

CHAPTER IV

Ninhydrin~~oxime~~ as an Analytical Reagent

Extraction and Spectrophotometric Determination of Cobalt

INTRODUCTION

Various oximes have been reported¹¹ to determine cobalt spectrophotometrically. Ninhydrinoxime 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 under optimum conditions. Taking advantage of this, a method has been devised to determine cobalt in micro quantities.

EXPERIMENTAL

Apparatus and Reagents :

A Shimadzu PR1 model recording spectrophotometer equipped with matched quartz cells of 10 mm optical path length was used for the absorbance measurement. The pH measurements were carried out with an ECL 5651 pH meter. Separatory funnels (coming) (50 ml) were used for extraction purpose.

A stock solution of cobalt(II) was prepared by dissolving 7.433 gm of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Analar) in 500 ml distilled water. This was standardised by complexometric titration using xylenol orange indicator¹⁰. Solutions of lower concentrations were prepared by appropriate dilution of the stock.

Buffer solutions of different pH were prepared by standard procedures : KCl-HCl (pH 1.0-2.0) K-H phthalate - HCl (pH 2.5-4.0), K-H phthalate - NaOH (pH 4.5-5.9) KH_2PO_4 -NaOH (pH 6.0-8.0), borax - HCl (pH 6.0-8.0), borax-NaOH (pH 9.5-10.8).

All other chemicals used were of analytical grade. Pyridine, α -Picoline, β -Picoline, γ -Picoline, 2,4,6-collidine were distilled before used.

Benzene, chloroform, carbontetrachloride, 1,2-dichloroethane, ethylacetate were also distilled before used.

Synthesis of Ninhydrin oxime :

Ninhydrin (2 gm) was dissolved in minimum amount of pyridine. To this was added 100 ml ethanolic solution of hydroxylamine hydrochloride (2 gm) and the mixture was refluxed for 2 hr. The product was filtered and recrystallized from ethanol. Yield 80%. (Found C-57; H-4.2; N-6.8; Calculated for $C_9H_7O_4N$: C,56; H,3.6; N,7.25).

0.5% ethanolic solution of the oxime was used in the present investigation.

Standard solutions of diverse ions were prepared from chlorides, nitrates or sulphates (in case of cations) and from sodium potassium or ammonium salts (in case of anions) to study interferences.

General procedure :

To an aliquot containing upto 40 μ g of cobalt(II) was added 1 ml of 0.5% ethanolic solution of ninhydrin oxime followed by 0.2 ml of pyridine in a separatory funnel.

Buffer solution was then added to adjust the pH to 4. The mixture was then left for 1 min to ensure complete complexation. The volume of the aqueous phase was maintained at 10 ml. This was then equilibrated with 10 ml of chloroform for 30 sec. After phase separation the organic extract was poured over anhydrous sodium sulphate to remove any retained water droplets. Finally the absorbance of the chloroform extract was measured at 330 nm against a blank. Amount of cobalt was computed from a calibration curve.

To test the interferences, the respective diversions were added to the system prior to addition of the reagents.

RESULTS AND DISCUSSION

Absorption spectra :

The spectral curves of cobalt(II)-nihydrinoxime complex, extracted into chloroform in presence of pyridine was recorded against a blank as shown in fig.1. The complex exhibits absorption maximum at 330 nm. The reagent itself shows high absorbance below 300 nm. However the absorbance becomes insignificant beyond 320 nm onwards. Wavelength of 330 nm was selected for all absorbance measurements.

Beer's law and calibration curve :

Different amounts of cobalt(II) were taken and extracted as in the procedure at pH 4.0 and the corresponding absorbance was measured against the reagent blank in order to observe the adherence of the colour system to Beer's law (table 1). The absorbance shows a linear response over the concentration of 4 ppm of cobalt (Fig.2). In each case the remaining aqueous phase after a single extraction, was clear and colourless. Furthermore the aqueous phase as tested by an independent method was void of cobalt.

The molar absorptivity and Sandell's sensitivity were evaluated to be $1.97 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and $0.003 \mu\text{g}/\text{cm}^2$ respectively at 330 nm.

Effect of ninhydrinoxime concentration :

The extent of absorbance has been examined with different amount of ninhydrinoxime keeping all other variables constant. It was found that 0.5 ml of 0.2% ethanolic solution of ninhydrinoxime along with 0.2 ml of pyridine was sufficient to extract $24 \mu\text{g}$ of cobalt in a single operation. Increased concentration of ninhydrinoxime did not bring about any significant

change in the maximum value of the absorbance. However higher concentration was avoided as the absorption of the blank goes high. The results are shown in table 2.

The nature of the extracted species was indicated to be 1:3 (Co:ninhydrinoxime) from mol ratio method.

Effect of pyridine concentration :

Keeping the other variable constant, the effect of pyridine has been examined in terms of absorbance. It was noted that 0.2 ml pyridine along with 0.5 ml of 0.5% ethanolic solution of ninhydrinoxime was sufficient to extract upto 40 μg of cobalt in a single operation. Higher concentration of pyridine gives lower absorbance.

Effect of other pyridine bases :

Apart from pyridine, some other bases were tested as auxiliary ligands. Use of β -picoline or γ -picoline did not bring about any significant change in the maximum value of absorbance. In presence of α -picoline or 2,4,6-collidine, the complex is not extractable into chloroform.

Effect of acidity :

The effect of acidity on the extractibility of cobalt was examined in terms of absorbance of the complex. The complex exhibits constant and maximum absorbance when the extractions were carried out from pH 3-6. On each case the aqueous phase after extraction was free from cobalt as tested by an independent method. This indicated a quantitative extraction of the metal in the aforesaid acidity range in a single operation. The absorbance decreases above or below this pH range. The pattern of the absorption spectra of the complex extracted from pH 1-10 remains unchanged, indicating the formation of single complex species in all cases. The absorbance as a function of pH has been shown in Fig.3. For our practical purpose pH 4.0 was selected.

Effect of solvents :

Apart from chloroform, other solvents like, 1,2-dichloroethane, ethylacetate, benzene and carbontetrachloride were tested as extracting solvents. Use of ethylacetate and 1,2 dichloroethane offered no special advantages over chloroform while lower absorbance resulted in case of benzene. Carbontetrachloride did not extract the complex.

Stability of colour :

The absorbance of the chloroform extracts, containing 24 μg of cobalt(II) extracted by the recommended procedure, was measured at the different intervals of time. The organic extract produced a steady absorbance for at least 24 hours at room temperature as seen from table 3.

Effect of diverse ions :

To test the effect of diverse ions cobalt was extracted according to the recommended procedure in presence of the desired foreign ions. Extraction pH was set at 4.0 with the buffer. An ion was considered to interfere if the recovery of cobalt differed by more than $\pm 3\%$ from the actual amount taken. Cobalt(II) (24 μg) could be determined without interference in presence 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), Mn(II), Be(II), Bi(III), Cu(II) and La(III). Rhodium interfered.

Among the anions tested, the followings did not interfere : ascorbate, oxalate, tartarate, arsenate, bromide, iodide, fluoride, phosphate, citrate, thiocyanate, EDTA, thiosulphate, and thiourea. However nitrite interfered. The results are shown in table 4.

Precision and accuracy :

The proposed method has been tested by analysing solutions containing a known amount of cobalt (II). The experimental results for the determination of cobalt are shown in table 5. The process is very simple and rapid requiring only 10-15 min for each run. The method has been compared to some other existing methods as seen from table 6.

Application :

In absence of real samples the proposed method has been tested by analysing some synthetic mixtures. The composition of the mixtures with percentage of recovery of cobalt are given in table 7. The results show that recovery of cobalt was satisfactory. Average of three determination was taken in each case.

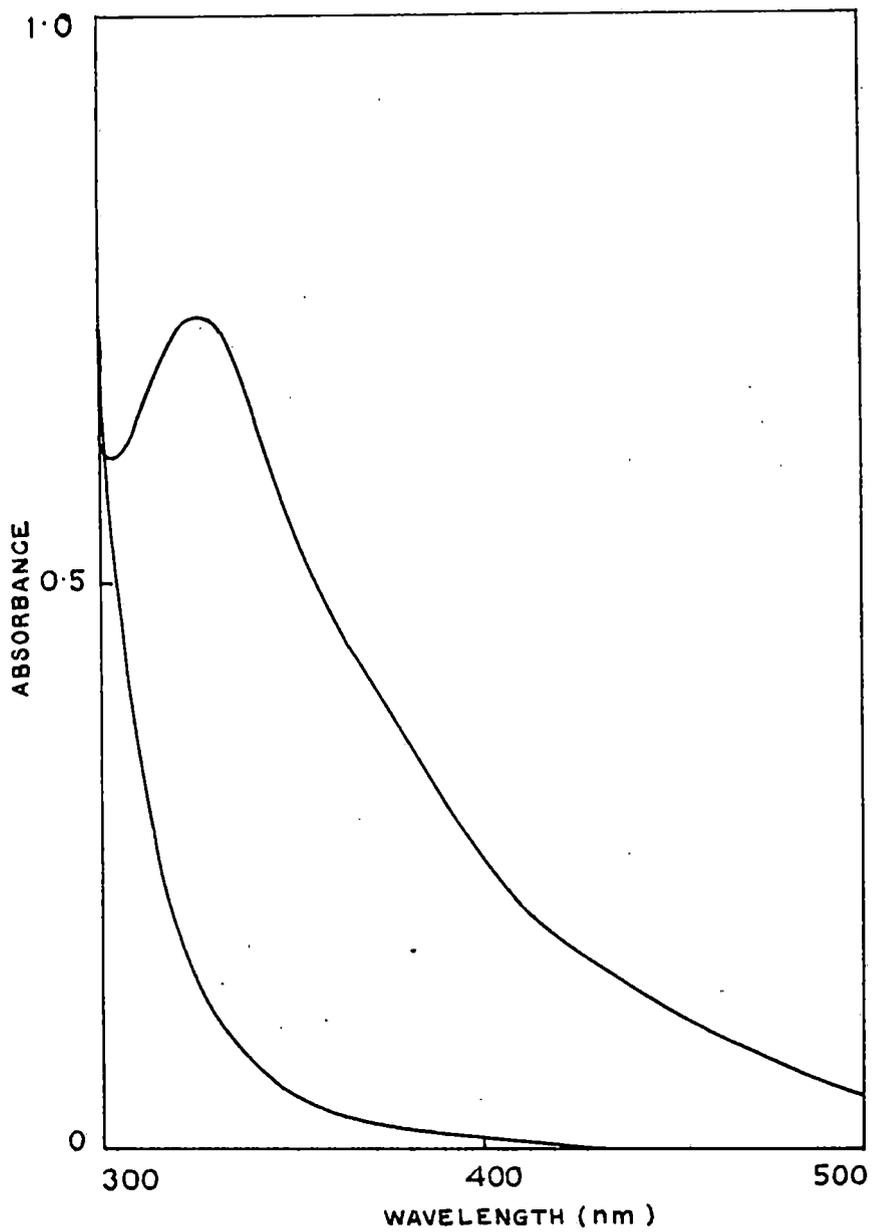


Fig-1. Absorbance spectra of (A) cobalt-Ninhydrin complex - Pyridine complex (2.4 ppm Co) and (B) reagent blank.

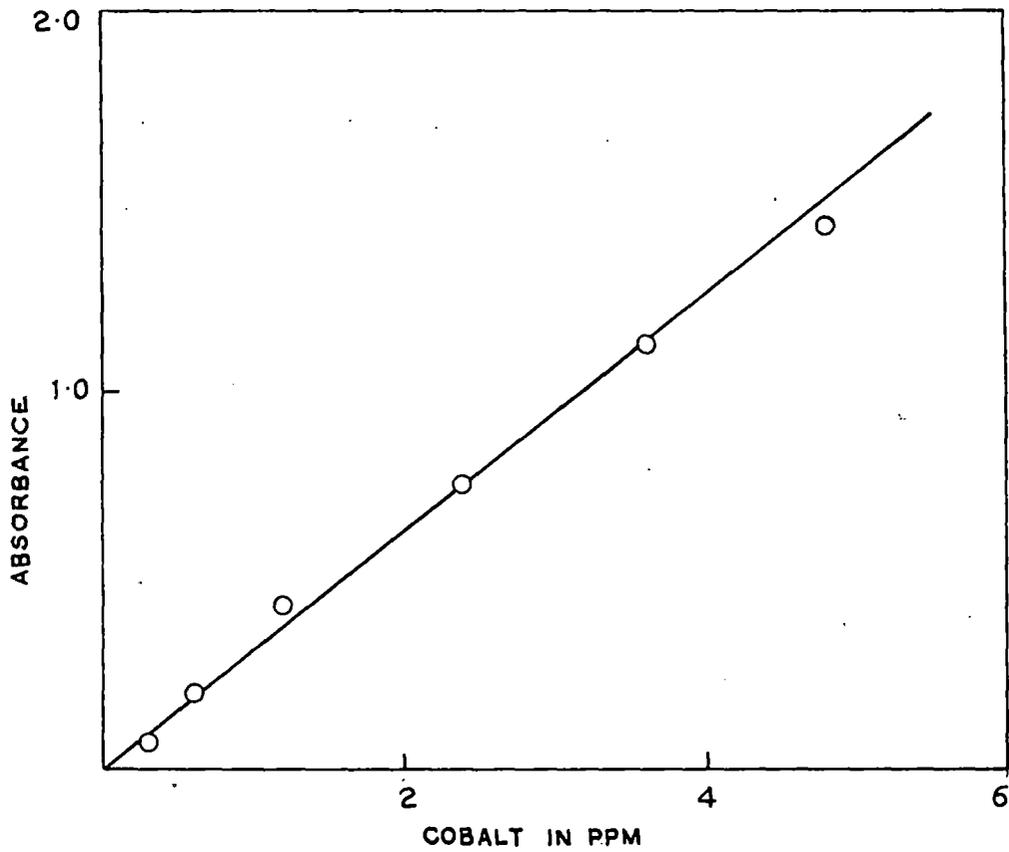


Fig-2: BEER'S LAW (Co-Ninhydrinoxime system)

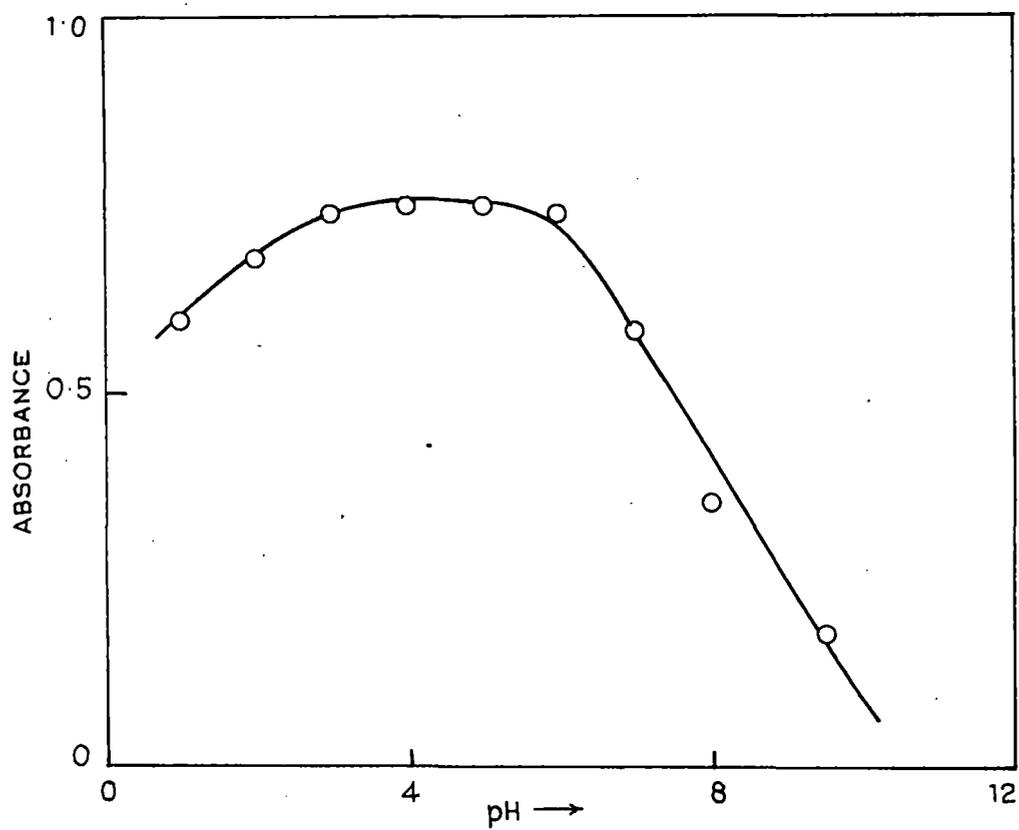


Fig-3. Absorbance as a function of pH (Co taken $24 \mu\text{g}$)

Table 1 : Adherence to Beer's law. Extraction pH-4.0

Cobalt concentration in ppm	Absorbance at 330 nm
0.3	0.080
0.6	0.105
1.2	0.440
2.4	0.752
3.6	1.120
4.8	1.460

Table 2 : Effect of ninhydrinoxime concentration (0.20%)

The aqueous phase (10 ml) contains 24 μg of cobalt (II) and 0.2 ml of pyridine. Extraction pH 4.0.

Amount added in ml	Absorbance (at) 330 nm
0.05	-
0.10	0.430
0.20	0.750
0.40	0.755
0.60	0.756
1.0	0.755

Table 3 : Variation of absorbance with time. Cobalt taken
24 μ g.

Time in hr after extraction	Absorbance at 330 nm
0.25	0.750
0.50	0.755
1.0	0.752
6.0	0.750
12.0	0.750
24.0	0.748

Table 4 : Effect of diverse ions on determination of
cobalt (24 μ g). Extraction pH-4.0.

Ion added	Amount tolerated, mg	Cobalt found μ g	Error %
Fe(III)	5.0	24.5	2.0
Ni(II)	5.0	23.8	0.8
Pd(II)	4.5	23.5	2.0
Pt(IV)	4.5	24.0	0.0
Th(IV)	6.0	24.2	0.8
Zn(II)	5.5	24.2	0.8
Cd(II)	4.5	24.8	3.3
Ca(II)	6.0	24.5	2.0
Ba(II)	6.0	24.0	0.0
Sr(II)	6.0	24.0	0.0

contd ...

Table 4 contd ...

U(VI)	5.0	23.5	2.0
Sn(II)	5.0	24.2	0.8
Cr(III)	5.0	24.2	0.8
Hg(II)	4.0	23.5	2.0
V(V)	5.0	24.0	0.0
Mo(VI)	4.5	24.0	0.0
Mn(II)	5.0	24.5	2.0
Be(II)	0.60	23.4	2.5
Bi(II)	0.50	23.5	2.0
Cu(II)	0.50	24.0	2.5
La(III)	0.50	23.4	2.5
Rh(III)	Nil	-	-
Ascorbate	10.0	23.5	2.0
Oxalate	10.0	23.8	0.8
Arsenate	10.0	23.4	2.5
Bromide	10.0	24.2	0.8
Iodide	10.0	24.0	0.0
Fluoride	10.0	24.0	0.0
Phosphate	10.0	23.5	2.0
Citrate	10.0	23.5	2.0
Tartarate	10.0	24.5	2.0
Thiocyanate	10.0	24.6	2.5
EDTA	0.4	23.5	2.0
Thiosulphate	0.4	23.4	2.5
Thiourea	0.4	23.4	2.5
Nitrite	Nil	-	-

Table 5 : Reproducibility of cobalt(II) recovery

Cobalt taken (μg)	Cobalt found (μg)	Mean (μg)	Std deviation (%)
12.0	10.5, 12.0, 12.5	12.26	1.08
	12.8, 12.0, 13.8		
24.0	24.5, 23.5, 24.0	24.46	0.60
	25.0, 24.8, 25.0		
36.0	37.5, 36.5, 36.0	36.91	0.73
	38.0, 36.5, 37.0		

Table 6 : Comparison of some existing methods for the spectrophotometric determination of cobalt

Reagent	λ_{max} (nm)	Molar absorptivity $1 \text{ mol}^{-1} \text{ cm}^{-1} \times 10^4$	Ref.
1. Acenaphthenequinone monoxime	400	1.18	1
2. Dimethyl glyoxime	435	1.08	2
3. Di-(2-Pyridylketoxime)	388	1.95	3
4. Dimedone dioxime	400	2.3	4
5. Nicotinamidoxime	540	0.59	5
6. Oxamidoxime	350	0.86	6
7. Phenanthrenaquinone monoxime	470	1.75	7
8. Pyridil monoxime	408	1.7	8
9. Present method	330	1.97	9

Table 7 : Analysis of synthetic mixtures
Extraction pH 4.0

Composition with amount taken (μg)	Recovery of cobalt(II) %
1. Co(II) 24, Fe(III) 100, Ni(II) 100, Cu(II) 100	98
2. Co(II) 24, Cr(III) 100, Mn(II) 100, Hg(II) 100	100
3. Co(II) 24, Pd(II) 100, Pt(IV) 100, Zn(II) 100	101
4. Co(II) 24, U(VI) 100, V(V) 100, Mo(VI) 100	98

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