



## Development of a flow injection method with amperometric detection for the indirect determination of copper in drinking water samples

ALEKSANDAR LOLIĆ<sup>1\*#</sup>, TATJANA TRIPKOVIĆ<sup>1</sup>, RADA BAOŠIĆ<sup>1#</sup>,  
SNEŽANA NIKOLIĆ-MANDIĆ<sup>1#</sup> and BOJANA STANIMIROVIĆ<sup>2</sup>

<sup>1</sup>Faculty of Chemistry, University of Belgrade, P. O. Box 158, 11001 Belgrade, Serbia  
and <sup>2</sup>Mol a.d., Company for Chemistry, Biotechnology and Consulting,  
Batajnički drum 2, 11080 Belgrade, Serbia

(Received 16 June, revised 1 September 2012)

**Abstract:** A gas-diffusion flow injection method with amperometric detection for the indirect determination of copper on a silver electrode was developed. The flow through system was equipped with two injection valves and a gas-diffusion unit. In the first step, a signal of a cyanide solution was recorded. In the subsequent step, the signal of cyanide in the presence of copper was measured. Interferences (Cd(II), Co(II), Ag(I), Ni(II), Fe(III), Hg(II) and Zn(II)) were investigated and successfully removed. The calibration graph was linear in the range 1–90  $\mu\text{mol dm}^{-3}$  of copper with a correlation coefficient of 0.993. The regression equation is  $I = (0.0455 \pm 0.0015)c + (0.4611 \pm 0.0671)$ , where  $I$  is the relative signal decrease in  $\mu\text{A}$  and  $c$  is concentration in  $\mu\text{mol dm}^{-3}$ . Relative standard deviation for six consecutive injections of 30  $\mu\text{mol dm}^{-3}$  copper(II) was 1.47 % and for 1  $\mu\text{mol dm}^{-3}$  copper(II), it was 3.40 %. The detection limit, calculated as  $3 s/m$  (where  $s$  is a standard deviation of nine measurement of a reagent blank and  $m$  is the slope of the calibration curve), was 0.32  $\mu\text{mol dm}^{-3}$ , which corresponds to 2.44 ng of copper(II) (the loop volume was 0.12  $\text{cm}^3$ ). The method enables 60 analyses per hour and it was successfully applied for the determination of copper in drinking water samples.

**Keywords:** copper determination; gas-diffusion; drinking water samples; copper cyano complex.

### INTRODUCTION

Copper is essential element with an important role in living organisms. A considerable number of highly sensitive and selective analytical techniques for the determination of copper are based on the use of large and expensive atomic

\* Corresponding author. E-mail: lolix@chem.bg.ac.rs

# Serbian Chemical Society member.

doi: 10.2298/JSC120616090L

spectrometric instrumentation (*e.g.*, flame atomic absorption spectrometry,<sup>1–5</sup> electrothermal atomic absorption spectrometry,<sup>6</sup> and inductively coupled plasma spectrometry with optical emission<sup>7</sup>). Less expensive optical<sup>8–14</sup> and electrochemical<sup>15–18</sup> detection techniques, which are amenable to miniaturization, have been successfully used in the development of flow injection (FI) methods for copper. Among electrochemical techniques, amperometry<sup>19–21</sup> has been used in FI systems for the development of biosensors for copper determination. The greatest disadvantages of biosensors are the regeneration of the modified surface of the working electrode and the not very sensitive determinations.

The purpose of this work was to develop a flow injection method for copper determination on a bare silver electrode. It is based on a previously optimized FI system for cyanide determination on a modified silver working electrode.<sup>22</sup> The system described in this paper was equipped with an additional flow stream, carrying copper solutions (samples), containing a single mixing coil and a gas-diffusion unit to increase selectivity. In the mixing coil, two competitive reactions, complex formation and formation of gaseous hydrogen cyanide, occurred. The obtained flow injection signal presents a decreased anodic current for cyanide in the presence of copper(II) ions. The method was successfully applied for copper determination in drinking water samples.

## EXPERIMENTAL

### *Reagents and chemicals*

All the chemicals used were of analytic reagent grade. Degassed and filtered water was used throughout. The copper standard solution was CertiPUR (Merck, Germany,  $\text{Cu}(\text{NO}_3)_2$  in  $0.5 \text{ mol dm}^{-3} \text{ HNO}_3$ ). The stock cyanide solution (KCN, Merck–Alkaloid, Macedonia) was prepared weekly as were other stock reagent solutions,  $0.1 \text{ mol dm}^{-3} \text{ HCl}$  solution (J.T. Baker, The Netherlands) and  $0.1 \text{ mol dm}^{-3}$  sodium hydroxide (Carlo Erba, Italy). Working solutions were prepared daily and the cyanide concentration was determined volumetrically using the Liebig method.

### *Sample preparation*

Drinking water samples were collected from several tap water units within one building. One liter of tap water was collected and acidified at the sampling location with  $1 \text{ cm}^3$  of concentrated nitric acid. The samples were filtered. If the pH value was lower than 2, it was adjusted carefully with sodium hydroxide solution ( $2 \text{ mol dm}^{-3}$ ) to the desired value (to match  $0.01 \text{ mol dm}^{-3} \text{ HCl}$ ). Samples were filtered again and injected into a flow injection analysis (FIA) manifold.

### *Apparatus*

The FIA manifold used for copper determination, equipped with a gas-diffusion unit and an amperometric detector, is presented in Fig. 1. Two peristaltic pumps, Model HPB 5400 (Iskra, Slovenia) and Model MS Reglo (Ismatec, Switzerland) with a flow rate control unit were used. Each of two injection valves, Model 5020 (Rheodyne, USA), were equipped with a  $0.12 \text{ cm}^3$  sample loop. The gas-diffusion unit was manufactured after a model that was provided by Shenyang Film Projector Factory, China. All connections were made with  $0.5 \text{ mm}$

i.d. tubing. Flow went through the amperometric cell, which was equipped with a working silver electrode (BASi, model MF-1008, USA), a reference Ag/AgCl electrode (BASi, model MF-2021, USA) and an auxiliary electrode made of stainless steel. The working electrode was polished with aluminum paste (BASi, 0.5  $\mu\text{m}$ , USA) and well rinsed with distilled water and methanol prior to every recording. The working potential was regulated with a polarograph MA 5450 (Iskra, Slovenia). The obtained FIA signals were recorded on a Servograph Model 61 recorder (Radiometer, Denmark).

Reference results were obtained on an atomic absorption spectrometer, Perkin-Elmer 2380, equipped with a graphite furnace unit. The determinations were performed at 324.8 nm, with slit 0.7 nm and a lamp current of 10 mA. A standard run was 5–150  $\mu\text{g dm}^{-3}$  of copper for the GF-AAS.

#### Procedure

All experiments were performed at room temperature. Prior to each recording, the silver electrode was optimized by injecting the cyanide solution (1 mmol  $\text{dm}^{-3}$ ) until the system reproducibility was better than 5 %; up to 10 injections were sufficient for this purpose. The system was equipped with two injection valves, one for cyanide solution injection,  $V_1$ , and the other for copper solution,  $V_2$ , Fig. 1. The anodic current,  $I_{\text{CN}}$ , was obtained by cyanide solution injection ( $n = 3$ ). Then, both the cyanide and copper solution were simultaneously injected ( $n = 3$ ) and current intensity was,  $I_{\text{CN}+\text{Cu}}$ , was measured. The decrease in the current responds to the copper concentration  $I_{\text{Cu}} = I_{\text{CN}} - I_{\text{CN}+\text{Cu}}$ . During system optimization, the relative decrease of the signal intensities were measured, and as optimal conditions were those under which the most prominent decrease was obtained. All waste solutions were collected in a saturated sodium hydroxide solution and disposed of adequately.

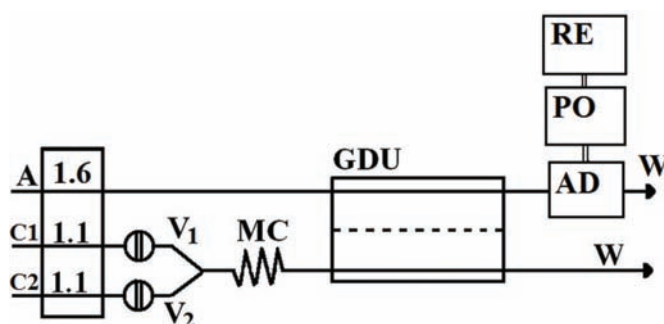


Fig. 1. Schematic presentation of the FIA manifold used for copper determination.

C1 – carrier for cyanide solution (0.02 NaOH mol  $\text{dm}^{-3}$ ); C2 – carrier for copper solution (0.01 HCl mol  $\text{dm}^{-3}$ ), A – acceptor (0.1 mol  $\text{dm}^{-3}$  NaOH),  $V_1$  – injection valve, for cyanide solution (0.120  $\text{cm}^3$ ),  $V_2$  – injection valve for copper solution (0.120  $\text{cm}^3$ ), MC – mixing coil (60 cm  $\times$  0.5 mm i.d.), GDU – gas diffusion unit, AD – amperometric detector, PO – potentiostat, RE – recorder, W – waste. Flow rates are given in  $\text{cm}^3 \text{min}^{-1}$ .

## RESULTS AND DISCUSSION

### Optimization of the flow system

In order to obtain optimal conditions for the copper determination, the effects of several parameters were investigated.

Working potential for all experiments was 0.0 V vs. Ag/AgCl, as there are many manuscripts describing cyanide amperometric determination at this potential.<sup>22</sup> This was confirmed by cyclic voltammetry.

Effect of the sample working volume (the gasket thickness effect) was part of a previously published work for the same amperometric flow cell.<sup>23</sup>

There are two competitive reactions occurring in the single mixing coil. One of them is cyano complex formation and the other is the formation of gaseous HCN. Both reactions are very pH sensitive, hence, strict control of the pH value in the mixing coil was mandatory. For the simultaneous injection of 100  $\mu\text{mol dm}^{-3}$  cyanide in 0.02 mol  $\text{dm}^{-3}$  NaOH and 30  $\mu\text{mol dm}^{-3}$  Cu(II) in 0.01 mol  $\text{dm}^{-3}$  HCl, a significant signal decrease was noticed.

The next experiment was to determine the optimal sodium hydroxide concentration as acceptor solution. Cyanide signals were recorded for following acceptor solution concentrations: 0.02, 0.05, 0.10 and 0.15 mol  $\text{dm}^{-3}$  sodium hydroxide. The most intensive decrease was obtained when 0.10 mol  $\text{dm}^{-3}$  hydroxide was used. With more concentrated hydroxide, an increase of cyanide signal in the presence of copper was noticed.

The length of the mixing coil was the subject of further investigations. Several mixing coils were used: 30, 60, 105 and 210 cm long. The most intensive decrease was obtained when 60 cm long mixing coil was used. Further increase of its length had no effect on the FIA signal.

The last parameter to be investigated was the effect of stream directions and rates. The rate of the donor stream was kept constant (1.1  $\text{cm}^3 \text{min}^{-1}$ ) while the rate of acceptor stream was varied (0.8, 1.6, 2.4 and 3.1  $\text{cm}^3 \text{min}^{-1}$ ). Obtained signals are presented in Fig. 2. All further experiments were performed with parallel streams and with the acceptor rate of 1.6  $\text{cm}^3 \text{min}^{-1}$ .

### *Interferences*

The interference study was investigated by injection of 100  $\mu\text{mol dm}^{-3}$  cyanide in the presence of 30  $\mu\text{mol dm}^{-3}$  copper, and a mixture of copper and the interferents (Cd(II), Co(II), Ni(II), Fe(III), Ag(I), Hg(II) and Zn(II)) of the same concentration. Silver, zinc and iron did not interfere with the copper signal intensity. When Fe(III) was present in higher concentration (60  $\mu\text{mol dm}^{-3}$ ), interference was noticed. Ni(II), Hg(II), Co(II) and Cd(II) also interfered with the copper determination when their concentration was 30  $\mu\text{mol dm}^{-3}$ . However, they did not interfere when their concentration was 3  $\mu\text{mol dm}^{-3}$ . The interferents were removed from the solution by known analytical methods.

### *Analytical performance*

The calibration graph was linear in the range 1–90  $\mu\text{mol dm}^{-3}$  of copper, with a correlation coefficient  $r^2$  of 0.993. The regression equation is  $I =$

$(0.0455 \pm 0.0015)c + (0.4611 \pm 0.0671)$ , where  $I$  is relative signal decrease in  $\mu\text{A}$ ,  $c$  is concentration in  $\mu\text{mol dm}^{-3}$ . The precision of the method was investigated by six repetitive injections of 30 and 1  $\mu\text{mol dm}^{-3}$  of copper and the relative standard deviations were 1.47 and 3.40 %, respectively. The detection limit, calculated as  $LOD = 3 s/m$  (where  $s$  is the standard deviation of nine measurements of a reagent blank, and  $m$  is the slope of the calibration curve), was 0.32  $\mu\text{mol dm}^{-3}$ , which corresponds to 2.44 ng of Cu(II) (the loop volume was 0.12  $\text{cm}^3$ ). The throughput of this method was 60 analyses per hour.

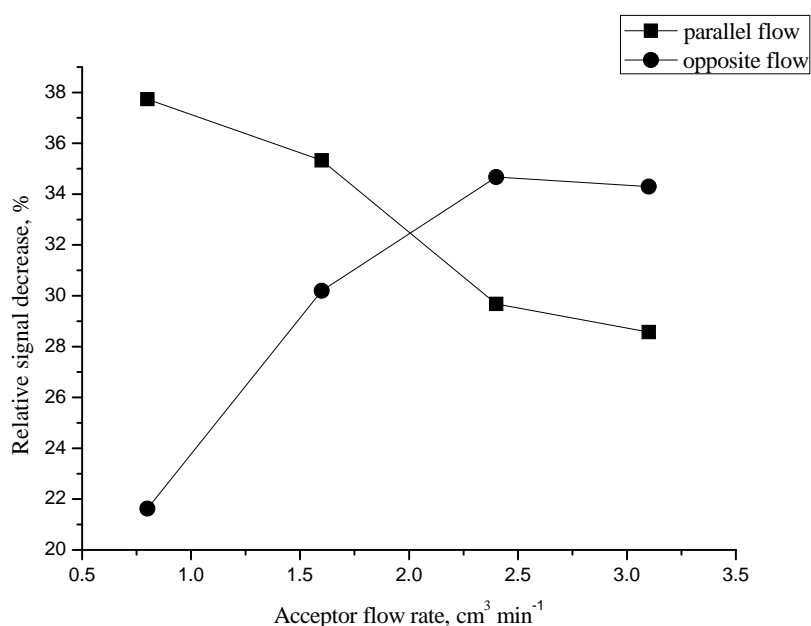


Fig. 2. Effects of parallel and opposite flow rates at different acceptor flow rates (0.8, 1.6, 2.4 and 3.1  $\text{cm}^3 \text{min}^{-1}$ ) for a constant donor flow rate (1.1  $\text{cm}^3 \text{min}^{-1}$ ) on the relative anodic current decrease for a cyanide solution (100  $\mu\text{mol dm}^{-3}$ ) in the presence of copper (30  $\mu\text{mol dm}^{-3}$ ).

### Application

To validate the developed method, it was applied to the determination of copper in drinking water samples (Table I). In order to investigate the recovery of copper(II), known amounts of copper(II) were added to the samples (100 and 150  $\mu\text{mol dm}^{-3}$ ). Obtained values were consistent with the values obtained by the reference method (GF-AAS), and the recoveries of about 100 % show that the copper determination was very accurate. The results also showed that interferences were successfully removed.

TABLE I. Determination of copper in drinking water samples. The results are expressed as the average of three replicates (mean value  $\pm$  SD)

Sample No.	Added Cu, $\mu\text{g dm}^{-3}$	Found Cu, $\mu\text{g dm}^{-3}$	Recovery, %	GF-AAS, $\mu\text{g dm}^{-3}$
1	0	103 $\pm$ 3	–	105.0 $\pm$ 0.6
	100	205 $\pm$ 7	102.00	
	150	250 $\pm$ 8	98.00	
2	0	107 $\pm$ 4	–	106.0 $\pm$ 0.6
	100	210 $\pm$ 7	103.00	
	150	261 $\pm$ 9	102.67	
3	0	73 $\pm$ 2	–	74.0 $\pm$ 0.3
	100	170 $\pm$ 6	97.00	
	150	228 $\pm$ 8	103.33	
4	0	127 $\pm$ 4	–	132.0 $\pm$ 1.0
	100	230 $\pm$ 8	103	
	150	275 $\pm$ 9	98.67	
5	0	71 $\pm$ 2	–	70.0 $\pm$ 0.3
	100	169 $\pm$ 6	98.00	
	150	223 $\pm$ 8	101.33	

## CONCLUSIONS

A simple and sensitive flow injection method with amperometric detection for copper determination was optimized. The anodic current vs. copper(II) concentration was linear over the concentration range 1–90  $\mu\text{mol dm}^{-3}$ . The precision was 1.47 % for 30  $\mu\text{mol dm}^{-3}$  and 3.40 % for 1  $\mu\text{mol dm}^{-3}$  of copper. The detection limit was 0.32  $\mu\text{mol dm}^{-3}$ , which corresponds to 2.44 ng of copper(II) (for an injection coil volume of 0.12  $\text{cm}^3$ ). Copper was successfully determined in drinking water samples after a simple preparation procedure. The developed method had a comparable or lower limit of detection compared to other methods for the amperometric determination<sup>19–21</sup> of copper found in the literature.

*Acknowledgement.* The authors acknowledge the grant from the Ministry of Education, Science and Technological Development of the Republic of Serbia, Project No. 172051.

## ИЗВОД

## РАЗВОЈ ПРОТОЧНЕ ИНЈЕКЦИОНЕ МЕТОДЕ ЗА ИНДИРЕКТНО ОДРЕЂИВАЊЕ БАКРА СА АМПЕРОМЕТРИЈСКОМ ДЕТЕКЦИЈОМ У ПИЈАЋОЈ ВОДИ

АЛЕКСАНДАР ЛОЛИЋ<sup>1</sup>, ТАТЈАНА ТРИПКОВИЋ<sup>1</sup>, РАДА БАОШИЋ<sup>1</sup>, СНЕЖАНА НИКОЛИЋ-МАНДИЋ<sup>1</sup>  
и БОЈАНА СТАНИМИРОВИЋ<sup>2</sup>

<sup>1</sup>Хемијски факултет, Универзитет у Београду, б.бр. 158, 11001 Београд и <sup>2</sup>Мол а.д., Акционарско друштво за хемију, биотехнологију и консалтинг, Бајрајнички друм 2, 11080 Београд

Циљ овог рада био је развој гасно-дифузионе проточно инјекционе методе са амперометријском детекцијом за индиректно одређивање бакра на сребрној електроди. Проточни систем је опремљен са два инјекциона вентила и гасно-дифузионом јединицом. У првом кораку снима се сигнал раствора цијанида, а у другом снима се сигнал при истовременом убризгавању раствора цијанида и раствора бакра. Сметње од Cd(II),

Co(II), Ag(I), Ni(II), Fe(III), Hg(II) и Zn(II) су испитане и успешно уклоњене. Калибрациона крива је линеарна у опсегу 1–90  $\mu\text{mol dm}^{-3}$  бакра, коефицијент корелације је 0,993, а једначина праве  $I = (0,0455 \pm 0,0015)c + (0,4611 \pm 0,0671)$ , где је  $I$  разлика висине сигнала у  $\mu\text{A}$ , а  $c$  је концентрација у  $\mu\text{mol dm}^{-3}$ . Релативна стандардна девијација за шест узастопних убризгавања раствора бакра концентрације 30  $\mu\text{mol dm}^{-3}$  је 1,47 %, а за 1  $\mu\text{mol dm}^{-3}$  раствор Cu(II) је 3,40 %. Лимит детекције, израчунат као  $3s/m$  (где је  $s$  стандардна девијација девет мерења следеће пробе и  $m$  је нагиб калибрационе праве), је 0,32  $\mu\text{mol dm}^{-3}$ , што одговара 2,44 ng Cu(II) (запремина петље за узорак је 0,12  $\text{cm}^3$ ). Метода омогућава 60 анализа по једном сату и успешно је примењена за одређивање бакра у пијаћој води.

(Примљено 16. јуна, ревидирано 1. септембар 2012)

#### REFERENCES

1. C. A. Şahin, I. Tokgöz, *Anal. Chim. Acta* **667** (2010) 83
2. C. A. Şahin, I. Tokgöz, S. Bektaş, *J. Hazard. Mater.* **181** (2010) 359
3. H. Shir Khanloo, H. Z. Mousavi, A. Rouhollahi, *J. Serb. Chem. Soc.* **76** (2011) 1583
4. R. Gong, D. Zhang, K. Zhong, M. Feng, X. Liu, *J. Serb. Chem. Soc.* **72** (2008) 249
5. K. Miranda, A. G. G. Dionisio, E. R. Pereira-Filho, *Microchem. J.* **96** (2010) 99
6. C. Zheng, R. E. Sturgeon, X. Hon, *J. Anal. Atom. Spectrom.* **25** (2010) 1159
7. L. Zhang, Z. Li, X. Du, R. Li, X. Chang, *Spectrochim. Acta A* **86** (2012) 443
8. D. Rekha, K. Suvadhan, K. S. Kumar, P. Peddyprasad, B. Jayaraj, P. Chiranjeevi, *J. Serb. Chem. Soc.* **72** (2007) 299
9. P. Rumori, V. Cerda, *Anal. Chim. Acta* **486** (2003) 227
10. R. J. Cassella, *Microchem. J.* **72** (2002) 17
11. Y. Sekine, I. Shitanda, M. Itagaki, K. Watanabe, S. Nakano, T. Kawashima, *Microchim. Acta* **170** (2010) 113
12. S. Lunvongsa, T. Tsuboi, S. Motomizu, *Anal. Sci.* **22** (2006) 169
13. J. J. Pinto, C. Moreno, M. Garcia-Vargas, *Talanta* **64** (2004) 562
14. T. Leelasattarathkul, S. Liawruangrath, M. Rayanakorn, W. Oungpipat, B. Liawruangrath, *Talanta* **70** (2006) 656
15. R. Chaisuksant, L. Pattanarat, K. Grudpan, *Microchim. Acta* **162** (2008) 181
16. B. C. Janegitz, L. H. Marcolino-Junior, S. P. Campana-Filho, R. C. Faria, O. Fatibello-Filho, *Sensor. Actuat., B* **142** (2009) 260
17. M. Lin, M. Cho, W. S. Choe, Y. Son, Y. Lee, *Electrochim. Acta* **54** (2009) 7012
18. S. Qiu, L. Xie, S. Gao, Q. Liu, Z. Lin, B. Qiu, G. Chen, *Anal. Chim. Acta* **707** (2011) 57
19. M. Lehmann, K. Riedel, K. Adler, G. Kunze, *Biosens. Bioelectron.* **15** (2000) 211
20. K. Tag, K. Riedel, H. J. Bauer, G. Hanke, K. H. R. Baronian, G. Kunze, *Sensor Actuat. B-Chem.* **122** (2007) 403
21. D. Compagnone, A. S. Lupu, A. Ciucu, V. Magearu, C. Cremisini, G. Palleschi, *Anal. Lett.* **34** (2001) 17
22. S. D. Nikolić, E. B. Milosavljević, J. L. Hendrix, J. H. Nelson, *Analyst* **117** (1992) 47
23. A. Lolić, S. Nikolić-Mandić, P. Polić, *J. Serb. Chem. Soc.* **66** (2001) 637.