

## Extractive Spectrophotometric Determination of Cobalt(II) with *p*-Methylisonitrosoacetophenonehydrazone

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A simple and rapid extractive spectrophotometric method for the determination of Co(II) is described. The complex formed between Co(II) and *p*-methylisonitrosoacetophenonehydrazone is extracted into chloroform from aqueous solution of pH 7.5. The extracted species has an absorption maximum at 520 nm and obeys Beer's law over a range of 0.2–6  $\mu\text{g mL}^{-1}$  of Co(II); the molar absorptivity being  $18.3 \times 10^3 \text{ L mole}^{-1} \text{ cm}^{-1}$ . Interference from foreign ions has also been studied.

### INTRODUCTION

Spectrophotometric methods coupled with a separation technique like solvent extraction can be advantageously applied for the determination of metals at low concentrations. Hydrazoximes<sup>1,2</sup> have been used for the extraction and spectrophotometric determination of metals at trace levels. *p*-Methylisonitrosoacetophenonehydrazone (HIMAPH) forms brown coloured complex with Co(II). The present work describes a method for the extractive spectrophotometric determination of Co(II) in aqueous solution using HIMAPH as a reagent and chloroform as the extracting solvent.

### EXPERIMENTAL

A Beckman-DU-2 spectrophotometer with optically matched quartz cells of 1 cm optical path was used for absorbance measurements and pH values were determined with an ELICO-LI-120 pH meter.

All chemicals and solvents were of analytical grade. A stock solution of cobalt having a strength of 1 mg/mL was prepared by dissolving Co(II) sulphate (AR) in sulphuric acid and standardised by thiocyanate-pyridine method gravimetrically.<sup>3</sup> Working solutions of cobalt were prepared using double distilled water.

The reagent HIMAPH was synthesized as per the procedure reported by Dey<sup>4</sup> for the preparation of phenylglyoxalhydrazoxime. Standard solutions of diverse

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ions were prepared from their chloride, nitrate or sulphate; or from sodium, potassium or ammonium salts using double distilled water.

An aliquot of cobalt solution containing  $0.1\text{--}20\ \mu\text{g mL}^{-1}$  of cobalt was treated with 2 mL of 0.5 M sodium acetate and 1 mL of 1% ethanolic solution of HIMAPH and the pH of the solution was adjusted to desired value using dilute solutions of  $\text{NH}_4\text{OH}$  and/or  $\text{HNO}_3$ . The resulting mixture was equilibrated for 2 min with 10 mL of chloroform. The organic layer was separated and its absorbance was measured at 520 nm against a reagent blank prepared under identical conditions.

Amounts of cobalt in unknown solutions were determined from the standard calibration curve. To study the interference, the respective foreign ions were added to the aqueous phase before extraction and pH adjustment.

## RESULTS AND DISCUSSION

Cobalt can be quantitatively extracted by HIMAPH into chloroform from an aqueous solution of pH 6.8–7.8. The organic solvents can be arranged in the following order on the basis of their extraction coefficient values:

Chloroform > diethyl ether > benzene > toluene > isobutanol > *n*-butanol > carbon tetrachloride > ethyl methyl ketone > ethyl acetate > nitrobenzene.

The absorption spectrum of Co : HIMAPH complex in chloroform shows an absorption maximum around 520 nm and Beer's law is obeyed over the concentration range  $0.2\text{--}6\ \mu\text{g mL}^{-1}$  of cobalt. Molar absorptivity of the extracted species is  $18.3 \times 10^3\ \text{L mole}^{-1}\ \text{cm}^{-1}$ . 1 mL of 1% ethanolic solution of HIMAPH was adequate for complete extraction of 50  $\mu\text{g}$  of cobalt and the colour of the complex was found to remain stable for 54 h at room temperature.

### Effect of foreign ions

Cobalt (50  $\mu\text{g}$ ) was determined in the presence of various ions. The following ions, when present in amounts indicated do not interfere in the spectrophotometric determination of cobalt:

10 Mg each of Li(I), Na(I), K(I), Sr(II), Mn(II); 5 mg each of Ca(II), Ba(II), Mg(II), Pb(II), Bi(III), As(III), V(V), Mo(VI), W(VI); 10 mg each of chloride, bromide, iodide, fluoride, chlorate, bromate, iodate, sulphate, thiosulphate, persulphate, sulphite, nitrate, nitrite, cyanate, acetate, thiourea and thiocyanate.

The interference by the ions Ag(I), Cu(II), Pd(II), Zn(II), Fe(III), Zr(IV), Th(IV), Ce(IV), U(VI), cyanide, citrate, tartrate, oxalate and EDTA can be removed using appropriate masking agents (Table-1).

The composition of the extracted species was found to be 1 : 3 (Co : HIMAPH) by Job's continuous variation method and mole ratio method.

Thus, present method proves to be very rapid and simple and provides an excellent recovery of cobalt in presence of most common ions.

The method was found to be quite suitable for the determination of cobalt in high speed steel alloy. The results of the analysis were found to be in good agreement with those obtained by Nitroso-R salt method<sup>5</sup> (Table-2).

TABLE-1  
MASKING AGENTS REQUIRED TO SUPPRESS THE INTERFERENCE  
OF FOREIGN IONS

Interfering ions	Masking agent added
Ag(I)	Potassium iodide
Cu(II)	Sodium thiosulphate
Pd(II)	Thiourea
Fe(III)	Thiourea
Zr(IV), Th(IV), Ce(IV), U(VI)	Sodium fluoride
Cyanide	Boiling with HNO <sub>3</sub> and formaldehyde
Citrate	Sodium molybdate
Tartrate	Sodium molybdate
Oxalate	Sodium molybdate
EDTA	Boiling with HNO <sub>3</sub>

TABLE-2  
RESULTS OF THE ALLOY ANALYSIS

Sr. No.	Alloy	Cobalt found %	
		Present method Average	Nitroso-R salt method Average
1.	High speed steel	46.29	46.27

### REFERENCES

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