

# Effect Of Glycine On Potentiometric Titration Of Cobalt (II) With Potassium Hexacyanoferrate (II)

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**Abstract:** Rapid and precise redox titration of cobalt (II) with potassium hexacyanoferrate (II) in the presence of glycine in alkaline medium is described. The strategy depends on the influence of glycine on the oxidation – reduction potential of cobalt ions in which it forms progressively stable complex with cobalt (III) than with cobalt (II) and the reaction has been studied by potentiometry as a function of pH and the concentration of glycine and cobalt. During the investigation it was found that the compound of divalent cobalt is stable at pH 7.0-10.0 in the presence of glycine, while the titration was impossible without glycine. The exactness and precision of the strategy was evaluated by the use of lack-of-fit test and other statistical techniques.

**Index Terms:** Cobalt (II), Glycine, Potassium Ferricyanide, Potentiometry, Redox Reactions.

## 1 INTRODUCTION

Cobalt is a transition component of high industrial significance in different field, for example, such as alloying, dyeing and steel making [1]. It acts as central metal cofactor in the vitamin B<sub>12</sub> complex as an essential micronutrient [2]. Cobalt is utilized in the creation of superior alloys [3,4], and for dental process as a substitute for nickel [5]. It finds application in the preparation of high-speed tools for improving heat and wear resistance [6]. The determination of cobalt using ferricyanide reaction was reported in recent studies by various techniques [7-11]. The increasing importance of cobalt usage in different places makes prime importance for determination of cobalt complexes. Determination of cobalt in an ammoniacal medium with Potassium ferricyanide as an oxidizing agent was carried out by Tomicek and Freiburger [12] and Dickens and Massen [13]. Within the sight of ammonia, a back titration is associated with which a solution of the sample is added to a standard ammoniacal solution of ferricyanide, and the overabundance being back titrated with a standard cobalt solution. The potentiometric titration of cobalt with potassium hexacyanoferrate was studied by many authors [14-15]. Lingane [16] investigated the potentiometric titration without other metals. Kopanica and Dolezal [17] put forward by using amino acids in the cobalt determination with ferricyanide. The use of ammonia and mixture of phenylalanine or alanine was given by Agasyan and Khakimova [18]. Quantitative oxidation of cobalt in the form of glycine complex with potassium hexacyanoferrate (II) has been studied by potentiometry as an effect of pH, concentration of glycine and concentration of cobalt. It was established in the course of work that the compound of divalent cobalt with glycine is stable with pH of 7.0-10.0, and that it is possible to oxidize it quantitatively along with manganese.

## 2 MATERIALS AND METHODS

### 2.1 Reagents

Every single chemical reagent has been set up from analytical grade and deionised double distilled water has been utilized to get solutions.

### 2.2 Cobalt (II) Sulphate Solution (0.1M)

It was prepared by dissolving 7.027g of cobalt sulphate in 250 ml of water and was standardized by EDTA method [19].

### 2.3 Potassium Ferricyanide Solution (0.1M)

A ferricyanide stock solution 0.1M has been made by dissolving 8.231g in distilled water and was standardized by sodium thiosulphate solution [19].

### 2.4 Glycine and Potassium Hydroxide Solution

A glycine (2.0 M) and potassium hydroxide (5.0 M) has been made by dissolving appropriate amount in distilled water.

### 2.5. Equipment

Digital pH meter (Elico, Model L1-120) measuring at a ambient temperature of 25°C with a precision of ±1 mv was used for entire titration analysis. The experimental set up consists of a titration cell (100 ml), mini burette, and a magnetic stirrer. The pH meter was calibrated by using standard buffer solutions.

### 2.6. Experimental Procedure

To a 100.0 mL titration cell, required amount of cobalt (II) sulphate solution was mixed with 20.0 mL of glycine solution (2.0 M) followed by 1.0-5.0 mL of 5.0 M KOH solution (pH 9.0) and diluted with double distilled water to 50.0 mL. Titration was carried out by adding standardized potassium ferricyanide in equal increments with constant stirring. The redox reaction might be taken as finished when the potential changed inside ± 2 mV min<sup>-1</sup> for every expansion. Potential measurements were estimations were trailed by utilizing indicator electrode (platinum) and a reference electrode (saturated calomel electrode). Six replicate titrations for various amount of cobalt were performed to establish the correctness of measurements. Interference study was performed to check the possible interference.

### 2.7. Statistical analysis

Systematic error in a newly developed method was also detected by applying linear regression analysis by plotting the

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amount taken on X-axis and the amount found on Y-axis. Use of the recently created technique was approved by comparing with standard method and assessment of the statistical results was trailed by application of F-test and student's t-test. Statistical examination of data was performed using programs written in BASIC.

### 3 RESULTS AND DISCUSSION

The direct titration of cobalt with potassium ferricyanide can be represented as,



The electrode potential of Cobalt (III)/ Cobalt (II) couple i.e ( $E_{\text{Co}}^0$  is 1.81 V) and that of the ferricyanide/ferrocyanide couple

is  $E_{(\text{ferri/ferrocyanide})}^0$  (0.36V). The calculated value of equilibrium constant for the oxidation – reduction reaction of Cobalt with ferricyanide ( $K_{\text{ferricyanide-cobalt}}$ ) is found to be  $10^{-24.75}$ . Thus direct titration is not possible.

If glycine forms complexes with cobalt (III) and cobalt (II), the redox potential of the Co(III)/Co(II) system can be composed as,

$$E'_{\text{Co}} = E_{\text{Co}}^0 + 0.059 \log \frac{\alpha_{\text{Co(II)(glycine)}}}{\alpha_{\text{Co(III)(glycine)}}} + 0.059 \log \frac{C_{\text{Co(III)}}}{C_{\text{Co(II)}}} \quad (3.20)$$

where  $\alpha$  denotes the reaction coefficient (side reaction) taking into consideration of the arrangement of cobalt (III) and cobalt (II) complex with glycine,  $C_{\text{Co(III)}}$  and  $C_{\text{Co(II)}}$  are the all out concentration of cobalt (III) and cobalt (II) respectively. The development of the cobalt glycine complex  $\text{CoGly}_3^{2-}$  is described by the high stability constant estimation of  $\log \beta_3 = 10.76$  [20]. The high stability of glycine complex with cobalt (III) than with cobalt (II) makes the direct titration of cobalt (II) with potassium hexacyanoferrate (II) possible, which is beyond the realm of imagination generally.

#### 3.1. Effect of pH

So as to fix an ideal pH range for the redox titration of 3.53 mg of cobalt (II) with potassium hexacyanoferrate (II) within the sight of 2.0 M glycine, the titrations were done at pH from 8.0-10.0 using platinum electrode and saturated calomel electrode. The required pH of the solution was maintained using 5.0 M KOH solution. The influence of the potassium hydroxide concentration on the reaction course was examined and found that reproducible results were obtained using 3.0-5.0 M KOH solution. 5.0 M KOH solutions were selected along with 2.0 M glycine because with the addition of few ml, the required pH can be maintained in the titration cell. Oxidation of cobalt (II) with potassium hexacyanoferrate (II) in the presence of 2.0 M glycine results with the development of pink colour cobalt (III)-glycine complex. The outcomes are examined in Fig. 1.0. A greatest potential difference of 34 mV was gotten at pH 9.0. The potentials were promptly settled in all cases in the immediate neighborhood of the titration end point within  $\pm 2$  mV. At pH values greater than 11.0, it is not possible to locate the equivalence point.

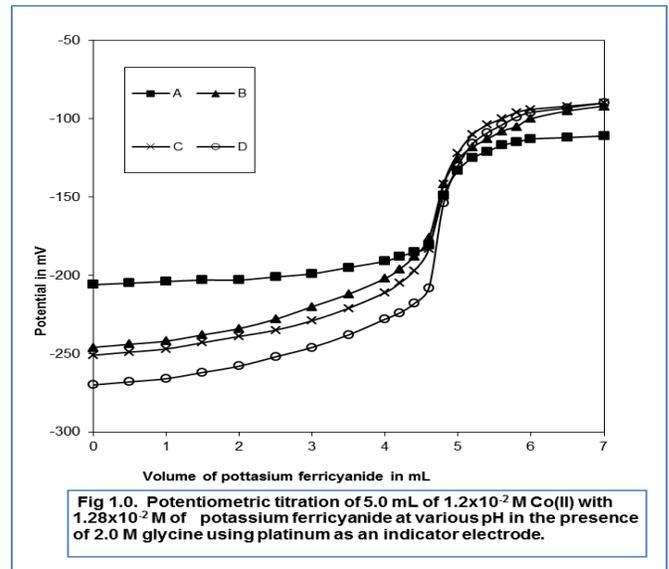


Fig 1.0. Potentiometric titration of 5.0 mL of  $1.2 \times 10^{-2}$  M Co(II) with  $1.28 \times 10^{-2}$  M of potassium ferricyanide at various pH in the presence of 2.0 M glycine using platinum as an indicator electrode.

#### 3.2. Effect of Concentration of Glycine

The effect of glycine on the redox titration of 3.53 mg of cobalt (II) with potassium hexacyanoferrate (II) at pH 9.0 was examined in the entire range 0.50-3.0 M. On increasing the concentration of glycine, the potential jump observed near the equivalence point also increases linearly. At more than 0.50 M glycine concentration, sufficient potential break was observed; when the glycine concentration was 2.0 M the potential changes by 30-40 mV on addition of 0.2 mL of ferricyanide solution. The greatest potential jump of 35 mV was seen at the proportionality point with the glycine concentration of 2.0 M. The results are discussed in Fig. 1.1. Under the specified conditions (i.e.) pH 9.0 and a glycine concentration of 2.0 M using a volume of 100.0 mL of solution, it is possible to determine 0.26-65.25 mg of cobalt with reasonable accuracy.

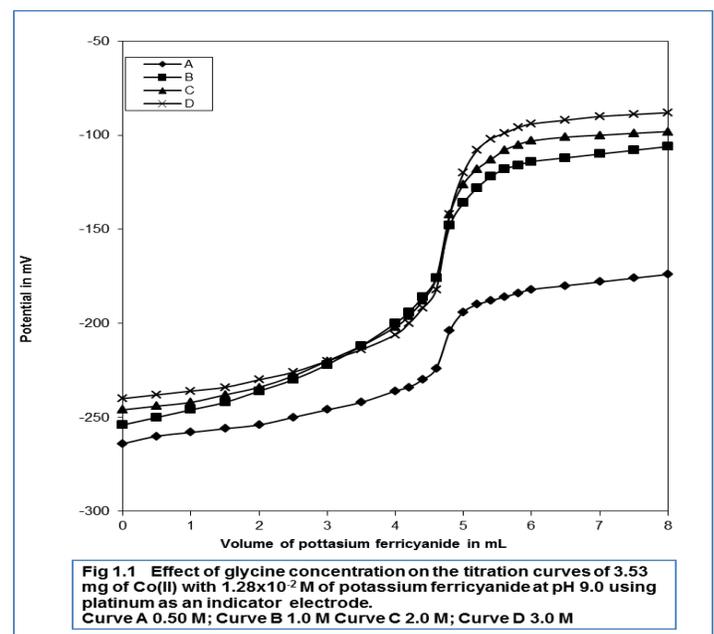
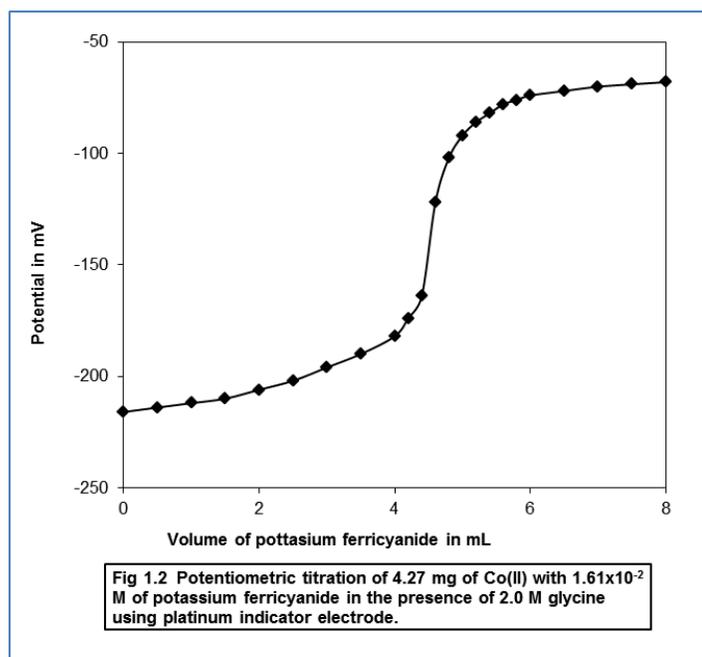


Fig 1.1 Effect of glycine concentration on the titration curves of 3.53 mg of Co(II) with  $1.28 \times 10^{-2}$  M of potassium ferricyanide at pH 9.0 using platinum as an indicator electrode. Curve A 0.50 M; Curve B 1.0 M Curve C 2.0 M; Curve D 3.0 M

#### 3.3. Effect of Other Ions

Chloride, sulfate, nitrate, zinc (II), bismuth (III), molybdenum (VI), nickel (II) and copper (II) in any event, when present in bigger sums they don't meddle. The nearness of iron (III)

together with the chromium (III) doesn't block with the test methodology. At the point when a lot of chromium (III) are available, it is required to permit the development of chromium (III) complexes with citrate or glycine at pH 5.0, after the complex has been framed a hold up of 5-20 min is required, Hydroxides of chromium (III) may be precipitated if proper waiting period is not maintained. Interference of manganese (II) will not happened even when citrate is not used. In smaller amounts vanadium (v) do not interfere but in some cases it does interfere when present with other elements in a combined form. The mechanism of action is not clear yet. Oxidation of cobalt (II) with potassium hexacyanoferrate (II) along with glycine was carried out using platinum electrode vs SCE. Plot of potential against volume of ferricyanide gave S-shaped curves (Fig 1.2). The potential increases linearly before the end point, when all the cobalt (II) has been oxidised by ferricyanide, a sharp increase in potential occurs. The rise in potential at the equivalence point was about 42 mV for platinum electrode vs SCE (for 4.27 mg of cobalt). Adjustment of potential was fast before and after the end point. A holding up time of 1-2 min was required toward the end point.



### 3.4. Precision and Accuracy

To check the exactness and accuracy of the given method six recreate titrations at ten concentrations of cobalt (II) containing 0.26-65.25 mg was performed using platinum electrode against SCE reference electrode. Potentiometric determination of cobalt (II) with potassium hexacyanoferrate (II) along with glycine was possible with reproducible results but a wait of around 1-2 min was required toward the end point. The outcomes acquired are examined in Table 1.00. The general mean recovery for 60 determinations of cobalt (II) was 100.05% and mean standard analytical error were 0.0122. Student's t-value was determined and the observed mean value was found to be 0.86 which was not exactly the basic estimation of critical value of 2.45 at essentialness level of 5% and 5 degrees of freedom. Regression examination and lack-of-fit test were performed for the data. F esteem was determined and was seen to be 0.84 which was not exactly the basic estimation of 2.10 at significance level of 5% and 8,

60 degrees of freedom. This indicated that there is no systematic error in the proposed method.

**Table 1. Potentiometric titration of cobalt (II) with potassium ferricyanide in the presence of glycine**

Amount Taken (mg)	Amount Found (mg)	Mean ( $\bar{x}$ ) $\pm$ Std.Dev	Mean Recovery (%)	Standard Analytical Error	Student's t
0.26	0.26, 0.26, 0.27, 0.25, 0.25, 0.26	0.258 $\pm$ 0.007	99.36	0.0031	0.54
0.55	0.54, 0.53, 0.54, 0.55, 0.55, 0.55	0.543 $\pm$ 0.008	98.79	0.0033	2.00
2.53	2.53, 2.54, 2.55, 2.55, 2.53, 2.54	2.540 $\pm$ 0.009	100.39	0.0036	2.74
4.65	4.65, 4.65, 4.63, 4.67, 4.66, 4.65	4.652 $\pm$ 0.013	100.04	0.0054	0.31
6.52	6.51, 6.52, 6.56, 6.55, 6.52, 6.53	6.532 $\pm$ 0.019	100.18	0.0079	1.47
10.25	10.21, 10.24, 10.28, 10.24, 10.23, 10.29	10.248 $\pm$ 0.031	99.98	0.0125	0.13
22.50	22.52, 22.57, 22.51, 22.56, 22.48, 22.50	22.523 $\pm$ 0.035	100.10	0.0143	1.63
35.32	35.27, 35.31, 35.33, 35.37, 35.34, 35.26	35.307 $\pm$ 0.042	99.98	0.0172	0.39
50.20	50.22, 50.28, 50.20, 50.15, 50.23, 50.16	50.207 $\pm$ 0.048	100.01	0.0196	0.34
65.25	65.22, 65.31, 65.38, 65.14, 65.21, 65.20	65.243 $\pm$ 0.086 Mean...	99.99 100.05	0.0353 0.0122	0.19 0.86

The calculated F-value in lack of fit test was 0.84.

## 4 CONCLUSIONS

The newly developed method is seen as exact, straightforward and precise assurance of cobalt along with glycine. In the presence of glycine as a complexing agent, the redox titration of cobalt (II) with potassium hexacyanoferrate (II) greatly improves the selectivity and sensitivity of the method, which is not possible in the absence of glycine. The strategy can be applied for the assurance of cobalt in ores and steel samples.

## 5. ACKNOWLEDGMENT

This is the work done during my Ph. D research work in the Department of Analytical Chemistry, University of Madras, Chennai, Tamil Nadu, and India.

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