Extractive spectrophotometric determination of cobalt with 5, 7-dichloroquinolin-8-ol and rhodamine 6 G

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A simple and sensitive method for extractive spectrophotometric determination of trace amounts of cobalt has been described. The method is based on the extraction of ternary ion-association complex viz., cobalt–5,7-dichloroquinolin-8-ol–rhodamine 6G into toluene. The colour reaction is sensitive (ε = 4.42 x 10^4 mol^(-1) cm^(-1)) and is employed for the determination of 0.7 to 7.0 μg of cobalt in 100 ml of aqueous phase. The method is precise and has been applied for the determination of trace amounts of cobalt in high purity ammonium sulphate samples.

Several reagents are described for the determination of cobalt including quinoline-8-ol and dithizone have been used for the determination of cobalt. But most of these have low sensitivity and selectivity. The reaction involving ternary complex formation provide good sensitivity and selectivity and a few reactions based on this system have been developed. Of these, the reactions based on (i) mixed ligand complexes, thiocyanate - ephedrin, (ii) surfactant sensitized systems 4,5-dibromomphenylfluorone-CPB and (iii) ion association systems and nitroso-R-salt-crystal violet offer better sensitivity compared to other similar reactions. We had reported the use of 5,7-dichloroquinoline-8-ol as one of the ligands which forms a binary amionic complex and subsequently by its association with rhodamine 6G could lead to sensitive and selective determination of neodymium and vanadium(IV). In continuation of this study, our investigations revealed that cobalt forms a ternary complex with 5,7-dichloroquinoline-8-ol and rhodamine 6 G which can be selectively extracted into toluene. This reaction offers good sensitivity (ε = 4.42 x 10^4 mol^(-1) cm^(-1)) for the determination of cobalt in the concentration range 0.007-0.07 ppm. The method has been applied for the determination of cobalt in high purity (NH₄)₂SO₄ samples.

Experimental

The spectrophotometric measurements were made on a Hitachi 220 microprocessor controlled double beam spectrophotometer. An ELICO digital pH meter. Model L1120 was used for the pH measurement. All the chemicals used were of AR grade. Cobalt solution (1000 ppm) was prepared by dissolving 0.2980 g of CoSO₄·7H₂O in 250 ml of doubly distilled water. The exact concentration was determined titrimetrically and diluted to lower concentrations as desired. The 5,7-dichloroquinoline-8-ol (0.05% m/v) was prepared by dissolving 0.025 g of the sample in methanol (50 ml). Rhodamine 6 G solution (0.01% m/v) was prepared by dissolving rhodamine6G (0.025 g) in water and diluting to 250 ml. The buffer solution (0.1 M) was prepared by dissolving ammonium acetate (1.93 g) in water and the solution was diluted to 250 ml.

Procedure

To an aliquot of cobalt solution, in a 100 ml volumetric flask (0.7-7.0 μg in 100 ml), 5 ml of 5,7-dichloroquinoline-8-ol, 20 ml of ammonium acetate buffer (pH 7) and 25 ml of rhodamine 6G were added and diluted up to the mark with water. The solution was transferred to a 125 ml separating funnel and shaken thoroughly for five min. with 10 ml of toluene. The organic layer was collected and centrifuged and the absorbance of the toluene layer was measured at 540 nm against the reagent blank.

Determination of cobalt in (NH₄)₂SO₄ samples

Suitable aliquots of 1% (NH₄)₂SO₄ solutions were subjected to the analysis using the procedure described above for the determination of cobalt.

Results and discussion

The absorption spectrum of the toluene extract containing the orange coloured Co(II)-5, 7-dichloroquinoline 8-ol-rhodamine 6G complex was recorded for 0.2 and 4 μg of cobalt(II) against water. The ternary ion-association complex showed absorption maximum at 540 nm.

The effect of pH on the extraction of 4 μg of cobalt(II) was studied in the pH range 5.0 - 9.0. At both higher and lower pH values, the extraction was incomplete. Maximum absorbance was recorded in the pH range 6.0 - 8.0. Hence all further extractions were carried out at pH 7.0 ± 1.0.

The optimum concentrations of 5,7-dichloroquinoline-8-ol and rhodamine 6G necessary for the formation of ternary ion-association complex were found by varying the concentrations from 0.1 to 2.0 ml of 0.05% 5,7-dichloroquinoline-8-ol solution in methanol and 1 to 4 ml of 0.01% rhodamine 6G. It was found that the maximum and constant absorbance was obtained in the range of 0.5 to 2 ml of 0.05% solution of 5,7-dichloroquinoline-8-ol and 2 to 4 ml of 0.01% rhodamine 6G present in a total volume of 10 ml. Hence, 0.5 ml of 0.05% solution of 5,7-dichloroquinoline-8-ol and 2.5 ml of 0.01% rhodamine 6G were used for further studies.
Various organic solvents were examined for the extraction of the complex. The ternary ion-association complex was found to extract completely into toluene and xylene, partially in benzene, cyclohexane, cyclopentane and diethyl ether and none in chloroform and n-butanol, hence toluene was chosen for all subsequent experiments. Further, it was found that on mixing 25,50 and 100 ml of aqueous phase with 10 ml of toluene there was no change in absorbance of toluene extract. Therefore, a volume of 100 ml of aqueous phase volume was chosen for further investigations. The order of addition of reagents was found to be not critical. Further, it was found that on shaking 100 ml of the aqueous phase with 10 ml of toluene for time periods ranging from 4 to 10 min. resulted in constant and maximum absorbance of the toluene extract and hence 5 min of equilibration time was chosen.

The ratio of cobalt to rhodamine 6G and 5,7-dichloroquinoline-8-ol in the complex was established by mole ratio, continuous variation and equilibrium shift methods. The results indicated that the ratio of cobalt to rhodamine 6G was 1:2 and that of cobalt to 5,7-dichloroquinoline-8-ol was 1:4. From these studies, it was concluded that the ion-pair formed in the reaction has the formula $R_1[Co(5,7-dichloroquinoline-8-ol)]$ where $R$ represents the rhodamine 6G cation.

Using optimal reaction conditions established above, a linear calibration graph was obtained by plotting the absorbances measured at 540 nm in the concentration range 0 to 7 $\mu$g of cobalt present in 100 ml of aqueous phase. The detection limit corresponding to a SNR value of 2 was found to be 0.4 $\mu$g of cobalt present in 100 ml of the aqueous phase. The molar absorptivity coefficient and Sandell sensitivity were calculated and found to be $4.42 \times 10^3$ l mol$^{-1}$ cm$^{-1}$ and 0.133 ng/cm$^2$ respectively. The proposed method showed good precision as the coefficient of variation for 10 successive determinations of 0.04 ppm of cobalt was calculated to be 4.68%.

**Effect of foreign ions**

The interfering effect of various cations and anions in the determination of 4 $\mu$g of cobalt was investigated. It was found that 1 mg amounts of Ba$^2+$,Ca$^{2+}$,Sr$^{2+}$,Mg$^{2+}$, Cd$^{2+}$,Hg$^{2+}$,Pb$^{2+}$, Pd$^{2+}$,Sb$^{3+}$,Te$^{4+}$,Br$^{-}$,Cl$^{-}$,NO$_3^-$,SCN$^-$,S$^{2-}$,SO$_4^{2-}$,MoO$_4^{2-}$ and VO$_4^{3-}$ and 0.01 mg amounts of Mn$^{2+}$, Al$^{3+}$, As$^{3+}$, Th$^{4+}$ and Cr$_2$O$_7^{2-}$ did not interfere in the determination of 4 $\mu$g of cobalt.

The addition of 2 ml of 5% thiourea was found to eliminate the interference from 1 mg amounts of Bi$^{3+}$. Similarly, the addition of 2 ml of 5% ascorbic acid eliminates the interference due to 1 mg of Cu$^{2+}$. The interference due to 1 mg of Cr$^{2+}$ was overcome by adding a mixture of 2 ml each of 5% thiourea and 5% ascorbic acid. However, Zn$^{2+}$ and Ni$^{2+}$ were found to interfere and have to be separated prior to the determination by the proposed method.

**Analysis of high purity (NH$_4$)$_2$SO$_4$ samples**

1% solution of (NH$_4$)$_2$SO$_4$ sample was analysed by the proposed method as described in experimental section. The results are shown in Table 1 from which it can be seen that the recoveries were satisfactory. Further, the results were compared with those obtained by standard atomic absorption spectrophotometric method (Table 1). It is clear from the table that the proposed method can reliably be used for the determination of cobalt in high purity ammonium sulphate samples.

**References**