



Trade Science Inc.

April 2007

Volume 5 Issue 1-6

Analytical CHEMISTRY

An Indian Journal

Full Paper

ACAIJ, 5(1-6), 2007 [130-133]

Solid Phase Spectrophotometric Determination Of Cobalt By Xylenol Orange



Corresponding Author

Jila Azad
Department of Chemistry, Faculty of science,
Alzahra University, Vanak, Tehran, (IRAN)
E-mail: Jazad@alzahra.ac.ir

Received: 10th December, 2006

Accepted: 25th December, 2006

Web Publication Date : 15th April, 2007



Co-Authors

Nahid Chalyavi¹, Kazem Kargosha²

¹Department of Chemistry, Faculty of Science, Alzahra University, Vanak, Tehran, (IRAN)

²Chem. And Chemi. Eng. Research Center of Iran, P.O.Box 14335-186 Tehran, (IRAN)

ABSTRACT

A simple and sensitive solid phase spectrophotometric method for the determination of cobalt is proposed based on the reaction between cobalt and xylenol orange (XO). The reaction product is fixed on the anionic exchanger resin sephadex QAE A-25 at pH= 5. The optical absorbance of the anionic gel like resin, packed in a 1.00 mm cell is directly measured at 588.0 nm. The linear range of calibration curve is found to be 100-1000 μgL^{-1} , with a detection limit of 13 ppb. The relative standard deviation for ten independent determinations is 2.1%. The effect of foreign ions is also studied. © 2007 Trade Science Inc. - INDIA

KEYWORDS

Solid phase;
Spectrophotometry;
Sephadex;
Cobalt;
Xylenol Orange.

INTRODUCTION

Cobalt is of considerable interest in many fields, and especially in the field of biochemistry because it is concerned with human biochemical metabolism^[1]. Cobalt is an essential trace element in human dietary intake, possessing anti-anemic properties and acting as the central atom of vitamin B₁₂ (cyanocobalamin), which is widely responsible for the production of red blood cells. However, it can be toxic at higher concentrations. Due to these properties, it often requires methods capable of quantitatively monitoring its presence at trace levels^[2-5].

The solid-phase spectrophotometry (SPS) is paid great attention recently^[6-8] since it was introduced in 1976^[9]. The reason is that this technique can provide various important advantages: the sensitivity (expressed as molar absorptivity) is much higher than the corresponding spectrophotometry in solution, it does not require an expensive instrumentation and the species interfering in spectrophotometry in solution can be excluded from the resin in proper conditions.

In this paper, solid phase spectrophotometry technique has been used for cobalt determination by fixation of a cobalt-xylenol orange complex on a

solid phase anion exchanger (Sephadex QAE A-25) and measurement of its optical absorbance directly at 588nm. Different variables affecting cobalt and XO reaction and also adsorption of cobalt complex on solid phase are studied.

EXPERIMENTAL

Apparatus

A Philips PU8800 double beam UV-Vis spectrophotometer and a pair of 1mm optical quartz cell were used for all spectral measurements. A Behdad centrifuge and a metrohm 691 pH meter with a combined glass calomel electrode were used for sample preparation and pH measurement respectively.

Reagents

All solutions were prepared using analytical grade reagents and freshly distilled and deionized water. A 1.0×10^{-2} M cobalt standard solution was prepared by dissolving 0.23793g $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in freshly deionized water and diluting it to 100 ml in a volumetric flask. 1.0×10^{-4} M and 5×10^{-5} M cobalt standard solutions were prepared by dilution.

A 1.0×10^{-2} M xylene orange solution was prepared by dissolving 0.38030g xylene orange (Sigma-Aldrich) in 50 ml of deionized water. This solution was further diluted to 1.0×10^{-4} M.

Acetate buffer solutions (pH= 3.5-6.0) were prepared by diluting appropriate volumes of 0.2 M acetic acid to 100 ml with 0.2 M sodium acetate solution. Phosphate buffer solutions (pH= 6.5) was prepared by diluting appropriate volume of 0.2 M sodium hydroxide to 100 ml with 0.2 M potassium dihydrogen phosphate.

The anionic resin (Sephadex QAE A-25 from pharmacia) in its chloride form was used as received from the supplier. To avoid contamination no pre-treatment was performed.

General procedure

An adequate volume of cobalt standard solution was transferred to a 25ml beaker to which 3ml buffer solution (pH=5.0), 50mg sephadex QAE A-25 ion exchanger resin and 1.2ml XO (1.0×10^{-4} M) were added. The mixture was stirred for 5 min and then

filtered. Resin beads together with a few drops of buffer solution were transferred to a 1mm quartz cell and the cell was centrifuged for 1 min. at 2000 rpm. Finally the absorbance of the sample was measured at 588 nm against a reference sample. This reference sample was prepared by applying the above procedure to a deionized water sample.

RESULTS AND DISCUSSION

Special characteristics

The XO-cobalt complex solution shows a maximum absorbance at 588nm. When the complex is fixed on sephadex anionic exchanger resin still a sharp peak is observed at the same wavelength. Spectrums of equal amounts of cobalt-XO complex (with cobalt concentration of 5×10^{-5} M) in liquid phase and adsorbed on sephadex surface are compared. The absorbance of the complex on the sephadex solid phase is large enough for determination of cobalt (Figure 1a) but no signal is observed in liquid phase (Figure 1b).

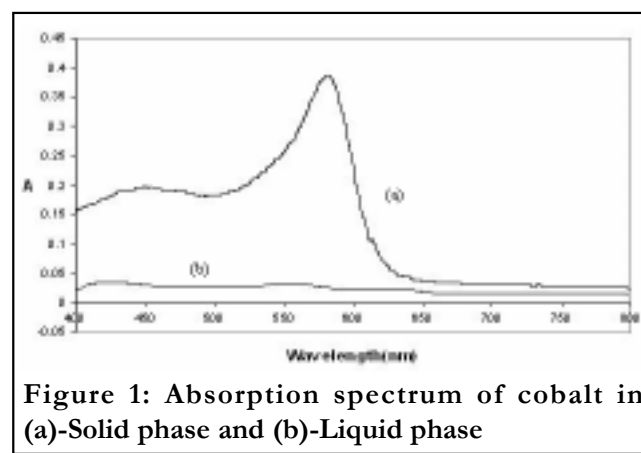


Figure 1: Absorption spectrum of cobalt in (a)-Solid phase and (b)-Liquid phase

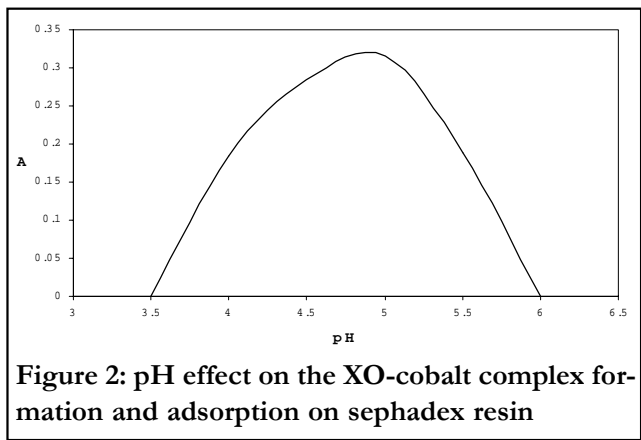
Optimization of variables

A series of experiments were conducted to establish the optimum values of variables. The optimized parameters include pH, XO concentration, the amount of anion exchange resin and duration of stirring period.

pH effect

The effect of pH was investigated over the pH range of 3.5-6.5. The pH was adjusted to the desired value using acetate buffer solution for the pH

Full Paper



range of 3.5-6 and phosphate buffer for the pH of 6.5. The absorbance of XO-cobalt complex fixed on the sephadex surface was measured at 588nm at different pH values. The changes in absorbance at different pH values are shown in figure 2. As can be seen from figure 2, the best pH value for complex formation and its fixation on the sephadex surface is 5. A significant decrease in the absorbance of complex was observed at pH values below and above 5. To fix the pH of the complex solution at 5, a sodium acetate-acetic acid buffer (0.2M) was used.

XO concentration

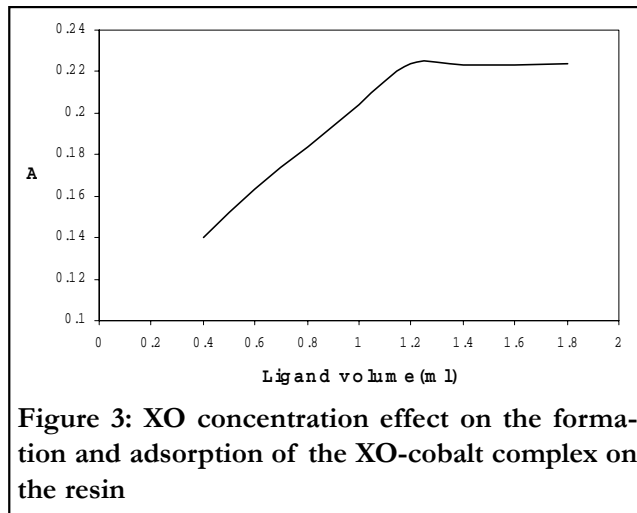
The effect of XO concentration on the formation and adsorption of the XO-cobalt complex on the solid phase was studied by adding different volumes of 1.0×10^{-4} M XO solution to the sample solution and measuring the absorbance of the complex adsorbed on the sephadex. The results are shown in figure 3. The optimum volume of 1.2ml XO was established.

Stirring time

The optimum stirring time was established and the best absorption was obtained in 15 minutes.

The amount of resin

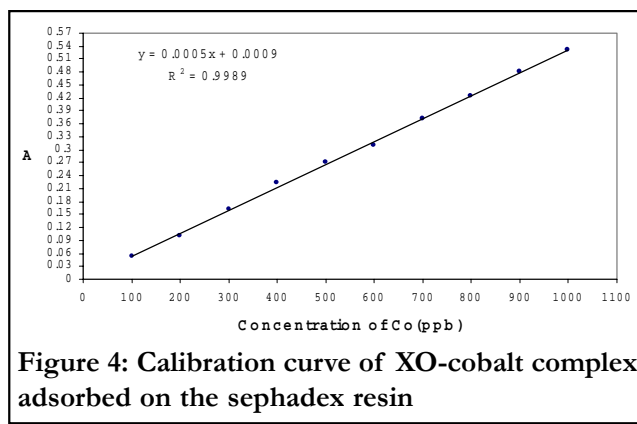
The optimum amount of resin for the adsorption of analyte was determined. Since the analyte concentrates on the solid support, the best sensitivity was obtained with the smallest amount of resin. Thus just enough amount of resin to fill the cell up to a suitable height for measurement was used. It was found to be 50mg of resin. By centrifugation of the gel contained in the cell an increased signal with



better reproducibility was observed. Thus the samples were centrifuged at 2000rpm for one min prior to the final measurement. After some experiments the following order of the addition of constituents was adapted: buffer, resin, cobalt and XO.

Analytical data

The calibration curve for the standard cobalt samples analyzed by the proposed method was linear at the concentration range of 100-1000 $\mu\text{g/L}$ with a correlation coefficient of 0.9989 (See figure 4).



The reproducibility of the method was determined and the relative standard deviation for analyzing ten independent samples containing $2\mu\text{g}$ cobalt was found to be 2.1%. A detection limit of 13 ppb was obtained using 3σ recommendation for its calculation.

Effect of foreign ions

The effect of several species on the cobalt signal was evaluated. Any species which changes the

TABLE 1: Effect of foreign ions on the determination of 29.46µg of cobalt

Inferent	Tolerance(µg)
Zn(II)	>654
Cu(II)	>436
Ni(II)	58.69
Fe(II)	233.4
Cl ⁻	283.6
CH ₃ COO ⁻	>590
SO ₄ ⁻	>960
NO ₃ ⁻	>620

TABLE 2: Analysis of cobalt in vitamin B₁₂

Sample	Cobalt found by proposed method, ppb	Cobalt found by ICP-AES, ppb
Vitamin B ₁₂	326.2 ^a	346.3 ^a

^a Both results are average of three determinations

cobalt signal by more than 5%, is considered as an interferant. The tolerance limit for the ions studied are shown in TABLE 1. As can be seen from the table Ni(II) ion is interfering seriously.

Applications

By using the recommended procedure, cobalt was determined in Vitamin B₁₂ ampul. The cobalt content of the sample was also directly determined by ICP-AES. As can be seen from data in TABLE 2, a very good agreement between these two sets of results is observed.

CONCLUSIONS

The proposed method is simple, rapid, sensitive and inexpensive. After addition of reagent the complex is formed and adsorbed immediately on the solid phase. Lower concentrations of cobalt could be determined comparing to liquid spectrophotometry.

The proposed method is applied to real sample analysis and the result is in very good agreement with standard method result which proves the validity of the method.

ACKNOWLEDGEMENTS

We express our special thanks to Dr. A.Molina Diaz for his endless support.

REFERENCES

- [1] E.J.Underwood; 'Trace Elements in Human and Animal Nutrition', 4th Ed., Academic Press, New York, (1977).
- [2] A.Carlosena, M.Gallego, M.Valcarcel; J.Anal.At Spectrom., **12**, 479 (1997).
- [3] F.Baruthio, F.Pierre; Biol.Trace Elem.Res., **39**, 21 (1993).
- [4] E.D.Caldas, M.F.Gine-Rosias, J.G.Dorea; Anal.Chim. Acta, **254**, 113 (1991).
- [5] B.Welz, M.Sperling; 'Atomic Absorption Spectrometry', 3rd Ed., VCH, Weinheim, (1999)
- [6] L.S.G.Teixeira, F.R.P.Rocha, M.Korn, B.F.Reis, S.L.C.Ferreira, A.C.S.Costa; Talanta, **51**, 1027 (2000).
- [7] L.S.G.Teixeira, A.C.S.Costa, J.C.R.Assis, S.L.C.Ferreira, M.Korn; Mikrochim.Acta, **137**, 29 (2001).
- [8] M.Lamotte, P.Violet, P.Garrigues, M.Hardy; Anal. Bioanal.Chem., **372**, 169 (2002).
- [9] K.Yoshimura, H.Waki, S.Ohashi; Talanta, **23**, 449 (1976).