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SEPARATION-SPECTROPHOTOMETRIC DETERMINATION OF Co(II) AND Mn(II) IN THE THIOCYANATE SYSTEM

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An investigation of complexes formed between Co(II) and Mn(II) and thiocyanate in hydrochloric acid solutions has been carried out, and the extractability of Co(II) by high molecular weight amine (HMWA) in organic solvent and its separation from Mn(II) was examined. The blue complex of Co(II)-SCN is quantitatively extractable into an organic phase containing tribenzylamine (TBA) a high molecular weight amine (HMWA), whereas the coloured complex of Mn(II)-SCN formed under the same conditions gets separated in the aqueous phase. Based on this selective extractability in the tribenzylamine (TBA), a method has been developed for the separation and spectrophotometric determinations of Co(II) and Mn(II). The extractability of the complex by a HMWA suggests that the coloured species is anionic.

INTRODUCTION

The use of high molecular weight amines (HMWA) as liquid anion exchangers" and extractant for anionic complex metal ions has been mainly confined to the separation of specific pairs of Ions[1-4]. An intensive study of many metal thiocyanates in ethyl ether at various NH_4CNS concentrations has been made by R. Bock[5]. More recently advantage has been taken of the use of thiocyanate complexing as a method of chemical separation[6]. Classan and his co-workers[7] extracted Mn(II) from acidified SCN solution by Allamine-336 and aliquat 336 in ph Me and CCl_4. Odashima Tsugi-katsu[8] determined trace amounts of cobalt in the trace manganese nodules using hydrazine derivatives as the extractant. Silver halides were used as trace collectors for chelate complexes and enrichment of trace element from Mn and Mn compounds with succeeding determination of Fe,Co,Ni, Ca etc. by A.A. spectrophotometer[9] whereas Nagoya and Yoshishique separated Co from Mn nodules by chlorination roasting [10]. Ion exchange properties were also used for the separation of cobalt and manganese[11-13]. A number of workers have used chromatographic methods[14-20] for the separation of Co from Mn.

These methods are inconvenient and time consuming as many steps of stripping and eluting are involved, whereas the extraction and separation methods used in the present study are easy and convenient. Moreover 100% of the separation is possible.

The most popular methods of extraction of metals is as the halo-complexes from HCl solution into an organic phase containing amine. The present authors after a study of the extraction of chloro-complexes used high molecular weight amine for the extraction of Co(II)-SCN system for the spectrophotometric determination of cobalt in the presence of iron [21]. In the belief that the species would be more likely to be anionic than as neutral complex, investigations were begun in this laboratory with the aim of using tribenzylamine to extract the species and if possible, use it for the separation and spectrophotometric determination of cobalt and manganese. The investigations were carried out and following the pattern of development and improvement in the method an analytical procedure was developed for the separation of Co(II) and Mn(II) by absorptiometric method. The method is based on the selective extraction of Co(II)-SCN system by tribenzylamine (TBA) in chloroform.

EXPERIMENTAL

Apparatus: Erma Spectrophotometer Model LS-7.

Reagents: Standard cobalt solution: lg of cobalt metal (100% purity) was dissolved in a minimum volume of (1:1) HCl and diluted to one litre. This solution was further diluted to get the required concentration.

Standard Manganese solution: Dissolved 1 g of pure manganese metal in a minimum volume of (1:1) HNO_3 and diluted to 1L with 1% (v/v) HCl. Further dilution was made from this stock solution. Potassium thiocyanate: 1.5M aq. solution. Tribenzylamine (TBA): 5% (w/v) in pure and redistilled chloroform. All other chemicals used were of analar grade.

Formation of Co(II)-SCN and Mn(II)-SCN complexes and the extraction of Co(II)-SCN by amine. The coloured complexes of Co(II)-SCN and Mn(II)-SCN were formed by adding thiocyanate into a solution containing cobalt and manganese in the presence of HCl. 5 ml of tribenzylamine (TBA) solution in organic phase were added to the coloured solution in a separating funnel and shaken for 2 minutes. The two phases were allowed to separate. The blue coloured complex of Co(II)-SCN was quantitatively extracted into organic phase and the reddish coloured complex of Mn(II)-SCN formed under the same conditions remained in the aqueous phase.

The organic phase was collected in a dried flask after passing it through a filter paper to remove the suspended water droplets. The absorption spectrum was determined with respect to a blank containing all the reagents but no cobalt and extracted in the same way. The spectrum shows the maximum absorption 620 mμ (Fig.1.) The absorption spectrum of Mn(II)-SCN in the aqueous phase was also measured against a blank using distilled water. The spectrum shows the maximum absorption at 480 mμ (Fig.2).

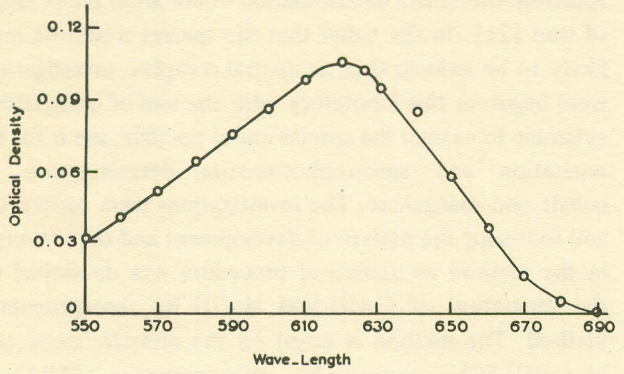

Fig. 1. Absorption curve of Co(II)-SCN after extraction into tribenzylamine.

Calibration, Sensitivity and Stability. A mixture of known concentrations of cobalt and manganese was taken. Co(II) and Mn(II) were estimated by the foregoing procedure. Their absorbances were measured at 620 mμ and 480 mμ respectively. These results are shown graphically in Fig.3. Beer's Law was closely obeyed for solutions containing 0.2-2 ppm of cobalt and manganese. The optical density of 0.005 corresponds to 1 μg of cobalt and 0.01 corresponds to 1 μg of manganese. The molar absorption coefficients of cobalt and manganese are 3.4×10^5 and 3.6×10^5 respectively. The blue coloured complex of Co(II)-SCN extracted into the organic phase was allowed to stand fortnightly but no change was observed in the optical density, which, therefore, shows the greater stability of the complex. The coloured complex of Mn(II)-SCN is stable only up to 24-hours. At the end of this period there is a gradual fading and lowering of intensity of colour.

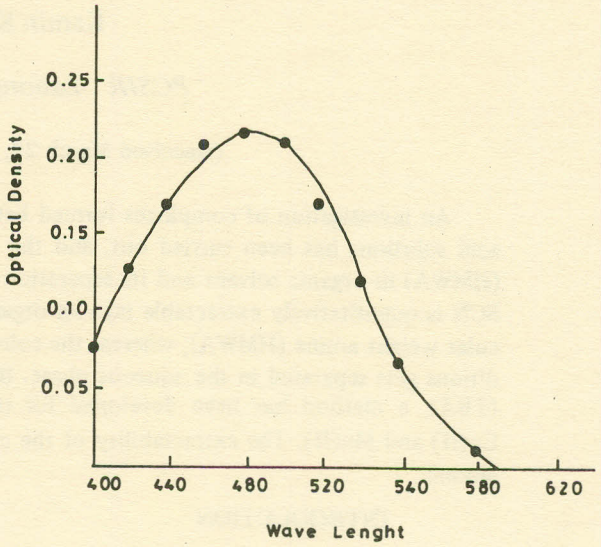

Fig. 2. Absorption curve of Mn(II)-SCN in aqueous phase.

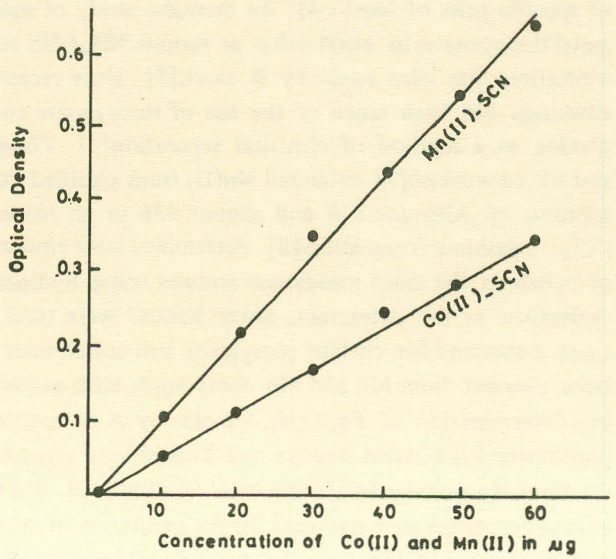

Fig. 3. Standard curve of Co(II)-SCN and Mn(II)-SCN.

Effect of Solvents and Extractants (HMWA). Two types of solvents i.e. benzene and chloroform and high molecular weight amines i.e. TBA and Allamine-336 were used to study their effects on the overall extraction and separation of cobalt and manganese. When benzene solution of TBA or Allamine-336 was used the mixture of cobalt and manganese became turbid and precipitated after shaking. A

chloroform solution of tribenzylamine (TBA) when used as extractant, a very clear solution was obtained, and 100% cobalt and a negligible amount of manganese were extracted. When Allamine-336 in chloroform solution was used, it was found that both cobalt and manganese were quantitatively extracted under the same conditions. This was in conformation with our earlier work in extraction and separation of metal anionic complex species[21].

Effect of Acid Concentration. The effect of hydrochloric acid concentration on the overall extraction was studied in the range of 0.1M – 0.35M. It was noted that 0.2M HCl is the most suitable concentration for maximum colour intensity and effecient extraction and separation. The results are shown in Fig.4.

Effect of Thiocyanate Concentration. The effect of thiocyanate concentration on the overall extraction and separation was also studied in the range of 0.1M-0.5M KCNS. Thiocyanate 0.3 – 0.35M concentration was found to be most suitable for maximum colour intensity and efficient extraction and separation. The results are shown in Fig. 5.

Procedure. Take 0.5 – 1.0 ml. of the mixture containing an equal amount of cobalt and manganese in a separating funnel and add 1 ml of thiocyanate followed by 1 ml of 1M HCl and dilute to 5 ml with distilled water. Add 5 ml tribenzylamine (TBA) solution in chloroform and shake the contents for 2 minutes. Allow the two phases to separate, filter the organic phase through a small filter paper to remove the suspended water droplets and measure the absorbance at 620 mμ. The manganese remained in the aqueous phase was also determined spectrophotometrically at 480 mμ.

As a final check one of us analysed a number of unknown mixtures for cobalt and manganese by the foregoing procedure. The results are shown as follows:

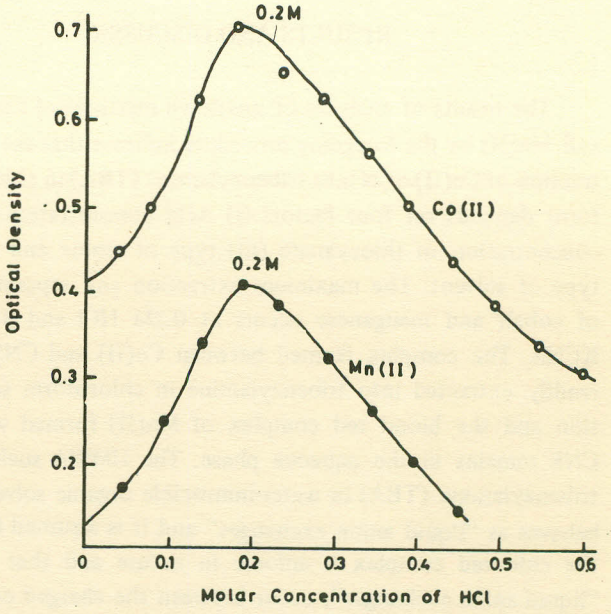

Fig. 4. Effect of HCl concentration on extraction and separation of Co(II) and Mn (II).

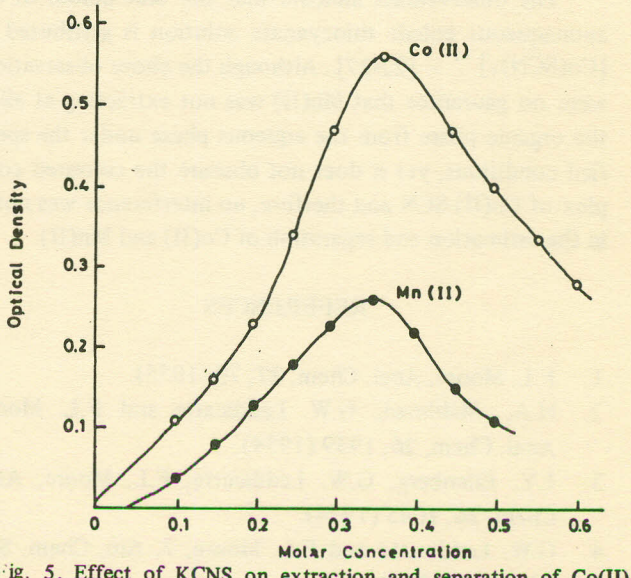

Fig. 5. Effect of KCNS on extraction and separation of Co(II) and Mn (II).

Analyses of unknown mixtures

S. No.	Cobalt		Error	Manganese		Error
	Present (μg)	Found (μg)	(μg)	Present (μg)	Found (μg)	(μg)
1.	10	10	0.00	10	10	0.00
2.	20	20	0.00	20	20	0.00
3.	30	29.9	–0.10	30	30.1	+0.10
4.	40	39.85	–0.15	40	40.2	+0.20
5.	50	50.10	+0.10	50	49.9	–0.10
6.	60	60.00	0.00	60	60.0	0.00
7.	80	79.50	–0.50	80	80.4	+0.40
8.	100	100.10	+0.10	100	99.95	–0.05

RESULTS AND DISCUSSION

The results of analyses of unknown mixtures of Co(II) and Mn(II) by the foregoing procedure indicate that the extraction of Co(II)-SCN into tribenzylamine (TBA) in chloroform depends on four factors (i) Acid concentration (ii) concentration of thiocyanate (iii) type of amine and (iv) type of solvent. The maximum extraction and separation of cobalt and manganese occurs at 0.2M HCl and 3.0M KCNS. The complex formed between Co(II) and CNS is readily extracted into tribenzylamine in chloroform solution and the blood red complex of Mn(II) formed with CNS remains in the aqueous phase. The HMWA such as tribenzylamine (TBA) in water-immiscible organic solvents behaves as "liquid anion exchanges" 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.

The observations indicate that the blue colour of the anonaqueous cobalt thiocyanate solution is attributed to $[Co(SCN)_4]^{-2}$ – [22-27]. Although the above observations were no gaurantee that Mn(II) was not extracting at all in the organic phase from the aqueous phase under the specified conditions, yet it does not obscure the coloured complex of Co(II)-SCN and therfore, no interference was noted in the estimation and separation of Co(II) and Mn(II).

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