# Catalimetric determination of nanogram amounts of copper (II) using the chemiluminescence method

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The kinetics of chemiluminescence oxidation of luminol by hydrogen peroxide in the presence of copper (II) salts has been studied using the discrete-mode photoelectric method. It has been found that equimolar amounts of iron (III) do not affect the initial intensity of the N2L-NaOH-H2O2-Cu (II) chemiluminescence system. The quantitative method of copper (II) determination in model solutions in the presence of equimolar amounts of iron (III) was developed. The RSD of $2,50*10^{-7}$ mol/l copper (II) analysis in the presence of $2,50*10^{-7}$ mol/l iron (III) was 0,03 at $\delta$ =0 % accuracy.

**Key words:** chemiluminescence kinetic method, determination of copper (II), effect of iron (III).

## INTRODUCTION

Controlling small amounts of copper (0,0001 to 0,001 mass %) in different objects (materials) is a challenge in modern pharmaceutical analysis. Copper is a microelement with an important role in the biochemical processes of live organisms (for instance, oxygen transport in tissues and iron fixation). However, excessive copper has an adverse effect on the human organism. It induces development of anaemia, neurological diseases, affects the liver and so forth [13, 14]. Developing new selective and sensitive techniques of quantitative analysis of copper (II) traces in the presence of other metals especially in an organic substances environment is a challenging analytical task.

Many studies in quantitative determination of copper (II) suggest using the chemiluminescence method [1, 2, 5, 6, 9, 10, 12].

Ukrainian researchers were the first to propose quantitative determination of copper (II) using the kinetic chemiluminescence method and the reaction of luminol with hydrogen peroxide as an indicator test [7].

Thus, early study [8] describes the technique of quantitative determination of copper (II) with luminol using the photoelectric method. The method is based on discrete-mode recording of chemiluminescence intensities occurring during the reaction of catalytic oxidation of luminol by hydrogen peroxide in an alkaline environment.

The study objective is developing an express and sensitive technique for quantitative determination of copper (II) in the presence of pro rata quantities of iron (III) using the chemiluminescence method and the reaction with luminol without masking agents.

## MATERIALS AND METHODS

Reagents of the chemically pure (c.p.) or the analytical reagent grade (a.r.g.) were used. Solutions were prepared with bidistilled water produced in a crystal distiller.

A reference (standard) solution of $1*10^{-3}$ mol/l copper (II) was prepared using the volumetric-weight method by dissolving 0,2497 g of a.r.g. blue copperas in bidistilled water in a 1-litre measuring flask. The solution obtained was standardised using the iodometric titration method [11]. Copper (II) smaller-concentration work solutions were prepared daily by diluting the stock solution with bidistilled water immediately before testing.

A standard solution with an exactly known concentration of 0,0100 mol/l iron salt (III) was prepared of c.p. iron-ammonium alum (ammonium ferrum (III) tetraoxosulphate (VI) hexahydrate $(NH_4Fe(SO_4)\cdot6H_2O)$) by acidifying with sulphate acid to pH 2 [4]. Work solutions with a smaller amount of iron (III) were prepared daily by diluting accurately the stock solution.

The stock 0,01 mol/l solution of *luminol* (5-amino-2,3-dehydro-1,4-phthalazinedion, $H_2L$
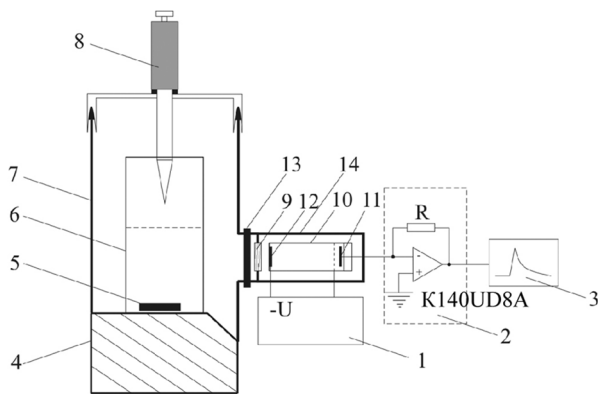
*Fig. 1. Installation for measuring chemiluminescence.*

*1– PEM power supply source (high-voltage stabiliser); 2 — current-voltage converter; 3 — recording potentiometer; 4 — magnetic mixer; 5 — impeller in Teflon; 6 — crystal measuring cell; 7 — opaque chamber; 8 — adjustable pipettor (P-1) with an opaque seal; 9 — light filter; 10 — photoelectric multiplier (PEM) FEU-84A; 11 — PEM anode; 12 — PEM cathode; 13 — blind; 14 — aluminium screen.*



*Fig. 2. Chemiluminescence (CL) kinetic graphs in the systems: $H_2L$-NaOH-$H_2O_2$-$Fe^{3+}$ (1) $H_2L$-NaOH-$H_2O_2$-$Cu^{2+}$(2). $c(H_2O_2)=9*10^{-3}$ mol/dm³; $c(H_2L)=1*10^{-4}$ mol/dm³; $c(Fe^{3+})=5*10^{-5}$ mol/dm³; $c(Cu^{2+})=5*10^{-5}$ mol/dm³.*

(*Chemapol*, additionally recrystallised from a saturated solution of sodium hydroxide) in a 0,01 mol/l solution of sodium hydroxide: 0,1772 g of luminol are dissolved in a 100,0 ml 0,1 mol/l solution of sodium hydroxide.

Preparing a sodium hydroxide solution without carbonates (using the Gillebrant technique), 0,1720 mol/l [3]. 50 g of bidistilled water was added to 50 g of c.p. sodium hydroxide, thoroughly mixed and leaved off for two weeks at 20° C. A sampling tube was used to transfer 10 ml of the solution to a 100-ml measuring flask. The solution volume was made up to mark by the freshly obtained bidistilled water and mixed. A lower-concentration solution was made by accurate dilution with bidistilled water stored in a tightly closed polyethylene vessel. The exact solution concentration was defined with amber acid us-
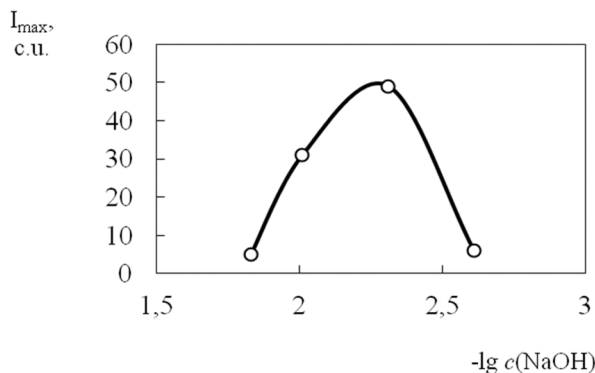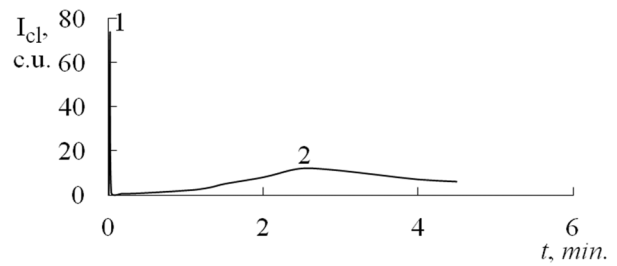
ing the method of acid-base titration with phenolphthalein.

A 3% and 0.3% (mass) solution of *hydrogen peroxide* was prepared from a 50% ultrapure (u.p.) preparation by diluting it with bidistilled water followed by permanganatometric control of the concentration [11].

Analytical damper scales of ADW-200 (2 class) were used for measuring to ±0,1 mg.

Chemiluminescence intensity was measured using an assembled chemiluminescence installation (Chemiluminometer-01) including photoelectric multiplier (PEM) FEU-84-A, weak current meter IMT-0,5 and fast-operating recording potentiometer LINE RECORDER TZ 4620 made by Laboratorni Pristroje (Czechia). The installation for measuring chemiluminescence is shown in Fig. 1.

When studying the impact of sodium hydroxide concentration on chemiluminescence in the catalytic system $H_2L$+NaOH+$H_2O_2$+$Cu^{2+}$, the following sequence of mixing reagents was observed: the pipettor was used to introduce into the crystal measuring cell 1,00 ml $1*10^{-3}$ mol/l of luminol ($H_2L$), X ml 0,0195 mol/l sodium hydroxide solu-



*Fig. 3. $I_{cl}$ graph in system $H_2L$+NaOH+$H_2O_2$+$Cu^{2+}$. $c(H_2O_2)=9*10^{-3}$ mol/l; $c(H_2L)=1*10^{-4}$ mol/l; $c(Cu^{2+})=5*10^{-7}$ mol/l.*
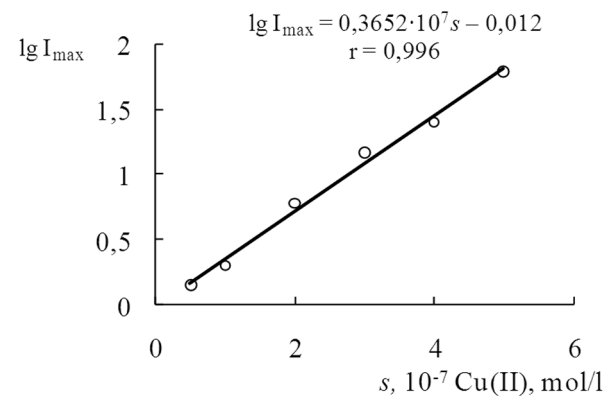


*Fig. 4. Concentration of $I_{cl}$ in the $H_2L$+NaOH+$H_2O_2$+Cu(II) system vs semilogarithmic coordinates. $c(H_2L)=1*10^{-4}$ mol/l; $c(H_2O_2)=9*10^{-3}$ mol/l; $c(NaOH)=4,8*10^{-3}$ mol/l.*

TABLE 1

**Quantitative determination of copper (II) in model aqueous solutions in the presence of iron (III).** $c$(Fe(III))=2,50*10$^{-7}$ mol/l

| Taken copper (II), mol/l | Found copper (II), mol/l | Metrological characteristics (P=0,95; n=5) |
|---|---|---|
| 2,50*10$^{-7}$ | 2,5*10$^{-7}$<br>2,6*10$^{-7}$<br>2,5*10$^{-7}$<br>2,4*10$^{-7}$<br>2,5*10$^{-7}$ | $\bar{x}$ = 2,50*10$^{-7}$<br>$\Delta x$ = 8,79*10$^{-9}$<br>S = 7,07*10$^{-9}$<br>S$_{\bar{x}}$ = 3,16*10$^{-9}$<br>RSD = 2,83%<br>$\varepsilon$ = 3,52%<br>$\delta$ = +0% |

tion, 1,00 ml 0,09 mol/l H$_2$O$_2$ solution, (10 — Y) ml bidistilled water and all this was mixed thoroughly (where Y is the total volume of all other components except for the hydrogen peroxide solution and a copper solution). The measuring cell was placed in the opaque chamber of the chemiluminometer, the blind was opened, the recording potentiometer was powered on and 0,50 ml 1*10$^{-5}$ mol/l copper (II) solution was added with the adjustable pipettor. It was fitted in a removable holder for isolating the photoelectronic multiplier photocathode from ambient light, and hence, allowing to work with ambient light. On the chemiluminescence intensity kinetic graph $I_{cl}$ vs time (*minutes*) the maximum chemiluminescence intensity is recorded in conventional units (mV). The experiment was repeated five times. The desired signal is the value of maximum chemiluminescence intensity obtained by averaging the values of five repeated experiments. The sensitivity is 2 mV and the motion velocity v=0.6 cm/min. All experiments were conducted at 18 to 20°C.

## RESULTS AND DISCUSSION

The chemiluminescence (CL) graphs in the H$_2$L-NaOH-H$_2$O$_2$-Fe$^{3+}$ system resemble a flash of light with fast CL extinction following an exponential law. At the same time, the I$_{cl}$ vs time graph in the presence of copper (II) has an S shape due to formation of a catalytically active complex of catalyst with luminol (Fig. 2).

Such a difference in the kinetics of occurrence of CL in the system being investigated allows for differentiated determination of copper (II) in the presence of iron (III) ions.

The optimal concentrations of CL system components were found experimentally.

Fig. 3 shows maximum intensity of chemiluminescence in the H$_2$L-NaOH-H$_2$O$_2$- Cu$^{2+}$ system vs alkali concentration. As obvious, maximum

luminescence is achieved at c(NaOH)=5*10$^{-3}$ mol/dm$^3$.

Fig. 4 shows maximum chemiluminescence intensity in the H$_2$L-NaOH-H$_2$O$_2$-Cu$^{2+}$ system vs Cu$^{2+}$ concentration. It is linear within 1*10$^{-7}$ mol/l to 5*10$^{-7}$ mol/l, and therefore can be used for quantitative determination of copper (II) using the calibration chart method. The calibration equation has the form: lg $I_{max}$=0,3652*10$^7$·$s$ — 0,012 (r=0,996).

Experimentally it has been found that commensurable molar quantities of iron (III) salts do not hinder the quantitative determination of copper (II) using the luminol reaction and the chemiluminescence method.

Table 1 shows the results of quantitative determination of copper (II) in model mixtures in the presence of iron (III) using the chemiluminescence method and the chemiluminescence reaction with luminol.

## CONCLUSION

A technique has been suggested for quantitative determination of copper (II) in model solutions in the presence of iron (III) using the chemiluminescence method and the reaction with luminol. When determining 2,50*10$^{-7}$ mol/l of copper (II) in model mixtures in the presence of equimolar quantities of iron (III), RSD=2,83% to +0% accuracy.

## REFERENCES

1. Bastos E.L. Evaluation of antiradical capacity by H$_2$O$_2$-hemin-induced luminol chemiluminescence / J. Agric. Food Chem. — 2003. — Vol. 51, №25. — P. 7481-7488.
2. Bolei Y. Determination of cobalt (II), copper (II) and iron (II) by ion chromatography with chemiluminescence detection / Yan Bolei, Paul J.Worsfold // Analytica Chimica Acta. — 1990. — Vol. 236. — P. 287-292.
3. Laitinen G.A. Chemical Analysis: Transl. from English / Ed. Yu.A.Kliachko. — 2md revised edition. — M.: Khimia Publishers, 1979. — 624 p.
4. Lazarev A.I. Handbook for Chemical Analysts / A.I.Lazarev, I.P.Kharlamov, P.Ya.Yakovlev, Ye.F.Yakovleva. — M.: Metalurgia Publishers, 1976. — 184 p.
5. Li Z.P. Study on catalytic effect of copper (II) complex on 1,10-phenanthroline-H$_2$O$_2$-CTMAB chemiluminescence reaction and its analytical applications / Z.P.Li, L.T.Dai, Z.J.Zhang // Microchemical Journal. — 1995. — Vol. 52. — Issue 2. — P. 208-215.
6. Podchainova V.N. Copper / V.N.Podchainova, L.N.Simonova. — M.: Nauka Publishers, 1990. — 279 p.
7. Ponomarenko A.A. On Chemiluminescent Quantitative Analysis / A.A.Ponomarenko // Rep. AS USSR. — 1955. — Vol. 102, №3. — P. 539-542.

8. Shcherbov D.P. Investigating chemiluminescence for analysis of mineral raw materials. Report I. Literature data and experimental validation of certain systems / D.P.Shcherbov, A.I.Ivankova and I.D.Vvedenskaya // Studies in chemical and physical methods of analysing mineral raw materials. — Alma-Ata, 1973. — Issue 3. — P. 5-18.

9. Skounas S. Kinetic studies and mechanism of hydrogen peroxide catalytic decomposition by Cu (II) complexes with polyelectrolytes derived from l-alanine and glycylglycine / S.Skounas, C.Methenitis, G.Pneumatikakis, M.Morcellet // Bioinorganic chemistry and applications. — 2010. — Vol. 2010. — P. 9-18.

10. Sorouraddin M.H. A novel captopril chemiluminescence system for determination of copper (II) in human hair and cereal flours / M.H.Sorouraddin, M.Iranifam, A.Imani-Nabiyyi // Journal of Fluorescence. — 2009. — Vol. 19, №4. — P. 575-581.

11. State Pharmacopeia of Ukraine / State Enterprise Research and Expert Pharmacopeia Centre. — Issue 1. — Kharkiv: RIREG, 2001. — 556 p.

12. Takahiro U. A new copper (II) complex as an efficient catalyst of luminol chemiluminescence / U.Takahiro, S.Shigeki // Organic letters. — 2007. — Vol. 9, №21. — P. 4383-4386.

13. Tulchynsky T.Kh. New Public Healthcare. Introduction to Modern Science / T.Kh.Tulchynsky, Ye.A.Varavikova. — Jerusalem: Amutah for Education and Health. — 1999. — 1024 p.

14. World Health Organization. Guidelines for Drinking Water Quality. 3rd ed. — Vol. 2. — Health Criteria and Other Supporting Information. — Geneva, 1996.

*И.Н.Боровская, Н.Е.Блажеевский, В.О.Евтухов. Каталиметрическое определение нанограмовых количеств меди (II) методом хемилюминесценции.*

*Ключевые слова:* кинетический метод хемилюминесценции, определение меди (II), влияние железа (III).

Изучена кинетика хемилюминесцентного окисления люминола перекисью водорода в присутствии солей меди (II) фотоэлектрическим методом в дискретном режиме. Установлено, что эквимолярные количества солей железа (III) не влияют на максимальную интенсивность хемилюминесценции в системе $H_2L$-NaOH-$H_2O_2$-Cu(II). Разработана методика количественного определения меди (II) в модельных растворах в присутствии эквимолярных количеств железа (III). При определении $2,50 \times 10^{-7}$ моль/л меди (II) в присутствии $2,50 \times 10^{-7}$ моль/л железа (III) RSD=0,03 ($\delta$=0%).

*I.Н.Боровська, Н.Є.Блажеєвський, В.О.Євтухов. Каталіметричне визначення нанограмових кількостей міді (II) методом хемілюмінесценції.*

*Ключові слова:* кінетичний метод хемілюмінесценції, визначення міді (II), вплив заліза (III).

Вивчено кінетику хемілюмінесцентного окислення люмінолу перекисом водню в присутності солей міді (II) фотоелектричним методом в дискретному режимі . Встановлено , що еквімолярні кількості солей заліза (III) не впливають на максимальну інтенсивність хемілюмінесценції в системі H2L-NaOH-H2O2-Cu (II). Розроблено методику кількісного визначення міді (II) в модельних розчинах у присутності еквімолярних кількостей заліза (III). При визначенні $2,50 \times 10^{-7}$ моль/л міді (II) у присутності $2,50 \times 10^{-7}$ моль/л заліза (III) RSD=0,03 ($\delta$=0%).