



J. Serb. Chem. Soc. 78 (5) 717–724 (2013)
JSCS–4452

Trace and selective determination of cobalt(II) in water and salt samples using cathodic adsorptive stripping voltammetry in the presence of Pyrogallol Red

FOROOZAN HASANPOUR¹, HOSSEIN TEIMORI², MASOUD FOULADGAR^{3*}
and MASOUMEH TAEI¹

¹Chemistry Department, Payame Noor University, 19395-4697 Tehran, Iran, ²Cellular and Molecular Research Center, School of Medicine, Shahrekord University of Medical Sciences, Shahrekord, Iran and ³Department of Biochemistry, Falavarjan Branch, Islamic Azad University, Falavarjan, Iran

(Received 5 March, revised 16 June 2012)

Abstract: A sensitive and selective procedure is presented for the voltammetric determination of cobalt. The procedure involves an adsorptive accumulation of cobalt Pyrogallol Red (PGR) complex on a stationary mercury drop electrode, followed by cathodic stripping voltammetry measurement of the reduction current of the adsorbed complex at -1.17 V (vs. Ag/AgCl). The optimum conditions for the determination of cobalt include pH 11.0, $35 \mu\text{M}$ Pyrogallol Red, an accumulation potential of -0.9 V (vs. Ag/AgCl) and scan rate 80 mV s^{-1} . The peak current is proportional to the concentration of cobalt over the concentration range 5.0 to 280 ng mL^{-1} with a detection limit of 1 ng mL^{-1} and an accumulation time of 140 s. The method was applied to the determination of cobalt in analytical grade NaCl and water samples.

Keywords: adsorptive cathodic stripping voltammetry, Pyrogallol Red, Co(II) determination.

INTRODUCTION

Cobalt is an essential trace element, a component of vitamin B₁₂ and it is non-specific activator of several enzymes. However, cobalt toxicity causes different diseases, including asthma, contact dermatitis, lung cancer and bronchitis.^{1,2} Cobalt(II) compounds can cause mutagenic effect in plants and mammal cells.³ Due to insufficient data, the allowed concentration level of cobalt in drink water has not been reported but in fresh water for aquatic life, the recommended maximum concentration of total cobalt is $110 \mu\text{g L}^{-1}$.⁴ The concentrations of cobalt in drinking water are generally in the range of 0.1 – $5.0 \mu\text{g L}^{-1}$.⁵

* Corresponding author. E-mail: Fouladgar@iaufala.ac.ir
doi: 10.2298/JSC120305070H



There are several methods for the determination of cobalt ions. The two most frequently used methods are flame atomic absorption spectrometry and electrothermal atomic absorption spectrometry.^{6–8} However, to decrease the detection limit of these methods, usually pre-concentration methods, such as liquid and solid phase extraction,^{9,10} cloud point extraction,^{11–14} adsorption,^{15,16} membrane filtration,¹⁷ *etc.*, are used.

A rather simple method for the determination of heavy metals is based on adsorptive accumulation. Stripping adsorptive accumulation of metal chelates is a widely accepted analytical tool because of its high sensitivity, selectivity and inexpensive instrumentation. Adsorption of surface-active complexes, prior to the reduction step in adsorptive cathodic stripping voltammetry (ACSV), causes the formation of a monomolecular layer of complex species on the surface of the electrode. This is followed by electrochemical reduction either of the element or the ligand in the complex.¹⁸ Due to the accumulation of most of the analyte in a mercury drop, the reduction current will be increased and the detection limit of the methods will be reduced.

Pyrogallol Red is well known as a complexing agent for some heavy metal ions.¹⁹ It forms a selective and stable complex with cobalt(II).²⁰

In this study, a simple adsorptive cathodic stripping voltammetry method was developed for trace determination of cobalt based on the effective accumulation of the cobalt(II)–Pyrogallol Red complex (Co(II)–PGR) on a stationary mercury drop electrode. The adsorbed complex was reduced through cathodic differential pulse polarography.

EXPERIMENTAL

Reagents

All employed chemicals were of analytical reagent grade (Merck, Fluka). Doubly distilled water was used throughout.

A fresh stock solution of Pyrogallol Red (Merck) in water (2×10^{-3} mol L⁻¹) was prepared every three days. A stock solution of cobalt(II) (1000 µg mL⁻¹) was prepared by dissolving cobalt nitrate hexahydrate in water and diluting to 250 mL; dilute solutions were prepared by diluting this solution with distilled water. Ammonia buffer (0.5 mol L⁻¹) was prepared by dissolving an appropriate volume of ammonia in water and diluting to 1.0 L. The pH of the solution was adjusted to 11.0 with hydrochloric acid solution (0.5 mol L⁻¹).

Apparatus

The electrochemical measurements realized using a computer driven µAUTOLAB type II analyzer equipped with a Metrohm VA STAND 663 and GPES ver. 4.9 software. The medium drop size was selected. A three-electrode arrangement with an Ag/AgCl, 3 mol L⁻¹ KCl reference electrode, a platinum wire counter electrode and a multi-mode mercury drop electrode were used. The pH values were controlled by a Metrohm 691 pH meter.

Procedure

About 5 mL of sample solution containing 1–800 ng cobalt was pipetted into a 10 mL volumetric flask and pH was adjusted to 11.0 by addition of the ammonia buffer (pH 11.0).

PGR solution ($180 \mu\text{L}$, $2 \times 10^{-3} \text{ mol L}^{-1}$) was added and the volume was adjusted to 10 mL with distilled water. The solution was transferred to the voltammetric cell. The stirrer was switched on and the solution was purged with argon gas for 5 min. A new drop was formed and accumulation was effected for 140 s at -0.9 V whilst stirring the solution. Then the stirrer was switched off, and the potential was scanned in a negative direction. When further volume of cobalt or PGR was added to the cell, the solution was deoxygenated with argon gas for 1 min.

Preparation of water and salt samples

Water samples were filtered using a $0.45 \mu\text{m}$ pore size membrane filter to remove suspended particles. A Metrohm UV-digester 705 with a temperature control was used. 10 mL water sample was irradiated and decomposed for 2 h at $90 \text{ }^\circ\text{C}$. The pH value was adjusted to 11.0 with ammonia buffer. Then the cobalt was determined using the recommended procedure.

One mL of a $0.5 \text{ mol L}^{-1} \text{ NaCl}$ salt (analytical grade) was transferred to the voltammetric cell and the pH was adjusted to 11.0 with ammonia buffer. Then the cobalt was determined using the recommended procedure.

RESULTS AND DISCUSSION

Adsorptive and voltammetric characteristics of the Co(II)–PGR complex

Preliminary experiments were performed to identify the general features that characterize the behavior of the C(II)–PGR complex at a dropping mercury electrode. No peak was found on cyclic voltammogram in a solution containing $1 \times 10^{-4} \text{ mol L}^{-1}$ PGR in ammonia buffer solution at pH 11.0 in the potential range 0 to -1 V .

The adsorption voltammograms of a solution of ammonia buffer at pH 11.0 containing PGR and after addition of Co(II) ions are shown in Fig. 1 as curve A and curves B–H, respectively. The peak potential of the reduction of adsorbed Co(II)–PGR in the ammonia buffer was -1.17 V . Cyclic voltammetry was used to investigate the electrode reaction. The Co(II)/Co(Hg) system showed irreversible behavior. This behavior was unchanged after the addition of PGR. The peak current of Co(II)–PGR *vs.* scan rate in the cyclic voltammetric mode was linear. This feature is characteristic of a reaction in which the reactant is adsorbed on the surface.²¹

The peak height increased with increasing deposition time. Cyclic voltammograms of the system between 0 to -1.5 V (*vs.* Ag/AgCl), after 0 and 60 s were obtained on a SMDE. The response increased dramatically when the accumulation period increased.

The apparent transfer coefficient could be estimated from the peak half-width, $W_{1/2}$, according to the Laviron Equation:²²

$$\alpha n = \frac{2.44RT}{W_{1/2}F} = \frac{62.5}{W_{1/2}} \quad (1)$$

The average peak half-widths for more than 10 measurements were $60.05 \pm \pm 0.04$ mV. From this value, an αn value of 1.04 was obtained. If the value of α was assumed to be 0.5, then a value for n of 2 was obtained. Therefore, the oxidation state of Co in the complex was 2. This result could be expected by comparison of the redox peak potential of Co(II)–PGR and Co(II)/Co(Hg) in Fig. 2. The peak height of Co(II)–PGR was found to depend on the PGR concentration as well as on cobalt concentration, the solution pH, the collection potential and the collection period.

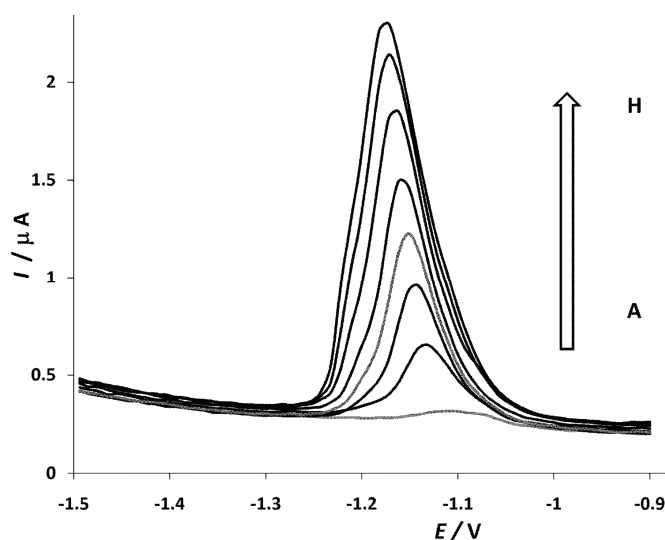


Fig. 1. Effect of Co(II) concentration on peak height of Ads voltammograms in ammonia buffer solution pH 11.0. Concentration of Co(II): A) 0.0; B) 32; C) 65; D) 139; E) 176; F) 201; G) 250; H) 265 ng mL⁻¹. [PGR] = 100 μmol L⁻¹; $E_{acc} = -0.9$ V; pulse height = 100 mV.

Optimization of the parameters

Several parameters, *i.e.*, pH, scan rate, PGR concentration, and accumulation potential and time had to be optimized to achieve maximum sensitivity in the determination of the cobalt concentration.

Effect of pH. The influence of pH on the stripping peak current was studied in the pH range 7–12. As can be seen in Fig. 3, the peak height was small when the pH value was lower than 9.0, and the peak current was approximately independent of pH when the pH value exceeded 10.5. The reason for decreasing peak height could be attributed to the weak complexing ability of PGR at pH values lower than 9.0. An optimum value of pH 11.0 was selected for the further experiments.

Effect of the accumulation potential. The effect of accumulation potential on the stripping peak current of the complex was examined over the potential range

of 0.1 to -1.1 V. The peak current increased with increasing accumulation potential from 0.1 to -1.0 V. A potential of -0.9 V was selected as the optimized accumulation potential.

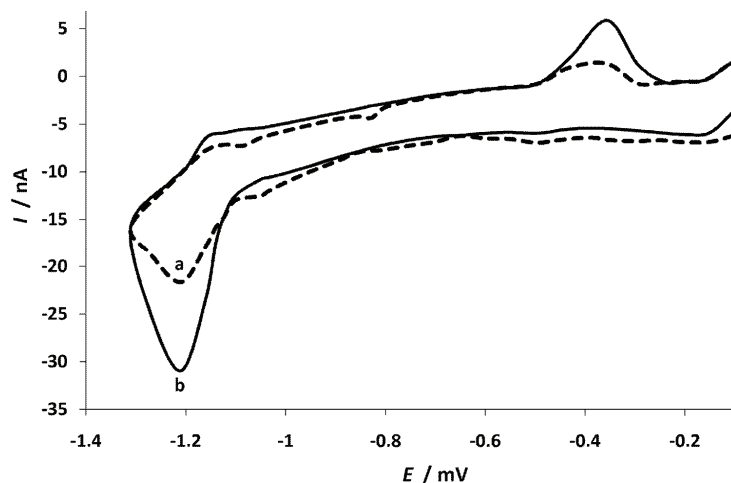


Fig. 2. Cyclic voltammograms of Hg electrode in the solution containing 50 ng mL^{-1} Co(II) for comparison of peak potential of a) Co(II)/Co(Hg) and b) Co(II)-PGR in $100 \text{ } \mu\text{mol L}^{-1}$ PGR.

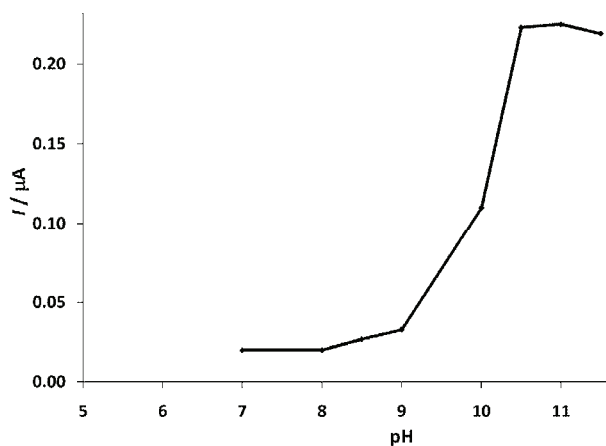


Fig. 3. Effect of pH on the cathodic peak current, after 80 s accumulation at -0.9 V, for 50 ng mL^{-1} of cobalt and $100 \text{ } \mu\text{mol L}^{-1}$ PGR.

Effect of accumulation time. The effect of accumulation time on the peak current was also studied. The peak current increased with increasing accumulation time up to 140 s and then starts to level off at longer accumulation times. Therefore, 140 s was selected as the optimum accumulation time.

Effect of the PGR concentration. The peak current for cobalt increased with increasing PGR concentration up to $32 \text{ } \mu\text{mol L}^{-1}$ PGR, and leveled off at higher concentrations. An optimum PGR concentration of $35 \text{ } \mu\text{mol L}^{-1}$ was selected for the further experiments.

Effect of scan rate. The effect of scan rate on the peak current was studied in the range 10–120 mV s⁻¹. When the scan rate was increased from 10–80 mV s⁻¹ (in the differential pulse mode), the peak current increased. However, at scan rates faster than 80 mV s⁻¹, there was no increase in the peak current height.

It was found that the peak current, I_p , of the complex varied linearly with potential scan rate v (in the cyclic voltammetric mode). There was a linear relation between $\log I_p$ and $\log v$ in the range 100 to 800 mV s⁻¹, with the a slope of 0.906, which indicates the target in the electrochemical process was adsorbed on the electrode surface.

Linear range, detection limit and reproducibility

Under the optimum experimental conditions, the calibration curve was linear over the range of 5.0 to 280 ng mL⁻¹ at pH = 11.0 (ammonia buffer), 35 $\mu\text{mol L}^{-1}$ PGR, accumulation potential of -0.9 V and accumulation time of 140 s, $v = 80$ mV s⁻¹. The detection limit $Y_{\text{LOD}} = \bar{X}_B + 3S_B$ (where Y_{LOD} is the signal for the detection limit, \bar{X}_B is the mean of the blank signal and S_B is the standard deviation of the blank signal) was obtained as 1 ng mL⁻¹. The precision for seven determinations of 50 ng mL⁻¹ of Co(II) was calculated to be 4 %.

Effect of foreign ions on the determination of cobalt

Possible interference by cations, anions and some surfactants were investigated in the adsorptive stripping voltammetric determination of cobalt by the addition of the interfering ion to a solution containing 50 ng mL⁻¹ of cobalt using the optimized experimental conditions. The results of this study are given in Table I.

TABLE I. Maximum tolerable concentration of interfering species for a cobalt concentration of 50 ng mL⁻¹

Foreign ions and surfactant	Tolerance limit, mole ratio [interferent]/[sample]
Alkaline and alkaline earth metals, Mn ²⁺ , Cu ²⁺ , Se ⁴⁺ , Cd ²⁺ , Al ³⁺ , Tl ⁺ , In ³⁺ , Fe ²⁺	800
Ce ³⁺ , Pb ²⁺ , Ni ²⁺ , CO ₃ ²⁻ , Br ⁻ , Cl ⁻ , NO ₃ ⁻ , HCO ₃ ⁻ , SO ₄ ²⁻	500
Ce ³⁺ , Tl ³⁺ , Cr ³⁺ , Ag ⁺ , Hg ²⁺ , CH ₃ COO ⁻ , CN ⁻	200
V ⁴⁺ , La ³⁺ , UO ₂ ²⁺ , Zr ⁴⁺ , CPC	100
TritonX-305	50
TritonX-100	10

Application of the method for the determination of cobalt in real samples

The utility of developed method was tested by determining cobalt in analytical grade NaCl and water samples (Tables II and III, respectively), using the recommended procedure. The data obtained for samples spiked with cobalt showed good recoveries.

TABLE II. Determination of Co in NaCl salt in pH 11.0 ammonia buffer

Concentration of cobalt, ng mL ⁻¹		Recovery, %
NaCl added	Total found	
0	5.74	–
8	13.2	96
11	16.48	98
14	19	96
17.8	23.98	101.8

TABLE III. Determination of Co in water samples

Concentration of cobalt, ng mL ⁻¹		Recovery, %
Added	Found	
0.0	25.1	–
20.0	48.3	107.1
40.0	62.4	95.8
50.0	70.6	94.0
80.0	108.7	103.4

CONCLUSIONS

The applicability of the proposed method using adsorptive cathodic stripping voltammetry (ACSV) for trace determination of cobalt(II) ions, based on the accumulation of Co(II)–PGR on a stationary mercury drop and using differential pulse polarography for stripping the mercury drop, was confirmed. This method has good selectivity for the determination of cobalt(II) in the presence of some other heavy metals and it was successfully employed for the analysis of water and NaCl salt samples. In addition, it has advantages, such as simplicity, rapidity and low detection limit, over some other methods.

ИЗВОД

СЕЛЕКТИВНО ОДРЕЂИВАЊЕ ТРАГОВА КОБАЛТА(II) У ВОДИ И УЗОРЦИМА СОЛИ
ПРИМЕНОМ КАТОДНЕ АДСОРПЦИОНЕ СТРИПИНГ ВОЛТАМЕТРИЈЕ
У ПРИСУСТВУ ПИРОГАЛОЛ ЦРВЕНОГ

FOROOZAN HASANPOUR¹, HOSSEIN TEIMORI², MASOUD FOULADGAR³ и MASOUMEN TAEI¹

¹Chemistry Department, Payame Noor University, 19395-4697 Tehran, Iran, ²Cellular and Molecular Research Center, School of Medicine, Shahrekord University of Medical Sciences, Shahrekord, Iran и

³Department of Biochemistry, Falavarjan Branch, Islamic Azad University, Falavarjan, Iran

У овом раду је описан осетљив и селективан поступак за волтаметријско одређивање кобалта. Поступак укључује адсорпцију комплекса кобалт–пирогалол црвеног (PGR) на стационарној капљућој живиној електроди, чему следи мерење струје редукције адсорбованог комплекса катодном стрипинг волтаметријом на 1,17 V (према Ag/AgCl). Оптимални услови за одређивање комплекса су: pH 11,0, концентрација пирогалол црвеног од 35 μM, потенцијал адсорпције од –0,9 V (према Ag/AgCl) и брзина промене потенцијала од 80 mV s⁻¹. Струја пика је пропорционална концентрацији кобалта у опсегу 5,0–280 ng mL⁻¹, са границом детекције од 1 ng mL⁻¹ и временом ад-

сорпције од 140 s. Метода је примењена за одређивање кобалта у NaCl аналитичког степена чистоће и узорцима вода.

(Примљено 5. марта, ревидирано 16. јуна 2012)

REFERENCES

1. M. De Boeck, M. Kirsch-Volders, D. Lison, *Mutat. Res.* **533** (2003) 135
2. V. Verougstraete, A. Mallants, J. P. Buchet, B. Swennen, D. Lison, *Am. J. Res. Crit. Care Med.* **170** (2004) 162
3. D. Beyersmann, A. Hartwig, *Toxicol. Appl. Pharm.* **115** (1992) 137
4. http://www.env.gov.bc.ca/wat/wq/BCguidelines/cobalt/cobalt_over.html, (accessed on 3 Feb, 2012)
5. C. Rojas, V. Arancibia, M. Góme, E. Nagles, *Int. J. Electrochem. Sci.* **7** (2012) 979
6. Y. Cai, G. Jiang, J. Liu, *Talanta* **57** (2002) 1173
7. S. Cerutti, S. Moyano, J. A. Gásquez, J. Stripeikis, R. A. Olsina, L. D. Martinez, *Spect. Chim. Acta, B* **58** (2003) 2015
8. Y. Wang, X. Luo, J. Tang, X. Hu, Q. Xu, C. Yang, *Anal. Chim. Acta* **713** (2012) 92
9. P. Berton, E. M. Martinis, L. D. Martinez, R. G. Wuilloud, *Anal. Chim. Acta* **713** (2012) 56
10. R. S. Praveen, S. Daniel, T. P. Rao, *Talanta* **66** (2005) 513
11. D. Citak, M. Tuzen, *Food Chem. Toxicol.* **48** (2010) 1399
12. M. Ghaedi, A. Shokrollahi, F. Ahmadi, H. R. Rajabi, M. Soylak, *J. Hazard. Mater.* **150** (2008) 533
13. G. L. Donati, C. C. Nascentes, A. A. Nogueira, M. A. Z. Arruda, J. A. Nóbrega, *Microchem. J.* **82** (2006) 189
14. J. Chen, K. Chuan Teo, *Anal. Chim. Acta* **434** (2001) 325
15. H. Minamisawa, H. Iwanami, N. Arai, T. Okutani, *Anal. Chim. Acta* **378** (1999) 279
16. X. Liu, Z. Fang, *Anal. Chim. Acta* **316** (1995) 329
17. I. Narin, M. Soylak, *Anal. Chim. Acta* **493** (2003) 205
18. Y. Li, Y.-H. Xie, F. Zhou, H. Guo, *Electroanalysis* **18** (2006) 976
19. T. Korenaga, S. Motomizu, K. Tōei, *Anal. Chim. Acta* **104** (1979) 369
20. A. A. Ensafi, A. Aboutalebi, *Sensors Actuators, B* **105** (2005) 479
21. A. J. Bard, L. R. Faulkner, *Electrochemical methods – Fundamentals and Applications*, Wiley, New York, USA, 1980, p. 179
22. E. Laviron, *J. Electroanal. Chem.* **52** (1974) 355.