

Extraction and Spectrophotometric Determination of Cobalt

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Isonitroso malon-di-anilide (HIMDA) is proposed as a new reagent for the selective extraction and photometric determination of Co(II). The reagent forms yellowish brown complex in the pH range 6.4 to 7. The complex can be extracted with chloroform and measured against solvent blank on spectronic λ_{20} at 410 nm. The effects of various experimental parameters such as pH, reagent concentration, equilibrium period and diverse ions have been studied and optimum conditions were evaluated to extract, separate and estimate cobalt at ppm level by spectrophotometry. The proposed method is selective and rapid for estimation of cobalt at trace level.

INTRODUCTION

Through ages, number of complexing agents have been used to determine cobalt in presence of other diverse ions. Oximes¹⁻⁶, xanthates⁷⁻¹⁰, hydrazones¹¹⁻¹³, thiosemicarbazone¹⁹⁻²³ and other chelating agents²⁴⁻²⁹ have been extensively used for the determination and separation of Co(II). In the present communication we report the applicability of isonitroso malon-di-anilide (HIMDA) for the liquid-liquid extraction and spectrophotometric determination towards cobalt. In slightly acidic medium cobalt forms a yellowish brown complex extractable into chloroform. Measurements at 410 nm show that Beer's law is valid over a concentration range 1-20 ppm. The method is simple and rapid. Effect of pH, reagent concentration, equilibration period, diverse ions etc. on the extraction behaviour have been studied. The nature of the extracted species has also been investigated.

EXPERIMENTAL

All reagents and chemicals of A. R. grade were used. A Lomb and Bausch spectronic-20 model with 1 cm glass cells were used for measurements of absorbance. Isonitroso malon-di-anilide (HIMDA) was synthesised and purified as reported³⁰. Freshly prepared 0.1% reagent solution in 50% alcohol was used for the spectrophotometric studies.

A stock solution of 0.01M cobaltous chloride was prepared in distilled water and standardised by known method³¹. The dilute solution of cobalt of desired concentration was prepared by appropriate dilution of stock solution.

Standard solutions of diverse ions were prepared from their chloride or sulphate or from alkali salts. Dilute HCl and/or NaOH were used to maintain different pH.

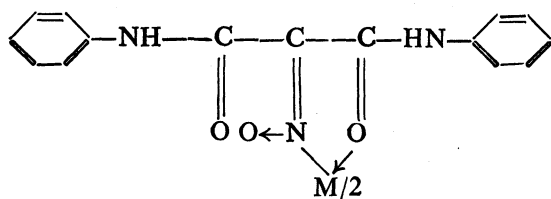
General Procedure :

To an aliquot of solution containing 20 μg cobalt and 1 ml of 0.1% HIMDA solution in 50% alcohol, adequate quantities of acetic acid (0.2M) and sodium acetate (0.2 M) were added to get pH 6.4 to 7.0 in 10 ml volume. The solution was equilibrated with 10 ml of chloroform for 1 min. The organic layer was separated and its absorption was measured at 410 nm against chloroform blank. The extracted cobalt complex was computed from calibration curve.

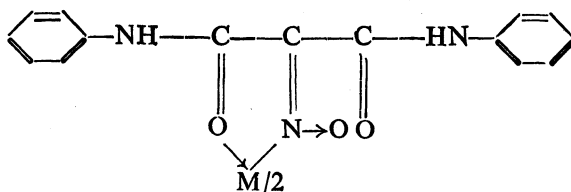
RESULTS AND DISCUSSION

IR spectrum of ligand by KBr disc method was recorded on Perkin-Elmer model, spectrum revealed characteristic stretching frequencies, as N-H at 3300 cm^{-1} , O-H stretching at 3080 cm^{-1} , carbonyl stretching at 1675 cm^{-1} , C-H aromatic stretching at 1600 cm^{-1} , N-O asymmetric stretching at 1420 cm^{-1} , N-OH stretching at 1060 cm^{-1} along with N-O at 910 and 925 cm^{-1} after formation of complex peaks were found to be shifted at C=O at 1650 cm^{-1} , aromatic C-H at 1590 cm^{-1} and M-N at 860 cm^{-1} and 890 cm^{-1} , N-H at 3300 cm^{-1} . This indicates that bonding is through oxygen of oxime group and through one of the carbonyl groups.

The possible structure of metal complex was found to be



Or



Absorption Spectra

The absorption spectrum of cobalt complex in chloroform shows an

intense peak at 360 nm, but the measurements were carried out at 410 nm using solvent blank because at this wavelength reagent shows negligible absorption. The sensitivity of the method as defined by Sandell is 0.004 $\mu\text{g}/\text{cm}$ at 410 nm. The system obeys Beer's law over the range of 0.1–2 ppm cobalt of chloroform. The complex is stable for 36 hrs.

Effect of pH and HIMDA Concentration

It is observed that the extraction is quantitative in the pH range 6.4 to 7.0. There is no extraction below pH 3.0. 1 ml of 0.1% of HIMDA solution in 50% alcohol is sufficient for quantitative extraction of cobalt.

Effect of Solvent

To have a proper choice of solvents for the extraction of cobalt (II) from aqueous phase, several solvents were tried, the percentage of extraction is shown in parentheses: chloroform (99.87), toluene (90.22), carbon tetrachloride (95.19), diethyl ether (93.43), *iso*-butyl methyl ketone (89.78), nitrobenzene (85.86), *iso*-butanol (9.50) and *iso*-amyl alcohol (76.22) etc. It is revealed that chloroform is the most suitable solvent for the present system. It is further noted that the extraction is quantitative in 1 minute after equilibration.

Composition of Complex

The composition of the yellowish brown Co(II) complex was determined by Job's continuous variation method and by mole ratio methods following the adopted procedures. Equimolar solutions of reagents and Co(II) (3×10^{-4} M) were mixed in complimentary mixture of 5 ml volume. The Co(II) : reagent ratio was found to be 1 : 2. The composition was verified by mole ratio method using 1 ml of 1×10^{-3} M and 0.5×10^{-3} M of same concentration of Co(II) and HIMDA, a plot of absorbance against increasing ligand concentration gave a break at metal to ligand ratio of 1 : 2.

Effect of Diverse Ions

The effect of diverse ions on the determination of 20 μg of Co(II) with the reagent was studied by extracting the complexes in presence of varying amounts of added foreign ions. Tolerance limit for the variation is fixed to cause $\pm 2\%$ error in the recovery of cobalt (Table-1). W(VI), Mo(VI) and Mg(II) had to be masked by fluoride. Cu(II) by thiosulfate and Mn(II) by citrate. Masking agents were used whenever absorption was varied by ± 0.02 optical density.

TABLE 1

S.No.	Amount of foreign ions added in mg	Ions
1	20.00	Chloride, bromide, iodide, fluoride, bromate, sulfate, sulfide, thiosulfate, nitrate, nitrite, acetate and citrate.
2	10.00	Perchlorate, iodate, phosphate and thiocyanate.
3	5.00	Pyrosulfate, permanganate, thiourea, tartarate, oxalate, Ca(II), Tl(I), Cd(II) and Zn(II).
4	2.50	Pyrophosphate, Pb(II), As(III), Cr(III), U(VI), Ce(VI), Mo(VI)* and Mn(II)*.
5	1.00	Be(II), Li(I), Th(IV), Ti(II), Sr(II) and V(V).
6	0.50	Ba(II), Fe(II), Fe(III), Ni(II), Pb(II), Mg(II)*, W(VI)* and Cu(II)*.
7	0.10	Pt(IV) and Ru (III).

*Masking agent used.

Accuracy and Precision

The average absorbance found for 20 μg of cobalt is 0.50 ± 0.0107 for eight determination. The relative standard deviation is $\pm 1.2\%$.

The method proposed here is simple, rapid, sensitive and reproducible at trace concentration of cobalt. It is possible to separate and determine cobalt from various ions.

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