



RESEARCH ARTICLE

CHEMISTRY

A COMPARATIVE STUDY OF COBALT (II) USING 4-HYDROXY 3, 5 DIMETHOXY BENZALDEHYDE 4-HYDROXY BENZOYL HYDRAZONE AND CINNAMALDEHYDE 4-HYDROXY BENZOYLHYDRAZONE IN PRESENCE OF MICELLAR MEDIUM BY SPECTROPHOTOMETRY

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ABSTRACT

Two simple, sensitive, rapid and selective spectrophotometric methods have been developed for the determination of Cobalt (II) by using newly synthesized reagents 4-Hydroxy3, 5dimethoxy benzaldehyde-4-hydroxybenzoylhydrazone (HDMBHBH) and Cinnamaldehyde 4-hydroxy benzoylhydrazone (CMHBH) in presence of neutral surfactant TritonX-100 (5%) (micellar medium). Cobalt (II) forms a yellow coloured water-soluble complex with HDMBHBH and CMHBH-in the pH range 9.0-12.0. The Co (II)-HDMBHBH complex shows maximum absorbance at λ_{max} 397 nm in the pH range 8.0-9.0 and Co (II)-CMHBH shows at λ_{max} 393 nm in the pH range 8.0-9.0. At these wavelengths (λ_{max}), the complex shows maximum absorbance while the reagent blanks shows negligible absorbance. Hence, analytical studies were carried out at λ_{max} 397 nm at pH 9.0 for HDMBHBH and 393 nm at pH 9.0 for CMHBH against reagent blanks. Beer's law is obeyed in the range 0.058-0.589 $\mu\text{g ml}^{-1}$ and the optimum concentration range from ringbom plot is 0.117-0.530 $\mu\text{g/ml}$ for Co (II)-HDMBHBH, and 0.029-0.294 ml^{-1} , 0.058-0.265 for Co (II)-CMHBH. The molar absorptivity and Sandell's sensitivity for the coloured solution were found to be $4.37 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and 0.0013- $\mu\text{g. cm}^{-2}$ for Co (II)-HDMBHBH, $6.5 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and 0.0009- $\mu\text{g. cm}^{-2}$ for Co (II)-CMHBH respectively. The interference effects of various diverse ions have been studied. Co (II) forms 1:1 complex with HDMBHBH and 1:2 with CMHBH stoichiometry with stability constant 11.47×10^6 for Co (II)-HDMBHBH and 3.07×10^{12} for Co (II)-CMHBH. The standard deviation in the determination of 0.117- $\mu\text{g ml}^{-1}$ of Cobalt (II) is 0.002 for HDMBHBH and 0.0024 for CMHBH. The Relative standard deviation is 2.53% for Co (II)-HDMBHBH and 2.3 % for Co (II)-CMHBH complex. First and second order derivative spectroscopic methods was developed at λ_{max} 434 nm and 470 nm for Co (II)-HDMBHBH and at 440 nm and 463 nm for Co (II)-CMHBH, for the determination of Cobalt (II) which is more sensitive than the zero order method. The developed method has been used for the determination of Cobalt (II) in Tealeaves, Vehicle exhaust, alloy samples and in vitamin B₁₂. The results are in good agreement with the certified values.

KEYWORDS

Comparative study of Cobalt (II), Spectrophotometry, Tealeaves, Vehicle exhaust, alloy samples, vitamin B₁₂, micellar medium, Triton x-100 (5%), HDMBHBH, CMHBH.

INTRODUCTION

The potential analytical applications of hydrazones and its derivatives have been reviewed by Singh et al ^[1]. Hydrazones are important class of known analytical reagents. Due to analytical potentialities of hydrazones herein we report the synthesis, characterization and analytical properties of reagents 4-Hydroxy, 5dimethoxybenzaldehyde-4-hydroxybenzoylhydrazone (HDMBHBH) and Cinnamaldehyde 4-hydroxy benzoylhydrazone (CMHBH). As the light of the above herein we report the direct and derivative spectrophotometric methods for determination of Cobalt (II) using HDMBHBH and CMHBH in Tealeaves, Vehicle exhaust, alloy samples and in vitamin B₁₂. Derivative spectrophotometry is a very useful approach for determining the concentration of single component in mixtures with overlapping spectra as it may eliminate interferences.

Cobalt is found generally in the form of ores. It is frequently associated with Nickel and Copper. So it is produced as a byproduct of Nickel and Copper mining activities. Cobalt is a micro nutrient for many living organisms, including human beings. Having 0.13 to 0.30 mg/kg of Cobalt in soils markedly improves the health of grazing animals. Cobalt plays an important role in the nitrogen fixation by bacteria and also an integral part of vitamin-B₁₂. Mammals required small amount of Cobalt salts. Plants and different food materials contain extremely low concentration of cobalt. Its deficiency leads to diseases like stunted growth, at high concentration it inhibits biosynthesis and enzyme activities.

Cobalt is also an important constituent in alloys like permanent magnetic alloys (3.36%) and in high strength, high temperature alloy (10-30%). Mostly Cobalt compounds have been used for centuries to impart a rich blue colour to glass, glazes, and ceramics. Several of its compounds are used in the industry. The metal is of wide use in the production of aircrafts, electromagnets, paints, varnishes and ceramics.

Cobalt alloys are also used in the manufacturing of turbine blades and cutting tools because of their sufficient hardness and resistive against oxidation at high temperatures. 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

For the determination of Cobalt (II), at microgram quantities, a number of hydrazone derivatives and several analytical techniques such as AAS, ICP-AES, ICP, X-Ray fluorescence spectroscopy and UV-visible spectrophotometry were employed. Among them, spectrophotometric methods are preferred because they are cheaper and easy to handle.

Hydrazones and its derivatives reacts with many metal ions forming colour complexes and act as chelating agents. In general the technique of solvent extraction is



widely used in the spectrophotometric determination of metal ions. However, organic solvents such as benzene and chloroform are often carcinogenic, toxic and cause environmental pollution. It is significant to develop a method which does not involve solvent extraction. A micellar solution has the ability to enhance the stability of metal complex and has been utilized as a medium for the spectrophotometric determination of the metal chelate [2-5].

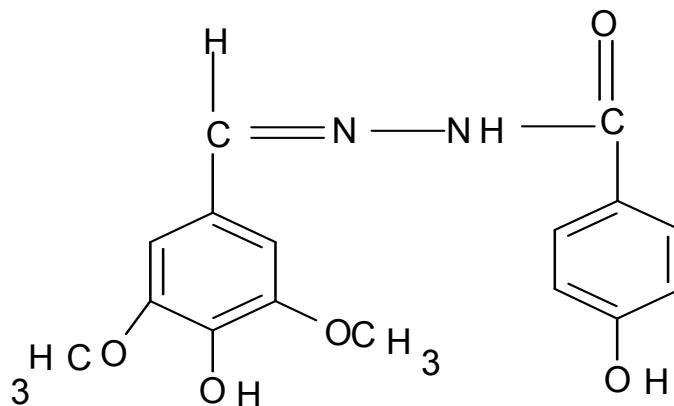
MATERIALS AND METHODS

The absorbance and pH measurements were made on a Shimadzu UV-visible spectrophotometer (Model UV-160A) fitted with 1.0 cm Quartz cells and Elico digital pH meter (Model LI 120) respectively. Suitable settings for derivative were as follows. The spectral band length was 5 nm, the wavelength accuracy was

0.5 nm with automatic wavelength correction and the recorder was a computer controlled thermal graphic printer with a cathode ray tube and one degree of freedom in the wavelength range 300 – 800 nm.

The reagents (HDMBHBH and CMHBH) were prepared by the Sah and Daniels [6] procedure

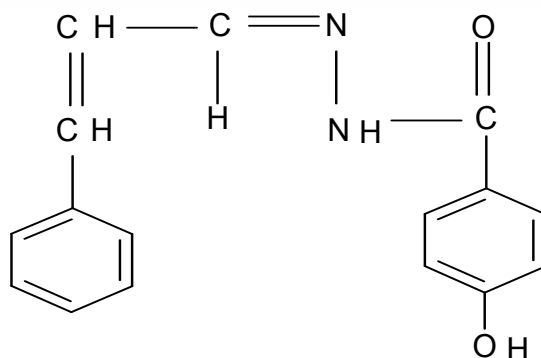
Preparation of HDMBHBH: 1.82 g of 4-hydroxy 3, 5 dimethoxy benzaldehyde and 1.52 g of 4-Hydroxy benzhydrazide were dissolved in sufficient volume of Carbinol and the mixture is refluxed for 4 hours. The contents were allowed to cool and the product was separated by filtration. A crude sample (yield 80%) is obtained ($C_{16}H_{16}N_2O_5$). The resultant product is recrystallised twice from hot methanol. Pure light greenish coloured crystals of 4-Hydroxy 3, 5 domethoxy benzaldehyde 4-hydroxy benzoylhydrazone (HDMBHBH) (m.p. 292-294°C.) was obtained.



Structure of HDMBHBH

Preparation of CMHBH:

1.32 ml of Cinnamaldehyde and 1.52 g of 4-Hydroxy benzhydrazide were dissolved in sufficient volume of methanol and the mixture is refluxed for 4 hours. The contents are allowed to cool and the product was separated by filtration. A crude sample (yield 80%) is obtained ($C_{16}H_{13}O_2N_2$). The resultant product is recrystallised twice from hot methanol. Pure light yellowish crystals of Cinnamaldehyde-4-hydroxy benzoylhydrazone (CMHBH) (m.p. 242-244°C.) was obtained.



Structure of CMHBH

Table: 1
Spectral data of Reagents (HDMBHBH and CMHBH)

Assignments	IR Spectral bands(cm^{-1}) of		Assignments	The ^1H NMR (300 MHz) spectrum of in DMSO solvent	
	HDMBHBH	CMHBH		HDMBHBH	CMHBH
ν NH stretching	3529	3452	NH	11.54 (S, 1H)	δ 11.57(S,1H)
ν OH stretching	3075	3218-3092	OH (phenolic)	10.13 (S, 1H)	10.74 (S, 1H)
ν > C=O stretching	1642	1620	N=C-H	8.1 (S, 1H)	8.19-8.22 (S, 1H)
ν C=N stretching	1609	1577	ArH (pyridine ring)	7.77 – 7.80 (D, 2H)	7.77 – 7.80 (D,2H)
			ArH (aldehydic)	6.84 –6.96 (M,4H)	7.60 – 7.62 (D,2H)
			-OCH ₃ (2 Methoxy)	6.63 (S, 6H)	

The mass spectrum of HDMBHBH and CMHBH shows that molecular ion peak at m/z 317.1 ($M+ 1$) and 267 ($M+ 1$) respectively. The structures of HDMBHBH and CMHBH were confirmed based upon above IR, NMR and mass spectral data

A 0.01M solutions of HDMBHBH and CMHBH in Dimethyl formamide (DMF) were employed in the present studies. The reagent (HDMBHBH and CMHBH) solutions (0.01M) were prepared by dissolving suitable quantity (0.316 g for HDMBHBH and 0.264 for CMHBH)

of the compound in 100 ml of dimethyl formamide. The reagent solution is stable for 6 hours in presence of micellar medium. The working solutions were prepared daily by diluting the stock solution to an appropriate volume. All other chemicals used were of analytical grade.

RESULTS AND DISCUSSION3



The reagents 4-Hydroxy 3, 5-dimethoxy benzaldehyde 4-hydroxy benzoylhydrazone (HDMBHBH) and Cinnamaldehyde 4-hydroxy benzoylhydrazone (CMHBH) were easily synthesized as any other Schiff base reagent. In basic medium, the ligands presumably

co-ordinates the metal ions as di-anion to give neutral complexes. The absorption spectra of reagents (HDMBHBH, CMHBH) and Cobalt (II) complex under the optimum conditions are shown in Figure 1 & 2.

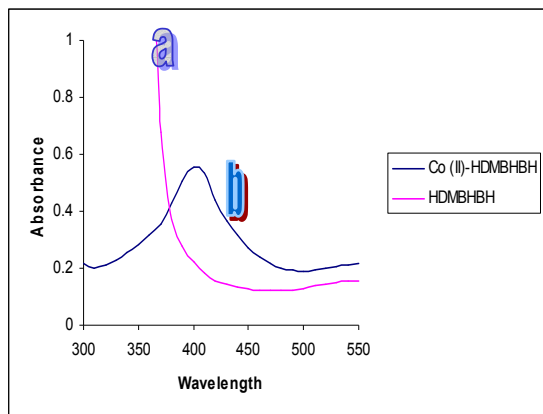


Fig-1 Absorption spectra of
(a) HDMBHBH Vs Buffer blank
(b) Co (II)-HDMBHBH Vs Reagent blank
HDMBHBH - 2×10^{-3} M (0.5 ml)
Co (II)- 2×10^{-4} M (0.5 ml)
pH 9.0 (3.0 ml)
Triton-X-100 (5%)-0.5 ml

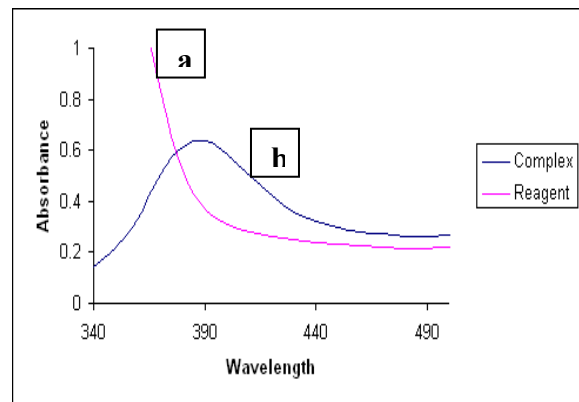


Fig-2 Absorption spectra of
(a) CMHBH Vs Buffer blank
(b) Co (II)-CMHBH Vs Reagent blank
CMHBH- 2×10^{-3} (0.5 ml)
Co (II)- 2×10^{-4} M (0.5 ml)
pH 9.0 (3.0 ml)
Triton-X-100 (5%)-1.0 ml

Effect of reagent (HDMBHBH and CMHBH) concentration

A 10-fold molar excess of reagent (HDMBHBH and CMHBH) was necessary for complex and constant colour development. Excess of the reagent has no effect on the absorbance of the complex. The absorbance of the complex solution was found independent of the order of the addition of the reagents.

Effect of time: Time stability of the coloured solution

The absorbance of the solution was measured at different time intervals to ascertain the time stability of the colour of the complex. The colour reaction between

Cobalt (II) with HDMBHBH and CMHBH was found to be instantaneous at room temperature. A slow decrease in absorbance was observed for the coloured species after 10 min. The stability of the complex was increased by adding neutral surfactant Triton X-100 (5%) and the colour remained stable for more than 6 hours.

The effect of surfactants

The effect of various surfactants such as TritonX-100, Sodium dodecyl benzene sulphonate (SDBS) and Cetyltrimethyl ammonium bromide (CTAB) on the absorption profiles of the system has been investigated



and presented in Table 2. In presence of Triton X-100 (5%) both complex were more stable and

exhibited maximum absorbance, hence Triton X-100 (5%) has been selected for further studies

Table : 2
Influence of different surfactants

Surfactant	Absorbance of Co (II)-HDMBHBH complex at λ_{max} 397 nm	Absorbance of Co (II)-CMHBH complex at λ_{max} 393 nm
None	0.335	0.328
Triton X-100 (5%)	0.563	0.634
CTAB (5%) (Cationic)	0.474	0.523
SDBS (5%) (Anionic)	0.445	0.456

Optical characteristics, precision and accuracy data.

Beer's law limits, molar absorptivity and Sandell's sensitivity values, regression equation and correlation coefficients for Cobalt (II)-

HDMBHBH and Cobalt (II)-CMHBH complex were compared and presented in Table 3. From this it was noticed that in derivative spectra the peak position shift towards higher wavelengths and Beer's law range was also improved compared to zero order method.

Table: 3
Optical characteristics, precision and accuracy data.

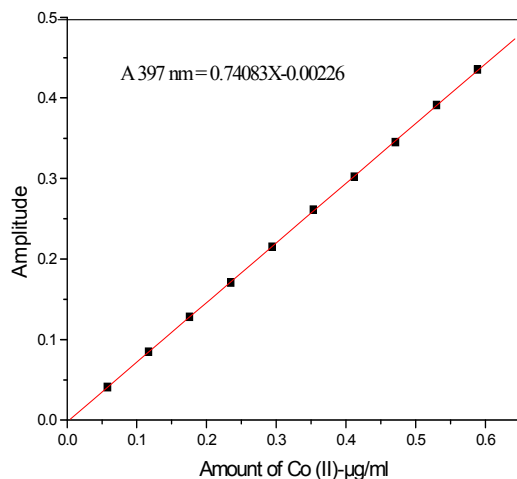
Characteristics	Results	
	HDMBHBH	CMHBH
λ_{max}	397 nm	393 nm
pH range	8.0-10.0	8.0-10.0
Optimum pH range	8.0-9.0	8.0-9.0
Mole of reagent required per mole of metal ion for full colour development	10 (folds)	10 (folds)
Molar absorptivity ($L \cdot mol^{-1} \cdot cm^{-1}$)	4.37×10^4	6.5×10^4
Sandal's sensitivity ($\mu g/cm^2$)	0.0013	0.0009
Beer's law validity range ($\mu g/ml$)	0.058-0.589	0.029-0.294
Optimum concentration range ($\mu g/ml$)	0.117-0.530	0.058-0.265
Composition of complex (M: L) obtained in Job's and molar ratio method	1:1	1:2
Stability constant of the complex	11.47×10^6	3.07×10^{12}
Standard deviation in the determination of 0.117 $\mu g/ml$ (HDMBHBH) and (CMHBH) of Cobalt (II) - for ten determinations.	0.002	0.0024
Relative standard deviation (%)	2.53	2.30
Regression coefficient	0.9997	0.99943
Detection limit ($\mu g/ml$)	0.006	0.0072
Determination limit ($\mu g/ml$)	0.018	0.0216

The calibration graph follows the straight-line equation $Y = a c + b$; where c is the concentration

of the solution, Y is measured absorbance or peak height and a and b are constants. By



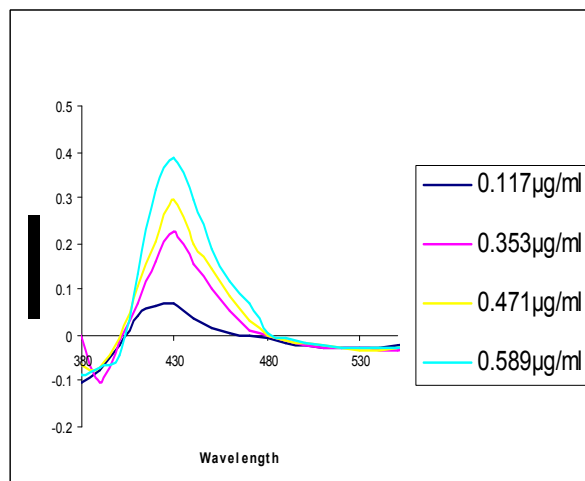
substituting the Co (II)- HDMBHBH complex experimental data in the above equation, the calibration equations were calculated as λ_{\max} 397 nm = 0.74083X-0.00226 for zero order data



Co (II)-HDMBHBH - Beer's law
Zero order
HDMBHBH- 2×10^{-3} M (0.5 ml)
Co (II) - 2×10^{-5} M (0.5 ml)
pH --9.0 (3.0 ml)
Triton-X-100 (5%)-0.5 ml
 λ_{\max} -----397 nm

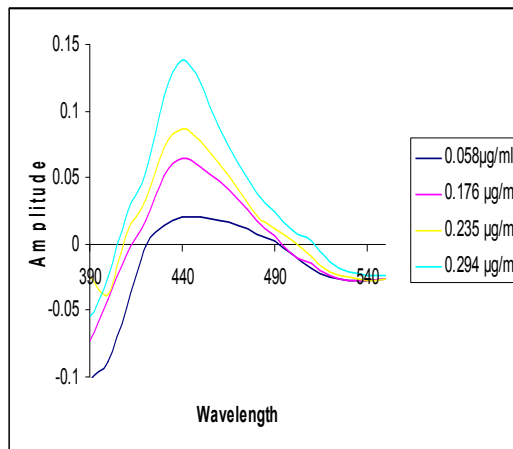
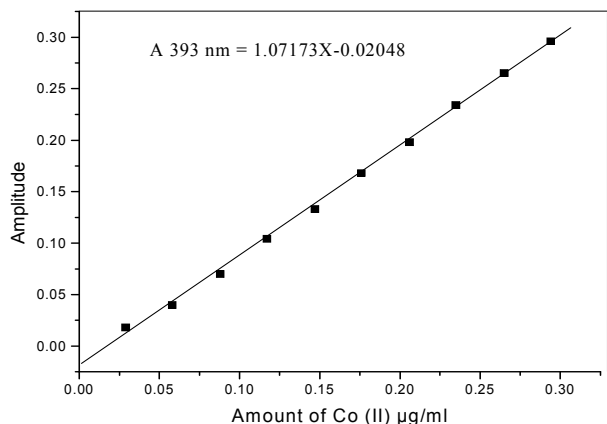
By substituting the Co (II)-CMHBH complex experimental data in the above equation, the calibration equations were calculated as λ_{\max} 393 nm = 1.07173X-0.02048 for zero order data

and λ_{\max} 434 nm = 0.65865X-0.00153 For first derivative data and λ_{\max} 470 nm = 0.90663X+ 8.93374 $\times 10^{-4}$ For second order derivative data which gives the straight lines.



Co (II)-HDMBHBH - Beer's law
first order derivative spectra
HDMBHBH- 2×10^{-3} M (0.5 ml)
Co (II) - 2×10^{-5} M (0.5 ml)
pH --9.0 (3.0 ml)
Triton-X-100 (5%)-0.5 ml
 λ_{\max} -----434 nm

and λ_{\max} 440 nm = 0.46004X+0.0031 for first derivative data, λ_{\max} 463 nm = 0.5256X+0.00262 for second derivative data which gives the straight lines.



Co (II)-CMHBH beer's law
Zero order
CMHBH - 1×10^{-3} M (0.5 ml)
Co (II) - 1×10^{-5} M (0.5 ml)
pH -9.0 (3.0 mL)
Triton-X-100 (5%)-1.0 ml
 λ_{max} -----393 nm

Co (II)-CMHBH beer's law
first order derivative spectra
CMHBH- 1×10^{-3}
Co (II) - 1×10^{-5} M (0.5 ml)
pH 9.0 (3.0 mL)
Triton-X-100 (5%)-1.0 ml
 λ_{max} -----440 nm

Zero order method: The developed spectrophotometric methods proposed in the present studies were applied for the determination of Cobalt (II) in Tealeaves, Vehicle exhaust, and alloy samples and in vitamin B₁₂. The results are in good agreement with the certified values.

APPLICATIONS

Preparation of tea leaf and vehicle exhaust samples:

(a)Tealeaf sample: The tealeaf samples were supplied by Andra Pradesh Agricultural Research Institute (APARI), Hyderabad, India. 0.1 g of tealeaf sample was taken in a beaker and dissolved in Conc. nitric acid (5

ml) with heating. The solution was cooled, diluted, and filtered. The filtrate was made up to 100 ml with distilled water in a calibrated flask.

(b)Vehicle exhaust sample: The vehicle exhaust sample was collected by using high volume air sampler. Vehicle exhaust particles (1 g) were dissolved in a mixture of 18 ml of Conc. nitric acid, 18 ml of Conc. perchloric acid, and 2 ml of Conc. hydrofluoric acid in a 100 ml Teflon beaker, evaporated to a small volume, filtered through a filter paper, and made up to 100 ml with distilled water. The amount of Cobalt (II) present in the above solutions was determined and results are presented in table 4

Table 4
Determination of Cobalt (II) in Tealeaves and Vehicle exhaust

Sample	Certified value	Amount of Cobalt (II) (mg/g)											
		HDMBHBH						CMHBH					
		Zero order	Error (%)	D1	Error (%)	D2	Error (%)	Zero order	Error (%)	D1	Error (%)	D2	Error (%)
Vehicle exhaust	3.3	3.26	-1.2	3.27	-0.91	3.29	-0.30	3.25	-1.5	3.28	-0.60	3.29	-0.30
Tealeaves	0.12	0.117	-2.5	0.118	-1.69	0.119	-0.84	0.121	0.82	0.123	2.43	0.123	2.43

**Average of three determinations

(c)Preparation of vitamin B₁₂ tablet solution:

The vitamin tablet was decomposed in a 50 ml round bottomed flask by heating with 10 ml of a mixture containing Conc. nitric and sulfuric acids (10+1) on a hot plate until near dryness. Drop wise addition of Conc. nitric acid is needed for obtaining a yellow residue. The

residue was neutralized with dilute sodium hydroxide solution, and then was diluted to 50 ml. The amount of Cobalt (II) present in the above solution was determined by the above procedure and the results are presented in table 5

Table: 5
Determination of Cobalt (II) in vitamin B₁₂ Tablet

Alloy Sample	AAS method	Amount of Cobalt (II) (µg/ml) found											
		HDMBHBH						CMHBH					
		Zero order	Error (%)	D1	Error (%)	D2	Error (%)	Zero order	Error (%)	D1	Error (%)	D2	Error (%)
Basiton forte**	7.42	7.415	-0.06	7.418	-0.02	7.40	-0.27	7.40	-0.27	7.41	-0.13	7.41	-0.13

* Average of three determinations, * composition (mg/tablet), amino mono nitrite (B1): 10, Riboflavin (B2): 10, Pyridoximehydro chloride: 3, Nicacinamide: 100, Calcium pentothenate: 50, Cyamocobalamine: 15, Sodium ascarbate: 150, Folic acid: 1.5.

(d)Preparation of alloy sample solution:

Alloy material (0.25 g) was dissolved in concentrated HCl (15 ml) by warming. A little concentrated nitric acid (1 ml) was added and slowly evaporated to dryness. The residue was dissolved in 10 ml of 1M HCl and the resulting solution was concentrated to ca. 5 ml, diluted

to ca. 50 ml with distilled water, filtered and made up to 100 ml. Suitable aliquots of the sample were analyzes for the determination of cobalt (II) by following the recommended procedure.

A suitable aliquot of the sample solution was taken in a 10 ml standard flask



containing 3.0 ml of buffer of pH 9.0, and 0.5 ml of reagent solution. The contents were diluted to 10 ml with distilled water and its absorbance was measured at λ_{max} against the reagent blank. The absorbance values were

referred to the pre-determined calibration plot to compute the amount of Cobalt (II) present. The results are presented in table 6

Table.6
Determination of Cobalt (II) in Alloy samples

Alloy Sample	Certified value	Amount of Cobalt (II) (mg/g)											
		HDMBHBH						CMHBH					
		Zero order	Error (%)	D1	Error (%)	D2	Error (%)	Zero order	Error (%)	D1	Error (%)	D2	Error (%)
^a Eligiloy-M-1712	40.00	39.15	-2.12	39.17	-2.07	39.19	-2.02	39.13	-2.22	39.36	-1.62	39.39	-1.54
^b High speed steel	09.25	9.21	-0.43	9.23	-0.21	9.23	-0.21	09.22	-0.32	09.23	-0.21	09.23	-0.21
^c Udimate-700c	18.00	17.95	-0.27	17.98	-0.11	17.98	-0.11	18.15	0.83	18.18	1.0	18.18	1.0

* Average of five determinations, a=Cr20% ; Ni 15% ; C 0.15% ; Fe 15% ;Mn 2% ; Mo 7% ; Fe 0.05% b= W18.5% ; Mo 5.5% ; Cr 4.15% ; Mn 0.40% ; Si 0.35% ; S 0.05% ; Rest Iron (Iron is masked by Phosphate). c =Cr 15% ; Al 4.3% ; Mo 5.21% ; C .08% ; B 0.003%.

Precision and accuracy

The precision and accuracy of the proposed methods were studied by analyzing (10 replicates) 0.117 $\mu\text{g/ml}$ of Cobalt (II) and the RSD values were found to be less than 2.5 %.

Effect of diverse ions

In order to assess the analytical potential of the proposed methods, the effects of some diverse ions which often accompany Cobalt (II) was examined by carrying out the determination of 0.294 $\mu\text{g/ml}$ Cobalt (II) in the presence of

foreign ions. An ion was considered to interfere in the determination if the absorbance observed differed by more than $\pm 2\%$ from that for Cobalt (II) alone. The results presented in Table 7 (a) indicate that many metal ions and anions do not interfere in the determination of Cobalt (II). However, Fe (III) and Cu (II) interfere seriously as they readily form coloured species with HDMBHBH and CMHBH. The tolerance limit of Fe (III) and Cu (II) were enhanced by using masking agents of fluoride, phosphate presented in Table 7 (b).

Table: 7 (a)
Tolerance limits of diverse ions in the determination of 0.294 µg/ml of Cobalt (II)

Ion Added	HDMBHBH			CMHBH		
	Tolerance Limit (µg/ml)			Tolerance Limit (µg/ml)		
	Zero order	D1	D2	Zero order	D1	D2
Iodide	1522	1765	1765	1015	1015	1015
Sulphate	960	960	960	288	480	480
Ascorbic acid	353	353	353	168	168	168
Urea	840	900	960	360	480	480
Thiocyanide	697	697	697	581	697	697
Bromide	1038	1198	1198	639	958	958
Thiourea	1141	1141	1141	608	608	608
Nitrate	372	439	439	744	868	930
Tetra borate	1474	1524	1524	737	737	737
Acetate	540	590	590	236	236	236
Phosphate	484	484	484	569	569	569
Chlorides	887	923	923	710	781	781
Tartrate	1125	1280	1280	500	500	500
Citrate	1702	1892	1892	606	606	606
Fluoride	418	418	418	228	228	228
Oxalate	1880	2256	2444	264	264	264
U ⁺⁶	35	38	40	9.5	12	12
Sn ⁺²	95	118	118	48	72	72
Al ⁺³	13	16	16	11	11	11
Ba ⁺²	315	343	343	110	110	110
Mo ⁺⁶	5.7	7.6	8.6	4	4	4
Hg ⁺²	28	34	46	20	20	20
Pb ⁺²	103	124	124	42	42	42
W ⁺⁶	183	220	220	73	73	73
Sr ⁺²	113	122	131	88	122	122
Se ⁺⁴	94	110	110	32	32	32
Bi ⁺³	24	27	31	7	7	7
Ti ⁺⁴	3	4.8	4.8	29	34	34
Ni ⁺²	5.8	5.8	5.8	4	5	5
Ce ⁺⁴	70	70	70	168	168	168
Fe ⁺³ *	1.11	1.11	1.11	2.79	3.35	3.35
Cu ⁺² **	1.27	1.27	1.27	1.0	1.0	1.0
Ru ⁺³	6.54	6.54	6.54	2	3	3
Pd ⁺²	3.19	3.19	3.19	4	4	4
Cd ⁺²	3.3	3.3	3.3	1.0	1.0	1.0
Mn ⁺²	4	4	4	3	4	4



Table: 7 (b)
Masking agents for interfering ions of HDMBHBH and CMHBH

Interfering ion	HDMBHBH	CMHBH
1. *Fe (III)	*Masked by Fluoride 418 µg/ml	*Masked by phosphate 569 µg/ml
2. **Cu (II)	** Masked by Thiourea 484 µg/ml	** Masked by Thiourea 608 µg/ml

Table 8
Comparison of spectrophotometric methods for the determination of Cobalt (II)

Reagent	λ_{max} (nm)	pH	Molar absorptivity $L \cdot mol^{-1} \cdot cm^{-1}$	Beer's law Range ($\mu g/ml$)	Reference
Iso vanillin thio semi carbazone	440	8.4	0.135×10^4	Upto 18.86	7
2-methylindol-3-carboxaldehyde-4-phenyl-3-thiosemicarbazone	388	8.8	7.0×10^3	0.39-1.38	8
Benzyl di thiosemi carbazone	589	4.0	7.3×10^3	1-8	9
Salicylhydroxamic acid	356	8.0	4.4×10^3	15ppm	10
8-hydroxy quinoline	398	10.0	2.74×10^3	0-50 µg/ml	11
Pyridine-2-acetaldehyde salicyloyl-hydrazone	415	1.0-6.0	1.04×10^3	0.5-7.0	12
2-hydroxy-4-methoxy benzophenonethiosemi carbazone	410	9.0	1.7×10^3	2.9-17.6	13
Phenanthrenequinonemono semicarbazone	470	9.0-10.8	1.7×10^3	7.08ppm	14
Furfuraldehyde semi carbazone (FAS)	356	8.1	1.28×10^5	0-10 µg/25ml	15
2,4-dihydroxy acetophenone oxime	390	9.5	2.74×10^3	0.12-1.8	16
2',4'-di hydroxy -5'-bromo chalcone oxime	400	8.0-10.0	2.384×10^3	Upto 18.86	17
4-Hydroxy 3, 5 dimethoxy benzaldehyde 4-hydroxy benzoyl hydrazone (HDMBHBH)	397	9.0	4.37×10^4	0.058-0.589	Present method
Cinnamaldehyde 4-hydroxybenzoylhydrazone	393	9.0	6.5×10^4	0.029-0.294	

CONCLUSION

The proposed methods are simple, accurate and have advantages over the reported methods which suffer from interference by large number of ions or require either heating or extraction or are less sensitive.

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