



UNIVERSITY OF NIŠ

The scientific journal "FACTA UNIVERSITATIS"

Series: "Physics, Chemistry and Technology" Vol. 1, No 1, 1994 pp. 64-73

Editor of Series: Predrag Dimitrijević

Address: Trg Bratstva i Jedinstva 2 YU-18000 Niš

Tel: (018) 23-953 Fax: (018) 24-488

KINETIC DETERMINATION OF ULTRAMICRO AMOUNTS OF Fe(III) IN CLEAR JUICE

G.Ž. Miletić and S.S. Mitić

Department of Chemistry, Faculty of Philosophy, University of Niš, 18000 Niš, Yugoslavia

Abstract. - A new kinetic method is suggested for determining traces of iron(III) on the basis of their inhibiting effect on the Co(II) catalysis of oxidation of purpurine with hydrogen peroxide. The sensitivity of the method is 20 ng/cm³. Kinetic equations were proposed for the investigated process. The effects of certain foreign ions upon the reaction rate were determined for the assessment of the selectivity of the method. The method was applied to determine Fe(III) in fruit juice.

1. Introduction

There are several indicator reactions that can be used as the basis of kinetic detection and determination of trace amounts of Fe(III) in solution [1-6]. Their sensitivity ranges from about 0.1 to 1 ng/cm³.

The oxidation of purpurine with hydrogen peroxide in borate buffer gives a colorless product. This reaction is catalysed by traces of Co(II), and is used for their kinetic-catalytic determination [7]. We have observed that small amounts of Fe(III) strongly inhibit the catalysis of this reaction by Co(II). The rate of the reaction decreases proportionately with increasing concentration of Fe(III) and this is used as the basis of kinetic method for determination of ultramicro amounts of Fe(III).

2. Experimental

Reagents

The hydrogen peroxide solution was 0.4 mol/dm³ and its concentration was determined by the permanganate method. Fe(III) solution (10 mg/cm³) was prepared from a more concentrated

FeCl₃·H₂O solution (1 mg/cm³) was prepared from a more concentrated CoCl₂·6H₂O solution and standardized electrogravimetrically. Borate buffer solutions with different pH values were prepared by mixing 0.1 mol/dm³ NaOH and 0.05 mol/dm³ Na₂B₄O₇ in a corresponding ratio [9]. The purpurine solution (1·10⁻³ mol/dm³) was prepared by dissolving PP in about 5 cm³ of 0.1 mol/dm³ NaOH, and the solution obtained was diluted to 100 cm³ with deionized water. Analytical - grade reagents, deionized water, and polyethylene vassels were used throughout.

Apparatus

During the oxidation of purpurin with hydrogen peroxide the solution gradually loses its color, so that one can observe the progress of the reaction spectrophotometrically by measuring the absorbance of the solution at a wavelength of 540 nm every 0.5 minute for 8 minutes from the reaction start. We used the PERKIN ELMER LAMBDA 15 spectrophotometer with an auxiliary thermostatic apparatus. The solution were thermostated at 23 ± 0.1°C before the beginning of the reaction. The pH-meter was a Radiometer PHM 29b, with a combined glass-calomel electrode, GK 2311-C.

Procedure

The initial concentration of each of the reactants in turn was systematically varied, the initial concentrations of the other reactants being kept constant.

The initial concentration of each of the reactants in turn was systematically varied, the initial concentrations of the other reactants being kept constant.

The selected volumes of the reactants were put into a 25 cm³ standard flask, in the order purpurin, buffer (2 cm³), catalyst, inhibitor, and water to make up exactly to a predetermined volume. The flask was kept in the thermostat for 10 min, then the solution was made up to the mark with hydrogen peroxide and water and vigorously shaken. The cell of the spectrophotometer was rinsed well and filled with the solution. The absorbance A was measured every 30 sec, for 5-8 min, the timing being started at the moment of hydrogen peroxide addition. Instead of the reaction rate (dc/dt), the quantity d log A/dt (which is proportional to it) was determined:

$$d \log A/dt = \epsilon \cdot l \cdot dc/dt = \tan \alpha$$

where t is the time, ε is the molar absorptivity, l the cell path-length, c the concentration of the purpurin.

The initial concentrations of the reagent solutions after the dilution to 25 cm³ were: 0.4 · 10⁻⁵ - 2.0 · 10⁻⁵ mol/dm³ purpurin, 1.6 · 10⁻³ - 1.12 · 10⁻² mol/dm³ H₂O₂, 0.8 - 2.4 ng/cm³ Co(II), 20 - 320 ng/cm³ Fe(III).

The measurements were done at 23 ± 0.1°C.

3. Results and discussion

The integral variant of the tangent method was used for processing the kinetic data, because there is a linear relation between the logarithm of the absorbance and time during the first 5-8 min.

Fig.1 shows the influence of pH on the rate of both reactions. In can be seen that the greatest difference between the reaction rates occurs at pH = 10.75, where iron(III) maximally decreases the catalytic reaction rate. From Fig.1, it appears that there is complicated relationship between the pH and the reactions rates, i.e., the order of reaction is variable with respect to hydrogen-ion concentration for the range of concentrations studied.

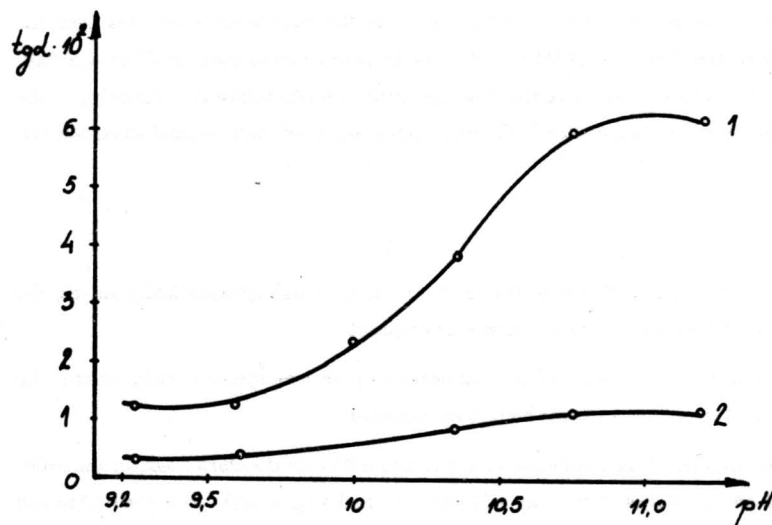


Fig. 1. Dependence of the reaction rate on pH. Initial conditions: $C_{PP} = 1.2 \cdot 10^{-5}$ mol/dm³, $C_{H_2O_2} = 8 \cdot 10^{-3}$ mol/dm³, $C_{Co(II)} = 2$ ng/cm³, $C_{Fe(III)} = 1$ mg/cm³; 1 - Catalysed reaction, 2 - Inhibited reaction.

The dependence of the reaction rates on the concentration of Co(II) is shown in Fig.2, which shows that with increasing Co(II) concentration the difference in the rates of the inhibited and catalytic reactions increases. Both reactions are of first order with respect to the Co(II) concentration. For further work an Co(II) concentration of 2 ng/cm³ was selected.

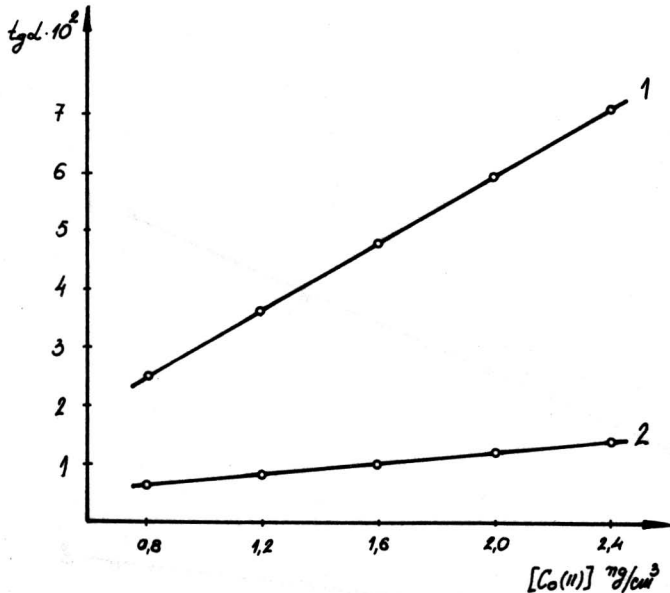


Fig. 2. Dependence of the reaction rate on the Co(II) concentration. Initial conditions: $C_{PP} = 1.2 \cdot 10^{-5}$ mol/dm³, $C_{H_2O_2} = 8 \cdot 10^{-3}$ mol/dm³, $C_{Fe(III)} = 1$ mg/cm³; 1 - Catalysed reaction, 2 - Inhibited reaction.

The dependence of $\tan \alpha$ on H_2O_2 concentration is shown in Fig.3, which shows that with increasing H_2O_2 concentration the difference in the rates of the inhibited and catalytic reactions increases. Both reactions are of first order with respect to the H_2O_2 concentration. For further work an H_2O_2 concentration of $4.8 \cdot 10^{-3}$ mol/dm³ was selected, because with higher concentrations the linear part of the kinetic curve ($\log A-t$) is rather shortened.

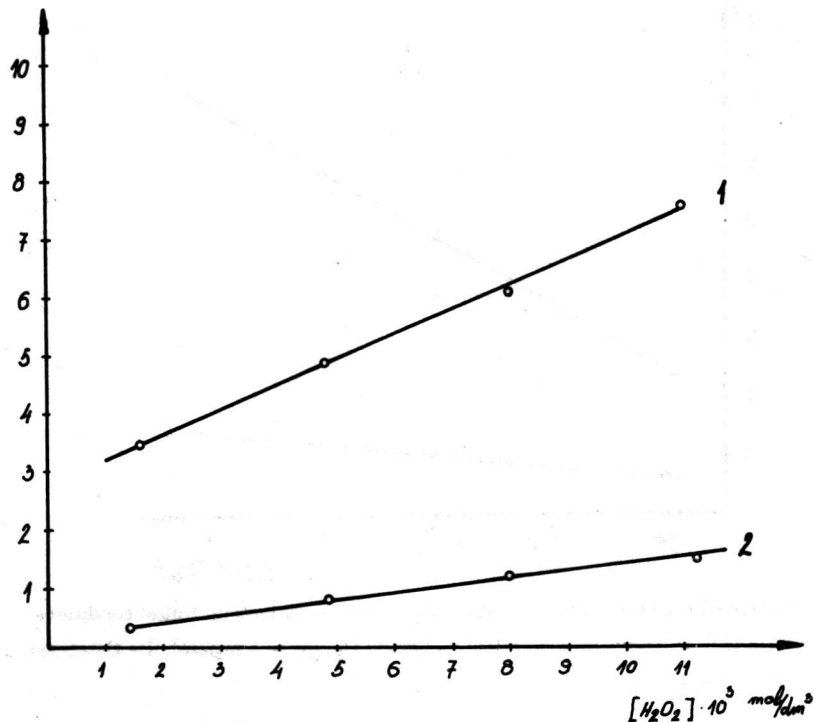


Fig. 3. Dependence of the reaction rate on the H_2O_2 concentration. Initial conditions: $C_{PP} = 1.2 \cdot 10^{-5} \text{ mol/dm}^3$, $C_{Co(II)} = 2 \text{ ng/cm}^3$, $C_{Fe(III)} = 1 \text{ mg/cm}^3$; 1 - Catalysed reaction, 2 - Inhibited reaction.

Figure 4 shows that $\tan \alpha$ is a linear function in the tested interval of purpurine concentrations, since both the catalytic and inhibited reactions are of the first order in respect to purpurine for further work the concentration of $1.2 \cdot 10^{-5} \text{ mol/dm}^3$ purpurin was chosen.

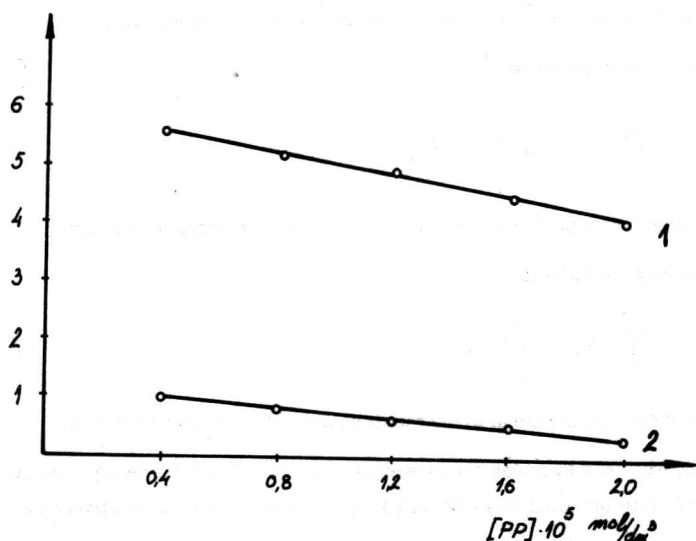


Fig. 4. Dependence of the reaction rate on the PP concentration. Initial conditions: $C_{\text{H}_2\text{O}_2} = 4.8 \cdot 10^{-3} \text{ mol/dm}^3$, $C_{\text{Co(II)}} = 2 \text{ ng/cm}^3$, $C_{\text{Fe(III)}} = 1 \text{ mg/cm}^3$; 1 - Catalysed reaction, 2 - Inhibited reaction.

Under optimal conditions of the reaction ($C_{\text{PP}} = 1.2 \cdot 10^{-5} \text{ mol/dm}^3$, $C_{\text{H}_2\text{O}_2} = 4.8 \cdot 10^{-3} \text{ mol/dm}^3$, $\text{pH} = 10.75$), Fe(III) concentration varied from 20 to 320 ng/cm^3 . Fig.5 shows calibration line which can be used for determination of Fe(III) concentration in the interval mentioned.

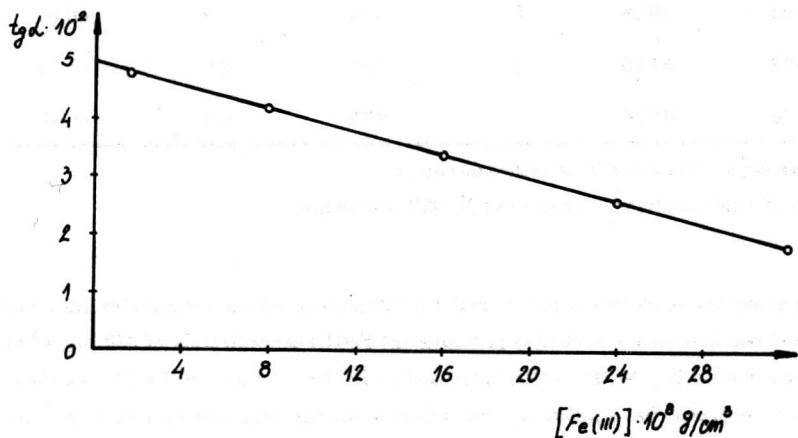


Fig.5. Dependence of the reaction rate on the Fe(III) concentration. Initial conditions: $C_{\text{PP}} = 1.2 \cdot 10^{-5} \text{ mol/dm}^3$, $C_{\text{H}_2\text{O}_2} = 4.8 \cdot 10^{-3} \text{ mol/dm}^3$, $C_{\text{Co(II)}} = 2 \text{ ng/cm}^3$, $\text{pH} = 10.75$, $t = 23 \pm 0.1^\circ\text{C}$.

The relationship between the reaction rates and the concentrations of the reacting components can be explained by the following kinetic equations (at constant pH).

For the inhibition reaction:

$$\frac{dx}{dt} = k_1 \cdot C_{PP} \cdot C_{H_2O_2} \cdot C_{Fe} \quad (1)$$

where k_1 is a constant proportional to the rate constant of the inhibited reaction.

For the catalysed process:

$$\frac{dx}{dt} = k_2 \cdot C_{PP} \cdot C_{H_2O_2} \cdot C_{Co} \quad (2)$$

where k_2 is a constant proportional to the rate constant of the catalysed reaction.

The accuracy and precision are presented in Table I. The relative error ranges from 0.8 to 4.3 % for Fe(III) concentrations from 320 to 20 ng/cm³. The method has relatively good accuracy.

Table I. - Accuracy and precision of Fe(III) determination

Taken (ng/cm ³)	Found (\bar{x}) (ng/cm ³)	n	S (ng/cm ³)	100ts/x√n %	(\bar{x} -μ)100/μ %
20.00	20.19	5	0.71	4.3	+0.95
80.00	81.00	5	1.83	2.8	+1.25
320.00	316.16	5	2.02	0.8	-1.20

\bar{x} - Mean value; μ - true value; S - standard deviation;

n - number of determinations; t - student's t for 95% confidence.

To assess the selectivity of the method, the influence of several foreign ions on the rate of the inhibited reaction rates was studied at a constant Fe(III) concentration of 320 ng/cm³ (Table II). It is seen that Cd(II), Ni(II), Cu(II), Zn(II) and Al(III) [in 1:1 ration to Fe(III)] interfere. The other ions investigated have practically no influence on the determination of Fe(III) by the method.

Table II. - Influence of some foreign ions on the determination of trace amounts of Fe(III);

$$C_{\text{Fe(III)}} = 320 \text{ ng/cm}^3; q = C_{\text{ion}}/C_{\text{Fe(III)}}$$

Ion	q	$\tan\alpha \times 10^2$	Ion	q	$\tan\alpha \times 10^2$
-	-	1.82	$\text{Cr}_2\text{O}_7^{2-}$	10	1.65
Ca^{2+}	10	1.95	WO_4^{2-}	10	1.70
Sr^{2+}	10	2.25	MoO_4^{2-}	10	1.90
Mg^{2+}	10	1.58	SO_4^{2-}	10^2	1.92
Ba^{2+}	10	1.80	PO_4^{3-}	10^2	1.98
Al^{2+}	1	1.20	CNS^-	1	2.02
Pb^{2+}	10	1.64	J^-	1	2.08
Zn^{2+}	1	1.23	Br^-	1	1.91
Cd^{2+}	1	0.92	F^-	1	2.06
Ni^{2+}	1	1.00	CH_3COO^-	10	1.86
Hg^{2+}	1	2.03	$\text{C}_2\text{O}_4^{2-}$	10	1.95
Cu^{2+}	1	1.15	$\text{H}_4\text{C}_4\text{O}_6^{2-}$	10^2	1.94
AsO_4^{3-}	10	2.00	citrate	10^2	1.85

The method was applied to the determination of iron in fruit juices. We have separated Fe(III) by extraction from other components of fruit juices [9]. The results are given in Table III. The values obtained by the method were confirmed by the AAS method.

Table III. - Determination of Fe(III) in clear juice

JUICE	kinetic determination				AAS determination
	method of calibration line		method of additions		
	Fe(III)(\bar{x})	error	Fe(III)(\bar{x})	error	
	$\mu\text{g}/\text{cm}^3$	%	$\mu\text{g}/\text{cm}^3$	%	
Cherry juice	2.70	2.5	2.82	1.4	2.80
Apple juice	0.97	5.0	0.98	1.9	1.10
Quince juice	1.30	4.3	1.37	1.6	1.38
Flum juice	4.45	1.4	4.52	1.2	4.60

 \bar{x} - Mean value

References

- [1] Krengold, S., Sosenkova, L.I., *Zh. Anal. Khim.*, **26** (1971) 332-337
- [2] Kawashima, T., Kozuma, Y., Nakano, S., *Anal. Chim. Acta*, **106** (1979) 355-360
- [3] Moreno, A., Silva, M., Perez-Bendito, D., Valcarcel, M., *Anal. Chim. Acta*, **157** (1984) 333-342
- [4] Dolmanova, I.F., Rychkova, V.I., Peshkova, V.M., *Zh. Anal. Khim.*, **28** (1973) 1763-1767
- [5] Nakano, S., Odzu, M., Tanaka, M., Kawashima, T., *Mikrochim. Acta*, **I** (1983) 403-411
- [6] Dolmanova, I.F., Rychkova, V.I., Peshkova, V.M., *Zh. Anal. Khim.*, **32** (1977) 1387-1393
- [7] Bognár, J., Jellinek, O., *Mag. Kém. Foly.*, **67** (1961) 73
- [8] Barsukova, Z.A., *Analytical Chemistry*, (1990) Moscow
- [9] Lure, Yu. Yu., *Handbook of Analytical Chemistry* (1990) Khemia, Moscow

KINETIČKO ODREĐIVANJE ULTRAMIKRO KOLIČINA Fe(III)
U BISTRIM SOKOVIMA

Gordana Ž. Miletić , Snežana S. Mitić

Predložena je nova kinetička metoda za određivanje tragova Fe(III) na bazi njihovog inhibitorškog dejstva na reakciju oksidacije purpurina vodonikperoksidom koja je katalizovana sa Co(II). Osetljivost metoda je 20 ng/cm^3 . Relativna greška se kreće od 0,8 do 4,3 % za interval koncentracije od 320 do 20 ng/cm^3 . Predložene su kinetičke jednačine za proučavani proces. Radi ocene selektivnosti metode ispitan je uticaj izvesnog broja stranih jona na brzinu reakcije. Metoda je primenjena za određivanje tragova Fe(III) u bistrim sokovima.