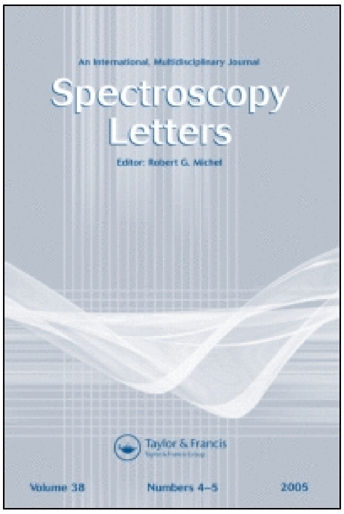

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INDIRECT KINETIC SPECTROPHOTOMETRIC DETERMINATION OF COBALT BASED ON THE REDOX REACTION WITH IRON(III) IN THE PRESENCE OF 1,10-PHENANTHROLINE

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ABSTRACT

An indirect kinetic spectrophotometric method is presented for determination of trace amounts of cobalt. The method is based on the redox reaction of cobalt with Fe(III) in the presence of 1,10-phenanthroline. In the presence of 1,10-phenanthroline, Fe(III) is reduced easily by cobalt(II) to a Fe(II)-1,10 phenanthroline complex ,which shows an absorption maximum at 514 nm. Linear calibration graphs were obtained over the range 0.25–12 $\mu g\,mL^{-1}$ of cobalt. The

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detection limit was $0.2\,\mu g\,mL^{-1}$ of cobalt. The relative standard deviation for the determination of $0.5\ \mu g\,mL^{-1}$, $2\ \mu g\,mL^{-1}$ and $5\,\mu g\,mL^{-1}$ cobalt ($n = 8$) were 1.4%, 0.6% and 0.8%, respectively. The method is free from most interferences, especially from Fe(II). The proposed method was successfully applied to the determination of cobalt in synthetic alloy solutions.

Key Words: Kinetic studies; Spectrophotometric analysis; Cobalt analysis; Redox reaction

INTRODUCTION

In a redox reaction of metal ions, the presence of complexing agent modifies the potential of a redox system.[1] By using this phenomenon, Kawashima et al., developed new methods for the potentiometric determination of chromium(VI) with iron(II),[2] copper(II) with iron(II),[2] vanadium(V) with iron(II)[3] and successive titration of chromium(VI) and iron(III) with cobalt(II)[4] in the presence of appropriate complexing agents. The flow injection analysis (FIA) methods for the determination of iron(II)[5] and vanadium(IV)[6] were also presented with photometric detection and were also developed for the determination of complexing agents such as EDTA, DTPA, NTA, diphosphate, etc., by means of ligand effects.[7,8] On the basis of this ligand effect, Kawashima et al.[9] described a new simultaneous FIA method for the determination of vanadium(IV) and vanadium(V) using redox reactions of vanadium(IV) with iron(III) and vanadium(V) with iron(II).

Cobalt is an important trace element in nature for example in the normal diet of man in the form of vitamin B_{12} (cyanocobalamin)[10–12] and also in industry. Although pure cobalt has few applications, its use as an alloying and as a source of chemicals makes it a strategically important metal.[13] The uses of cobalt-containing alloys include superalloys for aircraft engines, magnetic alloys for powerful permanent magnets, cemented carbides, wear resistance alloys, corrosion resistant alloys, etc. Cobalt chemicals, among their many applications, are used as pigments in the glass, ceramic and paint industries, as paint driers and as trace metal additives for agricultural and chemical use.[13] Thus, selective determination of traces of cobalt is important.

In the present work, we describe an indirect kinetic spectrophotometric method for determination of Co(II) by measuring the rate of formation of Fe(II)-phenanthroline, which is produced in the redox reaction of Fe(III) with Co(II) in the presence of phenanthroline.

EXPERIMENTAL

Apparatus

Absorption spectra were recorded on a Philips PU 8750 UV-Vis spectrophotometer. A Philips UV-Vis single beam spectrophotometer model PU 8625 with 1 cm glass cell was used for recording the change in absorbance vs. time. The temperature of the cell compartment was kept constant by circulating water from a thermostatic water bath model LO-TEMP-TROL 154 regulated at the reaction temperature.

Reagents

All reagents were of analytical grade. Triply distilled water was used throughout the study.

Stock solution of 1,10-phenanthroline hydrochloride (0.1 M) was prepared by dissolving 1.1734 g of 1,10-phenanthroline hydrochloride in water and diluting to 50 mL.

Cobalt stock solution ($1000\,\mu g\,mL^{-1}$) was prepared by dissolving 0.2466 g $Co(NO_3)_2$, $4H_2O$ in water and diluting to 50 mL.

Iron(III) stock solution ($1000\ \mu g\,mL^{-1}$) was prepared daily by dissolving 0.3600 g $Fe(NO_3)_3$, $9H_2O$ in water and diluting to 50 mL.

A stock solution of CTAB (0.1 M) was prepared daily by dissolving 0.3645 g of CTAB in water and diluting to 10 mL.

Stock solutions of interfering ions ($1\,mg\,mL^{-1}$) were prepared by dissolving their suitable salts in water.

Buffer solution pH 3 (Merck) was used.

Recommended Procedures

2 mL buffer solution (pH 3), 0.2 mL of stock solution of 1,10-phenanthroline hydrochloride, 0.1 mL of stock CTAB solution, 1 mL of Fe(III) ($100\,\mu g\,mL^{-1}$) and an appropriate volume of Co(II) solution containing $0.25–12\,\mu g\,mL^{-1}$ were added to 5 mL volumetric flask and made up to the mark with water. Time was measured just after the addition of the last drop of cobalt solution. The solution was mixed and a portion of that was transferred within 20 s into a 1 cm spectrophotometric cell to record the absorbance at 510 nm for 20–150 s after initiation of the reaction. Cobalt concentration of the test sample is determined from a calibration graph similarly prepared with cobalt working standard solution.

RESULTS AND DISCUSSION

The redox potential of a system involving metal ions is modified by complexation of metal ions with a suitable ligand. For the Fe(III)/Fe(II) system the conditional standard potential of the Fe(III)/Fe(II) couple, E'_{Fe}, in the presence of a ligand L (L = phen) can be written as:

$$\begin{aligned} E'_{Fe} &= E^0_{Fe} + 0.059 \log \alpha_{Fe(II)(L)}/\alpha_{Fe(III)(L)} \\ &\quad + 0.059 \log C_{Fe(III)}/C_{Fe(II)} \end{aligned} \tag{1}$$

where α denotes the side reaction coefficient taking into account the complex formation of iron(II) and iron(III) with L.[14] $C_{Fe(III)}$ and $C_{Fe(II)}$ are the total concentrations of iron(III) and iron(II), respectively. The potential of the Fe(III)/Fe(II) couple increases in the presence of phen because formation constants of iron(II)-phen complexes are higher than those of iron(III)-phen complexes,[15] i.e., the second term of Eq. (1) is positive.

The reaction of Co(II) with iron(III) in the presence of phen is very fast and kinetic monitoring of the reaction is not so easy. We found that the presence of a cationic surfactant such as cetyl trimethyl ammonium bromide (CTAB) causes a decrease in the rate of reaction, and thus, facilitating the kinetic study of the above system.

In this work, we have developed a method for the indirect kinetic spectrophotometric determination of Co(II) with iron(III) in the presence of 1,10-phenanthroline. In the presence of 1,10-phenanthroline (phen), Fe(III) is easily reduced by Co(II) to iron(II) and this ion reacts with phenanthroline to produce a red iron(II)-phenanthroline complex ($\lambda_{max} = 510$ nm). By plotting the graph of the difference between the absorbance of the red iron(II) complex at 20 and 150 s from initiation of the reaction vs. the concentration of Co(II), cobalt(II) can be determined at trace levels.

Effects of Operational Parameters

The effects of pH and CTAB on the kinetic signal were investigated to find optimum conditions. It should be noted that excessive amounts of iron(III) and 1,10-phenanthroline with respect to cobalt(II) (as described in the recommended procedure) were selected to insure complete reaction of cobalt(II).

Effect of pH

The effect of pH on the kinetic signal was studied in the pH range of 1.0–4.0 (Fig. 1). pH 3.0 was selected as the optimum pH for further studies.

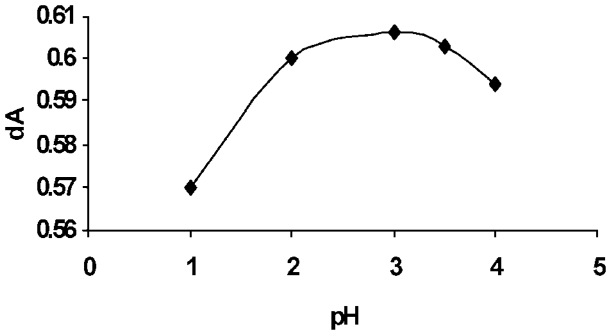

Figure 1. Effect of pH on the kinetic signal. Conditions: 1,10-phenanthroline hydrochloride 4.0×10^{-3}M, $20\,\mu g\,mL^{-1}$ Fe(III), CTAB 2.0×10^{-3}M, and $5\,\mu g\,mL^{-1}$Co(II).

Effect of CTAB

Figure 2 shows the effect of CTAB on the rate of the reaction. In the absence of CTAB, the reaction rate was very fast. However, addition of CTAB reduces the rate of reaction. A concentration of 2×10^{-3}M CTAB was selected as the optimum CTAB concentration.

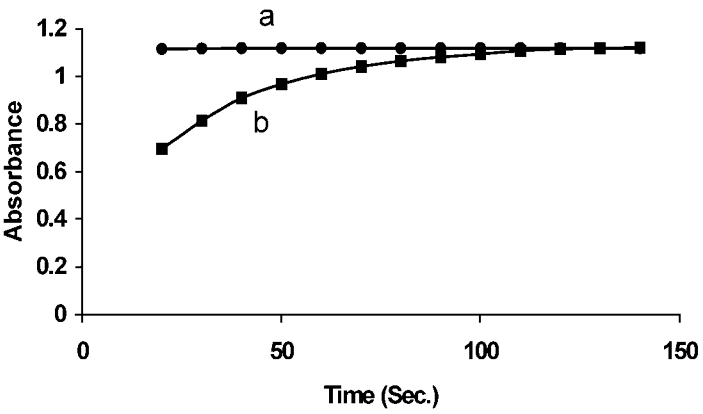

Figure 2. Effect of CTAB on the rate of reaction. (a): in the absence of CTAB; (b): in the presence of CTAB. Conditions as in Fig. 1.

Analytical Figures of Merit

The linear range for cobalt(II) determination was evaluated under the optimum conditions described above over a fixed time of 20–150 s from initiation of the reaction. The calibration graph for cobalt(II) was linear over the concentration of 0.25–12 $\mu g\, mL^{-1}$. The detection limit of the method is 0.2 $\mu g\, mL^{-1}$. A study of the precision and accuracy of the method was made with eight independent experiments and solutions of various concentrations (Table 1). The cobalt(II) concentrations were evaluated from a calibration graph.

Interference Study

The effect of co-existing ionic species on the determination of cobalt was investigated. More than thirty ions were examined for their possible interference in the determination of 5.0 $\mu g\, mL^{-1}$ cobalt under optimum conditions. The tolerance limit was defined as the concentration, which gave an error of 3.0% or less in the determination of 5.0 $\mu g\, mL^{-1}$ cobalt. The results showed that at least 500-fold As(V), Ni^{2+}, Cu^{2+}, Mn^{2+}, Cd^{2+}, Zn^{2+}, Al^{3+}, Bi^{3+}, Ce^{3+}, Te(IV), Se(IV), Se(VI), Pb^{2+}, V(V), Na^{+}, K^{+}, Ca^{2+} and anions $S_2O_3^{2-}$, HSO_3^{-}, SO_4^{2-}, SO_3^{2-}, F^{-}, Cl^{-}, CO_3^{2-}, MoO_4^{2-}, CH_3COO^{-}, NO_3^{-}. IO_3^{-} and NO_2^{-} do not interfere. It is also interesting to note that the presence of iron(II) in cobalt(II) samples did not have any interference on kinetic determination of cobalt(II). The reason is that although upon addition of the sample solution to the vessel containing 1,10-phenanthroline, the red complex of iron(II) and 1,10-phenanthroline forms almost instantaneously, but because we are measuring the rate of production of iron(II) (produced upon the reaction of iron(III) and cobalt(II)), after 20 s from initiation of the reaction, no contribution in the kinetic signal was observed from iron(II) present originally in the sample. Only V(IV) interfered at levels similar to that of cobalt.

Table 1. Results Obtained for Precision and Accuracy

Co(II) Present ($\mu g\, mL^{-1}$)	Co(II) Found ($\mu g\, mL^{-1}$)	RSD% (n = 8)
0.5	0.47	1.4
2.0	1.92	0.6
5.0	4.98	0.8

Table 2. Analysis of Real Samples by the Proposed Method

Alloy	Composition of Synthetic Mixture (μg mL^{-1})	Found Co(II) (μg mL^{-1})	
		Present Method	AAS Method
Cunico 1	Cu(50), Ni(21), Co(29)	28.95	29.10
Permivax	Fe(1.50), Co(1.25), Ni(2.25)	1.22	1.28
Alnico	Al(10), Ni(17), Co(13), Cu(6), Fe(54)	12.85	12.92

Real Sample Analysis

The proposed method was successfully applied to the determination of cobalt in several synthetic samples, the compositions of which have been prepared according to some known alloys.[16] The results for three determinations on each sample are summarized in Table 2 and are compared with those obtained by AAS. The concentration of cobalt obtained by the two methods agrees quite reasonably.

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