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KINETIC DETERMINATION OF ULTRAMICRO AMOUNTS OF Co(II)

UDC: 543.23

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Abstract. *A new catalytic reaction was proposed and a kinetic method was developed for the determination of ultramicro amounts of Co(II) in solution, based on its catalytic effect in the oxidation of the 4-hydroxycoumarinil-3-sulphonaminoacetic acid by $KMnO_4$ in acetate buffer. The sensitivity of the method is 0.25 ng/cm^3 Co(II). The probably relative error ranges between 2.5 and 10.9% for concentration interval 4.0 to 0.5 ng/cm^3 Co(II). Kinetic equations were proposed for the investigated process. The effects of certain foreign ions upon the reaction rate were determined for the assesment of the selectivity of the method.*

Key words: *cobalt, kinetic determination, 4-hydroxycoumarinil-3-sulphonaminoacetic acid*

1. INTRODUCTION

Lately, homogenous catalytic oxidation-reduction reactions are used for the analysis of Co(II) traces in solution where hydrogen peroxide is the oxidant and the reductor is, most frequently, a certain organic, aromatic oxy-compound [1-10]. Kinetic methods were elaborated, on the basis of those reactions, with wich Co(II) from about $1 \cdot 10^{-5}$ - $2 \text{ } \mu\text{g/cm}^3$ could be determined. They are all catalyzed by means of traces of Co(II) in a more or less alkaline medium, except for [10], and it can be the cause of lower selectivity.

The oxidation of 4-hydroxycoumarinil-3-sulphonaminoacetic acid (KS) by $KMnO_4$ in acetate buffer, is catalyzed by small amounts of Co(II). On the basis of this reaction the kinetic method was elaborated for Co(II) traces determination in the range from 0.25 - 5 ng/cm^3 . Diminution of the colour intensity of the oxidant ($KMnO_4$) was followed spectrophotometrically as the change of absorbance (A) in time (t).

2. EXPERIMENTAL

The dependence of absorbance on time was measured with a spectrophotometer MA 9524 Specol 221 Carl Zeiss-Iskra, equipped with thermostat system. A cell of path-length 10 mm, were used. The pH-values of solutions were verified by Radiometer PHM 29b pH-meter. All measurements were done on the wave-length of 525 nm. All solutions were kept in a thermostatic water-bath.

0.02 mol/dm³ KMnO₄ was prepared from an ampulla, produced by "Merck". Acetic acid and sodium hydroxide were used for preparation of acetate buffers [11]. 4-hydroxycoumarinil-3-sulphonaminoacetic acid solution (3·10⁻³ mol/dm³) was made by direct weighing of the solid KS, that have been previously recrystallized two times from the water-ethanol mixture (4:1) and dried on 105°C [12]. Co(II) solution with a concentration of 100 µg/cm³ was prepared from CoCl₂·6H₂O. The accurate concentration was electrogravimetrically determined from a more concentrated solution. Analytical grade reagents, redistilled water and polyethylene vessels were used for the preparation of all solutions.

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 10 cm³ standard flask, in the other KS, buffer (1 cm³), catalyst 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 KMnO₄ and water and vigorously shaken. The cell of the photometer was rinsed well and filled with the solution. The absorbance *A* was measured every 30 sec, for 5-8 min, the timing beign started at the moment of KMnO₄ addition. Instead of the reaction rate (dc/dt), the quantity d*A*/dt (which is proportional to it) was measured:

$$\frac{dA}{dt} = \varepsilon \cdot l \cdot \frac{dc}{dt} = \tan \alpha$$

where ε is molar absorptivity, *l* the cell path-length, *c* the concentration of the KMnO₄ and $\tan \alpha$ the slop of the linear part of the plot of *A* against *t*.

The initial concentrations of the reagent solutions after the dilution to 10 cm³ were: 1·10⁻⁴ - 1.6·10⁻³ mol/dm³ KS; 4·10⁻⁵ - 3.2·10⁻⁴ mol/dm³ KMnO₄; 0.125 - 5 ng/cm³ Co(II). The measurements were done at 25 ± 0.1°C.

3. RESULTS AND DISCUSSION

The differential variant of the tangent method was used for processing the kinetic data, because there is a linear relation between the absorbance and time during the first 2-5 min [1].

The effect of pH on the catalysed and uncatalysed reaction rates is shown in Fig. 1. From Fig. 1, it appears that there is a complicated relationship between pH and reaction rate, i.e., the order reaction is variable with respect to hydrogen-ion concentration for the range of concentrations studied. For further work a pH of 3.7 was chosen for quantitative applications.

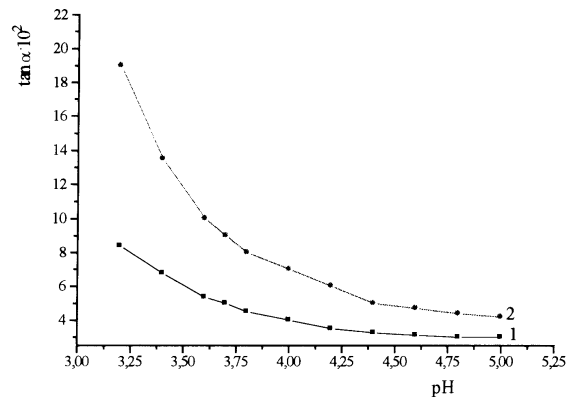


Fig. 1. Dependence of the reaction rate on pH. Initial conditions: $1.6 \cdot 10^{-4}$ mol/dm³ KMnO₄; $8 \cdot 10^{-4}$ mol/dm³ KS; 5 ng/cm³ Co(II); 1-uncatalysed reaction, 2-catalysed reaction.

The dependence of $\tan \alpha$ on KS concentration is shown in Fig. 2. The maximum difference between the rates of the catalysed and uncatalysed reactions is observed for concentrations of KS greater than $8 \cdot 10^{-4}$ mol/dm³. At lower concentrations, as already mentioned, both reactions are of the first order with respect to KS. For further work a KS concentration of $8 \cdot 10^{-4}$ mol/dm³ was selected.

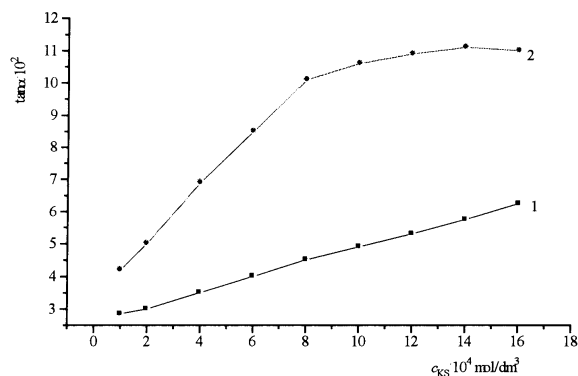


Fig. 2. Dependence of the reaction rate on the KS concentration. Initial conditions: $1.6 \cdot 10^{-4}$ mol/dm³ KMnO₄; 5 ng/cm³ Co(II); pH = 3.7; 1-uncatalysed reaction, 2-catalysed reaction.

The dependence of the reaction rates on the concentration of KMnO₄ is shown in Fig. 3. From Fig. 3, it appears that there is a complicated relationship between $c_{MnO_4^-}$ and reaction rate, i.e., the reaction order is variable with respect to MnO_4^- -ion concentration for the ranges of concentrations studied. For further work the concentrations of $1.6 \cdot 10^{-4}$ mol/dm³ KMnO₄ was chosen.

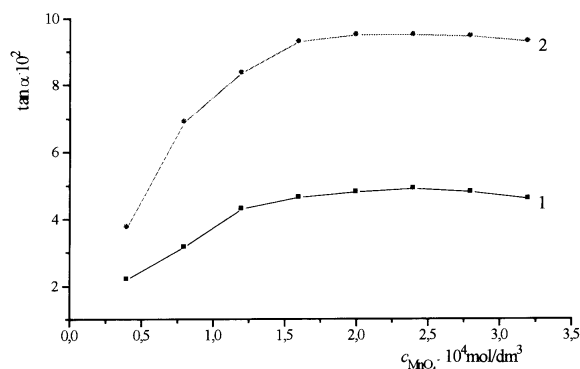


Fig. 3. Dependence of the reaction rate on the KMnO_4 concentration. Initial conditions: $8 \cdot 10^{-4} \text{ mol/dm}^3$ KS; 5 ng/cm^3 Co(II); $\text{pH} = 3.7$; 1-uncatalysed reaction, 2-catalysed reaction.

Under optimal conditions of reaction $c_{\text{KS}} = 8 \cdot 10^{-4} \text{ mol/dm}^3$, $c_{\text{KMnO}_4} = 1.6 \cdot 10^{-4} \text{ mol/dm}^3$, $\text{pH} = 3.7$ the Co(II) concentration was varied from 0.125 to 5 ng/cm^3 . Fig. 4 shows the two calibration lines which can be used for determination of Co(II) concentration in the interval mentioned. The relationship between the reaction rates and the concentrations of the reacting components can be explained by the following equations (at constant pH).

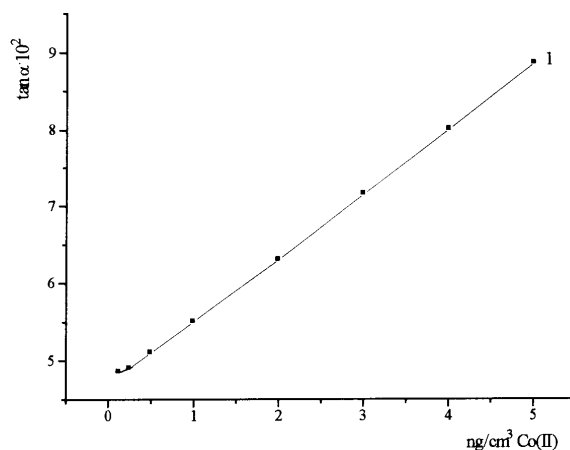


Fig. 4. Dependence of the reaction rate on Co(II) concentration. Initial conditions: $8 \cdot 10^{-4} \text{ mol/dm}^3$ KS; $1.6 \cdot 10^{-4} \text{ mol/dm}^3$ KMnO_4 ; $\text{pH} = 3.7$

For the catalysed reaction,

$$-\left(\frac{dc}{dt}\right) = k \cdot c_{\text{KS}} \cdot c_{\text{KMnO}_4}^x \cdot c_{\text{Co}} \quad \text{for} \quad c_{\text{KS}} \leq 8 \cdot 10^{-4} \text{ mol/dm}^3$$

where x is a variable and k is constant proportional to the rate constant of the catalysed reaction.

For the uncatalysed reaction,

$$-\left(\frac{dc}{dt}\right) = k_0 \cdot c_{KS} \cdot c_{KMnO_4}^y$$

where y is a variable and k_0 is a constant proportional to the rate constant of the uncatalysed reaction.

The accuracy and precision are presented in Table 1. The probably relative error ranges from 2.5 to 10.9% for Co(II) concentrations from 4 to 0.5 ng/cm³. The method has relatively good accuracy. To assess the selectivity of the method, the influence of several foreign ions on the catalysed reaction rate was investigated, at constant Co(II) concentration of 4 ng/cm³. The presence (individually, in the ratio to Co(II) that is given in brackets) of K⁺, NH₄⁺, Sr²⁺, SO₄²⁻ (10⁴:1), Mg²⁺, Ca²⁺, Ba²⁺, Cu²⁺, Cd²⁺, Cl⁻ (10³:1), Pb²⁺, Zn²⁺, Mn²⁺, Sn²⁺, citrate (10²:1) has practically no influence on the reaction rate. Fe³⁺ (1:1), Ni²⁺ (10:1) further catalyse the reaction. SCN⁻, PO₄³⁻, C₂O₄²⁻ (10:1) have a slight inhibiting effect.

Table 1. Accuracy and precision of Co(II) determination

Taken (ng/cm ³)	Found (x) (ng/cm ³)	n	100ts/x√n	(x-μ)100/μ (%)
0.50	0.53	5	10.9	6.0
1.00	1.01	5	6.5	1.0
2.00	2.03	5	4.0	1.5
4.00	3.95	5	2.5	-1.3

x-mean value; μ-true value; s-standard deviation, n-number of determination;
t-Student's for 95% confidence.

REFERENCES

1. K. B. Yatsimirskii, *Kinetic Methods of Analysis*, Khimia, Moscow, 1967 (in Russian)
2. V. Vershinin, B. Chuiko and B. Reznik, Determination of submicrogram amounts of cobalt using the catalytic reaction of alizarin s oxidation by hydrogen peroxide, *Zh. Analit. Khim.*, 26, 1710-1718 (1971)
3. T. Janjić and G. Milovanović, Determination of ultramicro quantities of cobalt by catalytic oxidation of pyrocatechol violet by hydrogen peroxide, *Bull. Soc. chim.*, Beograd, 37, 173-189 (1971)
4. I. Dolmanova, N. Ushakova and V. Peshkova, Kinetic determination of cobalt in the presence of nickel by reaction of diphenylcarbazone-tairon-hydrogen peroxide, *Zh. Analit. Khim.*, 28, 1131-1137 (1973)
5. I. Dolmanova, N. Ushakova, E. Smirnova and V. Peshkova, Selection of activators for the reaction of oxidizing diphenyl carbazone with hydrogen peroxyde catalysed with cobalt and nickel, *Ibid.*, 28, 1530-1534 (1973)
6. R. Pantalar, L. Alchimova, A. Bulgakova and I. Pulyaeva, Kinetic thermometric determination of cobalt microamounts, *Ibid.*, 30, 946-950 (1975)
7. R. Pantalar, L. Alchimova and A. Bulgakova, Comparative study of catalytic properties of complexes of manganese, iron and cobalt with 1,10-phenanthroline in reaction of hydrogen peroxyde decomposition, *Ibid.*, 30, 1834-1836 (1975)
8. R. Igov and M. Jaredić, Kinetic determination of ultramicro amounts of Co(II) by catalytic oxidation of 1,4-dioxyanthraquinone with hydrogen peroxide, *Bull. Soc. chim., Beograd*, 44 (11), 711-717 (1979)
9. R. Igov, S. Rančić, T. Pecev and J. Perović, Kinetic determination of Co(II) in solution, *I Regional Symposium: Chemistry and the Environment, Vrnjačka Banja, Yugoslavia*, 1995, SI-2
10. R. Igov, M. Jaredić and T. Pecev, Kinetic determination of ultramicro amounts of Co(II), *Bull. Soc. chim., Beograd*, 45 (9), 365-371 (1980)

11. Yu. Yu. Lure, *Handbook of Analytical Chemistry*, Khimia, Moscow, 1971 (in Russian)
12. M. Trkovnik, M. Kulaš, D. Kita and M. Ismaili, The reactions of 4-hydroxycoumarinil-3-sulphochloride with amino acids and amines, *Bull. Soc. Chem. and Technology, Sarajevo*, 33/34, 73-77 (1987/88).

KINETIČKO ODREĐIVANJE ULTRAMIKRO KOLIČINA Co(II)

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Predložena je nova katalitička reakcija i razrađena kinetička metoda za određivanje ultramikro količina Co(II) u rastvoru na osnovu njegove katalitičke aktivnosti pri oksidaciji 4-hidroksikumarinil-3-sulfonaminosirćetne kiseline sa $KMnO_4$ u acetatnom puferu. Osetljivost metode iznosi $0,25 \text{ ng/cm}^3$ Co(II). Verovatna relativna greška se kreće od 2,5 do 10,9% za interval koncentracija od 4,0 do $0,5 \text{ ng/cm}^3$ Co(II). Predložene su kinetičke jednačine za proučavani proces. Radi ocene selektivnosti metode ispitan je uticaj izvesnog broja stranih jona na brzinu reakcije.

Ključne reči: kobalt, kinetičko određivanje, 4-hidroksikumarinil-3-sulfonamino/sirćetna kiselina