KINETIC-CATALYTIC DETERMINATION OF ULTRAMICRO AMOUNTS OF Co(II) USING 4-HYDROXYCOUMARINE-PERMANGANATE REDOX REACTION

DRAGANA SEJMANOVIĆ[1*], RUŽICA MICIĆ[1], RANKO SIMONOVIĆ[1]

[1]Faculty of Natural Sciences and Mathematics, University of Priština, Kosovska Mitrovica, Serbia

ABSTRACT

Determination of Co(II) based on its catalytic effect on the reaction between 4-hydroxycoumarine and potassium permanganate, in the presence of acetate buffer was described. The method development includes optimization of the reagent concentration and temperature. Absorbance of potassium permanganate was measured at 525 nm. The calibration curve was linear in the range of 0.5 - 4 ng/cm^3 of Co(II). The relative standard deviation was in the interval 6.25-2.60 % of the concentration range of 0.6-3 ng/cm^3 Co(II), respectively. The interference effects of foreign ions were determined for the assessment of the selectivity of the method. The proposed method was found to have excellent sensitivity, relatively good selectivity and simplicity.

Keywords: cobalt(II), kinetic method, 4-hydroxycoumarine.

INTRODUCTION

Cobalt is an essential element in trace amounts for humans and animal as an integral part of the vitamin B_{12} complex; also necessary for the synthesis of a number of hormones, neurotransmitters and other compounds (Medina-Escriche et al., 1987). However, in higher concentrations cobalt is toxic to humans, animals and plants. The essentiality of cobalt has also been demonstrated in the environment elsewhere: as a micronutrient for some blue-green algae, required for nitrogen-fixation in legumes, in growth enhancement of some terrestrial plants at low concentration (Kiran et al., 2012). Cobalt is used as a pigment in glass, ceramics and paints; as a catalyst for the petroleum industry and in batteries. Cobalt is also found in low concentration in marine waters.

Although a number of methods are available for the determination of cobalt ions such as flame atomic absorption spectroscopy (FAAS), graphite furnace atomic absorption spectroscopy (GFAAS) (Jiang et al., 2008), inductively-coupled plasma optical emission spectroscopy (ICP-OES) (Mikula et al., 2007; Suleiman et al., 2007), inductively-coupled plasma coupled with mass spectrometry (ICP-MS) (Juvonen et al., 2002). These modern sophisticated sensitive methods are relatively expensive and require time for sample preparation, also can be applied after preliminary treatments such as preconcentration and extraction. Catalytic-kinetic methods have some advantages, including high sensitivity, short analysis time and minimum, low cost and easy available instruments (Mitić et al., 2009; Li, 1998; Safavi et al., 2002). Hence, due to these reasons simple colorimetric methods are still popular. Kinetic methods determined Co(II) as the catalyst of various reactions of oxidation with hydrogen peroxide or KIO_4 as the oxidant and different organic, aromatic oxy-compound, as the reductant. Different sensitive analytical methods including extractive spectrophotometry (Kamble et al., 2011), non-extractive derivative spectrophotometry, cloud-point extraction (Safavi et al., 2004), electro chemical detection (ECE) coupled with liquid chromatography (Suleiman et al., 2007) and kinetic spectrophotometric methods have been recognized as offering a valuable approach for the trace analysis (Bahram et al., 2012; Naseri et al., 2011; Wang et al., 2003; Ghasemi et al., 1998) of cobalt.

The aim of this study was to develop a simple trace kinetic-spectrophotometric method for the determination of cobalt(II) ions. An indicator reaction (oxidation 4-hydroxycoumarine by $KMnO_4$) has not previously been used for the kinetic determination of trace amounts of Co(II). The method is based on the catalytic effect of Co(II) on the oxidation 4-hydroxycoumarine by $KMnO_4$ in acetate buffer solution at pH=3.8, at 25±0.1°C. Diminution of the colour intensity of the oxidant ($KMnO_4$) was followed spectrophotometrically as the change of absorbance(A) in time (t).

EXPERIMENTAL

Reagents and Solutions

Analytical grade reagents, deionized water and polyethylene vessels were used throughout the study. A solution of $KMnO_4$ was prepared from an ampoule produced by „Merck" by dissolving in a volumetric flask. Before the experiment, the concentration of the solution was checked spectrophotometrically (at 525 nm). The solution of $KMnO_4$ was saved in a dark reagent flask.

A 1.25×10^{-3} mol/dm^3 solution of 4-hydroxycoumarine (in the text we have marked as 4-OHcoum.) was prepared by dissolving the appropriate amount of the solid compound. To improve its solubility, an equivalent amount of NaOH was

added. A stock solution of Co(II) (1000 ppm) was prepared by dissolving 1g of metal of cobalt analytical grade in 50 cm^3 of HCl (1:1) and diluted to 1 dm^3.

The exact concentration was determined electrogravimetrically from a more concentrated solution. A acetate buffer solution was prepared from 0.2mol/dm^3 CH$_3$COOH and 1 mol/dm^3 NaOH solutions.

Apparatus

A MA9524 SPECOL 221 (Carl Zeiss-Iskra) spectrophotometer equipped with thermostat system was used for spectrophotometric measurements. A cell of path-length 10mm, were used. The pH was measured by means of a radiometer (PHM 29b pH-meter) equipped with a GK 2311 C combined electrode. All solutions were kept in a thermostatic water-bath („Sutjeska", type 10) at 25±1°C before beginning the reaction.

Procedure

The method continual variations were performed, so the concentrations of the examined reactant was varied in given interval, while others were kept constant.

The selected volumes of the reactants were put into a 10 cm^3 standard flask in the following order: 4-hydroxycoumarine, acetate buffer, standard solution of Co(II) and water to make up exactly to the predetermined volume. The flask was kept in a thermostat for 10 min., and then the solution was made up to the mark with KMnO$_4$ and water. The content of the flask was mixed well. The cell of the photometer was rinsed well and filled with the prepared solution. Time changes of the abcorbance, dA/dt, were measured every 30s over a period of 5-6 min. during the reaction. The dA/dt was proportional to the reaction rate (dc/dt) expressed as:

$$dA/dt = \varepsilon \times l \times dc/dt = \tan \alpha$$

where ε is molar absorptivity, l the cell path-length, c the concentration of the KMnO$_4$, *tan α* the slope of the linear part of the A against t.

The initial concentrations of the reagent solutions after the dilution to 10 cm^3 were: 5×10^{-5}-2.5×10^{-4} mol/dm^3 of 4-hydroxycoumarine, 4×10^{-5}-3.2×10^{-4} mol/dm^3 KMnO$_4$, 0.5-4 ng/cm^3 Co(II). An unknown concentration of cobalt(II) was calculated from the equation (1).

RESULTS AND DISCUSSION

The exact mechanism of reaction and the nature of reaction products were not the main interest of our investigation, but only important analytical meaning. As the reaction progresses, the initial red color of the solution fades and the colorless reaction product forms. All spectrophotometric measurements were performed at the wavelength of the absorption maximum of KMnO$_4$ in acetate buffer (525nm).

Effect of the experimental conditions

For finding the optimum experimental conditions, the effect of pH, potassium permanganate concentration, concentration of 4-hydroxycoumarine and concentration of acetate buffer, on the reaction rate were studied by differential variant of the tangent method. The differential variant of the tangent method was used for processing the kinetic data, because there is a linear relation between the abcorbance and time during the first 2-5 min. after mixing.

Keeping concentrations of the other reactants constant we studied the effect of pH on the rates of catalytic and non-catalytic reactions in the range of 3.2-5.0.

The results are presented in Fig. 1. Figure 1 shows that there is complicated relationship between the pH and the catalytic and non-catalytic reaction rate in the studied pH range. The best results were obtained for the value pH of 3.80, and this value was selected as the optimum pH value for the system studied. At lower pH values, drastically increases the rate of reactions, and error in the determination of *tg α* becomes larger.
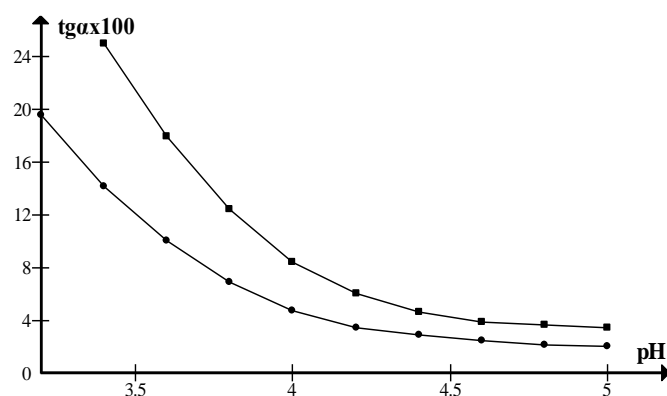

Figure 1. Effect of pH on determination of Co(II). Experimental conditions: 2×10^{-4} mol/dm^3 of KMnO$_4$, 1.5×10^{-4} mol/dm^3 of 4-OHcoum., 5ng/cm^3 of Co(II). (•)-catalytic reaction, (•)-non-catalytic reaction.
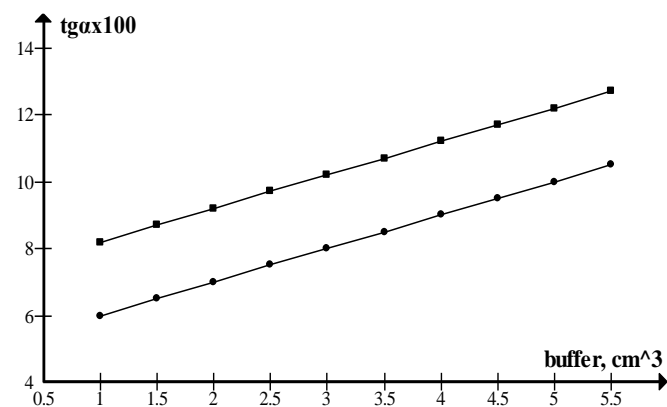
Figure 2. Effect of volume of acetate buffer on determination of Co(II). Experimental conditions: 2×10^{-4} mol/dm^3 of KMnO$_4$, 1.5×10^{-4} mol/dm^3 of 4-OHcoum., 5ng/cm^3 of Co(II). (•)-catalytic reaction, (•)-non-catalytic reaction.

The dependence of the volume of acetate buffer on the reaction rate was studied in the range of 1.0 to 5.5 cm³. The results are presented in Figure 2. In this interval both reactions show the first order dependence of the volume of acetate buffer. The concentration of acetate buffer: 6.5×10^{-2} mol/dm³ CH₃COOH, 7.3×10^{-3} mol/dm³ acetate ion chose as optimum concentration which respond the volume of 2.5 cm³ of acetate buffer. At higher concentration the rates of the catalytic and non-catalytic reaction accelerate.

The effect of 4-hydroxycoumarine concentration on the reaction rate was investigated in the concentration range of 5×10^{-5} to 2.5×10^{-4} mol/dm³ (Figure 3).
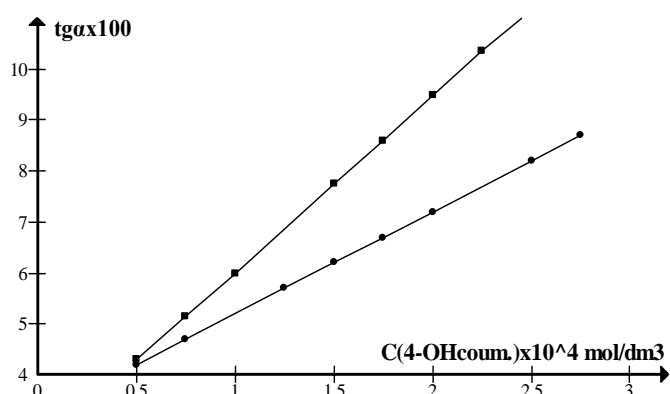
Figure 3. Effect of 4-OHcoum. concentration on determination of Co(II). Experimental conditions: 2×10^{-4} mol/dm³ of KMnO₄, 5 ng/cm³ of Co(II), pH=3.8. (▪)-catalytic reaction, (•)-non-catalytic reaction.
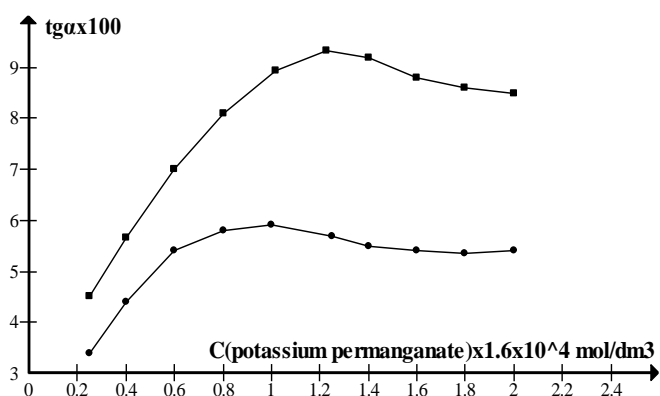
Figure 4. Effect of KMnO₄ concentration on determination of Co(II). Experimental conditions: 1.5×10^{-4} mol/dm³ of 4-OHcoum., 5 ng/cm³ of Co(II), pH=3.8. (▪)-catalytic reaction, (•)-non-catalytic reaction.

The catalytic and non-catalytic reactions were of the first order with respect to the concentration of 4-hydroxycoumarine. For further work a concentration of 4-hydroxycoumarine of 1.5×10^{-4} mol/dm³ was selected as the optimum concentration. At higher concentration of 4-hydroxycoumarine abcorbance significaully increased when the error of spectrophotometric measurement becomes higher (area of Beer's law validity).

The effect of oxidant concentration on the reaction rate was also investigated. The results are illustrated in Fig. 4. The relationship between the concentration of KMnO₄ and the reaction rate was complex. The reaction order depending on KMnO₄ concentration within the studied concentration of KMnO₄. For further work a concentration of 2×10^{-4} mol/dm³ of KMnO₄ was chosen. At higher concentration of 2×10^{-4} mol/dm³ leads to the formation of insoluble reducing the product of KMnO₄ adding the problem of contamination the cell of the photometer.

Calibration graph

For the optimal conditions described above (pH=3.8; $C_{4-OHcoum}=1.5\times10^{-4}$ mol/dm³; $C_{KMnO_4}=2\times10^{-4}$ mol/dm³) a calibration graph was constructed at two different temperatures at $25\pm0.1^{\circ}$C and $30\pm0.1^{\circ}$C. A Co(II) concentration under optimum conditions was varied from 0.5 ng/cm³ to 4 ng/cm³.

Figure 5 shows the corresponding calibration graph, which were used for determination of Co(II) concentration in the interval mentioned. The slopes of the calibration lines (1) and (2) were very similar, however the temperature of $25\pm0.1^{\circ}$C is recommended as appropriated.
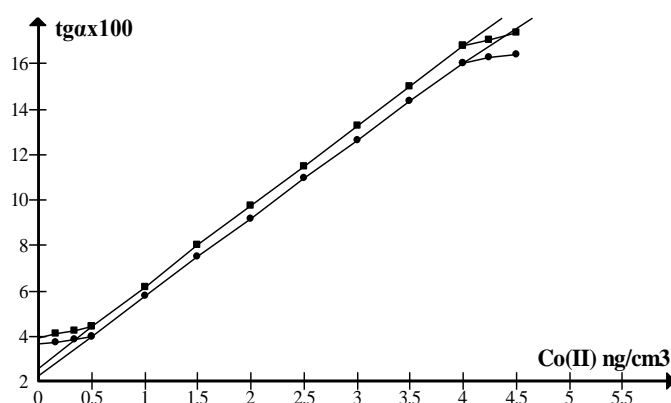
Figure 5. Effect of Co(II) concentration on the reaction rate. Experimental conditions: 2×10^{-4} mol/dm³ of KMnO₄, 1.5×10^{-4} mol/dm³ of 4-OHcoum., pH=3.8. (•)-temperature $25\pm0.1^{\circ}$C, (▪)-temperature $30\pm0.1^{\circ}$C

The unknown concentration of Co(II) was determined using the following equations which were obtained by the least-squares method:

$$C_{Co(II)}=(tg\alpha-0.026)/0.0346 \ (ng/cm^3) \qquad (1)$$

The following kinetic equations were deduced on the basis of the graphic correlations obtained for the investigated catalytic and non-catalytic reactions (at constant pH).

For the catalytic reaction:

$$-dc/dt=k_1\times C^m_{KMnO_4}\times C_{4-OHcoum}\times C_{Co(II)} \qquad (2)$$

where m is a variable, k_1 is a catalytic reaction rate constant.

For the non-catalytic reaction:

$$-dc/dt = k_0 \times C^p_{KMnO_4} \times C_{4\text{-}OHcoum} \qquad (3)$$

where p is a variable, k_0 is non-catalytic reaction rate constant.

Limit of detection (LOD) of the method was calculated as ($3\sigma/S$) is 0.0867 ng/cm^3 and limit of quantification ($10\sigma/S$) is 0.289 ng/cm^3, with coefficient of determination (R^2) of 0.9998.

Accuracy and precision

Four sets of working solutions with different concentrations of Co(II) were analyzed under the optimum conditions using a differential variant of the tangent method.

The results for estimated precision and accuracy are summarized in Table 1. The relative standard deviation ranged from 2.60 % to 6.25 % for Co(II) concentration range 3 - 0.6 ng/cm^3.

Table 1. Accuracy and precision of Co(II) determination

Taken(μ) (ng/cm^3)	Found($\bar{x}$) (ng/cm^3)	n	RSD (%)	($\bar{x}$-μ)/μ *100
0.60	0.64±0.04	5	6.25	6.60
1.00	1.02±0.05	5	4.90	1.50
2.00	2.02±0.05	5	2.48	1.00
3.00	3.07±0.08	5	2.60	2.33

$\bar{x}$-mean value ± standard deviation; μ-true value; RSD-relative standard deviation; ($\bar{x}$-μ)/μ*100-accuracy

Interference study

To study the selectivity of the method we undertook a systematic study of the effect of foreign ions on the catalytic reaction rate, under the optimal conditions mentioned above, at a constant concentration of Co(II) (4 ng/cm^3). Each ion was added in eight known concentration ratios (10^5:1, 10^4:1, 10^3:1, 10^2:1, 10:1, 1:1, 10^{-1}:1 and 10^{-2}:1) against the constant Co(II) concentration of 4 ng/cm^3.

The presence of K^+ and Cl^-, in the ratio 10^5:1, NH_4^+ and SO_4^{2-}, in the ratio 10^4:1, Mg^{2+}, Cu^{2+}, Mn^{2+}, I^-, in the ratio 10^3:1, Ca^{2+}, Ba^{2+}, Sr^{2+}, Pb^{2+}, Cd^{2+}, Sn^{2+}, in the ratio 10^2:1 has practically no influence on the reaction rate. The presence of Fe^{3+}, in the ratio 10^{-2}:1, Zn^{2+}, in the ratio 10^{-1}:1 and Ni^{2+}, in the ratio 10:1 further catalyzes the determination of cobalt. SCN^-, PO_4^{3-}, $C_2O_4^{2-}$, in the ratio 10:1 have a slight inhibiting effect. The results reveal that proposed method for Co(II) determination have a very good selectivity.

CONCLUSION

Development of the fast, simple, inexpensive and applicable kinetic-spectrophotometric method for the determination of Co(II) traces were reported in this paper. The method has very low detection limit, which falls within the range of more sensitive methods for Co(II) determination. Therefore, this method could be appropriate for the fast monitoring of traces amounts of Co(II) in different samples, with available and cheap chemicals and instrumentation.

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