

Kinetic determination of ultramicro amounts of Cu(II) ion in solution

Z. M. GRAHOVAC*, S. S. MITIĆ and E. T. PECEV

Faculty of Natural Sciences and Mathematics, Department of Chemistry, University of Niš, Višegradska 33, 18000 Niš, Serbia and Montenegro

(Received 19 September, revised 26 November 2002)

Abstract: A new kinetic method is described for the determination of ultramicro amounts of Cu(II) based on its catalytic effect on the oxidation of trisodium-2-hydroxy-1-(4-sulphonato-1-naphthylazo)naphthalene-6,8-disulphonato (red artificial color PONCEAU 4R) by hydrogen peroxide in borate buffer (B.B.) The detection limit given by Perez-Bendito is 0.8 ng/cm³, but the detection limit that we experimentally determined is 3.8 ng/cm³. The relative error ranges between 7.77 and 2.09 % for the concentration interval 3.8 to 50.1 ng/cm³. Kinetic equations are proposed for the investigated process. The effects of certain foreign ions upon the reaction rate were determined for an assessment of the selectivity of the method. The method was applied for the determination of Cu(II) ions in samples of alloy.

Keywords: kinetic method, copper(II) determination, PONCEAU 4R, samples of alloy.

INTRODUCTION

Copper is essential element for the function of many vital processes. It is extremely important in the processes of blood formation, stimulation of hemoglobin synthesis, growth and development of cells, as well as for the function of endocrine glands.

The human organism is supplied with copper through food and water. Therefore it is necessary to control its concentration in both, which necessitates its determination in both.¹

Copper is very important for plants too. It is significant in the process of photosynthesis and affects the absorption of nitrogen by plants.

Although copper is not a toxic element, its presence in freshwater, wastewater and drinking water is standardized, its concentration in drinking water is 0.05 mg/dm³.²

In recent years kinetic methods have become important in trace analysis and the application of catalytic reactions in trace analysis has been reviewed previously. Many methods for the kinetic determination of copper(II) are based on its catalytic effects on oxidation reactions including ligand-substitution reactions, or on the oxidation of organic compounds,

* E-mail: emapecev@yahoo.com

such as phenyl amines and phenols, by H_2O_2 or by oxygen. The oxidation of these compounds leads to the formation of colored products, hence the kinetics of trace reactions is usually followed spectrophotometrically. Most of these methods are very sensitive in the range of nanogramms and do not demand costly equipment.³⁻⁵

One of the kinetic method for the determination of Cu(II) is based on the reaction of the oxidation of Rodamine B with H_2O_2 in ammoniacal buffer. The detection limit is 20 ng/cm^3 . The method was applied for the determination of Cu(II) in serum.⁶

Zhang and associates proposed a catalytic-kinetic method for determination of Cu(II) ions, based on the reaction of the oxidation of Brilliant Yellow with H_2O_2 in ammoniacal medium. The detection limit of this method is 0.16 ng/cm^3 . The method was applied for the determination of Cu(II) ions in environmental samples.⁷

The kinetic method of the oxidation of 2,6-dichlorophenol-indophenol with H_2O_2 involved the photometrical monitoring of the oxidation of the leuco form at 562 nm. The method was applied for the determination Cu(II) ions in alloys, pharmaceuticals samples, and environmental samples. This method copper(II) can be determine allows the determination of Cu(II) ions in the concentration range from 5 to 300 ng/cm^3 .⁸

The indication reaction of the oxidation of Phenol Red with H_2O_2 was followed by Zhou and associates. The detection limit is 12 ng/cm^3 and the method was applied for the determination of Cu(II) ions in steel.⁹

A new kinetic method for the determination of Cu(II) ions, with a detection limit of 3.8 ng/cm^3 , is described in this paper. The oxidation of the indicator substance PONCEAU 4R with hydrogen peroxide in basic medium gives a colorless product. The reaction is catalyzed by traces of Cu(II) ions, and is used for their kinetic-catalytic determination.¹⁰ It was observed that small amounts of Cu(II) ions strongly catalyze this reaction. The rate of the reaction increases proportionally with increasing concentration of Cu(II) ions. This fact was used as the basis of the kinetic method for determining ultramicro amount of Cu(II) ions, with good accuracy and precision and with very good selectivity.

EXPERIMENTAL

Apparatus

A spectrophotometric method was used for following the rate of the investigated reaction. The dependence of the absorbance (A) on (t) was measured using a Perkin-Elmer Lambda 15 spectrophotometer, connected to a thermocirculating bath. The pH was measured by means of a Radiometer PHM 29b pH meter and a combined glass-calomel electrode, GK 2311C. The solution was thermostated at 22 ± 0.1 °C before the beginning of the reaction.

Reagents

A hydrogen peroxide solution was prepared from the 30 % reagent ($c = 1$ mol/dm^3) by diluting with deionized water.

A stock solution of the artificial color PONCEAU 4R ($c = 1 \times 10^{-3}$ mol/dm^3) was prepared by dissolving it in deionized water. The working PONCEAU 4R solution ($c = 1.6 \times 10^{-4}$ mol/dm^3) was obtained by dilution with water.

The borate buffer solution was prepared by mixing $\text{Na}_2\text{B}_4\text{O}_7$ ($c = 0.05$ mol/dm^3) with NaOH ($c = 0.1$ mol/dm^3).¹¹

The solution of CuCl_2 was prepared by dissolving CuCl_2 in water ($c = 1 \times 10^{-5} \text{ mol/dm}^3$). All chemicals were analytical reagent grade and were provided by Merck unless indicated otherwise. The artificial color PONCEAU 4R was obtained from the food industry "HISAR". The solutions were prepared using deionized water. All stock solutions were stored in polyethylene containers. The working solution of CuCl_2 and hydrogen peroxide were prepared immediately before use.

All the polyethylene containers and the glassware used were cleaned in aqueous HCl (1:1) and then thoroughly rinsed with deionized water.

Procedure

The selected volumes of reagents were transferred into a 10 cm^3 volumetric four compartment flask in (Bouderin flask) the order: borate buffer, PONCEAU 4, hydrogen peroxide and catalyst. Water was added to give the predetermined volume. The flask was thermostated for 10 min, and vigorously shaken. The spectrophotometer cell was rinsed well and filled with the solution. The absorbance at 478.4 nm was measured every 30 s over a period of 4 to 6 min after mixing. Instead of the reaction rate (dc/dt), the quantity dA/dt was used. The measurements were made at $22 \pm 0.1 \text{ }^\circ\text{C}$.

RESULTS AND DISCUSSION

Kinetic studies

An integral variant of the tangent method¹² was used for processing the kinetic data, because a linear correlation exists between the logarithm of the absorbance and time during the first 4 to 6 min after mixing. The reaction rate was followed by the change in the values of the tangent of the angle ($\text{tg } \alpha$) for the slope of the linear part of the kinetic curve to the abscissa in the coordinates $\log A-t$, because $\text{tg } \alpha = d \log A/dt$. Such a plot is shown in Fig. 1.

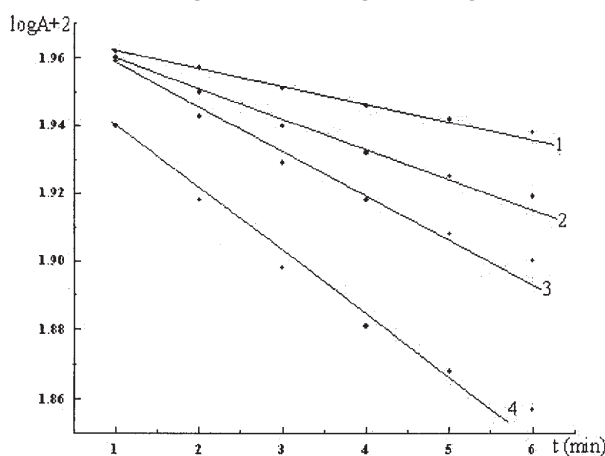


Fig. 1. Dependence of the logarithm of the absorbance of the solution on time. Initial conditions: $c_{\text{H}_2\text{O}_2} = 3 \times 10^{-2} \text{ mol/dm}^3$; $c_{\text{PONCEAU 4R}} = 8 \times 10^{-6} \text{ mol/dm}^3$; borate buffer pH 10.50; $c_{\text{Cu(II)}} \text{ ng/cm}^3$; 1-0.00; 2-3.8; 3-25.4; 4-50.1.

In order to determine the lowest possible determinable concentration of Cu(II) ions, the condition needed to be optimized. Therefore, the dependencies of the rates of both the catalyzed and the non-catalyzed reactions on the concentration of each of the reactants were determined.

The influence of pH on the rate of both reactions is shown in Fig. 2. It can be seen that the greatest difference between the reaction rates occurs at pH 10.50, when Cu(II) maximally increases the rate of the catalyzed reaction. For further work a borate buffer at pH 10.50 was selected.

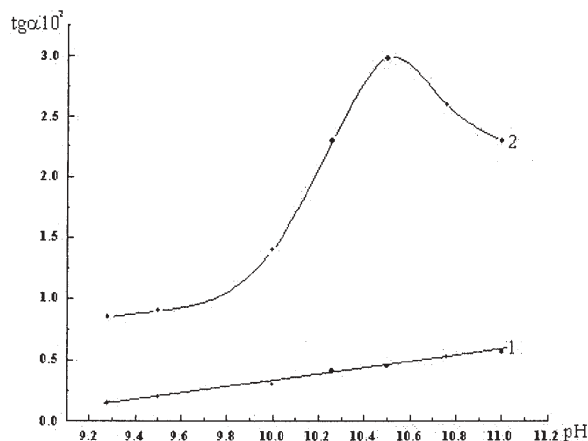


Fig. 2. Dependence of $\text{tg } \alpha$ on pH for the non-catalysed (1) and catalysed (2) reaction. Initial conditions: $c_{\text{H}_2\text{O}_2} = 3 \times 10^{-2} \text{ mol/dm}^3$; $c_{\text{PONCEAU 4R}} = 8 \times 10^{-6} \text{ mol/dm}^3$; $c_{\text{Cu(II)}} = 63 \text{ ng/cm}^3$; $t = 22 \pm 0.1 \text{ }^\circ\text{C}$.

From Fig. 2 it appears that there is a complicated relationship between the pH and the catalyzed reaction rate in the range of concentrations studied. A linear relationship between the logarithm of $\text{tg } \alpha$ and the logarithm c_{H^+} was found for the catalyzed reaction. The order of catalyzed reaction is -0.6 with respect to pH in the investigated pH interval from 9.28 to 10.50. The order of the non-catalyzed reaction is -1 order with respect to pH in the investigated interval.

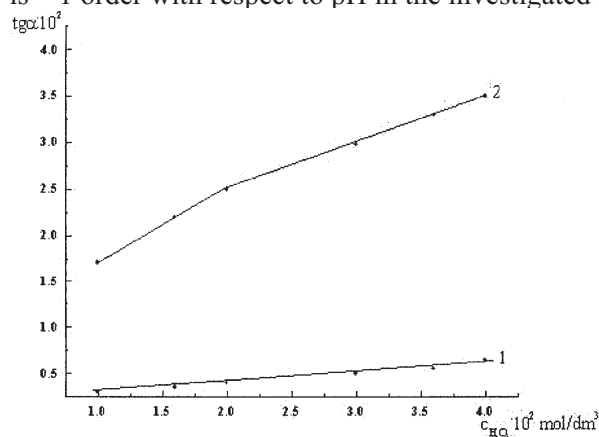


Fig. 3. Dependence of $\text{tg } \alpha$ on the H_2O_2 concentration for the non-catalysed (1) and catalysed (2) reaction. Initial conditions: borate buffer pH 10.50; $c_{\text{PONCEAU 4R}} = 8 \times 10^{-6} \text{ mol/dm}^3$; $c_{\text{Cu(II)}} = 63 \text{ ng/cm}^3$; $t = 22 \pm 0.1 \text{ }^\circ\text{C}$.

The dependence of the reaction rates on the concentration of H_2O_2 is shown in Fig. 3, from which it can be seen that both the catalyzed and non-catalyzed reactions are first order with respect to the H_2O_2 concentration. A H_2O_2 concentration of 0.03 mol/dm^3 was selected for further work.

The dependence of the reaction rates of the concentration of the color PONCEAU 4R is shown in Fig. 4. It can be seen that the greatest difference between the reaction rates occurs at $c_{\text{PONCEAU 4R}} = 8 \times 10^{-6} \text{ mol/dm}^3$. From Fig. 4 it can be seen that the catalyzed reaction is first order with respect to the PONCEAU 4R concentration from 4.8×10^{-6} to $8 \times 10^{-6} \text{ mol/dm}^3$, and the non-catalyzed reaction is zero order with respect to the PONCEAU 4R concentration.

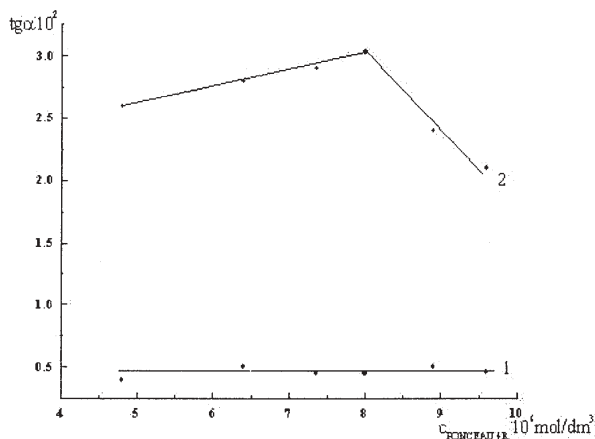


Fig. 4. Dependence of $\text{tg } \alpha$ on the PONCEAU 4R concentration for the non-catalyzed (1) and catalyzed (2) reaction. Initial conditions: borate buffer pH 10.50; $c_{\text{H}_2\text{O}_2} = 3 \times 10^{-2} \text{ mol/dm}^3$, $c_{\text{Cu(II)}} = 63 \text{ ng/cm}^3$; $t = 22 \pm 0.1 \text{ }^\circ\text{C}$.

Under the optimal reaction conditions:

pH 10.50 (borate buffer); $c_{\text{H}_2\text{O}_2} = 0.03 \text{ mol/dm}^3$; $c_{\text{PONCEAU 4R}} = 8 \times 10^{-6} \text{ mol/dm}^3$, the Cu(II) concentration was varied from 3.8 to 50.1 ng/cm^3 .

Figure 5 show the calibration line, at the temperature of 22 $^\circ\text{C}$, which can be used for the determination of the Cu(II) concentration in the interval mentioned.

The following kinetic equations were deduced on the basis of the graphic correlations obtained for the investigated process.

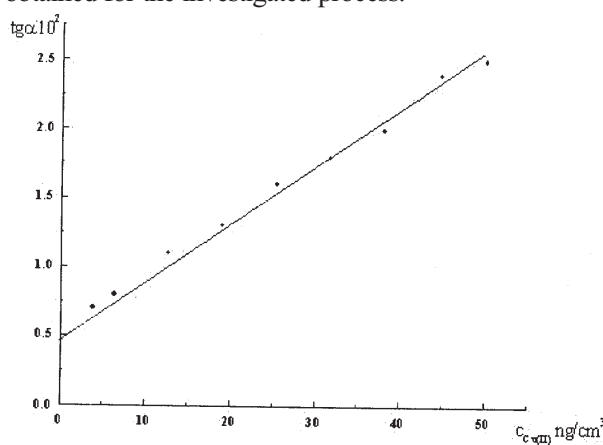


Fig. 5. Dependence of $\text{tg } \alpha$ on the Cu(II) concentration for the catalyzed reaction. Initial conditions: borate buffer pH 10.50; $c_{\text{H}_2\text{O}_2} = 3 \times 10^{-2} \text{ mol/dm}^3$; $c_{\text{PONCEAU 4R}} = 8 \times 10^{-6} \text{ mol/dm}^3$; $t = 22 \pm 0.1 \text{ }^\circ\text{C}$.

For the non-catalyzed reaction:

$$-dc/dt = k_0 c_{\text{H}^+}^{-1} c_{\text{H}_2\text{O}_2}$$

where k_0 is a constant proportional to the rate constant of the non-catalyzed reaction.

For the catalyzed reaction:

$$-dc/dt = k c_{\text{H}^+}^{-0.6} c_{\text{H}_2\text{O}_2} c_{\text{PONCEAU 4R}} c(\text{Cu(II)})$$

for the pH interval from 9.28 to 10.50 and for a concentration of PONCEAU 4R in the range from 4.8×10^{-6} to $8 \times 10^{-6} \text{ mol/dm}^3$ were k is a constant proportional to the rate con-

stant of the catalyzed reaction.

On the basis of these equations, the rate constants for the catalyzed and non-catalyzed reactions were calculated (Table I).

TABLE I. Rate constants for the non-catalyzed (k_0) and catalyzed (k) reactions at three temperatures

T/K	k_0	k
292	3.5×10^{-7}	6.46×10^{-2}
295	4.21×10^{-7}	8.33×10^{-2}
298	12.1×10^{-7}	11.6×10^{-2}

A linear relationship between the logarithm of the rate constant and the reciprocal of the absolute temperature was found for the non-catalyzed, as well as for the catalyzed reaction (Table II).

TABLE II. Logarithm of the rate constants for the catalyzed ($\log k$) and non-catalyzed ($\log k_0$) reactions at three different temperatures

$(1/T)/(10^{-4} \text{ K}^{-1})$	$\log k_0$	$\log k$
34.2	-6.44	-1.19
33.9	-6.37	-1.08
33.6	-5.91	-0.936

The activation energies were found to be $36.81 \text{ kJ mol}^{-1}$ for the catalyzed reaction and $74.81 \text{ kJ mol}^{-1}$ for the non-catalyzed reaction.

The accuracy and precision¹³ of the measurements are presented in Table III. The relative error ranges from 7.77 to 2.09 % for a Cu(II) concentration in the range from 3.8 to 50.1 ng/cm^3 .

TABLE III. Accuracy and precision of the Cu(II) determinations

Taken/ (ng/cm^3)	Found/ $(\bar{x})/(\text{ng/cm}^3)$	n	$S/(\text{ng/cm}^3)$	$G/\%$	$(x-\mu) \cdot 100/\mu \%$
3.8	3.64	5	0.228	7.77	-4.21
25.4	25.18	5	0.736	3.66	-0.866
50.1	50	5	0.856	2.09	-0.196

x – Mean value, μ – true value; n – number of determinations; S – standard deviation; G – relative error ($=100 \cdot t \cdot s/x \sqrt{n}$, where $n = 5$ and t is Student's for 95 % confidence)

The minimum concentration of Cu(II) which could be determined by this method may be calculated by the method given by Perez-Bendito and Silva.¹² The detection limit is 0.8 ng/cm^3 .

To assess the selectivity of the method, the influence of several foreign ions on the catalyzed reaction rate was examined, at a constant Cu(II) concentration of 25.4 ng/cm^3 (Table IV).

TABLE IV. Tolerance levels of interference in the kinetic determination of 25.4 ng/cm³ Cu(II) using the optimal conditions

Tolerance level $c_{\text{ION}}/c_{\text{Cu(II)}}$	Ion added
10 ²	Li ⁺ ; Na ⁺ ; K ⁺ ; NH ₄ ⁺ ; Mg ²⁺ ; Ca ²⁺ ; Ba ²⁺ ; Al ³⁺ ; CH ₃ COO ⁻ ; NO ₃ ⁻ ; VO ₃ ⁻ ; SO ₃ ²⁻ ; SO ₄ ²⁻ ; HPO ₄ ²⁻ ; C ₂ O ₄ ²⁻ ; F ⁻ ; Cl ⁻
10	Cr ₂ O ₇ ²⁻
1	Zn ²⁺ ; Ni ²⁺ ; Fe ³⁺ ; MoO ₄ ²⁻
1	Co ²⁺ interfere

Regarding selectivity as determined by the 2-s criterium¹⁴ for a Cu(II) concentration of 25.4 ng/cm³, it may be seen that Co(II) in a 1:1 ratio to Cu(II) interfere with the reaction. The other investigated ions have practically no influence on the determination of Cu(II) by this method. Hence, it can be concluded that the selectivity of the method is good.

DETERMINATION OF Cu(II) IONS IN SAMPLES OF ALLOY

The method was directly applied to the determination of the Cu(II) content in an alloy with Al using the calibration line kinetic method and the AAS method. These results are shown in Table V.

TABLE V. Determination of Cu(II) in a sample of alloy

Cu(II) proposed method/%	Cu(II) AAS method / %	$[(x-\mu)/\mu] 100 / \%$
0.048		
0.045	0.05	-2.00
0.045		

x – Mean value; μ – AAS value

Procedure

A sample of alloy (1 g) was added to 20.00 cm³ NaOH (20 %), and solution was heated. After the alloy had completely dissolved, the solution was diluted with 100.00 cm³ distilled water, and 40.00 cm³ HNO₃ with H₂SO₄. The solution was boiled for 5 min. After cooling, the solution was made up to 250.00 cm³ with distilled water, if necessary, depending on the Cu(II) content.

Acknowledgment: This research was supported by grant number 1211 from the Serbian Ministry of Sciences and Technology.

ИЗВОД

КИНЕТИЧКО ОДРЕЂИВАЊЕ МИКРОКОЛИЧИНА БАКРА У РАСТВОРУ

З. М. ГРАХОВАЦ, С. С. МИТИЋ и Е. Т. ПЕЦЕВ

Природно-математички факултет, Одсек за хемију, Универзитет у Нишу, Вишеградска 33, 18000 Ниш (E-mail: etarcecev@yahoo.com)

Предложена је нова индикаторска реакција и разрађена нова кинетичка метода за одређивање ултрамикро количина бакра на бази његовог каталитичког дејства на реакцију оксидације Тринатријум-2-хидрокси-1-(4-сулфонато-1-нафтилазо) нафтален-6,8-дисулфонат (прехрамбене боје PONCEAU 4R) водоник-пероксидом у боратном пуферу. Граница детекције методе је $3,8 \text{ ng/cm}^3$. Релативна грешка креће се од 7,77 до 2,09 % за интервал концентрације бакра од 3,8 до $50,1 \text{ ng/cm}^3$. Изведене су одговарајуће кинетичке једначине. Испитиван је утицај већег броја страних јона на брзину индикаторске реакције. Метода је примењена за одређивање бакра у легури алуминијума.

(Примљено 19. септембра, ревидирано 26. новембра 2002)

REFERENCES

1. N. V. Lazarov, *Vrednie veshchestva v promishljenosti*, Khimiya, Moskva, 1956
2. R. Feliks, *Standardne metode i normativi*, Niš, 1980 (in Serbian)
3. S. R. Crouch, A. Scheeline, E. S. Kirkor, *Anal. chem.* (2000), 72, 53R-70R
4. S. R. Crouch, A. Scheeline, E. S. Kirkor, *Anal. chem.* (1998), 72, 53R-106R
5. N. A. Motola, D. Perez-Bendito, *Anal. chem.* (1996) 68, 257R-289R
6. H. Mao, *Microchem. J.* **53** (1996) 303
7. W. Zhang, S. Sun, *Fenxi Shiyanski* **13** (1994) 49-51, [*C.A.* **122** (1995) 45145e]
8. M. I. Prodromidis, C. D. Stalikas, P. T. Veltsistas, M. I. Karayannis, *Talanta* **41** (1994) 1645
9. Y. Zhou, B. Geng, L. Zhou, *Yejin Fenxi* **15** (1995) 17, [*C.A.* **123** (1995) 24786v]
10. H. Müller, M. Otto, G. Werner, *Katalytische Methoden in der Säurenalyse*, Akademische Verlagsgesellschaft, Leipzig, 1980
11. Yu. Yu. Luruye, *Spravochnik po analiticheskoi khimii*, Khimiya, Moskva, 1989
12. D. Perez-Bendito, S. Silva, *Kinetic Methods in Analytical Chemistry*, Ellis Horwood, 1988, p. 256
13. M. L. Batuner, E. M. Pozin, *Matematicheskie metodi v khimicheskoy tekhnike*, Khimia, Leningradskoe odelenie, 1976, p. 609
14. G. F. Kirbright, *Talanta* **13** (1966) 1.