

## Spectrophotometric Determination of Cobalt(II) with Phenanthrenequinonemonosemicarbazone

H.C. RAI\*, SHIV RANJAN KUMAR† and K.B. SINGH†  
Department of Chemistry, L.S. College, Muzaffarpur-842 001, India  
E-mail: hcrail\_chem@yahoo.co.in

When phenanthrenequinonemonosemicarbazone reacts with cobalt(II), a red precipitate is formed on heating. The precipitate is partially soluble in ethanol and chloroform and soluble in dimethylformamide. Because of the intensity and stability of the colour formed with cobalt(II) this system has been studied in detail with a view to utilise this reaction for the spectrophotometric determination of the metal.

**Key Words:** Spectrophotometric determination, Co(II), Phenanthrenequinonemonosemicarbazone.

### INTRODUCTION

The principal oxidation states of cobalt are +2 and +3. The aqueous solution of cobalt(II), in the absence of any other complexing agents, contain the pink hexa aquo ion,  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  which is thermodynamically stable. Simple salts of cobalt(III) are uncommon and not stable in aqueous solutions containing no complex agent. However, complex compounds of cobalt(III) are numerous and stable and have played an important role in the development of coordination chemistry. In the presence of ligands such as ammonia and cyanide which stabilise the Co(III) state, the oxidation of cobalt(II) to cobalt(III) becomes more favourable and may be brought about by atmospheric oxygen. Co(III) exists mainly in low spin, octahedral complexes, especially those with nitrogen donor atoms, although for electrostatic reasons anionic ligands also bond strongly to  $\text{Co}^{3+}$ . Thus, the *tris* complex of 2-nitroso-1-naphthol with Co(III) is stable because the metal-ligand bonds involve both a nitrogen donor atom and an anionic oxygen. Ligands with high ligand-field strengths favour Co(III) because of large stabilisation associated with a low-spin  $d^6$  electronic configuration, so that Co(II) complexes; readily oxidise to Co(III). A low spin  $d^6$  configuration confers kinetic inertness on complexes, hence, once a species such as the *tris* complex of 2-nitroso-1-naphthol with Co(III) has been formed in weakly acidic solution and extracted into an organic solvent such as chloroform, it is not dissociated when shaken with strong hydrochloric acid.

---

†Research Scholars, Department of Physics, B.R.A. Bihar University, Muzaffarpur-842 001 (India).

Phenanthroquinone monosemicarbazone (PQSC) reacts with cobalt(II) forming orange red precipitate, extractable in chloroform and other organic solvents. The reaction is instantaneous and takes place in cold. The reaction appeared to be promising and it was considered worthwhile to investigate the feasibility of PQSC as a spectrophotometric reagent for the determination of cobalt.

### EXPERIMENTAL

Reagent grade cobalt sulphate heptahydrate was dissolved in double distilled water and the solution was standardised gravimetrically. Working solutions were prepared by diluting the stock solution with double distilled water.

#### Extraction procedure

An excess of ethanolic solution of PQSC is added to cobalt solution and the pH is adjusted with sodium acetate-sodium hydroxide buffer. To the precipitated complex, a known volume of chloroform is added and the contents are shaken on a shaking machine. The non-aqueous layer is pipetted out after equilibration, centrifuged to remove water droplets and the absorbance is measured.

#### Absorption spectra

The absorption spectra of the reagent and its cobalt complex are recorded in Fig. 1. The complex has an absorption maximum at 470 nm. Since the ligand also absorbs at this wavelength, all the absorbances were measured against the corresponding reagent blanks.

#### Effect of time

The absorbance of chelates, extracted in chloroform, were measured after different intervals of time and they were found to remain constant for nearly 24 h, after which measurements were discontinued.

#### Effect of reagent concentration

A series of solutions containing a fixed amount of metal ion (1 mL of  $5 \times 10^{-4}$  M) and varying amounts of the reagent at pH 10.0 were prepared. The absorbances, after extraction in 10 mL of chloroform, were recorded at 470 nm against the reagent blanks. The results are shown graphically in Fig. 1, from which it is seen that seven moles of the reagent per mole of metal ion are required for full colour development. During subsequent work, ten times molar excess of the reagent was maintained.

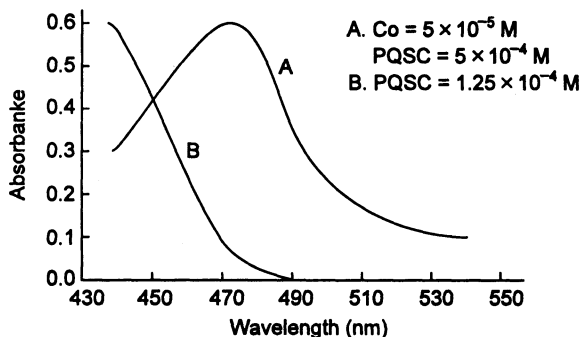


Fig. 1. Absorption spectra of the reagent and its cobalt complex. A. Complex vs. reagent blank B. Reagent vs. chloroform.

### Effect of pH

In order to investigate the role of pH of Co-PQSC system, solutions were prepared containing 1 mL of  $5 \times 10^{-3}$  M reagent. The pH was adjusted with sodium acetate-sodium hydroxide buffer, the contents were extracted in 10 mL of chloroform and the absorbances vs. pH (Fig. 2) shows that the absorbances remain constant in the pH range 9.0–10.8. In subsequent studies, therefore, pH of the solutions was adjusted to 9.8 with the help of acetate buffer.

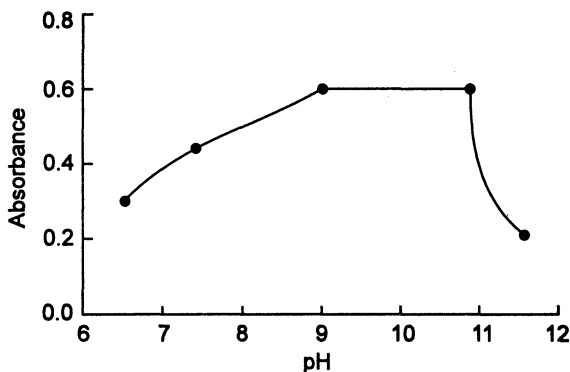


Fig. 2. Effect of pH on Co-PQSC complex.

### Stoichiometry of the complex

The molar composition of cobalt complexes was determined by the method of continuous variations<sup>1</sup>, extended to a two phase system by Irving and Pierce<sup>2</sup>. The plot of absorbance vs. the mole fraction of cobalt is shown in Fig. 3, from which it is deduced that the metal : ligand ratio in the complex is 1 : 3.

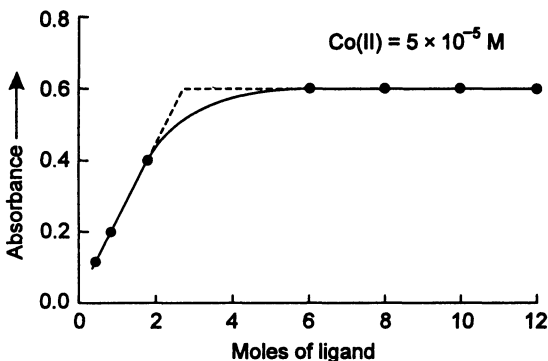


Fig. 3. Effect of reagent concentration on Co-PQSC complex.

### Adherence to Beer's law and sensitivity

A series of solutions containing an excess of the reagent and varying amounts of metal ion was prepared and the absorbances, after extraction, were measured at 470 nm. It has been found that the system obeys Beer's law up to 7.08 ppm. A plot of absorbance against varying amount of cobalt (Fig. 4) confirms this.

Mole ratio method<sup>3</sup> was employed for determining the composition of the

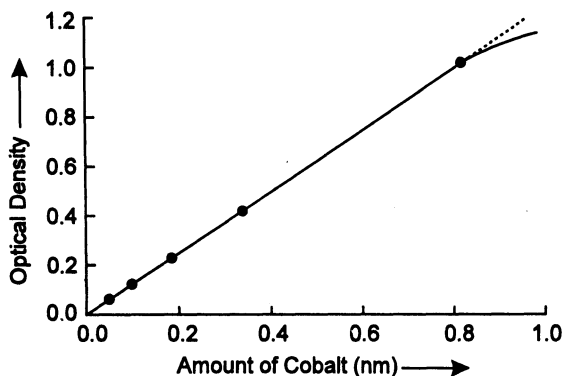


Fig. 4. Beer's law plot for Co(II)-PQSC complex, 1 mL = 2.95 ppm.

cobalt chelate. The results obtained are shown in Fig. 5 from which the formation of a 1 : 3 complex between cobalt and PQSC is indicated.

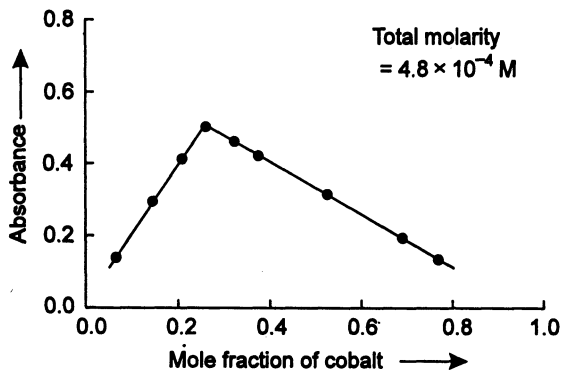


Fig. 5. Composition of cobalt-PQSC complex by Job's method.

### Working procedure

An aqueous solution of Co(II) containing 10.9–42.2  $\mu\text{g}$  of cobalt(II) is taken in a glass stoppered bottle and an excess of ethanolic solutions of the reagent is added. The pH is adjusted to 9.8 with sodium acetate and sodium hydroxide buffer in a total volume of 10 mL and 10 mL of freshly distilled chloroform is added. The contents are shaken in a shaking machine for 5 min and the mixture is allowed to stand for some time for equilibration. The chloroform layer is removed and centrifuged to remove any droplets of water remaining in the organic layer. The chloroform extract is removed with a pipette, transferred to the absorption cell and the absorbance is measured at 470 nm against a reagent blank prepared under identical conditions. Knowing the absorbance cobalt content is read from the calibration curve.

### Precision of the method

From measurements of the absorbance of six solutions containing a fixed amount (2.95 ppm) of cobalt and ten times molar excess of PQSC, diluted to 10 mL, absorbance deviations were calculated. The average absorbance was 0.595 with standard deviation of 0.0032 and relative deviation of  $\pm 0.386\%$ .

### Effect of diverse ions

The effect of foreign ions was studied by adding a solution of the ion concerned to the system before the reagent was introduced. Masking agents were used wherever necessary. Results of this study are given in Table-1.

TABLE-1  
EFFECT OF DIVERSE IONS IN THE DETERMINATION OF COBALT(II)

Cobalt taken = 2.95 ppm

Foreign ions	Amount liberated in ppm	Foreign ions	Amount liberated in ppm
Chloride	1000	Aluminium(II)	100
Bromide	500	Zinc(II)	10
Iodide	750	Cadmium(II)	50
Fluoride	800	Mercury(I) <sup>1</sup>	20
Sulfite	200	Osmium(VIII)	10
Perchlorate	1000	Iridium	50
Phosphate	70	Lead(II) <sup>2</sup>	100
Citrate	20	Manganese(II) <sup>1</sup>	100
Borate	100	Antimony(III)	50
Oxalate	50	Iron(III) <sup>1</sup>	100
Tartrate	200	Vanadium(IV)	20
Thiocyanate	100	Ruthenium(III)	40
Thiosulfate	10	Rhodium(III)	50
Nitrate	1000	Platinum(IV)	75
Barium(II)	500	Silver(I) <sup>1</sup>	35
Strontium(II)	500	Zirconium(IV)	50
Calcium(II)	500	Thorium(IV) <sup>1</sup>	30
Magnesium(II)	500		

1. Masked with fluoride.

2. Masked with iodide.

3. Removed by precipitation with chloride

Cyanide, nickel(II), palladium(II) and copper(II), however, interfere seriously.

### RESULTS AND DISCUSSION

Of the reagents used for the colorimetric determination of cobalt, the most important are thiocyanate<sup>4</sup>,  $\alpha$ -nitroso- $\beta$ -naphthol<sup>5-9</sup>, 2-nitroso-1-naphthol<sup>10-13</sup>, 3-nitroso-salicylic acid<sup>14</sup>, nitroso-R-salt<sup>15-18</sup>, and dithioamide<sup>19</sup>.

Thiocyanate method when used in aqueous acetone medium, is subject to many limitations. The complex formed is not intensely coloured and many elements interfere in the determination.  $\alpha$ -Nitroso- $\beta$ -naphthol is the most widely used reagent for cobalt. One of its derivatives, nitroso-R-salt, is generally used. It has been possible to avoid interference of copper and iron by the use of citrate but nickel interferes seriously. Hydrochloric acid has been used for the determination

of cobalt in which blue colour has developed in 11.4 N hydrochloric acid. This procedure has the inherent disadvantage that cobalt must be separated from large quantities of diverse ions. Secondly, conc. hydrochloric acid tends to lose strength due to evaporation. *o*-Nitrosocresol is also a sensitive reagent and the method has advantage over the nitroso-R-salt when the amount of cobalt to be determined is very small. The reagent is not available in the solid form; its solution must be prepared by the analyst and it is not very stable. Special precautions are to be taken to prevent the interference of traces of iron in the procedure; further, the cobalt complex absorbs in the ultraviolet region ( $\lambda_{\text{max}} = 360 \text{ nm}$ ).

The present method, using phenanthrenequinone monosemicarbazone as a reagent for cobalt(II) compares favourably with other methods known for the purpose. The sensitivity is greater than that of the thiocyanate method and comparable with dithioamide. The procedure is simple and the colour remains stable for a long time. The platinum metals which form complexes on heating do not interfere in the determination.

#### REFERENCES

1. P. Job, *Ann. Chim.*, **9**, 113 (1928).
2. H. Irving and T.B. Pierce, *J. Chem. Soc.*, 1565 (1959).
3. J.H. Yie and A.L. Jones, *Eng. Chem. Anal.*, **16**, 111 (1944).
4. E.B. Sandell, *Colorimetric Determination of Traces of Metals*, Interscience Publishers, Inc., New York (1959).
5. R. Lundquist, G.E. Markie and D.F. Boltz, *Anal. Chem.*, **27**, 1731 (1955).
6. N. Suzuki and H. Yoshida, *J. Chem. Soc.*, **80**, 1008 (1959).
7. M. Kawahata, H. Mochizuki and T. Misaki, *J. Analyst*, **9**, 1023 (1960); *Anal. Chem. Annual Rev.*, **34**, 66R (1962).
8. I. Subestian and B. Zitnansky, *Chem. Listy*, **56**, 948 (1963); *Anal. Chem. Annual Rev.*, **36**, 101R (1964).
9. E. Cogan, *Anal. Chem.*, **32**, 973 (1960).
10. R.S. Young, *The Analytical Chemistry of Cobalt*, Pergamon Press, London (1956).
11. C.E. Cardini, W. Jung and M. Fukeman, *Anales Assoc. Quim. Argentina*, **31**, 191 (1943).
12. H. Baron, *Z. Anal. Chem.*, **140**, 173 (1973).
13. A. Classen and R. Damen, *Anal. Chim. Acta.*, **12**, 547 (1955).
14. M.H. Perry and E.J. Serfass, *Anal. Chem.*, **22**, 565 (1950).
15. R.S. Young, *Anal. Chim. Acta.*, **4**, 366 (1950).
16. A.L.J. Rao and A.K. Manik *J. Indian Chem. Soc.*, **67**, 615 (1990).
17. W. Forester and H. Zoitllin, *Anal. Chim. Acta.*, **34**, 211 (1966).
18. J. Adam and R. Pribil, *Talanta*, **18**, 733 (1971).
19. W.D. Jacobs and J.H. Yoe, *Anal. Chim. Acta*, **20**, 332 (1959).