Spectrophotometric Determination of Cobalt(II) Using N-(2-pyrrolylmethylene)-2,4,6-triamino-1,3,5-triazine as a Chromogenic Reagent

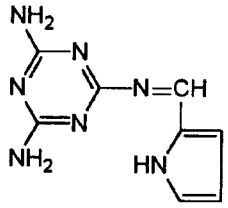
ZAHID H. CHOHAN* AND M. A. FAROOQ
Department of Chemistry, Islamia University, Bahawalpur (Pakistan)

(Received 7th May, 2001 revised 4th August, 2001)

Summary: A sensitive spectrophotometric method for the determination of cobalt(II) using a newly synthesised chromogenic reagent N-(2-pyrrolylmethylene)-2,4,6-triamino-1,3,5-triazine (PMTT) has been developed. The optimum conditions for the reaction of PMTT with cobalt(II) were studied. The calibration graphs were plotted. The molar absorptivity was found to be 1.83×10^5 dm^3 $mol^{-1}cm^{-1}$. To check the validity and sensitivity of PMTT, the method was applied for the determination of cobalt (II) in different samples [tablet, capsule and injection formulations] of vitamin B_{12}. The quantitative results of these studies show the presence of co(II) as 0.84, 0.82 and 0.81 ppm, respectively, in tablet, capsule and injection formulations in the tested vitamin. B_{12} samples.

Introduction

Determination of microamounts of cobalt(II) from the daily used food and other commodities has attracted a great deal of attention because of its environmental concern. Many spectrophotometric methods for its determination have been reported. Among those methods, using 5-(2-amino-4-hydroxy-benzeneazo)-*o*-benzenebromo-methylhydrazide [1], dithiazone [2], 4-(2-pyridylazo)resorcinol [3], thiooxamide [4], thioanide [5], dithiacarbamate [6], 6-amino-4-hydroxy-5-(2-hydroxy-4-nitobenzeneazo) naphthalene sulfoacid [7] and 4,4'-diazobenzene-diazoaminoazobenzene [8] are already known. However, most of these methods are either complicated, expensive, time consuming and also lack sensitivity.



(Figure 1)

In this paper, we wish to report a highly sensitive chromogenic reagent N-(2-pyrrolyl-methylene)-2,4,6-triamino-1,3,5-triazine (PMTT) (Figure 1) which has been synthesised, characterised and reported [9] earlier by us and now used to determine microamounts of cobalt(II) in different samples of vitamin B_{12} [tablet, injection and capsule formulations]. PMTT instantaneously reacted with cobalt(II) in sodium tetraborate buffer solution at pH-9.5 to form a red complex. The calibration graph was plotted which showed a linear relationship in the range 0-8μg per 25 ml cobalt(II). The molar absorptivity was 1.83×10^5 dm^3 mol^{-1} cm^{-1}. The colour system developed was stable for 48 h.

Results and Discussion

The chromogenic reagent (PMTT) is a stable compound and could be indefinitely stored as a solid and in a solution form. It was prepared by a standard Schiff-base reaction. It contains suitably placed donor atoms and gives an instantaneously a red coloured complex with Co(II) metal ion (Figure 2) in a stoichiometric ratio of metal : PMTT (1 : 2).

Effect of pH

Although at different pH values the maximum absorption was tested but, at pH 9.5, a maximum and constant absorption was achieved by using sodium tetraborate buffer solution. Therefore, at pH 9.5 all subsequent studies were made. Also, by keeping the amount of cobalt(II) constant at pH 9.5 and changing the concentration of PMTT the absorption was measured. It was found that by using 3 ml of PMTT (0.05 %), the maximum and constant absorption was obtained.

Effect of Temperature

The formation of a coloured complex of Co(II) with PMTT was instantaneous. The absorption

*To whom all correspondence should be addressed.

of the complex remained constant for at least 48 hours at room temperature. The effect of temperature on the absorbance was also studied. It was observed that increase in temperature to 50°C or above resulted in a gradual decrease of intensities of absorption.

Absorption Spectra

The absorption spectra of PMTT and of its complex with cobalt(II) are shown in Fig. 2. It is evident that the maximum absorption of the free PMTT is found at 430 nm and that of the complex is at 535 nm showing a difference of 105 nm.

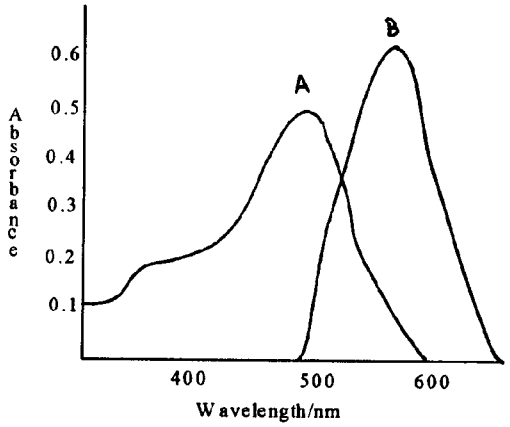


Fig. 2 Absorbance spectra of PMTT [A] and its cobalt(II) complex [B]

Beers' Law and Sensitivity

A calibration graph was plotted using the proposed method. Beers' law was obeyed in the range 0-8 μg of cobalt(II) per 20 ml. The proposed method was compared to other methods (Table 1). It was found that this method by using PMTT is much sensitive, more rapid, and cheaper than the other methods. Moreover, no use of any toxic solvents was involved.

Effect of Interfering Ions

A study of interfering ions in the determination of cobalt(II) was carried out and these species did not cause an error exceeding 5 %: 40 mg of Na^+, K^+, Cl^-, NO_3^-, SO_4^{-2}; 30 mg of Br^-, CO_3^{-2}, $S_2O_3^{-2}$ and PO_4^{-3}; 20 mg of Ca^{+2}, SCN^-, Mg^{+2} and 15 mg of $C_2O_4^{-2}$, Pb^{+2} and Cr^{+4}. However, Cu^{+2}, Ni^{+2} and Zn^{+2} caused positive interference at the concentration level as Co(II).

Experimental

Instrumentation

A Hitachi model U-2000 double-beam spectrophotometer using glass cells of 1 cm thickness was employed for measuring the absorbance. A Genway Model-3020 pH meter was used for pH measurements. Infrared spectra were recorded on a Philips Analytical PU 9800 FTIR spectrophotometer. ^{1}H-NMR spectra were obtained in DMSO-d_6 using a Brucker 250 MHz spectrometer. The CHN analysis was carried out by Butterworth Laboratories Ltd. All reagents and solvents used were of analytical reagent grade. Vitamin B_{12} samples, Methycobal injection (Eisal Pharmaceutical Comp Ltd, Japan), Mecobal tablets (Nabiqasim Pharmaceutical Comp Ltd, Karachi, Pakistan), Cobalmin tablets (Macter International Pharmaceutical Comp Ltd, Karachi, Pakistan) and Metran capsules (Daewon Pharmaceutical Comp Ltd, Seoul, Korea) were obtained from the respective Pharmaceutical Laboratories.

Buffer Solution

Buffer solution was prepared by dissolving $Na_2B_4O_7.10H_2O$ (10 g) in distilled water (250 ml) and adjusted the pH with sodium hydroxide (0.5 N) or hydrochloric acid (2N).

Cobalt(II) Stock Solution

It was prepared by dissolving cobalt (0.1 g) in nitric acid (9 M, 10 ml) and diluting to 100 cm^3 with distilled water in calibrated flask. A 5.0 μg ml^{-1} working standard solution was prepared by further dilution with distilled water.

(Table 1) Comparison of Reagents for Determination of Co(II)

Reagent	PH	λ_{max} (nm)	Co(II) (μg)	Ref
2-(2-T hiazolylazo)benzoic acid	5	650	0-12	[10]
2-(2-Bromobenzothiazolylazo)-5-dimethylamino-4,5-benzoic acid	4-5	710	0-10	[11]
2-(5-Nitro-2-pyridineazo)-5-dimethylamino benzoic acid	6-7	530	0-14	[12]
MPTT	9.5	535	0-8	Proposed

Chromogenic Reagent Solution

A solution of chromogenic reagent (0.05 % m/v) was prepared by dissolving PMTT (0.13 g) in ethanol (250 ml).

Preparation of Chromogenic Reagent (PMTT)

Pyrrol-2-carboxaldehyde (0.95 g, 0.01 M) in ethanol (15 ml) was added to a stirred hot ethanolic solution (20 ml) of melamine (1.26 g, 0.01 M). Then 2-3 drops of concentrated sulphuric acid were added and mixture refluxed for 2 h, during which a solid product was formed. The reaction mixture was cooled to room temperature, filtered and washed with ethanol (3x10 ml) to give a yellow solid product. It was recrystallised from hot ethanol, m.p 180°C. IR (KBr, cm^{-1}) 3220, 3160, 2932, 2020, 1695, 1630, 1615, 1605, 1545, 1110, 950, 785. ^{1}H-NMR (DMSO-d_6, 250 MHz) δ 5.5 (s, 4H, NH_2), 6.8 (s, 1H, azomethine), 6.15 (2H, dd, H-1,2), 7.75 (d, 1H, H-3), 7.9 (s, 1H, NH). Analysis Found C 47.33, H 4.42, N 48.29 Calculated for $C_8H_9N_7$ required C 47.31, H 4.33, N 48.25 %.

Recommended Method

General method

Cobalt(II) (5 μg) was added to a buffer solution (2 ml) in a 25 ml calibrated flask. Then PMTT solution (3 ml, 0.05%) was added in it and diluted to the mark with distilled water by mixing the solution well. The colour was developed and measured the absorbance at 535 nm against a reagent blank.

Method for the determination of cobalt(II) in samples

A suitable amount of sample containing not more than 8 μg of cobalt(II) was placed in a 25 ml calibrated flask. Then buffer solution (2 ml) and PMTT solution (3 ml) was added in it and mixed thoroughly. This solution was diluted with distilled water upto the mark. The absorbance was measured at 535 nm in a 1 cm cell against a reagent blank. The calibration graph was prepared for the standard cobalt(II) solution following the same method.

Table-2:Results of Determination of Co(II) in Vitamin B_{12} Samples

Sample	Measured Co(II) (ppm)	Certified Co(II) (ppm)
Vitamin B_{12} (tablets)	0.84	0.85
Vitamin B_{12} (capsules)	0.82	0.84
Vitamin B_{12} (injection)	0.81	0.82

Determination of cobalt(II) in vitamin B_{12} samples.

Cobalamin (vitamin B_{12}) sample was placed in a flask and added 2-3 ml of nitric acid in it for dissolution. This solution was transfered into 100 ml calibrated flask and diluted it upto the mark with distilled water. Then followed the steps as in general procedure. The results of determination are reproduced in Table 2.

References

1 H. M. Ma and X. S. Huang, *Hua. Xua. Xue. Bao.*, **52**, 1199 (1994).

2 W. D. Jacob and J. H. Yoe, *Anal. Chim. Acta.*, **20**, 332 (1959).

3 S. G. Maulive, I. V. Pyatritskii and L. K. Kolements, *Chem. Anal.*, **35**, 861 (1981).

4 J. Xavier, P. Ray and E. D. West, *Ind. Eng. Chem. Anal.*, **35**, 432 (1958).

5 A. V. Radhusev and B. V. Golomolzin, *Zh. Anal. Khim.*, **34**, 742 (1979).

6 A. K. De, S. M. Khopkar and R. A. Chalmer, "*Solvent Extrcation of Metals*", Van Nostrand Reinhold, N.York, 1970.

7 V. P. Dedkora, M. A. Azarashvihi and S. D. Swin, *Zh. Anal. Khim.*, **44**, 2012 (1989).

8 G. Jin, Y. Zhu, W. Jiang, B. Xie and B. Cheng, Analyst., **122**, 263 (1997).

9 Z. H. Chohan and M. A. Farooq,. *Pak. J. Pharmaceut. Sci.*, 7, 45 (1994).

10 H. Wada, T. Ishizuki and G. Nakagawa, *Anal. Chim. Acta.*, **135**, 333 (1982).

11 T. Katami, T. Hayakawa, M. Furukawa and S. Shibata, *Analyst*, **110**, 399 (1985).

12 Y. Tong, Y. P. Liu and J. C. Lou, *Fenxi. Shiyan. Shi.*, **12**, 25 (1993).