

## Direct and First Order Derivative Spectrophotometric Determination of Cobalt(II) using Diacetylmonoxime isonicotinoyl hydrazone

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Diacetylmonoxime isonicotinoyl hydrazone (DMIH) used as chromogen for cobalt(II)-DMIH reagent gives bright yellow coloured water-soluble complex in acidic buffer medium. The maximum absorbance is observed in the pH range 6–7. The molar absorptivity and Sandell's sensitivity of Co(II) at  $\lambda_{\max}$  334 was found to be  $1.25 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup> and 0.0047  $\mu\text{g}/\text{cm}^2$ . Beer's law validity range 0.235–2.35  $\mu\text{g}/\text{mL}$ . Cobalt forms 1 : 1 complex with DMIH and stability constant of the complex was  $1.75 \times 10^5$ . First order derivative technique has been developed. The derivative amplitude was measured by the peak zone method and shows maximum amplitude at 360 nm in basic buffer medium. The developed first order derivative spectrophotometric method was used for the determination of cobalt(II) in alloy samples.

**Key Words:** Cobalt(II), First order spectrophotometry, Diacetylmonoxime isonicotinoyl hydrazone (DMIH).

### INTRODUCTION

Oximes<sup>1</sup> and hydrazones are the two important classes of known analytical reagents. The potential analytical applications of hydrazone derivatives have been reviewed by Singh *et al.*<sup>2</sup> In the light of analytical potentialities of oximes and hydrazones herein we report the synthesis, characterization and analytical properties of reagents containing both functional groups, *viz.*, oximes and hydrazones. Diacetyl monoxime isonicotinoyl hydrazone (DMIH) was synthesized and characterized recently<sup>3</sup>. 1-Nitroso-2-naphthol proposed by Ilinsky *et al.*<sup>4</sup> was one of the first organic analytical reagents employed for the determination of cobalt. The reagent (DMIH) along with its isomer 2-nitroso-1-naphthol was used for the spectrophotometric determination of Co(II) in several real samples<sup>5–7</sup>. In the light of the above herein we report the derivative spectrophotometric determination of Co(II) using DMIH in alloy samples.

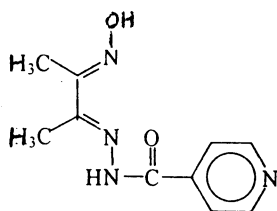
Derivative spectrophotometry is a very useful approach for determining the concentration of single component in mixtures with overlapping spectra as it may eliminate interferences. In this paper a first order derivative spectrophotometric method is described for the determination of cobalt(II) in alloys.

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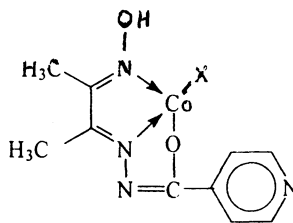
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## EXPERIMENTAL

The reagent diacetylmonoxime isonicotinoyl hydrazone (DMIH) was prepared by simple condensation of 1 mol of diacetylmonoxime with isonicotinic acid hydrazide. The structure of the reagent is as follows:



I. DMIH

II. Co(II)-DMIH complex  
where X = Cl or OH

A reagent solution (0.01 M) was prepared by dissolving suitable quantity (210 mg) of the compound in 100 mL of dimethylformamide. The reagent solution is stable for 1 h.

1 M hydrochloric acid-1 M sodium acetate (pH 0.5–3.5); 0.2 M acetic acid-0.2 M sodium acetate (pH 4–6) and 2 M ammonium chloride-2 M ammonium hydroxide (pH 8–11) buffer solutions were used in the determination of pK values of the reagents. The standard cobalt(II) solution ( $1 \times 10^{-2}$  M) was prepared using analytical reagent grade cobalt nitrate (AR, BDH). Solutions of diverse ions of suitable concentrations were prepared using AR grade chemicals.

Shimadzu 160A UV-Vis spectrophotometer equipped with 1.0 cm quartz cells and an Elico model LI-120 digital pH-meter were used in the present study.

### Recommended procedure

(a) **Determination of Cobalt(II) (Zero order):** An aliquot of the solution containing 0.12–2.82  $\mu\text{g/mL}$  of cobalt(II), 10 mL of buffer solution (sodium acetate and acetic acid) (pH 6.5) and 1 mL of 0.01 M reagent were taken in a 25-mL volumetric flask and the solution was diluted to the mark with distilled water. The absorbance of the solution was recorded at 334 nm against the corresponding reagent blank. The measured absorbance was used to compute the amount of cobalt from predetermined calibration plot.

(b) **First-order derivative spectrophotometric determination of Co(II):** For the above solutions, first-order derivative spectra were recorded in the wavelength range 300–600 nm. The derivative peak height was measured by peak-zero method at 362 nm. The peak height was plotted against the amount of cobalt(II) to obtain the calibration curve.

## RESULTS AND DISCUSSION

Diacetylmonoxime isonicotinoylhydrazone (I) is a blend of two functional groups, *viz.*, oxime and hydrazones. Therefore DMIH may be considered as a two-in-one ligand. This type of reagent is not exploited much for the spectrophotometric determination of metal ions.

The  $pK_a$  values are determined by recording the UV-Vis spectra of micromolar (ca.  $2 \times 10^{-4}$  M) solution of reagent at various pH values. The values of the deprotonation of the DMIH were found to be 5 ( $pK_1$ ) and 9 ( $pK_2$ ). The  $pK_1$  may be assigned to the deprotonation of imine ( $-\text{NH}$ ) through enolization while  $pK_2$  is assigned to the deprotonation of oxime hydrogen ( $=\text{N}-\text{OH}$ ).

The complex formation reactions between cobalt(II) with diacetylmonoxime isonicotinoylhydrazone have been studied in detail. Based on the composition of the complex as determined by using Job's and molar ratio methods, the structure II is suggested for Co(II)-DMIH complex. The various physico-chemical and analytical properties of Co(II)-DMIH complex are presented in Table-1.

TABLE-1  
PHYSICO-CHEMICAL AND ANALYTICAL CHARACTERISTICS  
OF Co(II)-DMIH COMPLEX

| Characteristics  | Results            |
|--|--------------------|
| $\lambda_{\text{max}}$ (nm)  | 334                |
| pH range (optimum)   | 6.0-7.0            |
| Mole of reagent required per mole of metal ion for full colour development                                   | 10 (folds)         |
| Molar absorptivity ( $\text{L mol}^{-1} \text{cm}^{-1}$ )  | $1.25 \times 10^4$ |
| Sandell's sensitivity ( $\mu\text{g}/\text{cm}^{-2}$ )   | 0.0047             |
| Beer's law validity range (ppm)  | 0.235-2.35         |
| Optimum concentration range (ppm)  | 0.47-2.12          |
| Composition of complex (M : L) obtained in Job's and molar ratio method                                      | 1 : 1              |
| Stability constant of the comolex  | $1.75 \times 10^5$ |
| Standard deviation in the determination of 1.17 $\mu\text{g}/\text{mL}$ of cobalt(II) for ten determinations | 0.0012             |
| RSD  | 1.2%               |

TABLE-2  
DETERMINATION OF COBALT(II) IN ALLOY SAMPLES

| Sample           | Cobalt (%)      |               |           |
|------------------|-----------------|---------------|-----------|
|                  | Certified value | Amount found* | Error (%) |
| Eligiloy-M-1712  | 40.00           | 39.60         | -1.00     |
| High speed steel | 09.25           | 09.40         | +1.60     |

\*Average of five determinations.

(a) Cr 20%; Ni 15%; Co.15%; Fe 15%; Mn 2%; Mo 7%; Fe 0.05%.

(b) W 18.5%; Mo 5.5%; Cr 4.15%; Mn 0.40%; Si 0.35%; S 0.05%; rest iron. Iron is masked by fluoride

### Interference

Derivative spectrophotometry is a very useful technique in the sense that it decreases the interference, *i.e.*, increases the tolerance limit value of foreign ions of metal ions having overlapping spectra. The recommended procedures have been employed for the first-order derivative spectrophotometric determination of cobalt(II).

The effect of various diverse ions in the determination of cobalt(II) was studied to find out the tolerance limit of foreign ions in the present method. The tolerance limit of foreign ions was taken as the amount of foreign ion required to cause an error of  $\pm 2\%$  in the absorbance.

The tolerance limit values of diverse ions in the determination of 1.17  $\mu\text{g/mL}$  of Co(II) are (values are given in  $\mu\text{g/mL}$  unless otherwise specified): tartrate (1104), iodide (761), thiosulphate (734), sulphate (588), thiourea (457), urea (360), bromide (256), acetate (236), thiocyanate (232), chloride (213), triethanolamine (110), citrate (97), phosphate (77), fluoride (76), oxalate (35), thioglycolic acid (26), tungsten(VI) (110), thorium(II) (93), manganese (29), tin(II) (24), cadmium(II) (18), aluminium(III) (16), zirconium(II) (15), lead(II) (08), bismuth (08), zinc(II) (05), chromium(VI) (04), palladium(II) (02), silver(I) (1.7); vanadium(V) (1.0), nickel(II) (1.0); mercury(II) (1.0); iron(III) (0.7), copper(II) (0.5). 3  $\mu\text{g/mL}$  of copper(II) was masked with 165  $\mu\text{g/mL}$  of thiourea and 10  $\mu\text{g/mL}$  of Fe(III) was masked with fluoride (55  $\mu\text{g/mL}$ ). An aliquot containing 120  $\mu\text{g/mL}$  Mo(VI), 43  $\mu\text{g/mL}$  aluminium(III), 41  $\mu\text{g/mL}$  lead(II) does not interfere in the presence of 1000 mg of triethanolamine. A 13  $\mu\text{g/mL}$  copper(II) does not interfere in the presence of 6 mg of thioglycolic acid. The tolerance limit values determined in first-order derivative method are higher than those in the zero order determination of cobalt(II).

### Applications

Alloy material (0.25 g) was dissolved in concentrated HCl (15 mL) by warming. A little concentrated nitric acid (1 mL) was added and slowly evaporated to dryness. The residue was dissolved in 10 mL of 1 M HCl and the resulting solution was concentrated to *ca.* 5 mL, diluted to *ca.* 50 mL with distilled water, filtered and made up to 100 mL. Suitable aliquots of the sample were analyzed for the determination of cobalt(II) by following the recommended first-order derivative procedure. The results are presented in Table-2.

### Conclusion

From the above discussion, it can be concluded that DMIH is a potential reagent for the derivative spectrophotometric determination of Co(II). It is very easy to synthesize DMIH, a novel class of reagent. The present derivative method is simple and rapid without the need for heating or extraction.

### REFERENCES

1. R.B. Singh, P. Jain and R.P. Singh, *Talanta*, **26**, 425 (1979).
2. ———, *Talanta*, **29**, 77 (1982).
3. K.B. Chandra Sekhar and K. Hussain Reddy, *J. Indian Chem. Soc.*, **78**, 340 (2001).
4. M. Llineky, G. Von and Knome, *Ber. Dtsch. Chem. Ges.*, **18**, 699 (1985).
5. B.E. Saltzman, *Anal. Chem.*, **27**, 284 (1955).
6. V.A. Nazaranko and G.G. Shitareva, *Zavadrk. Lab.*, **24**, 932 (1958).
7. E. Kogan, *Anal. Chem.*, **32**, 773 (1960).