

## Pyridine-2-acetaldehyde salicyloylhydrazone as reagent for extractive and spectrophotometric determination of cobalt(II) at trace level

S S Patil & A D Sawant \*

Inorganic Chemistry Division, The Institute of Science, 15, Madam Cama Road, Mumbai 400 032, India.

Received 10 September 1999; accepted 22 November 2000

An extractive spectrophotometric method is described for the determination of cobalt(II) using pyridine-2-acetaldehyde salicyloylhydrazone (PASH) as reagent. For the extraction of cobalt(II) various experimental parameters such as acidity, reagent concentration, equilibration time are systematically studied to establish optimum conditions for quantitative extraction. Cobalt(II) is extracted quantitatively in the pH range 1.0 - 4.0. The yellow coloured 1:2 metal:ligand complex in chloroform is determined spectrophotometrically at 415 nm. Beer's law was obeyed over the concentration range of 0.5-7.0  $\mu\text{g mL}^{-1}$  of cobalt(II). The molar absorptivity and Sandell sensitivity were found to be  $1.04 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  and  $5.63 \text{ ng cm}^{-2}$  respectively. The method is precise and simple. It was applied for the analysis of high speed steels and pharmaceutical samples for the estimation of cobalt(II).

Cobalt is industrially very important metal, also it has become increasingly important as constituent of high temperature, high duty steel alloys and super alloys. Though it has little importance as magnetic material when it is alloyed with iron and nickel it shows exceptional magnetic properties. Biologically it is a significant element playing micronutritive and toxic roles and environmentally pollutant capable of causing health risks even at trace levels. Considering versatile applications of cobalt, good and sensitive methods are often required for its separation and estimation.

Various methods have already been reported for determination of cobalt(II) in various samples by applying solvent extraction followed by spectrophotometric measurements. However these methods are time-consuming as they require heating at high temperature<sup>1-2</sup> and also less sensitive<sup>3-5</sup>. The conventional Nitroso-R-salt method<sup>6</sup> also has certain limitations as it requires heating after addition of reagent. Present method deals with application of PASH for extractive and direct spectrophotometric determination of cobalt(II). PASH forms complexes with various transition metals such as copper(II)<sup>7</sup>, palladium(II)<sup>8</sup>, nickel(II)<sup>9</sup>, lead(II)<sup>10</sup> etc.

### Experimental Procedure

The absorbance measurements were done on Shimadzu 1601 UV-VISIBLE spectrophotometer. An

Elico pH meter LI-10T was used for pH measurements. A stock solution of cobalt(II) ( $1000 \mu\text{g mL}^{-1}$ ) was prepared by dissolving  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in distilled water containing few drops of hydrochloric acid. The solution was standardised by known method<sup>11</sup>. Further dilutions of stock solution were made as necessary before use. The reagent PASH was prepared as reported in literature<sup>12</sup>. All reagents used were of AR grade.

To an aliquot of solution containing 5-50  $\mu\text{g}$  cobalt(II) pH was adjusted to 4.0 with ammonia - hydrochloric acid buffer and volume was made up to 10 mL. It was then equilibrated with  $7.83 \times 10^{-3} \text{ M}$  PASH in dimethyl formamide and chloroform for 1.0 min. The yellow coloured organic phase was separated and dried over anhydrous sodium sulphate to remove traces of water. The absorbance of chloroform extract was measured at 415 nm against reagent blank analogously prepared. The amount of cobalt(II) was determined from standard calibration plot.

### Results and Discussion

#### Extraction as a function of pH

Extraction of cobalt(II) with PASH was carried out over a wide range of pH (1.0 - 10.0). It reveals that the extraction of cobalt(II) with PASH into chloroform was maximum between pH 3.5 - 4.5 (Fig. 1). Hence, all the extractions were carried out at Ph 4.0.

\* For correspondence

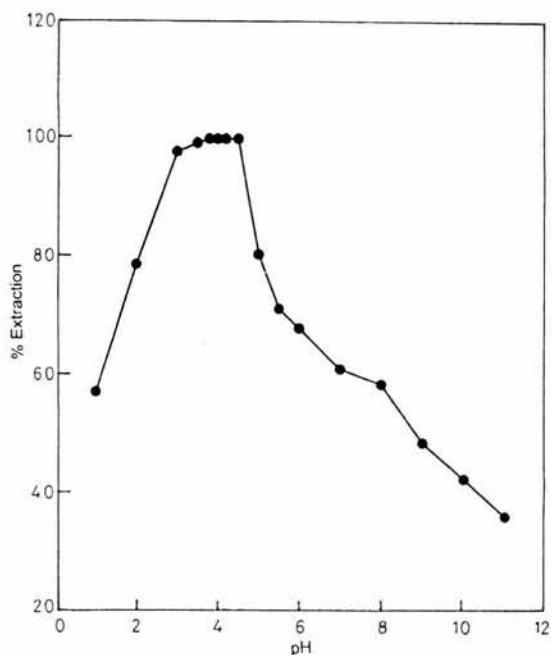


Fig 1—Extraction of cobalt(II) as a function of pH

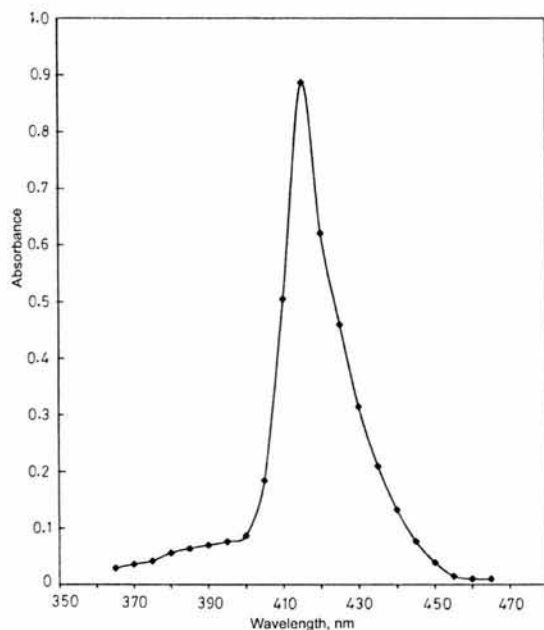


Fig 2—Absorption spectra for cobalt(II) complex extracted onto chloroform

**Extraction as a function of PASH concentration**

The optimum reagent concentration was ascertained by extracting cobalt(II) at different PASH concentrations ( $0.97 - 11.75 \times 10^{-3}$  M). It was noted that  $3.91 \times 10^{-3}$  M solution of PASH was sufficient

Table 1—Extraction of cobalt(II) with various solvents

| Solvent                | % Extraction | Distribution Ratio |
|------------------------|--------------|--------------------|
| Chloroform             | 99.77        | —                  |
| Dichloromethane        | 95.26        | 20.09              |
| Toluene                | 60.39        | 1.52               |
| Chlorobenzene          | 60.02        | 1.50               |
| Carbon tetrachloride   | 55.76        | 1.26               |
| 1,2-Dichloroethane     | 58.96        | 1.43               |
| Methyl isobutyl ketone | 54.70        | 1.20               |
| Benzene                | 52.50        | 1.10               |
| Xylene                 | 48.10        | 0.92               |

Table 2—Effect of diverse ions on the extraction of cobalt(II) with PASH (cobalt taken = 50  $\mu$ g)

| Tolerance Limit, $\mu$ g | Diverse ions   |
|--------------------------|--|
| 10,000                   | Li(I), Mg(II), Cl <sup>-</sup> , I <sup>-</sup> , Br <sup>-</sup> , F <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , ClO <sub>3</sub> <sup>-</sup> , IO <sub>3</sub> <sup>-</sup> , H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> , acetate, citrate, oxalate, tartarate, urea |
| 1,000                    | Al(III), Sr(II), W(VI)   |
| 500                      | Ca(II), Cr(III)  |
| 250                      | Cd(II), Mo(VI), Se(IV), As(III), Rh(III), Th(IV), Zr(IV), EDTA <sup>2-</sup> , S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>   |
| 100                      | V(V), Bi(III), Sn(II), Hg(II), Ni(II), Pd(II), Zn(II), Pb(II), SCN <sup>-</sup>  |
| Interfere                | 50 $\mu$ g Cu(II) & Pt(IV) masked with 500 $\mu$ g citrate, 50 $\mu$ g Mn(II) masked by 500 $\mu$ g oxalate  |

enough for complete extraction and maximum colour development for 50  $\mu$ g of cobalt(II). Further excess of reagent did not seem to have any significant effect on the absorbance. Hence  $7.83 \times 10^{-3}$  M reagent has been optimised for further analysis.

**Absorption spectra**

Absorption spectrum of cobalt(II)-PASH complex shows maximum absorbance at 415 nm (Fig. 2) where reagent has no significant absorbance. Hence all the spectral measurements were carried out at this wavelength.

**Effect of equilibration period**

Equilibration period is varied from 5 s to 5 min. It was found that equilibration time of 1 min. was adequate enough for complete extraction of 50  $\mu$ g of cobalt(II) and also longer shaking does not show any adverse effect.

**Stability of complex**

The absorbance of cobalt(II)-PASH complex in chloroform was measured at different intervals of

time to study the stability of the complex. The complex was found to be stable for 12 h.

#### Validity of Beer's law

The present studies indicate that the Beer's law was obeyed over the concentration range of 1- 6  $\mu\text{g mL}^{-1}$  of cobalt(II) with molar absorptivity and Sandell sensitivity being  $1.04 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$  and  $5.63 \text{ ng cm}^{-2}$  respectively. The practical working range was optimised as 1.5-5  $\mu\text{g mL}^{-1}$  of cobalt(II).

#### The composition of extracted species

The composition of the complex was determined by Job's continuous variation method and Mole ratio method. The results of the two methods were found to be in good agreement leading to the conclusion that the single complex forms having 1 : 2 metal : ligand stoichiometry.

#### Effect of diverse ions

The interference due to various diverse ions was studied (Table 2). The amount of diverse ions to bring about  $\pm 2\%$  variation in absorbance was taken as tolerance limit.

#### Determination of cobalt(II) in synthetic mixtures

The present method was applied for determination of cobalt(II) in various synthetic mixtures (Table 3). The results were found to be in good agreement with those obtained by standard Nitroso-R-salt method<sup>6</sup>.

Table 3—Determination of cobalt(II) (50  $\mu\text{g}$ ) in synthetic mixtures

| Synthetic mixtures         | Cobalt(II) found*<br>$\mu\text{g}$ | Nitroso-R-salt<br>method $\mu\text{g}$ |
|----------------------------|------------------------------------|--|
| Co(50), Pt(50),<br>Cr(50)  | 49.7                               | 49.9                                   |
| Co(50), Al(100),<br>Cr(50) | 49.9                               | 49.8                                   |
| Co(50), Al(50),<br>Cu(50)  | 49.7                               | 49.8                                   |

\* Average of five determinations

#### Determination of cobalt(II) in real samples

The proposed method is simple, rapid and selective and hence it was employed for the determination of cobalt(II) in real samples.

#### Determination of cobalt(II) in High Speed Steel

A sample of High Speed Steel (ITA LABS) (0.05 gm) was dissolved in aqua-regia. The solution was evaporated to dryness and oxides of nitrogen were expelled by treatment with concentrated hydrochloric acid. The residue was extracted with water. The working solution was diluted to 100 mL in a standard volumetric flask. An appropriate aliquot of the diluted solution was taken and its pH was adjusted to 4.0. Co(II) from the sample was extracted using 0.2% reagent in DMF : Chloroform and measured at 415 nm.

#### Determination of cobalt(II) in a pharmaceutical sample

To a Vitneurin injection (Glaxo) and Neurobion injection (Merck) sample (1 mL), concentrated sulphuric acid and nitric acid (1 mL each) were added and the mixture was evaporated to dryness. The treatment was repeated once again, followed by an evaporation with concentrated hydrochloric acid (3 mL). The residue was then taken up with water. The volume was made up to 50 mL and an appropriate aliquot was analysed for cobalt by the recommended procedure using PASH.

#### Determination of cobalt(II) in cobalt ink dryer

A sample of 1 mL of cobalt ink dryer (Rainbow Inks) was taken and evaporated to dryness and the residue was dissolved in aqua-regia. It was evaporated to dryness and oxides of nitrogen were expelled by treatment with concentrated hydrochloric acid. The residue was extracted in water and diluted to 100 mL. An appropriate amount of aliquot was taken for extraction and spectrophotometric determination of cobalt by the method developed in the present work.

Table 4—Determination of cobalt(II) in real samples

| S. N. | Sample                                  | Certified Value(%) | Nitroso-R-Salt Method(%) | Present Method(%)* |
|-------|---|--------------------|--------------------------|--------------------|
| I     | Alloy - High Speed Steel (ITA LAB 3082) | 4.82               | 4.79                     | 4.81               |
| II    | Co-Ink Dryer                            | 6.0                | 5.90                     | 5.89               |
| III   | Vitneurin Injection (Glaxo)             | 1.0 <sup>#</sup>   | 0.989 <sup>#</sup>       | 0.997 <sup>#</sup> |
| IV    | Neurobion Injection (Merck)             | 1.0 <sup>#</sup>   | 0.991 <sup>#</sup>       | 1.0 <sup>#</sup>   |

\* Average of five determinations

<sup>#</sup> Values in  $\mu\text{g}$

**References**

- 1 Zhang G & Zhang X, *Fenxi Huaxue*, 17(8) (1989) 713.
- 2 Singh A K, Katyal M & Singh R P, *Anal Chim*, CS (1-2) (1975) 109.
- 3 Pan J, Cheng S & Xu Z, *Yejin Fenxi*, 11(1) (1991) 11.
- 4 Burnsm D T & Tungkananuruk N, *Anal Chim Acta*, 182 (1986) 219.
- 5 Soni H K & Shah J R, *Acta Cienc Indiacca (Ser) Chem*, 11C(2) (1985) 122.
- 6 Vogel A I, *A Textbook of Quantitative Chemical Analysis*, 5 th ed.(ELBS, Longman, London) ,1991, 688.
- 7 Sinha S H, *Ph. D. Thesis*, Mumbai University, 1992.
- 8 Sinha S H & Sawant A D, *Bull Chem Soc, Jpn*, 65 (1992) 1622.
- 9 Sinha S H & Sawant A D, *Indian J Chem*, 30A (1991) 641.
- 10 Bale M N, Dave D P & Sawant A D, *Talanta*, 42 (1995) 1291.
- 11 Vogel A I, *A Textbook of Quantitative Chemical Analysis*, 3 rd ed. (ELBS, Longman, London), 1961, 443.
- 12 Vargas M G, *Microchem J*, 27 (1982) 519.