ISONITROSO-p-METHOXYACETOPHENONE AS AN ANALYTICAL REAGENT FOR EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF A BIOLOGICALLY AND INDUSTRIALLY IMPORTANT COBALT (II) METAL

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ABSTRACT

Oximes are found to be good chelating agents and are used as analytical reagents for spectrophotometric determination of metal ions. In this work, isonitroso-p-methoxyacetophenone (HINMAP) is used as an analytical reagent for the extractive spectrophotometric determination of cobalt (II). The optimum extraction conditions are evaluated by studying parameters like pH, equilibration time, organic solvent, reagent concentration and stability of complex etc. The reagent gives a golden yellow coloured complex with Co (II) and quantitatively extracted into carbon tetrachloride at pH 9.2. The absorption spectrum of Co-HINMAP shows maxima at 400 nm and it obeys Beer's law in the range of 1 to 12 ppm. The molar absorptivity and Sandell's sensitivity were 1.014×10^4 L mol^{-1} cm^{-1} and 0.0023μg mL^{-1} cm^{-2}, respectively. The composition of Co (II)-HINMAP is determined by Job's continuous variation method and further confirmed by mole ratio method. The standard deviation and variation from mean at 95% confidence limit were 0.48 and ± 0.34, respectively. The effects of diverse ions have been studied. The proposed method is rapid, sensitive and precise and has been applied for the determination of cobalt in synthetic and real, industrial and pharmaceuticals samples.

Key words: Cobalt, Solvent extraction, Spectrophotometry, Isonitroso-p-methoxyacetophenone.

INTRODUCTION

Cobalt is industrially and biologically significant[1], playing micro-nutritive and toxic roles. It is environmental pollutant and capable of causing health risks even at trace levels. The determination of cobalt in biochemical, bioenvironmental, geochemical and industrial systems is therefore important, which often requires its separation from other elements.

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Although there are a number of other organic complexing reagents containing an oxime group, which have been used for extractive spectrophotometric determination of cobalt; many of them suffer from the disadvantages[2,3] such as low sensitivity, incomplete extraction and/or interference from a large number of foreign ions. In this paper, we report an oxime *viz.* isonitroso-p-methoxyacetophenone, as a reagent for extraction and spectrophotometric determination of cobalt (II) metal.

EXPERIMENTAL

An Equiptronics EQ-614 digital pH-meter was employed for the pH measurements while absorbance measurements were carried out on Elico SL-150 digital UV-Visible Spectro-photometer. Stock solution of cobalt (II) (10000 μg/mL) was prepared by using $CoSO_4.7H_2O$ (Loba Chemicals, AR Grade) in deionized doubled distilled water containing 2 cm^3 of conc. H_2SO_4 and standardized by known method[4]. Working solutions were prepared by appropriate dilution from the stock solution. The reagent was prepared by using the procedure reported[5].

General procedure

To an aliquot of Co (II) solution, 0.3 mL of 0.1 percent solution of HINMAP in ethanol was added, followed by 3 mL of buffer to adjust the pH to 9.2. The volume was made to 10 mL with deionized double distilled water and equilibrated with 10 mL of carbon tetrachloride for 30s. The golden-yellow colored organic phase was separated and anhydrous sodium sulphate was added to remove traces of water. The absorbance of the organic phase was measured against a similarly prepared reagent blank at 400 nm. The amount of cobalt present was computed from the standard calibration curve[6].

RESULTS AND DISCUSSION

The absorption spectra of the carbon tetrachloride extract containing $[Co(INMAP)_2]$ complex were recorded against a similarly prepared reagent blank. It shows an absorption maximum at 400 nm. The reagent did not show any significant absorption around this wavelength. All the spectral measurements were therefore made at 400 nm. Apart from carbon tetrachloride, several other common organic solvents were also tested, but none of these offers special advantage over carbon tetrachloride, which shows maximum percentage extraction.

Extraction as a function of pH

The extraction of cobalt (II) with HINMAP into carbon tetrachloride was investigated

over the pH range 3.0 – 10.0. Cobalt (II) was quantitatively extracted in the pH range 9.0 - 9.4, where percentage extractions was found to be 99.8. Hence, all extractions of cobalt (II) were carried out at pH 9.2 by using Borax buffer prepared by dissolving 3.63 g of disodium tetraborate in 250 mL of doubled distilled water.

Extraction with various organic solvents

Cobalt (II) was extracted with HINMAP in different solvents. The extraction was found to be quantitative with carbon tetrachloride, while with iso-butyl methyl ketone, iso-amyl alcohol, n-butyl alcohol, dichloromethane, benzene, chlorobenzene, toluene, chloroform, xylene, ethyl acetate and n-hexane, the extractions were incomplete. Carbon tetrachloride is therefore used as solvent in further work.

Absorption spectra

The absorption spectrum (Fig. 1) of carbon tetrachloride extract containing [Co(INMAP)$_2$] complex, recorded against the reagent blank, showed maximum absorbance at 400 nm. The reagent did not show any significant absorbance around this wavelength. All the spectral measurements are therefore carried out at this wavelength.
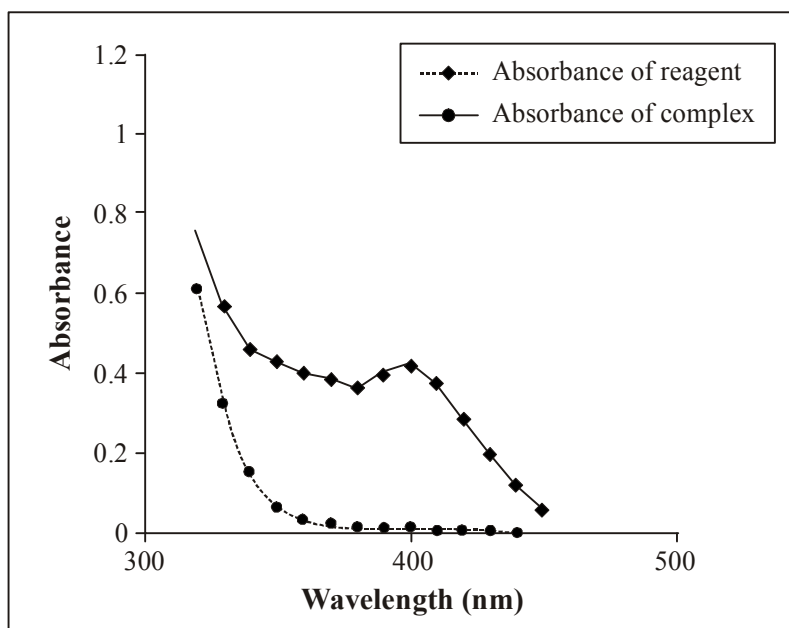

Fig. 1: Absorption spectra of reagent and complex

Extraction as a function of reagent concentration

The optimum reagent concentration was ascertained by extracting cobalt (II)-HINMAP at different reagent concentrations. It was found that 1.67×10^{-5} M of HINMAP in ethanol is sufficient for the extraction of cobalt (II). Higher concentration of reagent did not show any adverse effect on the extraction and spectrophotometric determination of cobalt (II). Hence, 1.67×10^{-5} M of HINMAP in ethanol solution was utilized for further work.

Effect of equilibration period

The extractions were carried out by varying equilibration period ranging from 20s to 90s. The optimum period of equilibration required for the complete transfer of the coloured complex into organic phase was found to be 30s. The equilibration period of 30s is therefore employed throughout the investigations. The studies on the absorbance of the organic extract at different time intervals revealed that the extracted $[Co(INMAP)_2]$ complex is stable for seven days.

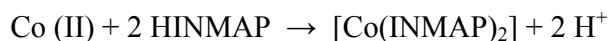**Validity of Beer's law**

The present studies indicate that Beer's law is obeyed for cobalt (II) over the concentration range 1-12 $\mu g\ mL^{-1}$ with molar absorptivity and Sandell's sensitivity being $1.014 \times 10^4\ L\ mol^{-1}\ cm^{-1}$ and $0.0023\ \mu g\ mL^{-1}\ cm^{-2}$, respectively. The Ringbom's concentration range was found to be 2-12 $\mu g\ mL^{-1}$

Composition of extracted species

The nature of the extracted $[Co(INMAP)_2]$ complex was ascertained by the Job's continuous variation method and it was found to be 1 : 2 (M : L) *i.e.* $[Co(INMAP)_2]$. This is confirmed by the mole ratio method, which shows a break corresponding to mole ratio 1 : 2.

The reaction of cobalt (II) with the reagent may therefore be represented as follows:

$$Co\ (II) + 2\ HINMAP\ \rightarrow\ [Co(INMAP)_2] + 2\ H^+$$

Effect of diverse ions

The effect of diverse ions on the extraction and determination of cobalt (II) was studied and the tolerance limits are determined (Table 1). The tolerance limit of foreign ion is taken as the amount required to cause an error of $\pm\ 2\ \%$ in the cobalt recovery.

Determination of cobalt in synthetic mixtures

The present method was applied to the determination of cobalt (II) in various synthetic mixtures (Table 2). The results are found to be in good agreement with those obtained by alternative method.

Table 1: Effect of diverse foreign ions

Interfering Ions	Tolerance limit (mg)
BrO_3^-, IO_3^-, Urea, F^-, Br^-, I^-, SO_4^{2-}, NO_2, Citrate, Li (I)	10
NO_3^-, SCN, Pb (II)	15
$S_2O_3^2$, Tartarate, SO_3^2, EDTA, Ca (II), Cd (II), Hg (II), Fe (II), Be, Ce	5
Sr (II), Acetate, Cr (III), Ba (II), Ag (I), Ni (II), W (VI)	3
Cu (II), Se (IV), V (V), Al (III), Fe (III)	2
Oxalate, Zr (IV), Th (VI), ClO_3^-	1
Cl^-, Pd (II) (masked by thiourea), As (III), Mo (VI)	Interfere

Table 2: Determination of cobalt in various synthetic and real samples

Names of samples	Amount found[*]	Certified value
Synthetic mixtures[a]		
Co (10) + Fe (50) + Hg (50)	9.81	-
Co (10) + Pb (100)	9.75	-
Co (10) + Ag (50)	9.8	-
Co (10) + Ni (30)	9.7	-
Standard samples		
Eldervit-12 (Elder)	108.6 µg mL^{-1}	108.7 µg mL^{-1}
Ovista capsules (Dr. Reddy's)	21.5 µg mL^{-1}	21.74 µg mL^{-1}
Cobalt in ink dryer	5.9 %	6 %
Cobalt sludge	36.8 %	37 %

[a]Values in parentheses are in µg. [*]Average of the three determinations

Determination of cobalt in real samples

In order to demonstrate the usefulness of the proposed method, it is applied to the determination of cobalt in standard samples for which cobalt content is known. The results obtained (Table 2) were found to be in good agreement with those reported and obtained by alternative method.

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