-3} Fe(III). U cilju utvrđivanja selektivnosti metode ispitan je uticaj prisustva različitih jona u reakcionoj smeši na brzinu reakcije. Zapaženo je da prisustvo oksalata i citrata u masenom odnosu 1:1 prema gvožđu, ometa određivanje gvožđa ovom metodom, pod odabranim eksperimentalnim uslovima. Metoda je primenjena za određivanje tragova gvožđa (III) u soku bele rotkve, a dobijeni rezultati su pokazali dobro slaganje sa rezultatima dobijenim metodom atomske apsorpcione spektrofotometrije.

Ključne reči: Fe(III), katalizator, kinetička spektrofotometrijska metoda, bela rotkva