

## EXTRACTION—SPECTROPHOTOMETRIC DETERMINATION OF Co(II) IN THE PRESENCE OF Fe(III).

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(Received March 14, 1981)

Formation of complexes between cobalt and iron and thiocyanate in the presence of hydrochloric acid has been examined. The blue coloured complex of Co(II)—SCN is quantitatively extractable into an organic phase containing tribenzylamine (TBA), (a high molecular weight amine: (H.M.W.A.)), whereas the blood red complex of Fe(III)—SCN formed under the same conditions is only partially extracted. This selective extractability by TBA has made possible the determination of cobalt in presence of iron.

### INTRODUCTION

Alkali thiocyanates have been used as complexing agents for the colorimetric estimation as well as a means of chemical separation of a number of metal ions by a number of workers [1].

Affsprung, and Portraz [2] precipitated thiocyanate complex of cobalt by 'onium' compounds such as tetraphenylarsonium chloride, extracted the complex into chloroform and estimated it spectrophotometrically. None of these methods could however, cut down interference by iron and other related ions.

Separation of iron and cobalt by the known techniques was still a problem. The method described in the present paper is based on the selective extraction of Co(II)—SCN complex from Fe(III)—SCN by tribenzylamine in chloroform. Separation of cobalt from iron is therefore, achieved.

### EXPERIMENTAL

Following reagents were used:

(i) *Standard Cobalt Solution.* 1 g cobalt metal of (100 % purity) supplied by E-Merck was dissolved in a minimum volume of HCl (1:1) and diluted to 1 litre with distilled water. This solution was further diluted with distilled water to get the required concentration.

(ii) *Standard Iron Solution.* 10 g of ferric chloride was dissolved in a few millilitres conc HCL, diluted to 1 litre with distilled water and standardised volumetrically.

(iii) *Tribenzylamine.* 5% (W/V) in chloroform.

(iv) *Potassium Thiocyanate:* 7.5 M potassium thiocyanate in distilled water.

*Formation of CO(II)—SNC Complex and Extraction by Amine.* The blue coloured complex of Co(II)—SCN was formed by adding thiocyanate (iv) into the cobalt solution (i) 5 ml TBA solution (iii) was added to the

coloured solution of cobalt in a separating funnel and shaken for 5 minutes. The two phases were allowed to separate and the blue coloured complex of Co(II)—SCN was quantitatively extracted into the organic phase.

The organic phase was freed of suspended water droplets by filtration and collected into a dried flask. The absorption spectrum of the complex was determined against a blank containing all the reagents, but no cobalt. (The spectrum of cobalt shows the maximum absorption at 620 m $\mu$  as shown in Fig. 2.).

*Calibration, Sensitivity and Stability.* Known concentrations of cobalt were extracted by the foregoing procedure and the absorbance measured at 620 m $\mu$ . The results are shown graphically in Fig. 1. Beer's law was closely obeyed for solutions containing 0.2–2 p.p.m. The optical density of 0.005 corresponds to 1  $\mu$ g of cobalt. The molar absorption coefficient is  $3.4 \times 10^5$ . The blue coloured complex of Co(II)—SCN extracted into organic phase was allowed to stand over night. No change was observed in the optical density. Repeated observations indicated no change for weeks, which therefore, shows the greater stability of the complex.

Similarly known concentrations of Fe(III) were mixed with potassium thiocyanate in presence of HCl and the optical density of the blood red coloured complex of Fe(III)—SCN in the aqueous phase was measured at 480 m $\mu$ . It was noted that the colour intensity fades away after 24 hr and is, therefore, less stable than cobalt.

*Effect of Acid Concentration.* The effect of hydrochloric acid concentration on the overall extraction of the complexes was studied in the range of 0.05 M–0.6M. Maximum colour intensity and efficient extraction was achieved at a concentration of 0.2 M HCl.

*Effect of Thiocyanate Concentration.* The effect of various concentrations of thiocyanate—in the range of 1.0–4.0 M was also studied. Maximum colour intensity of

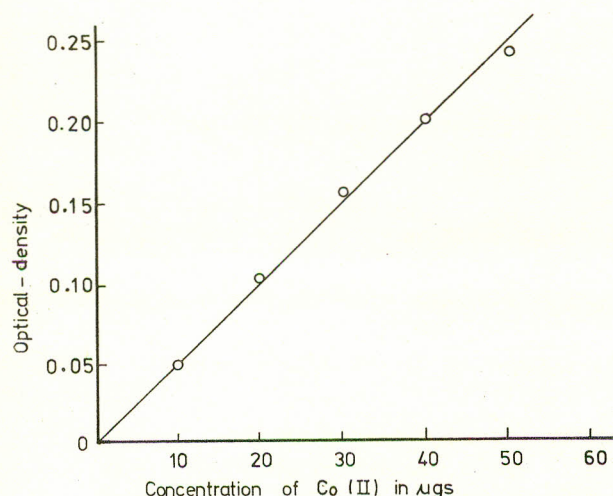


Fig. 1. Standard curve for CO(II)-SCN.

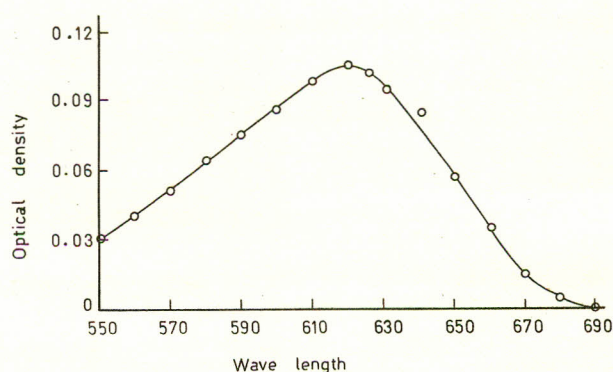


Fig. 2. Absorption curve for CO(II)-SCN after extraction into tribenzylamine.

cobalt was observed at 2.8–3 M thiocyanate concentration.

**Procedure.** 0.5–1 ml of a mixture containing equal amounts of cobalt and iron were taken in a separating funnel and 2 ml of potassium thiocyanate followed by 1 ml of 1 M HCl were added. The whole was diluted to 5 ml with distilled water. 5 ml of TBA solution in chloroform were added and the contents were shaken for 5 min. and the two phases were allowed to separate. The organic phase was filtered to remove suspended particles and absorbance taken at 620 m $\mu$ .

## RESULTS AND DISCUSSION

Results of analyses of unknown mixtures of cobalt and iron are given in Table 1. The estimation of cobalt as Co(II)-SCN and its extraction into TBA seems to depend upon the acid and thiocyanate concentrations. The maximum extraction of cobalt occurs at 0.2 M HCl and 3 M KCNS.

Two types of high molecular weight amines, i.e. tribenzylamine and allamine-336 were used in present studies. It was found that allamine-336 extracted both

Affsprung and his Coworkers[2] extracted cobalt as tetraphenylarsonium cobalt thiocyanate. The absorption spectrum of their studies shows two maxima. Also the standard curve of cobalt, indicated nearly a linear relationship between 30 and 80 % absorbancy, whereas in the present findings the standard curve for cobalt is almost a straight line and the spectrum obtained shows only one peak.

B.E. McClellan and V.M. Benson[3] separated and determined cobalt and iron in chloride system after extraction into high molecular weight amines i.e. trioctylamine and tri-iso-octylamine etc. The extracted 93–94 % of cobalt at the maximum and used inconvenient and time consuming method which involves several steps of stripping and extractions. Whereas, the present method makes 100 % extraction of cobalt and there is no need of repeated stripping. The extraction of cobalt is easy and convenient and the complex is stable for almost 15 days.

Table 1. Analyses of mixtures of cobalt and iron.

S.No.	Cobalt present (u9)	Iron present (u9)	Cobalt found (u9)	Error (u9)
1.	20	20	20	0.1
2.	40	40	39.9	-0.1
3.	60	60	60.0	0.0
4.	80	80	79.0	-0.2
5.	100	100	100	0.0

iron and cobalt quantitatively under the same conditions, whereas TBA extracted 100 % of cobalt and negligible amount of iron as a coloured thiocyanate complex. Also the concentration of iron thiocyanate extracted does not obscure the colour of cobalt complex. Similar observation had previously been made in an earlier publication by one of the present authors in a study on the extraction of Mo(VI)–Sn(II)–CNS system by tribenzylamine[4]. The tribenzylamine in chloroform acts as “liquid anion exchanger” and it is assumed that the coloured complex is anionic in nature and that the liquid anion exchanges occur between the charged complex and the high molecular

weight amine.

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