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Spectrophotometric Determination of Cobalt(II) Using a Sulphur, Nitrogen and Oxygen Donor Ligand

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A simple sensitive spectrophotometric method is proposed for the determination of cobalt(II) using 4-salicylideneamino-3-mercapto-6-methyl-1,2,4-triazine(4*H*)-5-one as a chromogenic reagent. Accurate and reproducible results were obtained upto 32 ppm of Co(II). The average value of molar absorptivity and Sandell's sensitivity were computed and are 4.612×10^2 L mol^{-1} cm^{-1} and 5.5×10^{-3} μg cm^{-2}, respectively. The composition of the complex was studied by Job's method of continuous variation and mole ratio method and is found to be of ML_2 type. Interference of various cations and anions were also studied.

Key Words: Spectrophotometry, Cobalt determination, Sulphur, Nitrogen, Oxygen donor ligand, Sandell's sensitivity.

INTRODUCTION

Absorption spectrophotometry in the ultraviolet and visible region is mainly used for the quantitative analysis of many metal ions. The method is remarkable for its versatility, sensitivity and precision. The spectrophotometry of micro amounts of cobalt has recently attracted much attention owing to environmental concerns. Various spectrophotometric methods for the determination of cobalt using sulfosalicylic acid[1], phenanthraquinone monothiosemicarbazone[2], 2-diethylamino-5-nitroso-1,4,5,6-tetrahydropyrimidine-4,6-dione[3], 2,2,1-dipyridyl-2-pyridyl hydrazine[4], 1,2-diamino cyclohexane tetra acetic acid[5], 1-nitroso-2-naphthol[6], 5-[-O-carbophenyl-azo]2,4-dihydroxy benzoic acid[7], 4-benzyl piperidine dithiocarbamate[8], pyridoxal 3-phenyl-3-thiosemicarbazone[9], Cyanex 23[10], 2-[1-(2-hydroxy-5-sulfophenyl)-3-phenyl-5-formazano]benzoic acid mono sodium salt[11], nitroso R salt[12], 2-hydroxy-3-methoxy benzaldehyde thiosemicarbazene[13] *etc.*, have already been reported.

A highly sensitive chromogenic reagent, 4-salicylideneamino-3-mercapto-6-methyl-1,2,4-triazine(4*H*)-5-one [SMMT] has been synthesized and used to determine trace amounts of cobalt by spectrophotometry. 4-Salicylideneamino-3-mercapto-6-methyl-1,2,4-triazine(4*H*)-5-one reacted instantaneously with cobalt to form a light yellow coloured 1:2 complex in a buffer solution of pH 4. The colour of the system was stable for 24 h. Accurate and reproducible results were obtained upto 32 ppm of Co(II). The average value of molar absorptivity and Sandell's sensitivity were computed and are 4.612×10^2 L mol^{-1} cm^{-1} and 5.5×10^{-3}

μg cm^{-2}, respectively. The composition of the complex was studied by Job's method of continuous variation and mole ratio method and is found to be of ML_2 type. A systematic study of interfering ions in the determination of the composition of cobalt(II) was also made.

EXPERIMENTAL

For the pH measurement Elico pH meter was employed. Beckman Du-6 spectrophotometer was used with 10 mm quartz cell for the absorbance and transmittance measurement.

All chemicals used were of AR grade and all solutions were prepared in double distilled water.

A stock solution of cobalt(II) was prepared by dissolving $Co(NO_3)_2.6H_2O$ in distilled water and standardized using standard methods[14]. Working solutions were prepared by suitable and accurate dilutions of the stock solution.

The reagent 4-salicylideneamino-3-mercapto-6-methyl-1,2,4-triazine(4*H*)-5-one was prepared by the reported procedure[15]. Doubly recrystallized reagent was dissolved in alcohol to prepare 0.1 % reagent solution.

Buffer solutions: Buffer solutions of suitable pH were prepared by mixing KCl, HCl, NaOH, Potassium hydrogen phthalate, Potassium hydrogen phosphate, borax, $NaHCO_3$ in proper proportions[16].

General procedure: An aliquot of the sample solution containing 8-32 ppm of Co(II) was transferred quantitatively into a 25 mL standard flask. Excess of 0.1 % alcoholic solution of 4-salicylideneamino-3-mercapto-6-methyl-1,2,4-triazine(4*H*)-5-one was added to the flask and made up to mark using buffer solution of pH 4. The solution was mixed well and the absorbance of the solution was measured at 400 nm, using 10 mm matched cells against the reagent blank.

RESULTS AND DISCUSSION

Absorption spectra: The absorption spectra of cobalt(II)-SMMT complex was studied for a wavelength range from 350 to 550 nm and shown in Fig. 1. The coloured Co(II)-SMMT complex had a maximum absorption at 400 nm and at this wavelength the absorbance of the reagent is very small and hence negligible. The complex formation reaction between Co(II) and the reagent SMMT was found to be fast and the maximum colour was developed instantaneously at room temperature.

In aqueous medium at a pH of 4, cobalt(II) forms a light yellow coloured complex with SMMT reagent. The colour of the complex was stable for at least 24 h and there was no considerable change in the absorption value.

Composition of the complex : The composition of Co(II)-SMMT complex was studied using mole ratio method[17] and Job's method of continuous variation[18]. In mole ratio method (Fig. 2) a break was observed when the Co(II)-SMMT ratio was 1:2, indicating a ML_2 type complex formation. The plot of Job's method (Fig. 3) also confirms the formation of a ML_2 type composition for the complex.

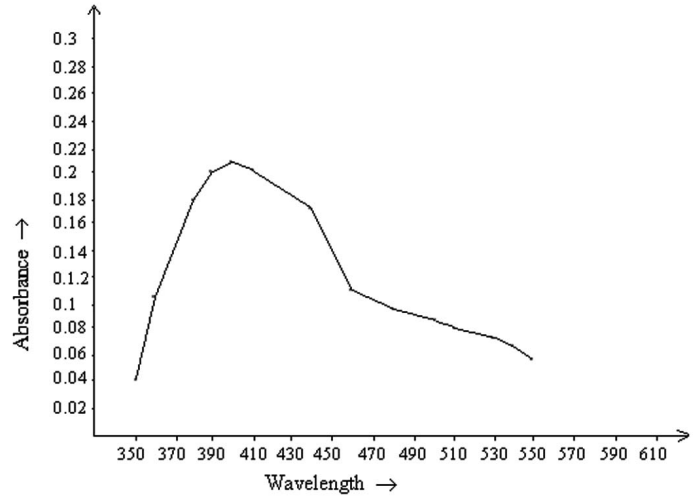

Fig. 1. Absorption spectrum for Co(II)-SMMT system

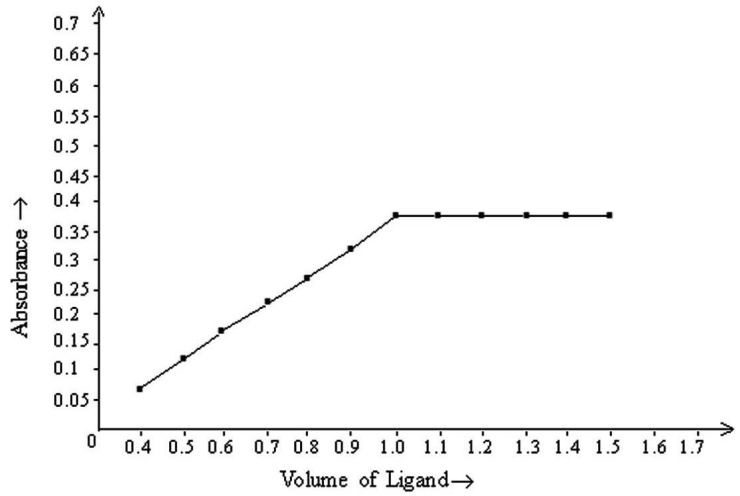

Fig. 2. Mole-ratio graph for Co(II)-SMMT system

Effect of pH: A series of buffer solutions of pH ranging from 1 to 13 were prepared[16] and using these buffer solutions the variation of absorbance of Co(II)-SMMT complex was studied. It was observed that the absorbance value was maximum and constant for the coloured complex at a pH of 4. Hence for all subsequent studies, the pH was maintained at the optimum level of 4.

Effect of metal concentration: The effect of metal concentration on the intensity of the colour development was investigated by treating the cobalt(II) solution with various amounts of the reagent. When 0.5 mL of 0.1 % solution of SMMT was added to 20 ppm of Co(II) solution, maximum and constant absorbance was observed.

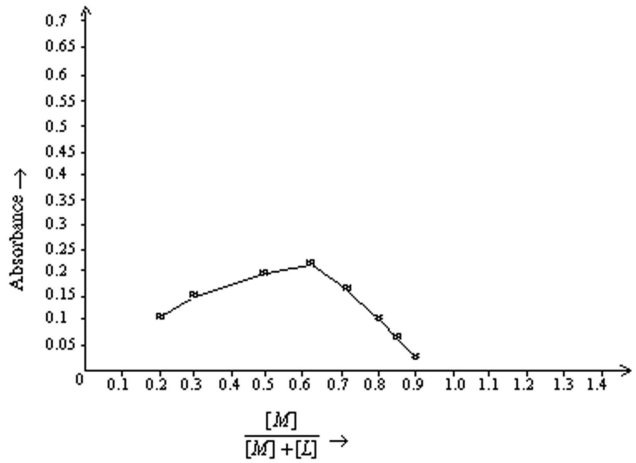

Fig. 3. Continous-variation graph for Co(II)-SMMT system

Beer's law and optimum range: The adherence of the Co(II)-SMMT system to the Beer's law was studied by measuring the absorbance values of solutions of varying Co(II) concentration. A graph was drawn by plotting absorbance against concentration of metal ion. A straight line graph was obtained which passes through the origin at zero ppm concentration. From the plot, it could be noted that at 400 nm the Beer's law was valid upto 32 ppm of Co(II) (Fig. 4).

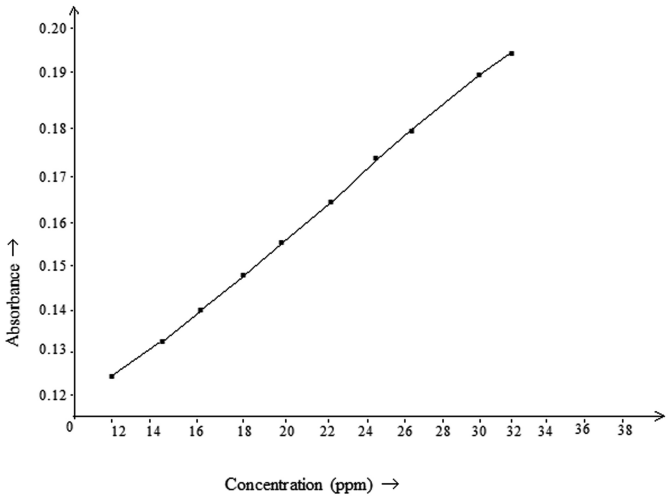

Fig. 4. Verification of Beer's Law for Cobalt(II)-SMMT system

The optimum concentration range for maximum precision was deduced from Ringbom's plot[19]. The percentage transmittance was plotted against the logarithm of metal concentration. The linear portion of the curve indicates that the range was 12-28 ppm of Co(II) (Fig. 5).

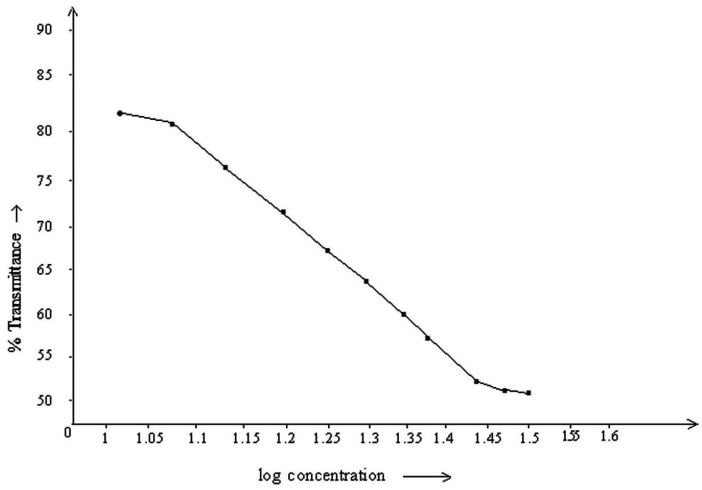

Fig. 5. Ringbom's plot for Co(II)-SMMT system

Molar absorptivity and sensitivity: By measuring the absorbance of solutions at different concentration levels of cobalt(II), the molar absorptivity was calculated. The mean value was found to be 4.612×10^2 L mol^{-1} cm^{-1}. The Sandell's sensitivity[20] was calculated and was found to be 5.5×10^{-3} μg/cm^2.

Effect of foreign ions: A systematic study of interfering ions in the determination of cobalt(II) was made and summarized in the Table-1. The studies clearly showed that almost all anions did not provide any interference in the determination. Cations like Zn(II), Cu(II), Ce(IV) and Ni(II) offered serious interference.

TABLE-1
EFFECT OF FOREIGN IONS ON ABSORBANCE

Foreign	Absorbance	Foreign	Absorbance
Co(II)	0.230	V(V)	0.280
Fe(II)	0.210	Ce(IV)	0.170
Zr(IV)	0.230	W(VI)	0.196
Ca(II)	0.230	Ni(II)	0.198
Na(I)	0.230	Cu(II)	0.280
K(I)	0.230	Mg(II)	0.240
Zn(II)	0.250	Mo(IV)	0.220
Mn(II)	0.200	–	–

Conclusion

(i) The proposed reagent, 4-salicylideneamino-3-mercapto-6-methyl-1,2,4-triazine(4*H*)-5-one (SMMT) develops a stable colour with cobalt(II) instantaneously at room temperature.

(ii) The method provides a rapid, simple and accurate procedure for the spectrophotometric determination of Co(II) in ppm levels.

(iii) The reagent has the advantages of high sensitivity, selectivity, wide optimum pH range and low absorbance of the reagent blank.

(iv) The sensitivity and the molar absorptivity of the method is comparable to the most of the methods reported.

(v) The method neither needs heating for the complete colour development nor extraction into any organic phase.

(vi) The proposed reagent could be synthesized easily and is stable at room temperature.

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