

Spectrophotometric Determination of Cobalt(II) with Mordant Blue 9 -Application to Vitamin B₁₂ (Injections and Powder)

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ABSTRACT

A spectrophotometric method has been developed for determination of cobalt with Mordant Blue 9 in presence of cetyltrimethylammonium bromide (CTAB) in order to form an intense violet-colored chelate which exhibits maximum absorption at 586 nm at pH 3. Beer's law is obeyed over the range of 0.004 -1 ppm with a molar absorptivity $3.97 \times 10^4 \text{ l.mol}^{-1}.\text{cm}^{-1}$, Sandell's sensitivity index of 1.484 ng.cm^{-2} , while LOD (limit of detection), LOQ (limit of quantitation) are found to be 4.006 ng/ml (n=10) and 13.353 ng/ml (n=10), respectively. The method has been applied for determination of Co(II) in pharmaceutical preparations.

Keywords: cobalt, Mordant Blue9, vitamin B₁₂, CTAB, spectrophotometry.

التقدير الطيفي لفلز الكوبلت (II) مع كاشف المورديانات الأزرق 9- التطبيق على فيتامين B₁₂ (الباودر والإبر)

المخلص

طورت طريقة طيفية لتقدير الكوبلت تعتمد على تفاعل الكوبلت مع كاشف Mordant blue 9 لتكوين معقد كيليتي بنفسجي اللون (بوجود CTAB كمادة فعالة سطحيا) والذي أعطى أعلى امتصاص عند طول موجي 586 نانوميتر عند pH 3 وكانت حدود تطبيق قانون بير في مدى التركيز 0.004 - جزء بالمليون من الكوبلت وكانت الامتصاصية المولارية $10^4 \text{ لتر.مول}^{-1}.\text{سم}^{-1}$ ودلالة ساندل للحساسية 1.484 نانوغرام/سم² و حد الكشف 4.006 نانوغرام/مل (n=10) والحد الكمي 13.353 نانوغرام/مل (n=10). وقد تم تطبيق الطريقة ونجاح في تقدير الكوبلت في مستحضرات صيدلانية مختلفة.

الكلمات الدالة: فلز الكوبلت (II)، كاشف المورديانات الأزرق 9 ، فيتامين B₁₂، التقدير الطيفي، CTAB.

INTRODUCTION

Cobalt is an essential element in human body as a component of vitamin B₁₂ and it is clear that monitoring of body fluids for cobalt is essential for the control of nutritional deficiencies, and perhaps prevention of its toxic effect in cases of occupational exposure (Todorovska *et al.*, 2003). Although cobalt is not highly toxic, but its acute and chronic poisoning gives rise to symptoms such as pulmonary edema, nausea, allergy, gastro-intestinal tract disorders, diarrhea and other disorders (Gupta *et al.*, 2004).

Cobalt (II) ions are also genotoxic and carcinogenic (Ahmed and Hossan, 2008). This metal ion is among the significant toxic metals for environmental surveillance food control occupational medicine, toxicology and hygiene (Enafi *et al.*, 2000). Cobalt (II) has also been employed in the production of sensors (Oiyee *et al.*, 2009; Pedrosa and Berttoi, 2007) and alloy (Hamood and Abed, 2012). Cobalt occurs predominantly in the II oxidation state. In some complexes, it is readily oxidized to Co(III). It forms amine, cyanide, tartrate and EDTA complexes (Marcezonko and Balcerzak, 2000).

Several methods have been reported for the determination of cobalt including, spectrophotometry (Ahmed, 2013; Divarova *et al.*, 2013), electrothermal atomic absorption spectrometry (Dragan *et al.*, 2009), flame atomic stripping voltammetry (Morfobos *et al.*, 2004), adsorptive stripping voltammetry (Orolczuk, 2005), plasma emission spectrometry, (Zhao *et al.*, 2012) and high performance liquid chromatographic separation (Khuhawar and Lanjwani, 1998).

The present article describes a spectrophotometric method for trace determination of cobalt based on its colored-complex formation with the chromogenic mordant blue 9 in acidic medium and in the presence of cetyltrimethylammonium bromide. The method has been found successful in determination of cobalt in pharmaceutical preparations.

EXPERIMENTAL

Apparatus

Spectral and absorbance measurements were carried out using Shimadzu UV-160, spectrophotometer with 1-cm plastic cells.

Atomic absorption spectroscopy (Perkin, USA, 2005)

The pH measurements were carried out using (HANNA pH-211) pH meter

Reagents

All chemicals used are of the highest purity available.

Stock cobalt(II) solution (100µg/ml). The solution was prepared by dissolving 0.1235 g of cobalt (II) nitrate hexahydrate (Hopkin and Williams) in distilled water and the volume was completed to 250 ml with distilled water in a volumetric flask. Dilute cobalt solution were prepared by diluting this stock solution.

MB9 reagent solution (5×10^{-4} M).

The solution was prepared by dissolving 0.1247 g of MB9 (Aldrich, 50% dye content) in distilled water and the solution was diluted to 500 ml in a volumetric flask and then transferred to a dark bottle. This solution was stable for one week at least.

Buffer solution (pH 3) (Perrin and Dempsey, 1974). This solution was prepared by mixing 10 ml of 2M citric acid and 6 ml of 2M NaOH and the volume is completed to 100 ml with distilled water in a volumetric flask.

CTAB solution (1×10^{-3} M). This solution was prepared by dissolving 0.3645 g of cetyltrimethylammoniumbromide (CTAB), (BDH) in distilled water and the volume was completed to 1000 ml.

Vitamin B₁₂ (injection and powder)solution. This solution is prepared by igniting vitamin B₁₂ injection or powder in a furnace for one hour at 700 °C. Then 0.3-3 ml of concentrated HNO₃ is added with heating until complete dissolution. This solution is adjusted to pH 7 with NaOH before dilution to the suitable volume with distilled water in a volumetric flask.

RESULTS AND DISCUSSION

Recommended procedure and calibration graph

The well-known equation for spectrophotometric analysis in a very dilute solution is derived from Beer's law. The effect of the metal concentration is studied according to the optimum reaction conditions, by transferring aliquots of cobalt solution into 25 ml volumetric flasks to cover the range 0.1 - 35 µg Co(II) ion. Then 4 ml of 5×10^{-4} M MB9, 4 ml of 1×10^{-3} M CTAB and 5 ml of citric acid buffer were added and the volume completed to the mark with distilled water. The absorbances at 586 nm were measured for reaction mixtures against the reagent blank prepared in the same manner but without cobalt. The resulting calibration graph obtain is shown in Fig. 1.

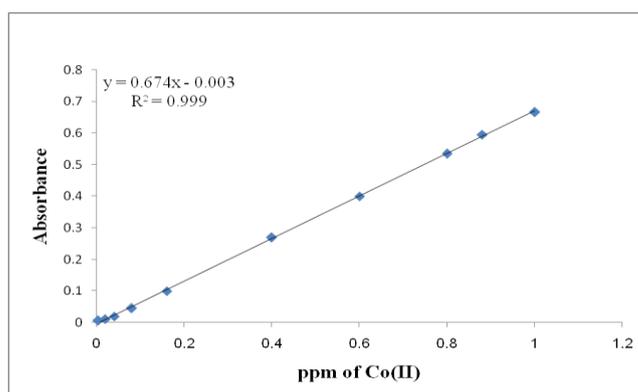


Fig. 1: Calibration graph for cobalt (II) determination with MB9 reagent

The graph is a straight line passing through the origin. The absorbance is linear for 0.1 - 25 μg Co(II)/25 ml; i.e., 0.004 - 1 ppm. The molar absorptivity of the complex is calculated from the equation of calibration graph and found to be $3.97 \times 10^4 \text{ l.mol}^{-1}.\text{cm}^{-1}$ with Sandell's sensitivity index of 1.484 ng.cm^{-2} , while limit of detection (LOD), limit of (LOQ) (Valcarcel, 2000) found to be 4.006 ng/ml and 13.353 ng/ml, respectively. At higher concentration of Co(II) ion, a negative deviation is observed Fig. 1. The r^2 (coefficient of determination) is 0.999, showing an excellent linearity.

Preliminary Investigations:

The visible spectra of the violet colored compound was formed by mixing 20 μg of cobalt(II) solution(M), 2 ml of 5×10^{-4} M MB9(R), 5 ml of 1×10^{-4} M CTAB(S) and 3.5 ml of 0.01 M HCl in different orders of addition as shown in Table 1.

Table 1 : Preliminary check of the colored system

Reaction components	Order number	Absorbance of sample	λ_{max}	Absorbance of blank	λ_{max}
M + S + R + HCl	I	0.104	587.5	0.382	515.5
M + S + HCl + R	II	0.003	463.0	0.389	515.0
M + R + HCl + S	III	0.025	571.0	0.389	516.0

From Table 1, order I is chosen for the following work.

Study of Optimum Reaction Conditions:

The effects of various parameters on the absorption intensity of the colored compound are studied and optimum conditions have been selected for the determination of cobalt with MB9 reagent in aqueous solution.

Effect of pH

The investigation of pH has been firstly investigated since most of the organic reagents used for the metal determination are of the weak-acid type and these are affected by pH change. The extent of compound formation and hence, the absorbance of the final solution and λ_{max} are found to be a function of hydrogen ion concentration. Therefore, a volumes of 0.01M HCl or NaOH solutions are added to aliquots of solution containing 20 μg Co (II), 5 ml of 1×10^{-3} M CTAB and 2 ml of 5×10^{-4} M MB9 reagent. The pH of the final colored solution after dilution to 25 ml was measured and the absorbance of each colored solution against its corresponding reagent blank was recorded. The results indicated that optimum pH could be considered as 2.6-3.5, since color contrast and sample absorbance rather good. pH 3 is chosen for the following experiments.

To maintain the optimum pH concentration, buffers of different composition pH 3 have been examined. These buffers are: potassium hydrogen phthalate + HCl (B₁), formic acid + sodium formate (B₂), glycine + HCl (B₃), tartaric acid + NaOH (B₄) and citric acid + NaOH (B₅) (Perrin and Dempsey, 1974). The effect of these buffers solutions on the absorbance of the Co(II)-MB9 complex is shown in Table 2.

Table 2 : Effect of buffers on absorbance

MI of buffer solution	Absorbance / ml of buffer added				
	B ₁	B ₂	B ₃	B ₄	B ₅
1	0.225	0.210	0.239	0.222	0.227
	B* 0.086	0.068	0.072	0.070	0.074
2	0.211	0.213	0.239	0.214	0.236
	B 0.059	0.068	0.072	0.067	0.073
3	0.232	0.210	0.234	0.214	0.268
	B 0.049	0.068	0.070	0.069	0.074
4	0.219	0.215	0.257	0.228	0.267
	B 0.046	0.068	0.070	0.066	0.073
5	0.257	0.221	0.239	0.250	0.275
	B 0.049	0.068	0.066	0.071	0.076
7	0.262	0.220	0.242	0.265	0.268
	B 0.039	0.071	0.070	0.066	0.073
10	0.277	0.218	0.240	0.286	0.276
	B 0.037	0.071	0.074	0.071	0.076
Final pH of the reaction mixture	3.12-3.44	3.98-3.17	3.15-3.55	3.19-3.35	3.19-3.36

* The blank value at λ_{\max}

From the Table 2, five ml of B₅ solution was chosen for the subsequent work, since it gives a good absorbance for the standard and a lower blank value.

Effect of masking agents

To enhance the selectivity of the organic reagent (MB9) used, it has been called for the addition of some of the commonly - used masking agents: tartaric acid, citric acid, oxalic acid, ascorbic acid, sodium flourid, 5-sulphosalicylic acid (5-SSA), ethylene diaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), diethylenetriamine pentaacetic acid (DETPA), and trans-1,2-diamino-cyclohexane tetraacetic acid (DCTA).

The results shows that neither any of the masking agents used were useful. Therefore, they neglected in the next steps of the work.

Effect of surfactant amount

Surfactants can induce favorable shifts in equilibrium constant and spectral properties, inhibit undesirable reactions, such as hydrolysis and photolysis, stabilize reaction intermediates, co-solubilize non-polar and polar samples, derivatization reagents and products and speed up reactions, by means of micellar catalysis (Esteve- Romero *et al.*, 1995; Sulaiman *et al.*, 2013). In this respect, cationic CTAB, anionic SDS and non-ionic (TritonX-100, Tween 80 and Gelatin) surfactants with different amounts and different amount of 5×10^{-4} M MB9 have been examined. The results shows that, 4 ml of 1×10^{-3} M CTAB with 4 ml of 5×10^{-4} M MB9 were the best therefore chosen in the subsequent experiments since they give the colored system longer stability period.

Effect of time and reagent amount on absorbance

The effect of time on the development and stability of the colored complex with different amount of reagent has been investigated under the optimum experimental conditions described above. The formation of the colored complex has been completed after 15 minutes using 4 ml of 5×10^{-4} M MB9 and the absorbance of the complex remained constant for at least 60 minutes.

Order of addition of reagent

The reagent used in the investigation have order of addition added to the metal ion solution in different orders to find the optimum. The results are given in Table 3.

Table 3: The order of addition of reagent

Reaction components	Order number	Absorbance
M + R + S + B	I	0.495
M + R + B + S	II	0.261
M + S + R + B	III	0.369

M= Co(II)

S= CTAB

R= MB9

B= Buffer

Order I is recommended in the subsequent investigation for its relatively higher absorbance.

Final absorption spectra

Under the optimum conditions, the absorption spectra of the coloured complex and that of the corresponding reagent blank are shown in Fig. 2. The spectrum of the violet colored compound showed maximum absorption at 586 nm. The reagent blank showed maximum absorption at 510 nm. The wavelength of maximum absorption at 586 nm has been used for the calibration curve.

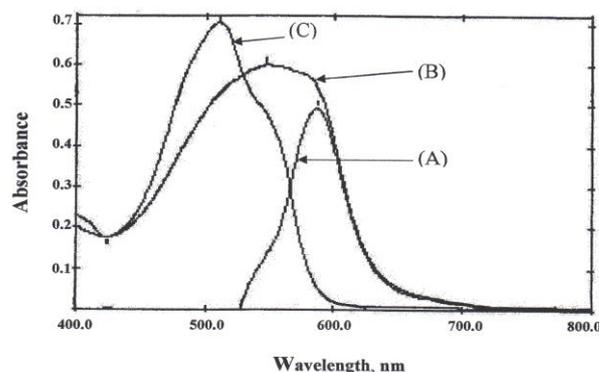


Fig. 2: Absorption spectra of 20 μ g of Co(II)/25 ml treated as the procedure and measured: (A) against blank, (B) against distilled water and (C) blank against distilled water.

Accuracy and precision of method

To check the accuracy and precision, cobalt is determined under the above-established conditions at two different concentrations.

The results shown in Table 4 indicate that the calibration curve is accurate and precise.

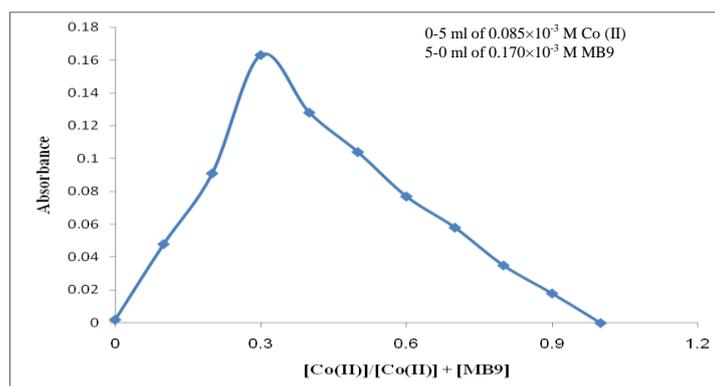
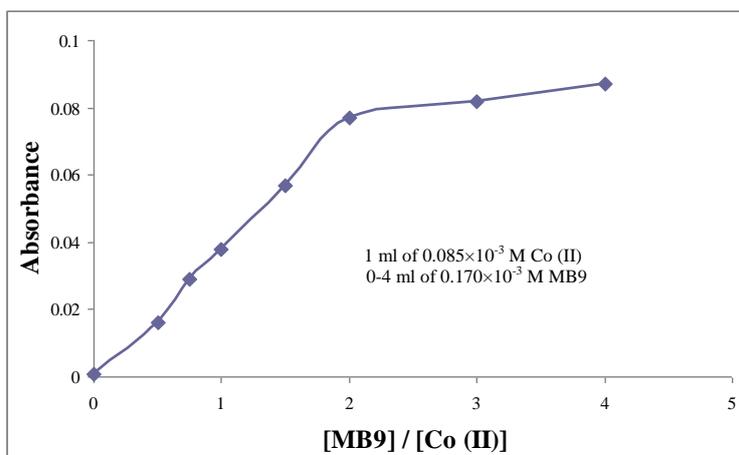
Table 4: Accuracy and precision

Cobalt (II) taken $\mu\text{g}/25\text{ml}$	RE%*	SD%*	RSD%*
10	- 0.42	± 0.20	± 0.84
20	+ 0.35	± 0.21	± 0.42

* Average from five determination

Nature of the complex

Job's method of continuous variations and mole-ratio (Hargis, 1988) method are used to evaluate the combining ratio of cobalt(II) to MB9 in the compound. The results represented in Fig. 3 and 4 relieve that Co(II) reacts with MB9 in a ratio of 1:2. The concentration of the reagent has been different from the concentration of metal because it has 50% dye.

**Fig. 3: Job's plot for cobalt(II) with MB9****Fig. 4: Mole-ratio plot for cobalt(II) with MB9**

The proportion of CTAB in the complex is determined by Job's method of continuous variations as shown in Fig. 5.

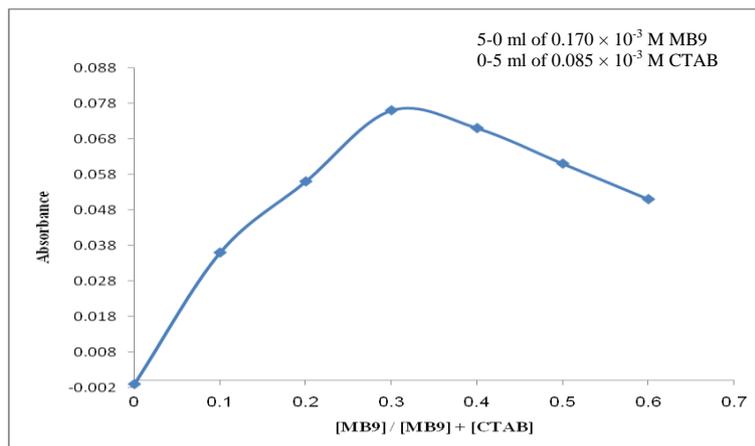


Fig. 5: Job's plot for MB9-CTAB

Fig. 5 indicates that a molar ratio of MB9 to CTAB is 1:2. The complex is thus, formulated as $\text{Co}(\text{MB9})_2(\text{CTAB})_4$.

Solutions are formulated to contain exactly one proportion of cobalt(II) to two of the MB9 reagent. The interaction between the metal (M) and ligand (L) proceeds according to:



Knowing the value of α from the equation:
$$\alpha = \frac{A_m - A_s}{A_m}$$

Where A_m is the absorbance of the solution containing excess amount of ligand and A_s is the absorbance of the solution containing stoichiometric amounts of ligand and C are essentially the same as the concentration of Co(II) ion. The conditional constant (K) readily be calculated Table 5.

Table 5: Stability constant of Co (II)-MB9 complex

MI of 0.085×10^{-3} M Co(II) /25ml	Absorbance		α	K M^{-2}
	A_s	A_m		
1.0	0.069	0.105	0.343	3.5209×10^{11}
1.5	0.115	0.165	0.303	2.4083×10^{11}

The stability constant value found shows that the chelate is stable.

Study of Interferences

The recommended procedure for the determination of cobalt using MB9 reagent is followed to study the interfering effects of foreign species by determination $20\mu\text{g}$ of cobalt in presence of each interfering ion. The results are shown in Table 6.

Table 6: Study of interferences

Foreign ion	Form added	Interferences*				
		%				
		Amount added, µg				
		5	15	25	50	100
Al ³⁺	Al(NO ₃) ₃ .9H ₂ O	+20.47	-8.41	-20.69	-24.78	-
Ba ²⁺	BaCl ₂ .2H ₂ O	-1.42	+0.81	-0.20	-1.22	+0.41
Be ²⁺	BeSO ₄ .4H ₂ O	-21.13	-31.61	-43.93	-59.23	-83.86
Ca ²⁺	Ca(NO ₃) ₂ .4H ₂ O	-1.66	+1.04	+0.41	-2.49	-2.28
Cd ²⁺	Cd(CH ₃ COO) ₂ .2H ₂ O	-12.43	-6.22	-4.26	-3.20	-6.22
Cr ³⁺	CrCl ₃ .6H ₂ O	+3.17	+4.16	-13.27	-40.40	-79.21
CrO ₄ ²⁻	K ₂ CrO ₄	+1.67	+0.42	+3.57	+4.81	+4.81
Cu ²⁺	CuCl ₂ .2H ₂ O	+5.65	-0.42	-14.02	-38.49	-26.78
K ⁺	KCl	+26.54	+18.05	+11.04	+11.88	+6.79
Li ⁺	LiClO ₄	-10.23	Turbid	Turbid	Turbid	Turbid
Mg ²⁺	Mg(NO ₃) ₂ .6H ₂ O	-0.21	-3.13	-2.5	-3.75	-2.92
Mn ²⁺	MnCl ₂ .4H ₂ O	-4.60	+4.60	-4.66	-2.51	-3.56
Mo ₇ O ₂₄ ⁶⁻	(NH ₄) ₆ Mo ₇ O ₂₄	-1.49	-2.55	-2.34	-9.15	-22.34
Na ⁺	NaCl	+3.66	-2.58	+2.80	+0.65	+4.95
Ni ²⁺	Ni(NO ₃) ₂ .6H ₂ O	-9.20	-27.43	-46.18	-87.32	-95.14
Sr ²⁺	SrCl ₂ .6H ₂ O	+0.21	+0.82	-1.04	-1.25	+1.46
WO ₄ ²⁻	Na ₂ WO ₄ .4H ₂ O	+0.21	-0.63	-0.63	-1.90	+0.21
Y ³⁺	YCl ₃ .6H ₂ O	-1.46	-7.28	-15.59	-49.06	-87.73
Zn ²⁺	ZnSO ₄ .7H ₂ O	+0.66	+3.52	+3.74	-2.86	-12.09
Tl ⁺	TlCl	-0.19	-2.70	-2.12	+0.39	+1.54
Sc ³⁺	Sc ₂ (SO ₄) ₃ .6H ₂ O	-2.20	-32.31	-70.99	-103.96	-101.76
Cl ⁻	KCl	+2.12	-1.54	+2.03	+2.12	+0.19
CO ₃ ²⁻	Na ₂ CO ₃	-3.07	+1.73	+1.15	-3.07	-0.19
HCO ₃ ⁻	NaHCO ₃	-3.65	-0.96	+1.92	+2.88	-2.30
I ⁻	NaI	-0.58	-4.22	-3.26	-5.18	-9.41
NO ₂ ⁻	NaNO ₂	-0.38	-5.82	-2.25	-6.57	-2.25
SO ₄ ²⁻	Na ₂ SO ₄	-1.54	-1.15	-1.34	-0.38	-2.50
SCN ⁻	KSCN	-0.19	-3.45	-2.30	-2.69	-1.73
NO ₃ ⁻	NaNO ₃	-0.58	-1.35	+2.13	-2.71	-2.51
CH ₃ COO ⁻	Na(CH ₃ COO).3H ₂ O	-3.26	-1.15	-0.96	-2.88	-1.34
CN ⁻	KCN	-17.44	-22.74	-32.99	-58.29	-91.97
Pb ²⁺	Pb(NO ₃) ₂	-1.21	-3.02	-5.43	-6.04	-1.01
SO ₃ ²⁻	Na ₂ SO ₃	-3.58	-6.56	-6.16	-3.58	-11.93
S ₂ O ₃ ²⁻	Na ₂ S ₂ O ₃	-2.72	+0.09	-0.19	-1.97	-0.66

*For at least four replications

The high negative error observed in case of some ions, is due to the competition of these ions with Co(II) for the reagent and formation of their own complexes (appearance of pink color) then depleting the reagent available for the Co(II) ion.

The present reagent cannot differentiate between cobalt(II) and nickel(II). Therefore, a preliminary separation step is necessary.

Applications

The method has been applied for the determination of Co(II) in pharmaceutical preparations, in the form of vitamin B₁₂ ampoules and powder.

Cobalt has been determined with the proposed method and compared with the results obtained by atomic absorption spectrometry. The pretreatment of vitamin samples has been done for both methods, proposed method and AAS method. The results are shown in Table 7.

Table 7: Determination of cobalt (II) in some pharmaceutical samples

Sample	Co ⁺² added, µl/25 ml	Recovery* %,	
		present method	AAS method
Vitamin B ₁₂ injection (MAKHBRÜCKE, E. K. Co., Germany)	0.1	100.0	101.0
	15	100.0	101.0
	25	99.01	101.0
Vitamin B ₁₂ injection (Trittau- Germany)	0.2	100.0	100.0
	25	101.0	100.0
Vitamin B ₁₂ injection (Sane and Smart, London, U.K)	0.1	100.0	100.1
	15	100.0	100.1
	25	99.99	100.1
Vitamin B ₁₂ injection (Nanjing Hyaxn Biopharam. Co.LTD. China)	0.1	100.0	99.90
	15	99.91	99.90
	25	98.00	99.90
Vitamin B ₁₂ powder (N.D.I- Iraq)	0.1	100.0	100.0
	15	101.0	100.0
	25	102.0	100.0

* From three determinations

Results in Table 7 indicate that the proposed method can be successfully applied to the determination of Co(II) in vitamin B₁₂ formulations.

Comparison of Method

Table 8 shows the comparison of spectrophotometric method of cobalt(II) determination based on chelating with MB9 reagent with a literature thiocyanate method (Marcezonko and Balcerzak, 2000).

Table 8: Comparison of methods

Analytical parameter	Present method	Literature method
pH	3	-
λ_{\max} (nm)	586.0	620.0
Reagent	MB9	Thiocyanate
Amount of reagent solution	4 ml of 5×10^{-4} M	5 ml of 50%
Range of cobalt determination, (ppm)	0.004-1	-
Molar absorptivity ($\text{l.mol}^{-1}.\text{cm}^{-1}$)	3.97×10^4	1.9×10^3
RSD (%)	± 0.63	-
Determination coefficient (r^2)	0.999	-
K ($\text{l}^2.\text{mol}^{-2}$)	2.9646×10^{11}	-
Nature of complex(Co:Reagent)	1:2	-
Application of the method	Vitamin B ₁₂ (ampoules and powder)	Vitamin B ₁₂

The present method seems to be good method for the determination of cobalt in vitamin B₁₂.

CONCLUSION

A sensitive spectrophotometric method for determination of cobalt ion with MB9 (in presence of CTAB) as a chromogenic reagent in aqueous solution has been developed. The colored complex is violet shows maximum absorption at 586 nm with a molar absorptivity of $3.97 \times 10^4 \text{ l.mol}^{-1}.\text{cm}^{-1}$ and adheres to Beer's law over the range 0.004-1 ppm. Sandell's sensitivity index of 1.484 ng.cm^{-2} , while LOD, LOQ are found to be 4.006 ng/ml and 13.353 ng/ml, respectively. The method has been applied to determination of Co(II) in pharmaceutical preparation.

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