



# PHYSICAL CHEMISTRY 2008

## *Proceedings*

*of the 9th International Conference on Fundamental  
and Applied Aspects of Physical Chemistry*

### *Volume I*

---

The Conference is dedicated to the 200th Anniversary of the University in Belgrade



---

September 24-26, 2008,  
Belgrade, Serbia



# PHYSICAL CHEMISTRY 2008

## *Proceedings*

*of the 9th International Conference  
on Fundamental and Applied Aspects of  
Physical Chemistry*

*Volume I*

ISBN 978-86-82475-16-3  
Title: Physical Chemistry 2008. (Proceedings)  
Editor: Prof. dr A. Antić-Jovanović  
Published by: The Society of Physical Chemists of Serbia, Studentski trg 12-16, P.O.Box 47, 11158 Belgrade, 218, Serbia  
Publisher: Society of Physical Chemists of Serbia  
For publisher: Prof. dr S. Anić, president of the Society of Physical Chemists of Serbia  
Printed by: "Jovan" Printing and Published Comp;  
250 Copies; Number of Pages: x + 468; Format B5;  
Printing finished in September 2008.  
Text and Layout: Aleksandar Nikolić

*250 – copy printing*

The Conference is organized by  
the Society of Physical Chemists of Serbia

in cooperation with  
Institute of Catalysis, Bulgarian Academy of Sciences

Boreskov Institute of Catalysis,  
Siberian Branch of the Russian Academy of Sciences

Faculty of Physical Chemistry, University of Belgrade

Institute of Chemistry, Technology and Metallurgy, Belgrade

Institute of General and Physical Chemistry, Belgrade

## DETERMINATION OF COPPER AND NICKEL BY ION CHROMATOGRAPHY AND VOLTAMMETRY

K.R. Kumrić, T.M. Trtić-Petrović and J.J. Čomor

*Vinča Institute of Nuclear Sciences, Laboratory of Physics (010), P.O. Box 522,  
11001 Belgrade, Serbia*

### Abstract

Simultaneous determination of copper(II) and nickel(II) by ion chromatography (IC) has been optimized and the detection limits of the new method were compared to stripping voltammetry. The best eluent enabling fast and efficient separation of Cu(II) and Ni(II) is a mixture of 8 mM citric and 0.3 mM oxalic acid using a Metrosep C2 (Metrohm) IC column. The detection limits are significantly lower using stripping voltammetry, while IC is considerably faster.

### Introduction

The radionuclide  $^{64}\text{Cu}$  combines three types of decay ( $\beta^+$ ,  $\beta^-$  and internal conversion followed by Auger electron emission), making it suitable for applications in positron emission tomography (PET) imaging and targeted radiotherapy of different diseases. The nuclear reaction  $^{64}\text{Ni}(p,n)^{64}\text{Cu}$  performed with small medical cyclotrons, is the most suitable production route for  $^{64}\text{Cu}$  for nuclear medical applications. The most frequently used method for the separation of  $^{64}\text{Cu}$  from the enriched nickel target is ion exchange chromatography [1,2].

Our future work will be orientated towards the optimization of separation of Cu(II) and Ni(II) by membrane-based solvent extraction. In order to find adequate separation conditions for Cu(II) and Ni(II), and to investigate the physicochemical parameters of transport of Cu(II) and Ni(II) across the membrane, a suitable analytical method that would enable the determination of low (ppm) and very low (ppb) concentrations of non-radioactive Cu(II) and Ni(II) is needed. Ion chromatography (IC) and stripping voltammetry (anodic, ASV, and cathodic, CSV) are promising techniques for the determination of trace quantities of Cu(II) and Ni(II).

The aim of this study was to find optimum conditions for the determination of Cu(II) and Ni(II), in terms of separation factors, detection limits, linearity and duration.

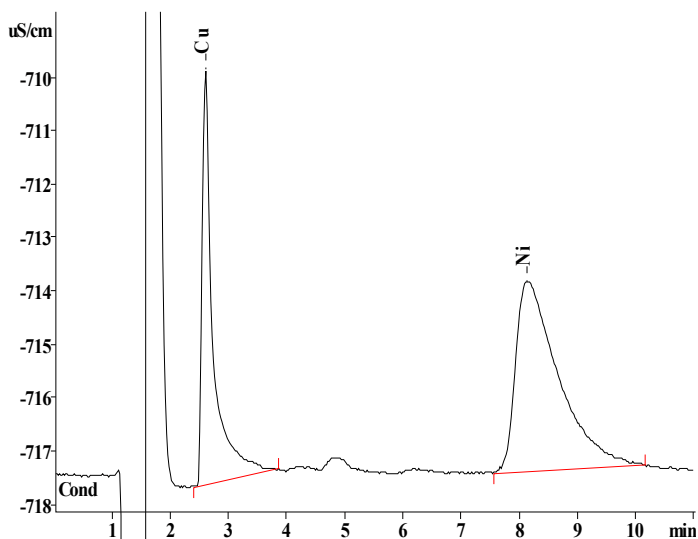
### Results and Discussion

Ion chromatographic separation of transition metals is performed by cation-exchange columns with eluents which contain a complexing agent such as tartaric acid, oxalic acid, citric acid and pyridine-2,6-dicarboxylic acid. Metals form complexes of differing stabilities with the anions and as a result their charge density is reduced. As this occurs in accordance with the kinetics of complex

formation and stability constants of the complexes, differences in selectivity increase and separation becomes possible [3]. Retention of cations is controlled by the concentration of the complexing agent and the pH of the eluent. Ion chromatographic measurements were performed by the 861 Advanced Compact IC system (Metrohm, Switzerland) with conductivity detector and analytical column Metrosep C2 (Metrohm, 150 mm x 4 mm, particle diameter of 7  $\mu\text{m}$ ). All reagents used were of analytical reagent grade. Working solutions of Cu(II) and Ni(II) were prepared by diluting their stock standard solutions (1000 ppm) with 2 mM  $\text{HNO}_3$ .

Considering the stability constants of complexes, the separation of Cu(II) and Ni(II) was tried using eluents which are different mixtures of complexing acids: tartaric and dipicolinic, tartaric and oxalic, tartaric and citric, oxalic and ascorbic, citric and oxalic. By changing the eluent composition and concentrations, the main task was to find a suitable eluent which would enable elution of Cu(II) and Ni(II) in a reasonable period of time.

The best results for the separation of Cu(II) and Ni(II) were obtained using 8 mM citric and 0.3 mM oxalic acid as eluent (Fig. 1). Retention times for the Cu(II) and Ni(II), are 2.6 and 8.1 min, respectively. Duration of the analysis is 11 min, which fulfills the requirements for short and efficient analysis.



**Fig. 1.** Chromatogram of Cu(II) and Ni(II) obtained using 8 mM citric acid and 0.3 mM oxalic acid (flow rate = 1 ml/min, injection volume = 100  $\mu\text{l}$ )

Concentration ranges of Cu(II) and Ni(II) between 0.1 and 25 ppm were investigated. The obtained conductivity vs. concentration dependences were linear, with correlation coefficients of 0.999 for Cu(II) and 0.998 for Ni(II) determination. Detection limits for the determination of Cu(II) and Ni(II) are 0.2 ppm for both ions.

Voltammetric determinations of Cu(II) and Ni(II) were done according to Metrohm's procedure No. 231/2e using a 797 VA Computrace analyser (Metrohm, Switzerland). The electrolyte used for the determination of Cu(II) and Ni(II) by ASV and CSV, respectively, was 0.05 M ammonium-chloride buffer with pH 9.4. For the determination of Ni(II) addition of 0.1 cm<sup>3</sup> of 0.1 M dimethylglyoxime is necessary.

Cu(II) gives a well developed ASV peak, with peak potential,  $E_p$ , at -0.10 V. Three concentration ranges of Cu(II) were investigated: (0.001 – 0.015) ppm, (0.01 – 0.15) ppm and (0.15 – 1.5) ppm. Depending on the concentration range, Cu(II) was deposited at -1.15 V for a period of 30 to 120 s. The obtained current vs. concentration dependences were linear with correlation coefficients of 0.994, 0.999 and 0.998, respectively. The detection limit of this method is 1.0 ppb.

Ni(II) gives a well developed CSV peak, with a half wave potential,  $E_p$ , at -0.95 V. Two concentration ranges of Ni(II) were investigated: (0.1 – 1) ppb and (1 – 10) ppb. Depending on the investigated concentration range, Ni(II) was deposited at -0.7 V for a period of 90 to 120 s. The obtained current vs. concentration dependences were linear with correlation coefficients of -0.998 and -0.999, respectively. The detection limit of this method is 0.1 ppb. Duration of both analysis, ASV and CSV, is at least 30 min.

For the determination of Cu(II) and Ni(II) concentrations higher than 1 ppm and 0.03 ppm, respectively, polarography on static mercury drop electrode (SMDE) can be applied.

## Conclusion

Ion chromatography and stripping voltammetry are complementary methods regarding the determination of low (ppm) and very low (ppb) concentrations of Cu(II) and Ni(II). Detection limits for Cu(II) and Ni(II) by ion chromatography are 0.2 ppm, while ASV and CSV provide significantly lower determination limits of 1.0 ppb and 0.1 ppb, respectively. The main drawback of stripping voltammetry is that Cu(II) and Ni(II) can not be determined during one single run, which implies longer time for the analysis.

IC of Cu(II) and Ni(II) is performed during a single run and provides a fast and efficient method for simultaneous determination of Cu(II) and Ni(II). IC is the method of choice for the determination of Cu(II) and Ni(II) concentrations of 0.2 ppm or higher.

## References

- [1] D. W. McCarthy et al., Nucl. Med. Biol., 1997, **24**, 35-43.
- [2] X. Hou et al., Appl. Radiat. Isotopes, 2002, **57**, 773-777.
- [3] C. Eith et al., Monograph: Practical Ion Chromatography, Metrohm, 2001.