J.Serb.Chem.Soc. 69(2)123–135(2004)
JSCS – 3136

UDC 546.733+546.98:543.23
Original scientific paper

Investigation of Pd-catalyzed Co(III)-EDTA/hypophosphite inhibition reaction kinetics, mechanism and the evaluation of its analytical application possibilities

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(Received 28 July, revised 1 October 2003)

Abstract: The reaction between Co(III)-EDTA and hypophosphite ion, catalyzed by Pd(II) was chosen as the indicator reaction. The inhibition kinetics of this catalytic reaction have been investigated by a mechanistic approach in the presence of some inhibitors. Catalysts other than $PdCl_2$, that is Pt, Au, Ni salts, did not exhibit any effect on the reaction. An original reaction mechanism is proposed based on the experimental data. The important variables were optimized for maximum sensitivity. The calibration graph, which was prepared following the inhibition kinetic method, showed a linear relationship ($r = -0.9878$) between the initial rate and iodide in the concentration range of 2–35 ng/cm^3 I^- with a detection limit of 1.2 ng/cm^3 I^- ($3S_b/m$ criterion). The RSDs of the method, ($N = 5$) for 7 and 14 ng/cm^3 were 1.19 and 0.81 %, respectively, depended on iodide concentration. The method was only applied to the determination of iodide in water, urine, iodized table salt and some drug samples and was compared with the modified Sandell–Kolthoff method.

Keywords: Co(III)-EDTA/hypophosphite, inhibition kinetics, iodide and some amino acid determination, kinetic spectrophotometry and initial rate method.

INTRODUCTION

The determination of iodide in natural waters, foodstuffs and biological samples (such as urine, plasma, blood and hair) is important for environmental and biochemical reasons. Not may only a lack of iodine but also a gross excess of iodine (>20 mg/day) in a diet cause a lot of disorders, including endemic goiter and hypothyroidism. For this reason it was decided to investigate an alternative method of iodine defermination.[1]

Especially, cystine and cysteine are two amino acids of great interest in biochemical and nutrition research. They are often found together in a variety of samples since cysteine is easily converted into cystine by dissolved oxygen in neutral to weakly alkaline media and cystine is hydrolysed to cysteine in water.[2]

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A number of methods have been developed for the determination of these amino acids in urine.[3–7]

Iodine has also been determined by catalytic methods[8,9] in addition to spectroscopic, electroanalytic and MS spectrometric methods. Two main methods are employed in this context. One is based on the redox reaction between cerium(IV) and arsenic(III), which was first demonstrated and exploited for the determination of iodide at the μg/cm^3 level by Sandell and Kolthoff and subsequently modified.[10–13] The other method is based on the catalytic action of iodide on the decomposition of the $FeSCN^{2+}$ complex ion. The indicator reaction is characterized by an induction period, the length of which depends on the reagent concentration, pH and temperature.[14,15]

Especially, the former reaction was adopted as a standard method for iodide determination in natural and waste waters and in food and biological samples.[16] However, high inter-laboratory relative standard deviations have frequently been reported for this method.[17] This might be partly attributed to the limitations of method to quantitatively detect or tolerate iodate ions (IO_3^-) that are found in natural waters and/or formed during the ashing steps of food samples.[16] Hence, the need for a low-cost or economical, rapid, more sensitive and selective method still exists.

In this work, a detailed study of the appropriate conditions for the inhibitory effects of iodide, cystine, cysteine and *N*-acetyl cysteine on the Pd(II)-catalyzed reduction of Co(III)-EDTA by the hypophosphite ion in weakly acidic media was performed. The reaction was monitored spectrophotometrically at 540 nm by measuring the change in the absorbance with time using the tangent (initial rate) method.

EXPERIMENTAL

Apparatus

Absorbance measurements were performed in 1 cm quartz cuvettes at 540 nm, the wavelength at which the Co(III)-EDTA solutions exhibit maximum absorbance, using a Jasco-UV/Visible 550 double beam spectrophotometer attached to a computer and recorded as absorbance–time curves, A=f(t).

A Grant LTD-6G Model Thermostatic bath (operating in the –20 and 100 ºC temperature range) was used to control the reaction temperature with ± 0.1 ºC accuracy.

High precision micropipettes of 50, 500 and 1000 μL volume (Volac, UK) were used for pipetting the solutions.

Reagents

Analytical reagent grade chemicals and doubly-distilled water were used throughout the experiments.

Co(III)-EDTA stock solution, 0.04 mol/dm^3 : 40 cm^3 of 0.1 mol/dm^3 Co(II) nitrate (Merck) and 40 cm^3 of 0.1 mol/dm^3 Na_2H_2EDTA (Merck) were pipetted into a 250 cm^3 beaker. 2.4 g dipotassium peroxodisulphate (Merck) was then added and the solution adjusted to pH 6 with ammonia solution (1+1, v/v, d:0.88 g/cm^3) and boiled gently for about 20 min in order to decompose the excess peroxodisulphate. The solution was made up to volume with water in a 100 cm^3 volumetric flask.

Sodium hypophosphite stock solution, 3 mol/dm^3: 7.95 g of $Na_2H_2PO_2{\cdot}H_2O$ (Riedel-de Haen) dissolved in water and diluted to 25 cm^3 in a volumetric flask. This solution was prepared each week and stored in a dark bottle and place.

Palladium dichloride (Sigma), 5.0×10^{-3} mol/dm^3: Prepared in 0.2 mol/dm^3 HCl and stored in a dark bottle and place.

Standard iodide solution, 1000 mg/dm^3, was prepared by dissolving 0.1308 g potassium iodide (Merck), dried at 105 ºC for 2 h, in water and diluted with water to 100 cm^3 in a volumetric flask. Working solutions were prepared daily by suitable dilution with water.

Citrate–phosphate–borate buffer solution, pH 2–12 was prepared according to the literature. Preparation of the citrate–phosphate–borate buffer solution has been described elsewhere.[17]

Potassium tetrachloro-platinate(II) of 1.0×10^{-3} mol/dm^3, chloro auric acid of 1 % (w/v), palladium nitrate of 1 % (w/v), platinum dichloride of 7.5×10^{-4} mol/dm^3 and ammonium hexachloroplatinate of 0.01 mol/dm^3 stock solutions were prepared daily by dissolving K_2PtCl_6, $HAuCl_4{\cdot}4H_2O$, $Pd(NO_3)_2$, $PtCl_2$ and $(NH_4)_2PtCl_6$ salts with water, dilute HNO_3 or HCl solution, respectively.

Sandell–Kolthoff reagents were prepared and used in the analysis according to recommendations in the appropriate literature.[11,12]

General procedures

Determination of the reaction rate. The indicator reaction was carried out with respect to the literature values without using any inhibitor[34] and the rate of this reaction was monitored spectrophotometrically.

The kinetic study on the catalytical reaction with and without inhibitor was accomplished by the initial rate method where the initial slope of the reaction was measured as has been described[19] and then the slope of the curve ($dA/dt = \tan\alpha$) taken as a measure of the initial reaction rate. The absorbance–time curves were recorded at 540 nm. A calibration graph was obtained by plotting the change in the catalyzed-reaction rate for sample solution *versus* the iodide concentration as inhibitor.

For the determination of iodide in iodized table salt, water and urine samples, samples were analyzed either directly using a suitable aliquot of a sample solution or using a suitable aliquot of its diluted solution.

RESULTS AND DISCUSSION

It has been stated in previous studies that the reduction reaction of Co(III)-EDTA by $H_2PO_2^-$ ion is catalyzed by Pd(II) and that it occurs in micro heterogeneous reaction medium.

According to the results of the experiments, it is proposed that the following mechanism is permissible thermodynamically:

In the reaction of $H_2PO_2^-$ ion and Pd(II):

$$Pd^{2+} + H_2PO_2^- + H_2O = Pd^0 + H_2PO_3^- + 2H^+ \quad (1)$$

metallic Pd is produced. Then in the reaction between metallic Pd and Co^{3+} ions:

$$2Co^{3+} + Pd^0 = 2Co^{2+} + Pd^{2+} \quad (2)$$

the Co^{3+} ions are reduced to Co^{2+} ions by Pd^0.

If the equations of reaction (1) and (2) are combined, the resultant equation is the equation of the overall reaction:

$$2Co^{3+} + H_2PO_2^- + H_2O = 2Co^{2+} + H_2PO_3^- + 2H^+ \quad (3)$$

The first step (1) is slow, and second step (2) is fast. If the second step of this reaction is considered dominant, according to Dutt and Mottola,[20] in this second step Co(III) is reduced by active H_2 molecules as is the case in the reduction of hypophosphite dyes by the catalysis of Pd(II). Our results cast some doubts about this comment of the authors. If the reduction of Co(III), was by active H_2 molecules, the following events would be realized:

1. Like Pd^0, metals and metal cations, such as Ni, Au, Pt, which can produce active H_2 molecules should also catalyze this reaction. All the experiments performed using the above mentioned catalyst did not confirm this conclusion. Among these catalysts only the $Pd(NO_3)_2$ solution was not as stable as the $PdCl_2$ solution. Salts of Pd(II) are more suitable as a catalyst according to our experiments.

2. No indication of black-colored metallic palladium production was observed on the walls of the spectrophotometry cell in which the reaction occurred. This shows that almost all of the produced Pd^0 was used up.

3. During the monitoring of the reaction, no obvious H_2 gas production from the reaction mixture was observed; but just before the reaction ends and even after the reaction had ended, gaseous bubbles were observed.

According to these experimental results it can be conduded that Co(III) was reduced by Pd^0 microcrystals rather than by active H_2 molecules.

The strong inhibitory effect of iodide on the reaction can be explained by stable complex formation between Pd^{2+} and iodide ions, the latter replacing the chloride ions in $PdCl_2$. The formation of the PdI_4^{2-} complex blocks the reduction of Pd^{2+}, or at least delays it.

Also, the amino acids which inhibit the reaction contain an active –SH group (thiol group). These –SH groups are immobilized on the active centers of the Pd, which explains the inhibitory effects of these amino acids.

It was experimentally observed that iodide, cystine, cysteine and *N*-acetyl cysteine considerably decrease the catalytic effect of Pd(II) on the reaction of the Co(III)-EDTA/$H_2PO_2^-$ system in acidic media, *i.e.,* it proceeded much slower.

The rate of decrease of the reaction rate (tan α) was suppressed by ions of these inhibitor substances in that the overall reaction rate is much smaller compared to the catalyzed reaction (decreasing slope).

Therefore, trace amounts of iodide could be determined using this system due to the linear relation between the decrease in the reaction rate and the iodide concentration.

Effect of reaction variables on the inhibited reaction

In order to increase the selectivity and sensitivity of the inhibition kinetic method in the determination of inhibitor species, the effects of several variables on the rate of the catalyzed and inhibited catalyzed reactions were studied.

The effect of the Co(III) concentration on the catalyzed and inhibited catalyzed reaction rate was studied in the concentration range of $(0.65–6.5)\times10^{-3}$ mol/dm^3 both with and without inhibitor, while the iodide concentration was kept constant at 10 ng/cm^3; cystine at 0.34 μmol/dm^3; cysteine at 0.83 μmol/dm^3 and *N*-acetyl cysteine at 1.67 μmol/dm^3. The influences of the Co(III) concentration on both of the reaction rates and on the inhibition % for the various inhibitors were separately measured by the same method with varying Co(III) concentrations. The inhibition % was calculated from the following equation:

$$\text{Inhibiton \%} = (\text{rate}_{\text{without inh.}} - \text{rate}_{\text{with inh.}}) / \text{rate}_{\text{without inh.}} \times 100$$

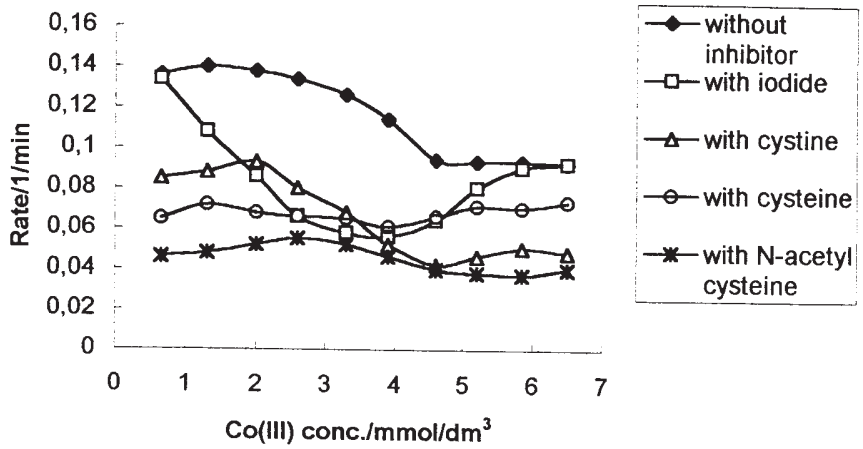

Fig. 1. Influence of the Co(III) concentration on the reaction rate and inhibitory effect of various substances. Conditions: 0.4 mol/dm^3 $H_2PO_2^-$; 0.33 μmol/dm^3 Pd(II); 3.2 pH; 10 ng/cm^3 I^-; 0.34 μmol/dm^3 Cystine; 0.83 μmol/dm^3 Cysteine; 1,67 μmol/dm^3, *N*-acetyl cysteine. Temperature 25 ± 0.1 ºC, wavelength 540 nm.

The best result was obtained with a Co(III) concentration of 3.2 $\times 10^{-3}$ mol/dm^3 for iodide that was to be determined analytically. This concentration had both the maximum percentage inhibition and the maximum reaction rate. Therefore, it was chosen as the optimum Co(III) concentration for the subsequent studies (Figs. 1 and 2).

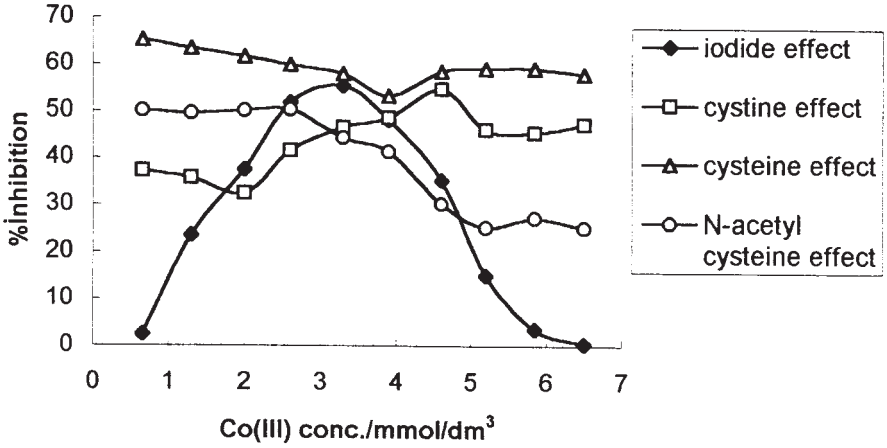

Fig. 2. Influence of the Co(III) concentration on the inhibition % in the presence of various inhibitors. Conditions: 0.4 mol/dm^3 $H_2PO_2^-$; 0.33 μmol/dm^3 Pd(II); pH 3.2; temperature 25 ± 0.1 ºC, wavelength 540 nm.

Effect of the hypophosphite concentration on the catalyzed and inhibited catalyzed reaction rate was studied in the concentration range of 0.1 – 1.00 mol/dm^3 both with and without inhibitor while the inhibitor concentrations were kept constant at the above mentioned optimum values. The experiments were repeated three times for the same hypophosphite concentration and their average values were taken into consideration. The rate of sample reaction and the rate of blank reaction increased with increasing hypophosphite

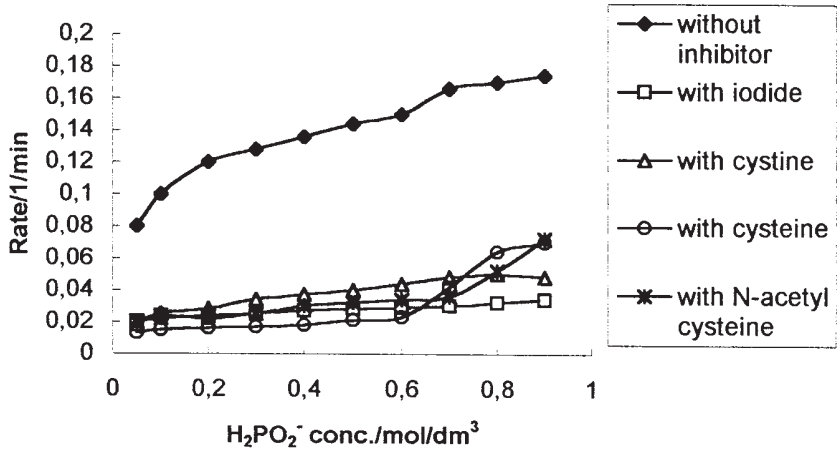

Fig. 3. Influence of the hypophosphite concentration on the reaction rate and inhibitory effect of various substances. Conditions: 3.2×10^{-3} mol/dm^3 Co(III); 0.33 μmol/dm^3 Pd(II); pH 3.2; 10 ng/cm^3 I^-; 0.34 μmol/dm^3 Cystine; 0.83 μmol/dm^3 Cysteine; 1.67 μmol/dm^3 *N*-acetyl cysteine. Temperature 25 ± 0.1 ºC, wevelength 540 nm.

concentration. However, the rate of sample reaction increased up to 0.4 mol/dm^3 $H_2PO_2^-$ and at higher hypophosphite concentrations the reaction rate and inhibition % slowly decreased. In addition, above a hypophosphite concentration of 0.4 mol/dm^3, the inhibition % remained approximately constant; thus a concentration of 0.4 mol/dm^3 hypophosphite was used for the subsequent studies (Figs. 3 and 4).

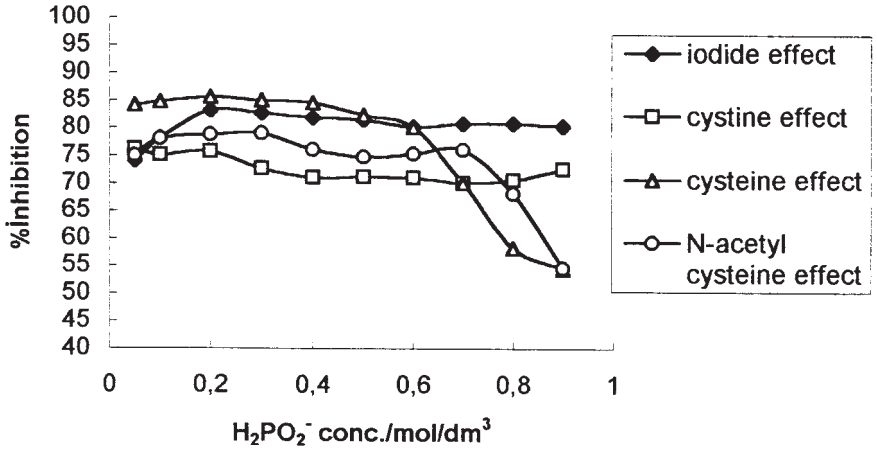

Fig. 4. Influence of the hypophoshite concentration on the inhibition % in the presence of various inhibitors. Conditions: 3.2×10^{-3} mol/dm^3 Co(III); 0.33 μmol/dm^3 Pd(II); pH 3.2 and temperature 25 ± 0.1 ºC, wavelength 540 nm.

Effect of pH on the catalyzed and inhibited catalyzed reaction was studied in the pH range 2.0 – 5.4 at the optimum reagent concentrations both with and without inhibitor while the inhibitor concentrations were kept constant at the above mentioned opti-

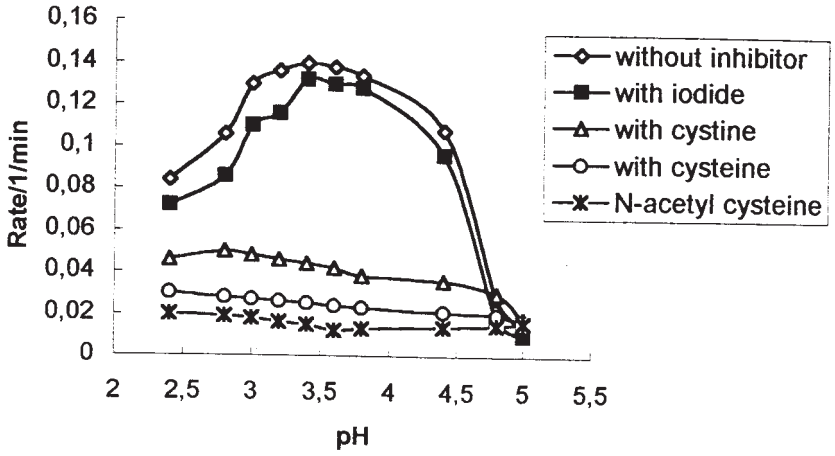

Fig. 5. Influence of pH on the reaction rate and inhibitory effect of various substances. Conditions: 3.2×10^{-3} mol/dm^3 Co(III); 0.4 mol/dm^3 $H_2PO_2^-$; 0.33 μmol/dm^3 Pd(II); 10 ng/cm^3 I^-; 0.34 μmol/dm^3 Cystine; 0.83 μmol/dm^3 Cysteine; 1.67 μmol/dm^3 *N*-acetyl cysteine. Temperature 25 ± 0.1 ºC, wavelength 540 nm.

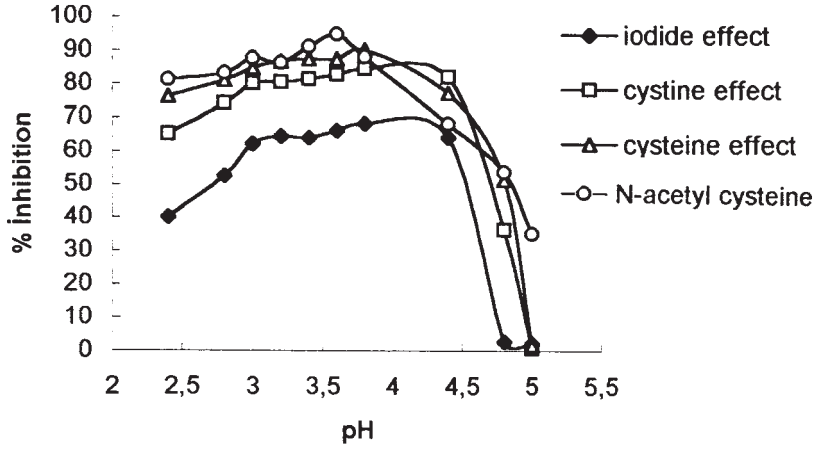

Fig. 6. Influence of pH on the inhibition % in the presence of various inhibitors. Conditions: 3.2×10^{-3} mol/dm^3 Co(III); 0.4 mol/dm^3 $H_2PO_2^-$; 0.33 μmol/dm^3 Pd(II). Temperature 25 ± 0.1 ºC, wavelength 540 nm.

mum values. The rate of the catalyzed and inhibited catalyzed reaction increased with increasing pH up a value of 3.2. At higher pH values the rate of the catalyzed and inhibited catalyzed reaction decreased significantly. Therefore, a pH value of 3.2 was selected as the optimum pH value in order to compromise between sensitivity and reaction rate (Figs. 5 and 6).

The effect of the Pd(II) concentration on the catalyzed and inhibited catalyzed reaction rate was studied in the concentration range of 0.08 –1.20 μmol/dm^3 both with and without inhibitor while the inhibitor concentrations were kept constant at the above mentioned optimum values. The experiments were repeated for the same Pd(II) concentrations

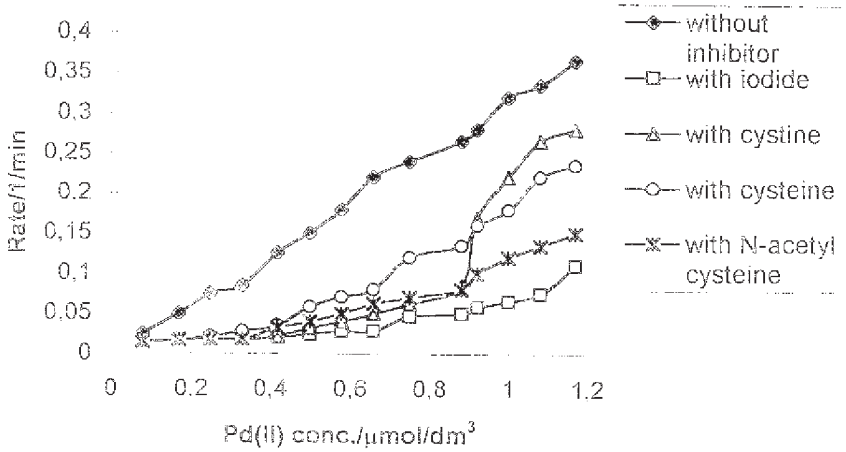

Fig. 7. Influence of Pd(II) concentration on the reaction rate and inhibitory effect of various substances. Conditions: 3.2×10^{-3} mol/dm^3 Co(III); 0.4 mol/dm^3 $H_2PO_2^-$; 3.2 pH; 10 ng/cm^3 I^-; 0.34 µmol/dm^3 Cystine; 0.83 µmol/dm^3 Cysteine; 1.67 µmol/dm^3 *N*-acetyl cysteine. Temperature 25 ± 0.1 ºC, wavelength 540 nm.

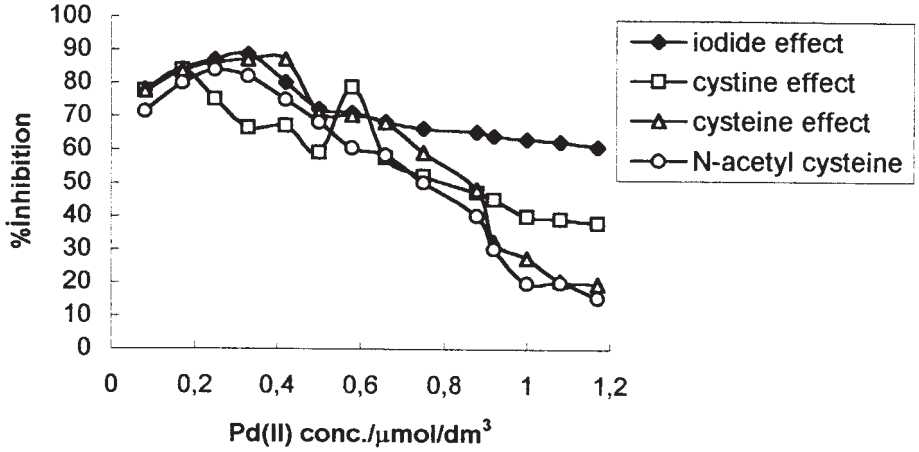

Fig. 8. Influence of Pd(II) concentration on the inhibition % in the presence of various inhibitors. Conditions: 3.2×10^{-3} mol/dm^3 Co(III); 0.4 mol/dm^3 $H_2PO_2^-$; pH 3.2. Temperature 25 ± 0.1 ºC, wavelength 540 nm.

and their average values were taken into consideration. The rate of the catalyzed reaction strongly increases while that of the inhibited catalyzed reaction slowly increases in this concentration range. The best result was obtained at a Pd(II) concentration of 0.33 µmol/dm^3. This concentration was chosen as the optimum one because the maximum percentage inhibition was then the greatest (Figs. 7 and 8)

The effect of the temperature on the rate of the inhibited catalyzed reaction was studied in the 10–55 ºC temperature range at the optimum reagent concentrations both with and without inhibitor while the iodide concentration was kept constant at 10 ng/cm^3. The

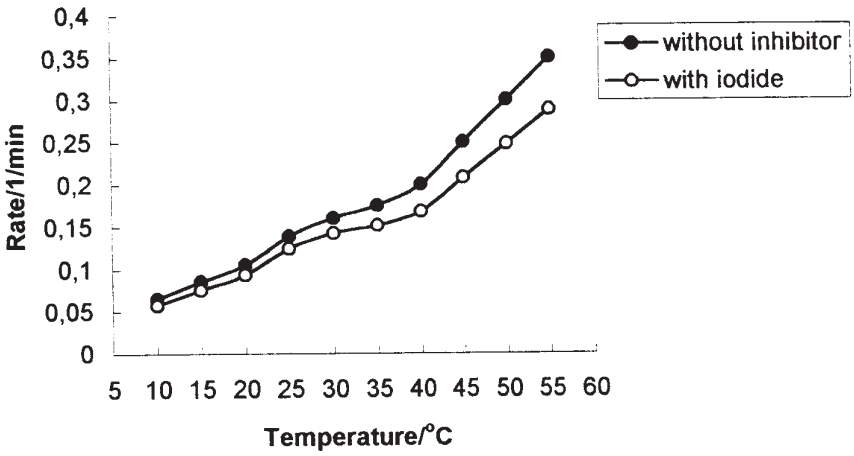

Fig. 9. Influence of temperature on the catlayzed and inhibited catalyzed reaction rate with and without iodide. Conditions: 3.2×10^{-3} mol/dm^3 Co(III); 0.4 mol/dm^3, $H_2PO_2^-$; 0.33 μmol/dm^3 Pd(II); pH 3.2 and 10 ng/cm^3 I^-. Wavelength 540 nm.

results are given in Fig. 9, which shows that the rate of the inhibited catalyzed reaction increases proportionally with increasing temperature. The results show that 25 ºC is the best suited, since at higher temperatures the inhibition effect of iodide decreases and, hence, inconveniently (high) reaction rates result. Therefore, 25 ºC was selected as the optimum temperature for technical reasons.

No attempt was made to maintain the ionic strength constant as changes in ionic strength were considered to have no significant effect on the inhibited catalyzed reaction rate under almost all conditions of constant ionic strenght.

Inhibitory effects of iodine, cystine, cysteine and N-*acetyl cysteine*

The slopes of the reaction rate curves both with and without inhibitor were taken into consideration as analytical parameter. The reaction rate found by the tangents method was 0.138 1/min without any inhibitor.

The inhibitory effect of iodide on the indicator reaction was investigated in the concentration range of 2–35 ng/cm^3 I^-. The results of the rate measurements were used to determine the iodide ion concentration with a satisfactory of regression relation under the previously optimised conditions. The optimum reaction conditions are as follows: 3.2×10^{-3} mol/dm^3 Co(III); 0.4 mol/dm^3 $H_2PO_2^-$; 0.33 μmol/dm^3 Pd(II); pH 3.2 and temperature 25 ± 0.1 ºC.

The inhibitory effects of cystine, cysteine and *N*-acetyl cysteine on the reaction rate were independently investigated in the concentration ranges of 0.13–2.5 μmol/dm^3, 0.17–5.00 μmol/dm^3 and 0.17–5.83 μmol/dm^3, respectively. The reaction rates and inhibition % were studied in a similar manner. However, strict calibration studies were not carried out for these amino acids.

Calibration

The calibration graph gave a linear relationship ($r = -0.9878$) between the initial reaction rate and the iodide concentration up to 35 ng/cm^3 iodide. The least squares equation for the calibration graph is $100 \times \tan \alpha$ (1/min) = 12.52–0.401 [I^-] where [I^-] is the iodide concentration expressed in ng/cm^3.

The theoretical limit of the detection $LOD = K.S_b/m$ was 1.2 ng/cm^3 of iodide, where $K = 3$, S_b is the standard deviation of the blank signals and m is the slope of the calibration plot. The *RSD*s for five replicate determinations of iodide were 1.19 and 0.81 % for 7 and 14 ng/cm^3 of iodide, respectively.

Analytical applications

The iodide inhibition kinetic method was tested on four real samples: tap water, iodised table salt, urine and drug samples. To check the accuracy of the method, known concentrations of iodide standard were spiked into definite volumes of the samples prepared directly or after appropriate dilution. The accuracy of the analysis was checked by the procedure of standard iodide addition and compared to the results of the modified Sandell–Kolthoff method. The recovery of each method was separately determined from five repeated measurements of the iodide spiked samples.

TABLE I. Recoveries of iodide spiked into different samples by the inhibition kinetics method

Sample	Added/(ng/cm^3)	Found±*SD*[a]/(ng/cm^3)	*RSD*/%	Recovery/%
Tap water	25	25.20 ± 0.53	2.10	100.80
	35	34.07 ± 0.93	2.74	97.34
	50	48.34 ± 1.90	3.93	96.68
Urine	25	24.00 ± 1.18	4.94	96.00
	35	35.01 ± 0.10	0.28	100.03
	50	51.97 ± 1.01	1.94	103.94
Table salt	25	25.06 ± 0.15	0.61	100.24
	35	34.03 ± 1.10	3.25	97.23
	50	48.02 ± 2.22	4.63	96.04

[a] Mean and standard deviation of five replicate determinations

TABLE II. Recoveries of iodide spiked into different samples by the modified Sandell–Kolthoff method

Sample	Added/(ng/cm^3)	Found±*SD*[a]/(ng/cm^3)	*RSD*/%	Recovery/%
Tap water	25	25.05 ± 0.19	0.79	100.20
	35	34.99 ± 0.12	0.34	99.97
	50	48.99 ± 1.15	2.34	97.98

TABLE II. Continued

Sample	Added/(ng/cm^3)	Found±*SD*[a]/(ng/cm^3)	*RSD*/%	Recovery/%
Urine	25	24.10 ± 1.01	4.18	96.40
	35	37.01 ± 2.25	6.09	105.74
	50	48.96 ± 1.17	2.40	97.92
Table salt	25	24.99 ± 0.18	0.74	99.96
	35	35.98 ± 1.11	3.08	102.80
	50	48.80 ± 1.39	2.85	97.60

[a] Mean and standard deviation of five replicate determinations

The results obtained by both methods are shown in Tables I and II. These results show that there is good agreement between the results obtained by the two methods. However, direct determination of iodine in the appropriately diluted drug samples could not be accomplished by either method.

CONCLUSIONS

The results of this work show that the Co(III)-EDTA–$H_2PO_2^-$–Pd(II) system can be successfully applied for the quantitative determination of trace amounts of I^-.

The gross advantage of this new method, as an alternative to the standard Sandell–Kolfhoff method, for iodide determination is that no pre-treatment of the samples is required before measurement. Additionaly, a time-consuming alkaline ashing preparative procedure is necessary in order to apply the standard method.

Our method, as an alternative to the standard method, is fast, practical, economical and easy requiring readily available reagents and equipment.

The inhibitory effect of iodide on the indicator reaction at pH 3.2 is very sensitive and the method based on this indicator reaction has a detection limit as low as 1.2 ng/cm^3 I^- and also an analytical working range of 2–35 ng/cm^3 I^-. The determination of iodide at low concentrations as low as 1.2 ng/cm^3 I^- is possible without any pre-concentration or pre-treatment step. No attempt was made to prevent interference because the interference effect was only controlled by the standard addition method for the determination of iodide contents of real samples. The proposed method is comparable with other kinetic-catalytic methods and instrumental methods, such as, ICP-MS (1.0–9.0 μg/dm^3),[23,24] ICP-AES (40.0–470.0 μg/dm^3),[25,26] except for NAA (0.1 – 0.2 μg/dm^3)[21,22] and IC (0.1 – 0.8 μg/dm^3)[27,28] in view of simplicity, cheapness, detection limit, convenience and relative selectivity. However, these instrumental methods have several disadvantages, such and as very high costs and the need for pre-concentration and/or separation.

Finally, it can be stated that our study from the mechanistic approach on the inhibition kinetics of the reaction of Co(III)-EDTA and $H_2PO_2^-$ suggest new areas of research, in-

cluding the application of this method for analytical purposes, which would necessitate the determination of analytical criteria, such as precision, bias, sensitivity, detection limits and concentration range.

Acknowledgements: This work was supported by grants from Research Fund Accountancy of Ege University. The authors wish to express their gratitude to the University of Dokuz Eylül, Medical School, Department of Biochemistry for enabling experimental work. We would also like to thank Dr. Cengiz Bicer for his contribution and assistance.

ИЗВОД

ИСПИТИВАЊЕ КИНЕТИКЕ ИНХИБИЦИЈЕ РЕАКЦИЈЕ Co(III)-ЕДТА СА ХИПОФОСФИТОМ КАТАЛИЗОВАНЕ СА Pd. РЕАКЦИОНИ МЕХАНИЗАМ И РАЗМАТРАЊЕ МОГУЋНОСТИ ЊЕНЕ ПРИМЕНЕ У АНАЛИТИЦИ

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Проучавана је реакција Co-EDTA са хипофосфит јоном, која је катализована јонима Pd(II), као индикаторска реакција. Инхибициона кинетика ове катализоване реакције проучавана је са гледишта механизма реакције у присуству неких инхибитора. Осим $PdCl_2$, други катализатори, као соли Pt, Au, и Ni нису имали никаквог ефекта на реакцију. На основу резултата експеримената предложен је оригинални реакциони механизам. Важни параметри оптимизовани су за постизање највеће осетљивости. Калибрациони дијаграм за ову методу инхибиционе кинетике био је линеаран (r = – 0,9878) у области између иницијалне брзине и брзине у присуству јодида у области концентрација 2 – 35 ng/cm^3 I^- уз границу детекције од 1,2 ng/cm^3 I^- (критеријум $3S_b/m$). *RSD* критеријум (N = 5) а за 7 и 14 ng/cm^3 I^- био је 1,19 и 0,81 %. Метода је примењена за одређивање јодида у води, урину, јодираној соли и неким узорцима лекова и компарирана је са модификованом методом Sandell-a и Kolthoff-a.

(Примљено 28. јула, ревидирано 1. октобра 2003)

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