

**Spectrophotometric study of Cobalt(II) Using Organic
Reagent 2-[(6-Methyl-2-Benzothiazolylazo)-4-Chloro
Biet tin gi chua, vao day coi di
<http://gaigoibaucat.xlphp.net>
phenol .**

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(Received on 6/5/2008)

(Accepted for publication 16/7/2008)

Abstract

A sensitive and selective spectrophotometric method was proposed for studying of Co(II) using 2-[(6-Methyl-2-Benzothiazolylazo)-4-Chloro Phenol (6-MeBTACIP). The reaction between Co(II) and (6-MeBTACIP) reagent is instantaneous at pH=6.1, and the absorbance remains stable for over 24 h. The method allows for the determination of Co(II) over the range (0.3 - 10.0) $\mu\text{g.ml}^{-1}$, with molar absorptivity of (1884.8) $\text{l.mol}^{-1}.\text{cm}^{-1}$ and a detection limit of 0.27 $\mu\text{g.ml}^{-1}$ at 600 nm. Recovery and relative error values of precision and accuracy of method were found to be R.S.D%=1.22%, Re%=96.68% ,and Erel=3.32% . Study of complex nature shows that (M: L) ratio was 1:2 at pH=6.1 ,and the stability constant of $(8.33 \times 10^7) \text{l}^2. \text{mol}^{-2}$. The interferences of ions (NH_4^+ , I^- , Hg^{2+} , Al^{3+} , Cu^{2+} , Ni^{2+} , F^- , $\text{S}_2\text{O}_3^{2-}$) on absorbance were studied. A suitable masking agents were used for eliminating of seriously interfering ions.

-4-[(-2- -6)]-2

(II) . (II)

24 6.1 =

1- (10.0-0.3) (II)

1- (0.27) 1- . 1- (1884.4)

600

%Erel) (%96.68=Re) (% 1.22=R.S.D)

.(% 3.32 =

6.1 = (2:1)

NH_4^+ , I^- , Hg^{2+} , Al^{3+} , Cu^{2+} , Ni^{2+} ,) $2- .^2 (8.33 \times 10^7)$

(F^- , $\text{S}_2\text{O}_3^{2-}$

Introduction

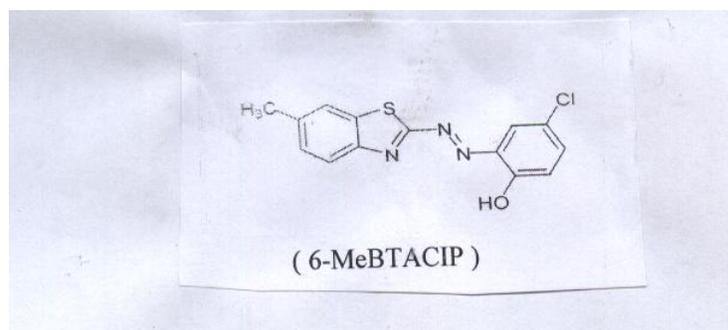
Cobalt is an essential element for the functioning of many vital processes. It is extremely important in the processes of blood formation, stimulation of hemoglobin synthesis, and the functioning of vitamins, enzymes and hormones. This metal has a very positive influence on the metabolism of vitamins, such as ascorbic acid and vitamin B12. Cobalt is an essential element in the human body as a component vitamin B12 and it is clear that the monitoring of body fluids for cobalt is important for the control of nutritional deficiencies and, perhaps, the prevention of its toxic effect in cases of occupational exposure. Finally, it is also necessary for the synthesis of a number of hormones, neurotransmitters, and other compounds, such as bile acids and DNA.^(1,2)

Some chromogenic reagents have been used in spectrophotometric methods of determination of cobalt such as, 2-[2-(5-

methylbenzothiazolyl)azo]-5-dimethyl amino benzoic⁽³⁾, 2-(2-Quinolylazo)-5-Diethylamino aniline⁽⁴⁾, 4-benzylpiperidinedithiocarbamate⁽⁵⁾, 2,2'-dipyridyl-2-pyridyl hydrazone(DPPH)⁽⁶⁾, 2-Hydroxy-3-Methoxy Benzaldehyde Thio semicarbazone⁽⁷⁾, 4, 4' diazobenzenediazoamioazobenzene (BBDAB)⁽⁸⁾, 2, 2'-dipyridyl ketoxime⁽⁹⁾, and 2-(5-bromo-2-pyridylazo)-5-diethylamino phenol⁽¹⁰⁾.

Thiazolylazo compounds have attracted the attention, as they are sensitive chromogenic reagents in addition to being important complexing agents. These dyes are useful in spectrophotometric determinations due to their good selectivity over a wide range of pH and because they are relatively easy to synthesize and purify⁽¹¹⁾.

In this paper, 2-[(6-Methyl-2-Benzothiazolyl)azo]-4-Chloro Phenol (6-MeBTACIP) chromogenic reagent, which was prepared by Aqeel et al⁽¹²⁾, used in simple method involving spectrophotometric study of cobalt(II).



Experimental

Apparatus

Absorption spectra were made with a Shimadzu 1650 UV-Visible spectrophotometer scientific equipment with 1.00 cm cell. The PD-303 spectrophotometer, Apel, Japan, was used in other measurements of

absorbance of solutions. The pH-meter, 720-WTW, Germany was used for measuring pHs of solutions. The water bath - 90, Hambury, England was used for adjusting temperatures of solutions.

Reagents;

All reagents were of analytical grade . Freshly distilled water was used for solutions preparations .

-Stock Co(II) solution ;A solution of Co(II) ($100 \mu\text{g}\cdot\text{ml}^{-1}$) was prepared by dissolving (0.04035)g of $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ in (100 ml)distilled water. Other standard solutions of Co(II) were prepared freshly by dilution of stock solution .

- 3×10^{-4} M (6-MeBTACIP) prepared by dissolving (0.0045)g in 50 ml of absolute ethanol .

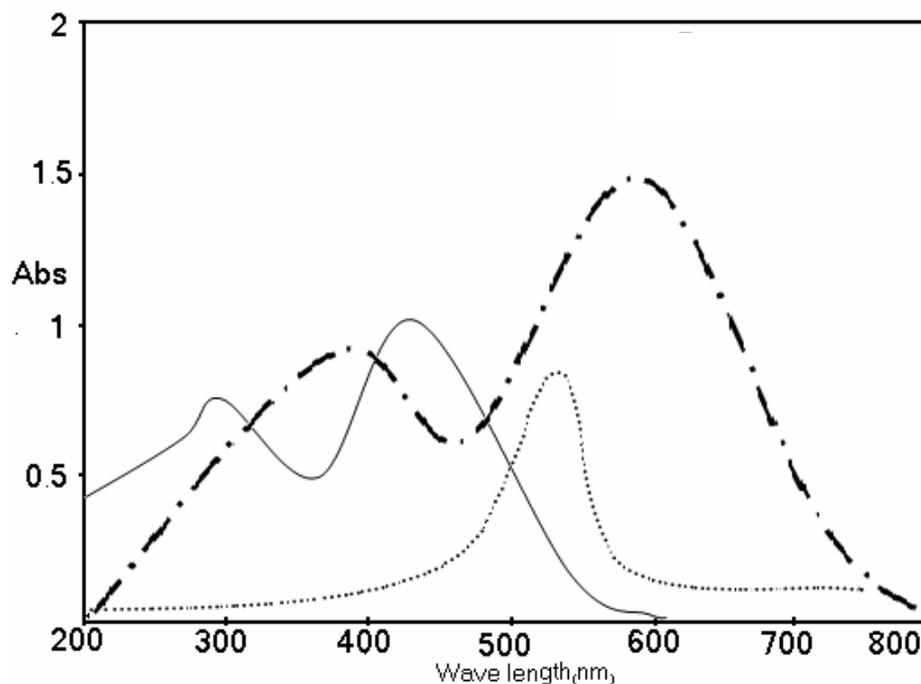
Procedure

To an aliquot containing $\leq 10 \mu\text{g}\cdot\text{ml}^{-1}$ of Co(II) in a 10-ml volumetric flask , was added 2 ml of buffer solution , and 3 ml of (3×10^{-4} M)of (6-MeBTACIP) solution .The solution

was diluted to the mark with ethanol, and absorbance was measured at 35°C and wave length of 600 nm against the reagent solution as a blank solution prepared under the same conditions.

Results and Discussion**Study of Cobalt (II)_(6-MeBTACIP) complex****Absorption spectra**

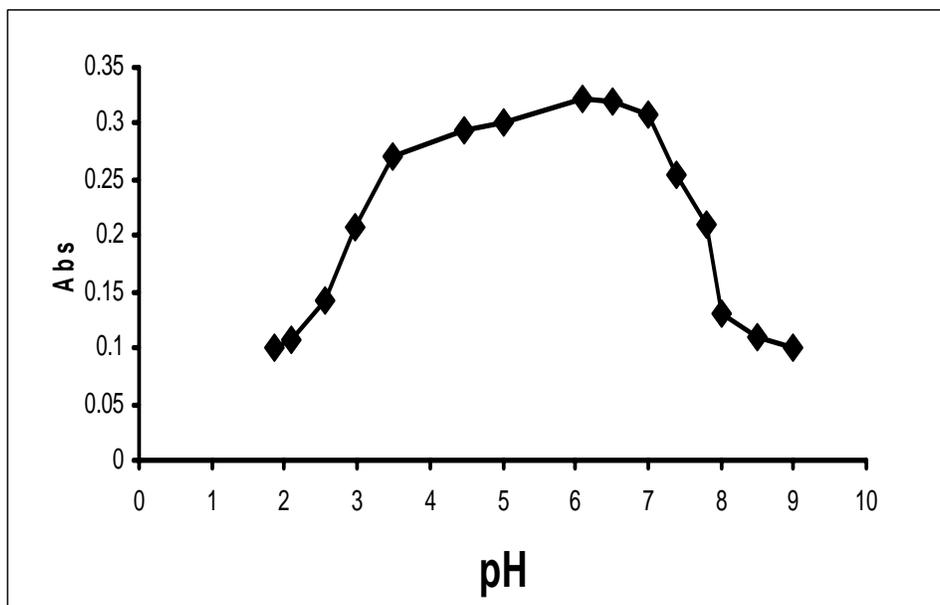
Ultra violet - visible absorption spectra of (6-MeBTACIP) reagent , Co (II) ion , and Co(II) - (6-MeBTACIP) complex solutions are shown in fig(1).The reagent showed an absorption maximum at 430 nm , the cobalt ion at 510 nm , and the complex at 600 nm .



Fig(1);Absorption spectra of :----- Co-(6-MeBTACIP) complex at pH=6.1
 ——— 6-MeBTACIP, 3×10^{-4} M .
 Co(II) solution, 2×10^{-2} .

Effect of pH

The influence of pH was studied over the range (2-8) adjusted by means of dilute HCl and NaOH solution; fig(2)shows the relationship between absorbance and pH , where the maximum absorbance obtained in the range of pH=(5.0 – 6.5) . At $7.0 \leq \text{pH} \leq 5.0$ a decrease in absorbance . Therefore , the optimum pH was 6.1 , where the absorbance was maximum and stable.



Fig(2);Effect of pH on the absorbance of Co- (6-MeBTACIP) complex

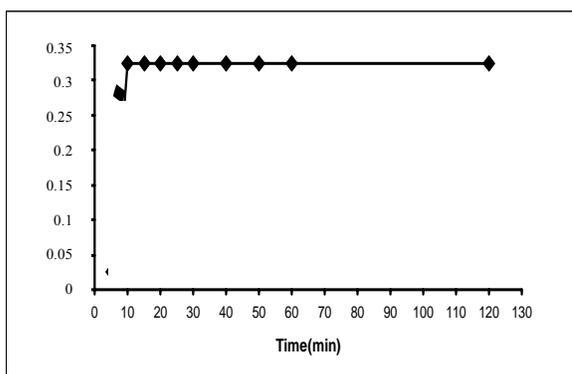
Effect of Time

The stability of absorbance of complex was studied from (0-120)min at different time of intervals. Fig (3) shows the maximum absorbance reached at 10 min , after that the absorbance remains stable till 24 h.

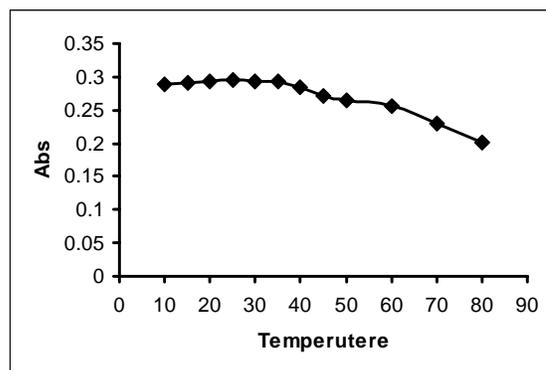
Effect of Temperature

The effect of temperature on the absorbance of complex was studied

.The study was performed at temperature between (10-80) °C .Fig (4) shows the maximum absorbance obtained at temperature 35°C which was regarded as a proper temperature of complex formation .At temperatures higher than 50°C the absorbance decrease due to dissociation of complex gradually.



Fig(3) Effect of time on the stability of complex

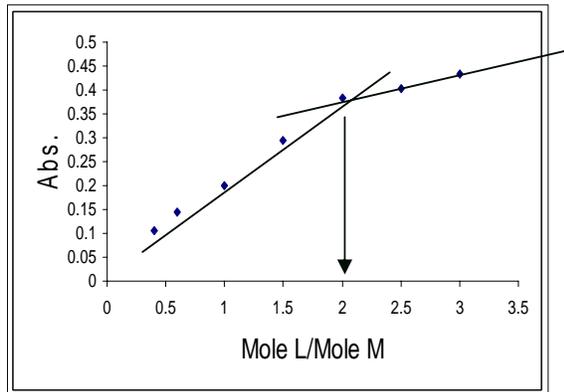


Fig(4) Effect of temperature on stability of complex

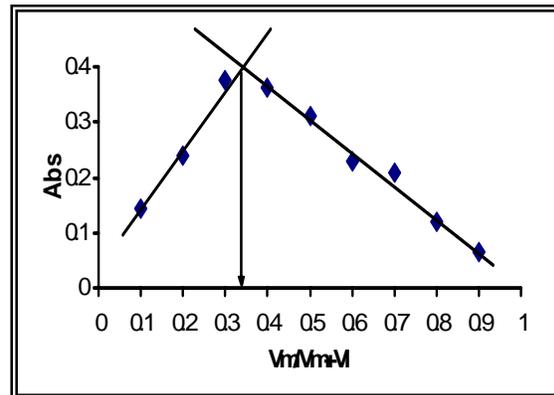
Determination of stoichiometry and formation constant

The composition of complex was studied by Jobs method of continuous variations and (mole-ratio) method ^(13,14) Fig(5,6). Both

methods indicate that the ratio of metal ion to reagent molecules (M:L) was (1:2) at pH=6.1 . The formation constant calculated by applied procedure ⁽¹⁵⁾ was found to be $(8.33 \times 10^7) \text{ l}^2 \cdot \text{mol}^{-2}$.



**Fig(5); Mole ratio plot [Reag]=[Co²⁺]
=3x10⁻⁴,pH~6.1**



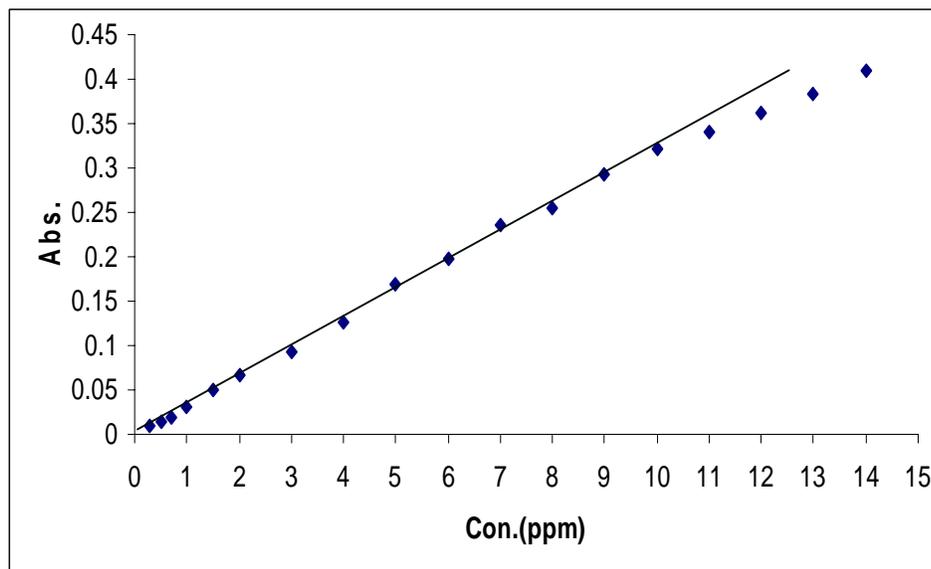
**Fig(6); Jobs plot [Reag]=[Co²⁺]
=3x10⁻⁴,pH~6.1**

Analytical characteristics

Calibration curve

Linear calibration graph through the origin was obtained which obeyed Beers law over the range (0.3 – 10.0)

$\mu\text{g} \cdot \text{ml}^{-1}$ of Co^{2+} .The average molar absorptivity was found to be $(1884.8) \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$.The sandells sensitivity ⁽¹⁵⁾ was $(0.0312) \mu\text{g} \cdot \text{Co}^{2+} \cdot \text{Cm}^{-2}$, and correlation coefficient (r) was 0.9986.



Fig(7); Calibration curve of Co (II) - (6-MeBTACIP) complex

Precision and accuracy

The relative standard deviation (R.S.D%), evaluated from seven independent determination of $5 \mu\text{g.ml}^{-1}$ of Co^{2+} was 1.22%, this result shows that this method is highly precise. Also the accuracy of this method was determined by calculating the $\text{Erel}\%$ for (5) ppm standard solution of Co (II) which was found to be 3.32% and $\text{Re}\%=96.68\%$.

Effect of Foreign Ions

A study of potential interferences in the determination of cobalt was performed. An error of

$\pm 5\%$ in absorbance reading was considered tolerable. Solutions containing cobalt ($8 \mu\text{g.ml}^{-1}$) and other ions were prepared and the developed procedure was applied. The tolerance limits of various foreign ions are given in table (1). These results demonstrate that the effect of NH_4^+ , F^- , I^- , Hg^{2+} and thiosulphate are negligible, while the effect of Cu^{2+} , Ni^{2+} , Al^{3+} are seriously interfering. Suitable masking agents were examined for eliminating the effect of the interfering ions of Al^{3+} , Ni^{2+} , Cu^{2+} , Hg^{2+} as shown in table(2).

Table(1) : Tolerance limit of foreign ions on study of cobalt ($8 \mu\text{g.ml}^{-1}$) by proposed procedure.

Ions	Maximum tolerable ion amount/ $\mu\text{g.ml}^{-1}$
NH_4^+	1100
Cu^{2+}	5
Ni^{2+}	8
Al^{3+}	0.1
F^-	850
I^-	750
Hg^{2+}	1000
$\text{S}_2\text{O}_3^{2-}$	1350

Table(2) : Masking agents for eliminating seriously interfering ions on study of cobalt($10 \mu\text{g.ml}^{-1}$) by proposed procedure.

Foreign ion / ppm	Masking agent ()ml , []
$\text{Cu}^{2+} / 5$	NaI (1) , [0.5]
$\text{Hg}^{2+} / 20$	NaI (2) , [0.2]
$\text{Ni}^{2+} / 10$	$\text{Na}_2\text{S}_2\text{O}_3$ (1) , [0.3]
$\text{Al}^{3+} / 0.1$	NaF (2) , [0.5]

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