

Non-extractive Spectrophotometric Determination of Cobalt (II) using 2-Hydroxy-3 Methoxy Benzaldehyde Isonicotinoyl Hydrazone (HMBIH)

S. Vidyasagar Babu^{1*} and M .Jaya Ramudu²

¹Department of Chemistry, Sri Krishnadevaraya University College of Engineering and Technology, Anantapur-515 003.Andhra Pradesh, India.

Abstract: Spectrophotometric determination of cobalt(II) using 2-Hydroxy-3-Methoxy Benzaldehyde Isonicotinoyl hydrazone (HMBIH). This method is based on the formation of yellow-colored complex between cobalt(II) and the reagent in acidic media. The complexes exhibit maximum absorbance at 394 nm (HMBIH) respectively. The method was optimized for pH, reagent concentration, and reaction time. Beer's law was obeyed in the concentration range of 0.06–1.18 µg/mL for reagent. The molar absorptivity, Sandell's sensitivity, and stability constant of the complex were determined. The method was successfully applied to determine cobalt (II) in tea leaves, and vitamin B12 tablets with high accuracy and precision.

Keywords: Cobalt(II), Spectrophotometry, HMBIH, Complexation, Beer's Law, Vitamin B12, Tea Leaves

Introduction

Hydrozones are important reagents widely used for the spectrophotometric determination of metal ions. Cobalt is an important essential element. It is present in vitamin B₁₂ which is involved in the production of red blood cells and the prevention of pernicious anemia¹. Insufficient natural levels of cobalt in feed cause cobalt deficiency diseases characterized by anemia, loss of weight, or retarded growth². Cobalt-60 is used as an efficient radioactive tracer and an anticancer treatment agent in medicine. Cobalt is also important to human nutrition as it is an essential part of vitamin B₁₂ (cyanocobalamine). Therefore, the determination of cobalt is valuable for the quality control of artificial and biological samples in a simple, selective and sensitive manner^{3,4}.

Hinsky et al⁵. proposed the first organic analytical reagent, (1-Nitroso-2- naphthol) for the determination of cobalt(II). 1-Nitroso-2-naphthol and its isomer 2- nitroso-1-naphthol were used for its spectrophotometric determination of cobalt^{6,7} in several real samples. A number of photometric methods making use of oximes and their derivatives, azo compounds and several often organic reagents for cobalt⁸⁻¹² were reported in the literature. Many organic reagents having sulphur as coordinating atom were employed in the determination of cobalt (II).

They were dithiozone^{13,14}, dithioximide (rubeanic acid) and its N,N-bis (3-dimethyl amino propyl) derivative equinoxaline 2,3-dithiol^{15,16}, thioglycolic acid and its derivative. This dibenzoyl methane, thiotropolone¹⁷, I-Phenyl thiosemicarbazide, N,N- ethylene-bis (o- mercapto-benzamide), and thiohemol tri fluoro acetone. However, the author is interested in use of isonicotinoylhydrazones as spectrophotometric reagents¹⁸

A brief account of various hydrazones employed for the spectrophotometric determination of cobalt(II). It gives various chromogenic reagents¹⁹ used for the spectrophotometric determination of cobalt(II). This study introduces a reagent, 2-hydroxy-3-methoxy benzaldehyde isonicotinoyl hydrazone (HMBIH) is a chelating agent that forms a highly stable and colored complex with Co(II) without requiring organic solvent extraction. This method is based on the selective reaction of HMBIH with Co(II) in a suitable pH range, producing a complex with a distinct absorbance.

Experimental

Reagents and Instruments

All chemicals used were of analytical grade. Cobalt(II) solutions were prepared from cobalt chloride. The reagent HMBIH was synthesized and characterized. A UV-Vis spectrophotometer was used for absorbance measurements.

Procedure

The spectrophotometric determination of cobalt(II) was carried out by mixing cobalt(II) solution with HMBIH in acidic medium pH 6.5. The absorbance of the resulting complex was measured at 394 nm. The effects of pH, reagent concentration, and reaction time were studied to optimize the conditions.

Results and discussion

Absorption Spectra

The absorption spectra of the cobalt(II)-HMBIH complex showed maximum absorbance at 394 nm, respectively. The reagent blanks showed minimal absorbance at these wavelengths, indicating the formation of a stable complex.

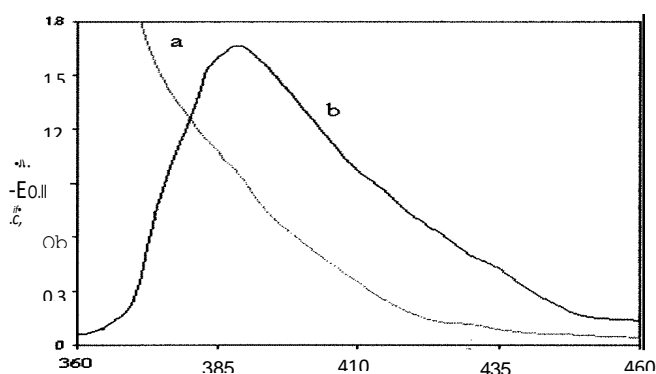


Fig.1. (a) Absorption spectra of HMBIH vs buffer blank. (b) Co(II)-

HMBIH complex vs reagent blank $[Co(II)] = 4 \times 10^{-5}$, $[HMBIH]$ pH = 6.5

Table .1. Physico-Chemical and analytical characteristics of Co(II)-HMBIH complex

S.No	Characteristics	Results
1	Wavelength (nm)	395
2	pH range (Optimum)	5.5-7.0
3	Mole of reagent required permole of metal ion for full colour development	5(folds)
4	Molar absorptivity ($L \cdot mole^{-1} \cdot cm^{-1}$)	3.2×10^4
5	Sandell's sensitivity ($\mu g/cm'$)	0.0018
6	Beer's law validity range ($\mu g/ml$)	0.060-1.18
7	Optimum concentration range ($\mu g/ml$)	0.236-1.061
8	Composition of complex (M:L) obtained in Job's and mole Ratio method	1:2
9	Stability constant of the complex	$5.86 \times 10^1 M$
10	Standard deviation in the determination of $1.17 \mu g/ml$ of Co(II) for ten determinations	0.0005
11	Relative standard deviation(%)	0.1

Effect of pH

The optimum pH range for maximum absorbance was found to be 6.0–7.0 for HMBIH. A buffer solution of sodium acetate-acetic acid was used to maintain the pH.

Effect of Reagent Concentration

A 5-fold molar excess of HMBIH and a 10-fold molar excess of sufficient to achieve maximum absorbance. The absorbance remained constant with further increases in reagent concentration.

Effect of Time

The color development was instantaneous, and the absorbance remained stable for over 2 hours, indicating the stability of the complex.

Beer's Law and Sensitivity

Beer's law was obeyed in the concentration range of 0.06–1.18 $\mu g/mL$ for the reagent. The molar absorptivity was found to be $3.2 \times 10^4 L \cdot mol^{-1} \cdot cm^{-1}$ for HMBIH. The Sandell's sensitivity was 0.0018 $\mu g/cm^2$ for HMBIH.

Tolerance of Foreign Ions

The method showed high selectivity for cobalt(II). Common cations and anions did not interfere significantly, except for Fe^{3+} and Cu^{2+} , which were masked using fluoride and thiourea, respectively given in table Table .2.

Table: 2. Tolerance limit of foreign nions in the determination of $1.47\mu\text{g/ml}$ of Co(II).

Ion added	Tolerance Limit ($\mu\text{g/ml}$)	Ionadded	Tolerance Limit ($\mu\text{g/ml}$)
Hypo	3606	Th^{4+}	67
Bromide	1996	Sb_{2+}	51
oxalate	1521	Sn^{2+}	40
Thiourea	1045	Pd^{2+}	34
Urea	1003	Mo^{6+}	28
Acetate	953	Zr^{4+}	26
Thiocyanate	904	Al^{3+}	7
Chloride	773	Hg^{2+}	4
Iodide	570	W^{6+}	4
Fluoride	450	Cu^{2+}	4
Tartarate	241	Fe^{3+*}	3.0
Phosphate	87	Zn^{2+}	2.0
Citrate	85	V^{5+}	2.0

*Masked with Fluoride ($300\mu\text{g/ml}$),

Masked with thiourea ($986\mu\text{g/ml}$)

Masked by thiourea ($720\mu\text{g/ml}$),

Applications

The method was successfully applied to determine cobalt(II) in tea leaves, vehicle exhaust, and vitamin B12 tablets. The results were in good agreement with certified values, with relative errors of less than 2% is given table 3 and 4.

Table 3. Determination of Co(II) in tealeaves and vehicle exhaust.

Sample	Amountof Co(II)(mg/g)		Error($\frac{3}{4}$)
	Certifiedvalue	Presentmethod*	
Tealeaves	0.12	0.123	+2.23

*Average of three determinations

Table.4. Determination of Cobalt(II) in vitamin B₁₂ Tablet

Sample	AmountofCobalt($\mu\text{g/ml}$)		Relative error(%)
	Certified	Present method*	
Basitonforte**	7.42	7.53	+1.48

*Average of three determinations

**composition (mg/tablet)

Thiamin mononitrite (B1): 10, Riboflavin (B2): 10, Pyridoxime hydrochloride: .
3, Nicotinamide: 100, Calcium pantothenate: 50, Cyanocobalamin: 15, Sodium ascorbate: 150, Folic acid: 1.5.

Conclusion

The proposed spectrophotometric method using HMBIH reagent, sensitive, and selective for the determination of cobalt(II) in various samples. The method offers high accuracy and precision, making it suitable for routine analysis in environmental and biological samples.

Acknowledgments

The authors thank the Department of Chemistry, S.KUCET, Anantapur, for providing the necessary facilities to carry out this work and special thanks to timely helped M. Jaya Ramudu for the purpose of work field.

References

1. P. Vicini, F. Zani, P. Cozzini and I. Doytchinova, Hydrozones of 1,2-benzisothiazole hydrazides: Synthesis, antimicrobial activity and QSAR investigations, *Eur J Med Chem* 37 **553** (2002)
2. C.D. Klaassen, "Casarett and Doull's Toxicology" the basic science of poisoning", 6th ed., McGraw-Hill, Medical Publishing Division, New York, 839 (1986).
3. S. Vidyasagar Babu, K. Hussain Reddy and Y. Lingappa "Spectrophotometric determination of cobalt in biological samples using 2-acetylpyridine semicarbazone." *J. Indian Chem. Soc.*, Vol 86, 312-315 (2009).
4. S. Vidyasagar Babu, S. Eswaramma and K.S.V. Krishna Rao. "Synthesis, Characterization, luminescence and biological activities of lanthanide complexes with a hydrozone ligand." *Main Group Chemistry*, 17, 99-110 (2018).
5. Cogan, E. "Separation of Cobalt from Its Alloys and Ores with 1-Nitroso-2-Naphthol." *Analy. Chem.*, 32(1960)973.
6. Marczenko, Z., Spectrophotometric determination of metal ions, Ellis Horwood. Ltd., England, 239 (1976).
7. Snell, F.D., Photometric and Fluorometric methods of analysis (metals), Wiley Inter Science Pub. Part I., chapter 5, 273 (1978).
8. Marczenko, Z., Separation and spectrophotometric determination of elements, Horwood Chichester, (1986).

9. Orishi, H., Photometric determination of traces of metals, Part-IIA Individual metals, Aluminium to Lithium, Wiley, New York (1986).
10. Marczenku, Z., Crit. Spectrophotometric determination of trace elements, Rev.Anal.Chem.,11,195(1981).
11. Forester, W. and Zeitlin, H., Spectrophotometric determination of Nickel in Sea Water with Quinoxaline-2,3-Dithiol.Anal.Chem., 38,649(1966).
12. Monnier, D., Haerdi, W., Vogel, J. and Wnger, P.E., Helv. Macro-et microdosage de Traces de cobalt II. Separation de traces de cobalt par extraction au moyen de dithizone. Chem. Acta., 42, 1846 (1959).
13. Burke, R.W., and Yoe, J.H., Simultaneous Spectrophotometric Determination of Cobalt and Nickel with 2,3-Quinoxalinedithiol. Anal. Chem., 34, 1378 (1962).
13. Chemomorcherko, L.I., Chuiko, T.V. and Akhmetshin, A.G., Zh. Analit Khim., 27, 2265 (1972).
14. Dalziel, J.A., and Shawinski, A.K., Improved method for the simultaneous absorptiometric determination of cobalt and nickel with quinoxaline-2,3-dithiol. Talanta., 15, 367 (1968).
15. Burke, R.W., and Deardorff, E.R. Simultaneous spectrophotometric determination of cobalt, nickel and copper with 2,3-quinoxaline-dithiol. Talanta., 17, 255 (1970).
16. Uhlemann, E., and Miller, H.,Chelate von β -dicarbonyverbindungen and ihren derivaten 1 Thiodibenzoylmethan als extraction sphotometricsches und gravimetrisches reagent fur kobalt Anal. Chim. Acta., 48, 115 (1969).
17. Srivastava, J.N., and Singh, R.P., Thiotropolone as achromogenic reagent for the simultaneous determination of cobalt (II) and nickel(II). Talanta., 48, 1210 (1973).
18. Kobylecka, J., Chemia Analityczna., 37 (3), 369 (1992).
19. Shraydesh, B.F., Zhuri, A. Z. A and Hannoun, M.,Spectrophotometric Determination of Trace Amounts of Cobalt and Copper with 3-(2-Thiazolylazo)-2,6-Diaminopyridine Spectroscopy Lett., 25 (7), 1049 (1992).