

## References

1. H. W. NURNBERG, *Proc. Anal. Div. Chem. Soc.*, 1978, **15**, 276
2. J. J. DULKA and T. H. RISBY, *Anal. Chem.*, 1976, **48**, 640A.
3. P. SHARMA and R. C. KAPOOR, *Int. J. Environ. Anal. Chem.*, 1987, **30**, 51.
4. D. N. HUME and I. M. KOLTHOFF, *J. Am. Chem. Soc.*, 1943, **65**, 1897.
5. M. SANKARANARAYANAN, C. A. BASHA and R. VIJAYAVALLI, *Bull. Electrochem.*, 1985, **1**, 517.
6. V. K. JINDAL, A. K. MOHAMMAD, R. M. BHATNAGAR and S. VERMA, *Anal. Chem.*, 1985, **57**, 380.
7. "Differential Pulse Stripping Voltammetry of Water and Waste Water, Application Brief W-1", Princeton Applied Research Corporation, New York, 1976.
8. H. WILLARD, L. MERRIT and J. DEAN, "Instrumental Methods of Analysis", 5th. ed., D. Van Nostrand, New York, 1974, p. 659.

### Extractive Spectrophotometric Determination of Cobalt(II) with Ninhydrin Oxime in Presence of Pyridine

P. K. PARIJA\*, T. K. THOKDAR and S. K. MAJUMDAR

Department of Chemistry, North Bengal University,  
Darjeeling-734 430

Manuscript received 16 February 1988, revised 28 December 1989,  
accepted 22 January 1990

THE most sensitive colourimetric methods for determination of cobalt are based on its reaction with compounds containing the grouping  $=C(OH)-C(OH)=$ . Various oximes have been reported<sup>1</sup> to determine cobalt spectrophotometrically. In pH 3–6 ninhydrin oxime forms a yellowish brown complex with cobalt, which by itself is not extracted into organic solvents. In presence of pyridine, the complex is extractable into chloroform. Measurement of absorbance of this extract shows a linear response with cobalt concentration. Taking advantage of this, a method has been devised to determine cobalt in micro quantities.

#### Experimental

Absorbance measurements were made with a Shimadzu PR1 spectrophotometer. A ECL 5651 pH-meter was used to measure the pH. A stock solution of cobalt(II) was prepared by dissolving  $CoCl_2 \cdot 6H_2O$  (AnalaR) in distilled water. This was standardised by complexometrically using xylenol orange as indicator<sup>2</sup>. Pyridine, chloroform and other organic solvents were distilled before use. Potassium hydrogen phthalate–hydrochloric acid buffer was used to adjust the pH.

**Synthesis of ninhydrin oxime:** To a solution of ninhydrin (2 g) dissolved in pyridine (2 ml), was added ethanolic solution (100 ml) of hydroxylaminehydrochloride (2 g) and the mixture was refluxed for 2 h. The resulting solid was recrystallised from ethanol (80%) (Found: C, 57; H, 4.2; N, 6.8.  $C_9H_7O_4N$  calcd. for: C, 56; H, 3.6; N, 7.25%).

**General procedure:** To an aliquot containing upto 40  $\mu g$  of cobalt(II) was added 0.6% ethanolic solution (1 ml) of ninhydrin oxime followed by pyridine (0.2 ml). Buffer solution was then added

to adjust the pH to 4. The mixture was left for 1 min and the volume of the aqueous phase was made upto 10 ml. This was then equilibrated with chloroform (10 ml) for 30 s. After phase separation, the organic extract was poured over anhydrous sodium sulphate to remove water droplets. Finally the absorbance of the chloroform extract was measured at 330 nm. Amount of cobalt was computed from a previously prepared calibration curve. To test the interferences, the respective diverse ions were added to the system prior to the addition of the reagents.

#### Results and Discussion

The complex exhibits  $\lambda_{max}$  at 330 nm. The reagent itself shows high absorbance below 300 nm. However, the absorbance becomes insignificant beyond 320 nm. The complex exhibits constant and maximum absorbance when the extractions were carried out at pH 3–6. In each case, the aqueous phase after extraction was free from cobalt. The pattern of the absorption spectra of the complex extracted at pH 0–10 remains unchanged, indicating the formation of the single complex species in all cases. Apart from chloroform, other solvents like ethyl acetate, 1,2-dichloroethane, benzene and carbon tetrachloride were tested as extracting solvents. The use of ethyl acetate and 1,2-dichloroethane offered no special advantages over chloroform. Lower absorbance resulted in case of benzene. Carbon tetrachloride did not extract the complex. Apart from pyridine, some other bases were tested as auxiliary ligands. The use of  $\beta$ -picoline or  $\gamma$ -picoline did not bring about any significant change in the maximum value of absorption. In presence of  $\alpha$ -picoline or 2,4,6-collidine, the complex is not extractable into chloroform. The nature of the extracted species is 1 : 3 (M : L) (mole ratio method).

The system conforms to Beer's law. The absorbance of the cobalt complex in chloroform shows a linear response upto 4 ppm of cobalt at 330 nm and the molar absorptivity of the complex is  $1.97 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  with Sandell's sensitivity  $0.003 \mu g \text{ cm}^{-2}$ .

Cobalt (24  $\mu g$ ) could be determined without interference in presence of 200-fold excess of the following ions:  $Fe^{III}$ ,  $Ni^{II}$ ,  $Pd^{II}$ ,  $Pt^{IV}$ ,  $Th^{IV}$ ,  $Zn^{II}$ ,  $Cd^{II}$ ,  $Ca^{II}$ ,  $Ba^{II}$ ,  $Sr^{II}$ ,  $U^{VI}$ ,  $Sn^{II}$ ,  $Cr^{III}$ ,  $Hg^{II}$ ,  $V^{V}$ ,  $Mo^{VI}$  and  $Mn^{II}$ . The system tolerated less than 25-fold excess of  $Be^{II}$ ,  $B^{III}$ ,  $Cu^{I}$  and  $La^{III}$ .  $Rh^{III}$  interfered. The following anions did not interfere when present in 400-fold excess: ascorbate, oxalate, arsenate, bromide, iodide, fluoride, phosphate, citrate, tartrate and thiocyanate. Less than 50-fold excess of EDTA, thiosulphate and thiourea were permissible. Nitrite interfered.

#### References

1. R. B. SINGH, B. S. GARG and R. P. SINGH, *Talanta*, 1979, **26**, 425.
2. A. I. VOGEL, "A Textbook of Quantitative Inorganic Analysis", Longmans, London, 1978.