

## **Spectrophotometric Determination of Cadmium ( II ) Using 2 – ( 6 – Methyl – 2 – benzothiozolyazo ) – 4 – benzyl phenol**

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### **Abstract**

The present paper describes the use of 2-( 6 – Methyl – 2 – benzothiozolyazo ) – 4 – benzyl phenol ( 6 – MeBTABP ) as a sensitive and selective analytical reagent for the spectrophotometric determination of cadmium ( II ) . ( 6 – MeBTABP ) reacts with cadmium ( II ) in the PH range (3 - 9 ) to form a colored complex shows a maximum absorbance at 598 nm . The calibration curve is linear between 1 and 20  $\mu\text{g} \cdot \text{ml}^{-1}$   $\text{Cd} ( \text{II} )$  , detection limit of 0.7  $\mu\text{g} \cdot \text{ml}^{-1}$  with molar absorptivity and Sandal's sensitivity values of  $L \ 1056 \ \text{mol}^{-1} \cdot 0.0045 \ \text{cm}^{-1}$  ,  $\mu\text{g} \cdot \text{cm}^{-2}$  , respectively . The composition of the  $\text{Cd} ( \text{II} ) - (6 - \text{MeBTABP} )$  complex is established as 1 : 2 by molar ratio and conductivity measurement methods . An excellent linearity with a correlation coefficient value of ( 0.9999 ) is obtained for the complex . The relative standard deviation , recovery and relative error values of precision and accuracy of method were found to be  $R . S . D . \% = \%$  ,  $\text{Re} \% = \%$  and  $\text{Erel} \% =$  The stability constant of the complex calculated is  $L^2 \ 73 \times 10^{10} \cdot \text{m}^{-2} \text{ol}$  , at room temperature . The interferences of foreign ions on the determination of cadmium ( II ) and suitable masking agents were used .

**الخلاصة :-**

يصف هذا البحث استخدام 2 - ( 6 - مثيل - 2 - بنزوثيرازوليل ازو ) - 4 - بنزاييل فينول ( MeBTABP - 6 ) في التقدير الطيفي لأيون الكاديوم ( II ) بطريقة تحليلية سهلة وسريعة وحساسة . يتفاعل ( MeBTABP - 6 ) مع الكاديوم ( II ) ضمن مدى من PH يتراوح بين ( 3 - 9 ) لتكوين معقد ملون عند الطول الموجي للامتصاص الاعظم 598 نانومتر . الخطية لمنحني المعايرة بين ( 1 - 20 ) مايكروغرام كاديوم ( II ) . مليلتر<sup>-1</sup> ، بحد كشف 0.7 مايكروغرام . مليلتر<sup>-1</sup> اما معامل الامتصاص المولاري وحساسية ساندل فكانت 1056 ، لتر . مول<sup>-1</sup> . سم<sup>-1</sup> ، 0.0045 مايكروغرام . سم<sup>-2</sup> على التوالي . المعقد المتكون ( II ) - Cd ( MeBTABP - 6 ) يمتلك نسبة مولية 1 : 2 من الايون الفلزي الى الكاشف وتم حساب ثابت الاستقرار للمعقد المتكون فكان  $10^{10} \times 73$  لتر<sup>2</sup> . مول<sup>-2</sup> ، اما قيمة  $R^2 = 0.999$  وحدد دقة وضبط الطريقة التحليلية المتبعة فكانت قيمة . S . D . R ، % Re ، % Erel هي 1.6 % ، 101.1 % و 1.1 % على التوالي . كذلك تم دراسة حجب الايونات التي تتداخل عند تفاعل الكاشف ( MeBTABP - 6 ) مع ايون الكاديوم ( II ) باستخدام عوامل حجب قياسية .

**Introduction :-**

Cadmium can be incorporated to the blood by absorption in stomach or on lungs after inhalation . An excess of cadmium produces adverse health effects on human beings , in addition , cadmium is a severe toxic metal and therefore needs to determination of cadmium in several matrices <sup>(1)</sup> .

Many of the analytical techniques such as flam atomic absorption spectrometry ( FAAS ) <sup>(2)</sup> , inductively coupled plasma atomic emission spectrometry ( ICP - AES ) <sup>(3)</sup> and

inductively coupled plasma mass spectrometry ( ICP – MS )<sup>(4)</sup> are available for the determination of trace metals with enough sensitivity for the most applications . However , the spectrophotometric method is a widely used technique and is one of the most powerful tools in chemical analysis , because its simplicity , lower cost of instrumentation , and usually is precise and accurate .

Heterocyclic azo reagents , especially thiazolylazo , are of a great importance in inorganic trace analysis . They are widely used in spectrophotometry in visible region and in liquid chromatographic methods<sup>(5)</sup> . The thiazolylazo dyes form colored complexes with many metals in acidic solutions . Armeanu and Dragusin have shown that cadmium forms a 1 : 2 complex with BTADCl at PH = 5.5 , which is one of the few cadmium complexes with maximum absorption in acidic solution<sup>(6)</sup> .

This spectrophotometric method for determination of micrograms quantities of cadmium by using 2 – ( 6 – Methyl – 2 – benzothiazolylazo ) – 4 – benzyl phenol , which prepared by A . Hussein<sup>(7)</sup> , is sensitive and rapid at room temperature and do not require complicated equipment .

## Experimental

### Reagents and apparatus

Cadmium ( II ) stock solution (  $250 \mu\text{g} \cdot \text{ml}^{-1}$  ) . Prepared by dissolving 0.0507 gm of  $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$  in 100 ml of distilled water working solutions were prepared by dilution of the stock solution .

2 – ( 6 – Methyl – 2 – benzothiazolylazo ) – 4 – benzyl phenol ( 6 – MeBTABP ) Solution . Prepared by dissolving 0.0897 gm of pure reagent in 250 ml of absolute ethanol .

A spectrophotometer ( Cintra 5 – GBC scientific Equipment ) for recorded Absorption spectra while absorption measurements were obtained with Spectrophotometer T , RSP – 721 Triup International Corp , both with matched 1 cm quartz cells . PH of the solutions was measured using a Microprocessor 211 PH meter ( PH  $\pm$  0.001 ) , and 214 HANNA instruments conductivity meter was also used .

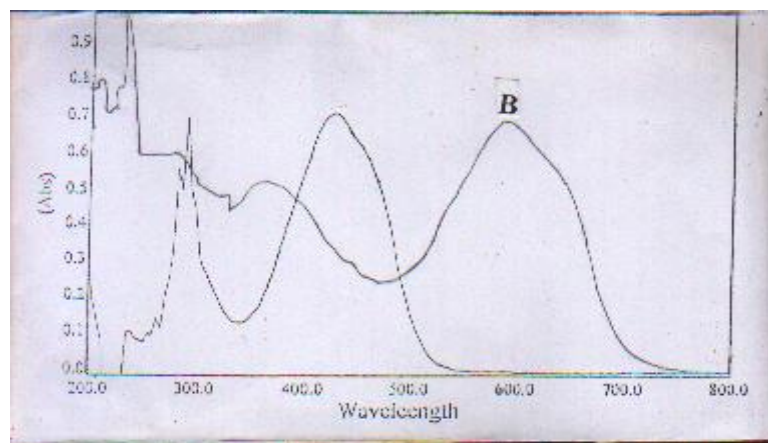
### **Analytical procedure**

1 ml of sample solution containing less than 100  $\mu\text{g} \cdot \text{ml}^{-1}$  of cadmium (II) was transferred to a 10 ml calibrated flask and adjust the PH to 6 with acetic acid acetate buffer , add 3 ml of  $1.5 \times 10^{-5}$  M ethanolic ( 6 – MeBTABP ) solution and diluted to the mark with water . Measure the absorbance of the resultant solution after 3 min . at 598 nm at 25°C against blank solution prepared the same procedure .

### **Results and Discussion**

#### **Absorption Spectra**

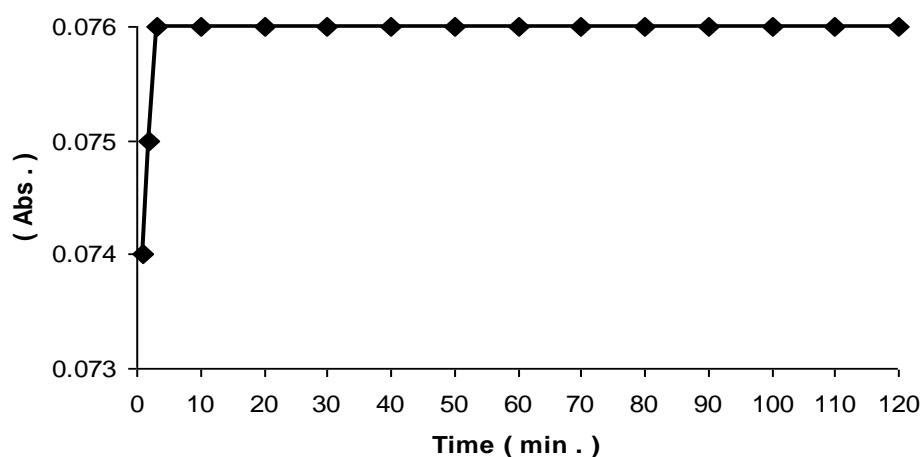
Figure . 1 shows the absorption spectre of a cadmium complex with ( 6 – MeBTABP ) and the reagent were an absorption maximum for the complex at 598 nm . The reagent has no absorbance at this wavelength .



**Fig . 1 : Absorbtion spectra of A : 6 – MeBTABP , B : Cd – 6 – MeBTABP complex**

### **Effect of some factors on the absorbance**

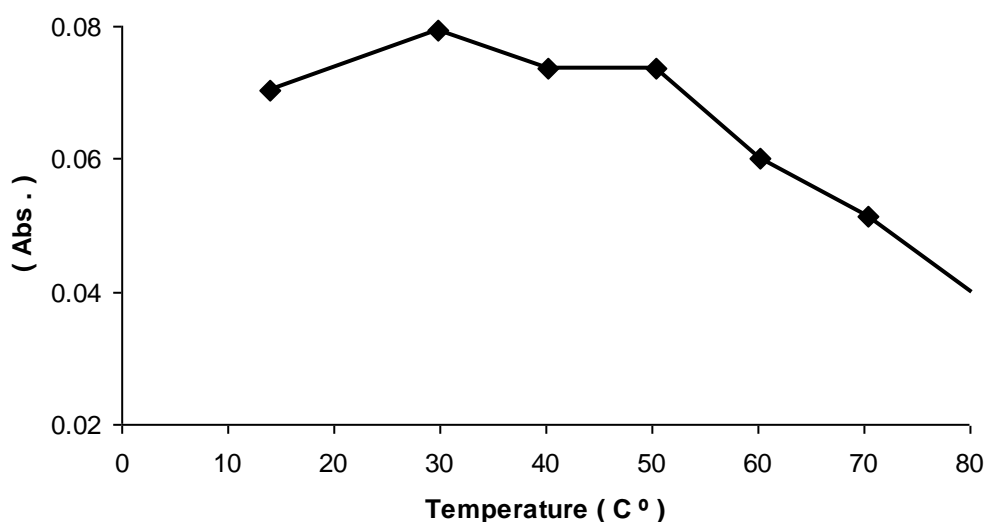
The effect of factors on the absorbance was investigated according to an analytical procedure . Effect of time on the absorbance of cadmium complex was studied . The maximum absorbance was reached at the 3 min and remains stable for at least 24 h ( Fig . 2 ) .



**Fig . 2 : Effect of time on the absorbance of cadmium complex**  
 **$\text{Cd ( II )} = 15 \mu\text{g} \cdot \text{ml}^{-1}$**

The influence of temperature on the Cd ( II ) - ( 6 – MeBTABP ) complex was studied at temperature between 10 °C and 70 °C and the results showed the maximum absorption was obtained when the temperature was varied between 20 °C

and 30 °C , at temperature higher than 30 °C the absorbance gradually decreased with increasing temperature , which may be due to dissociation of the complex .

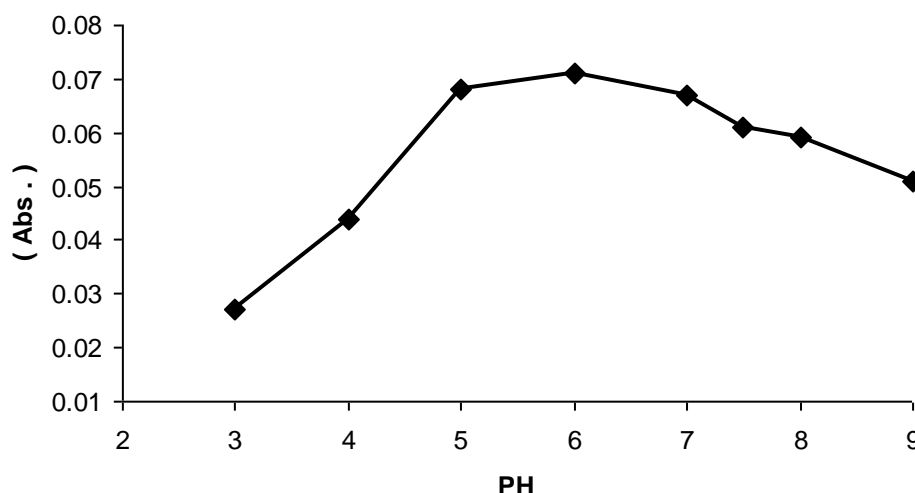


**Fig . 3 : Effect of temperature on the absorbance of cadmium complex       $\text{Cd ( II )} = 15 \mu\text{g} \cdot \text{ml}^{-1}$**

The reagent amount sufficed to complete the reaction was found 3 ml of  $1.5 \times 10^{-5} \text{ M}$  ( 6 – MeBTABP ) solution added to  $20 \mu\text{g} \cdot \text{ml}^{-1}$  of cadmium ( II ) .

### Effect of PH

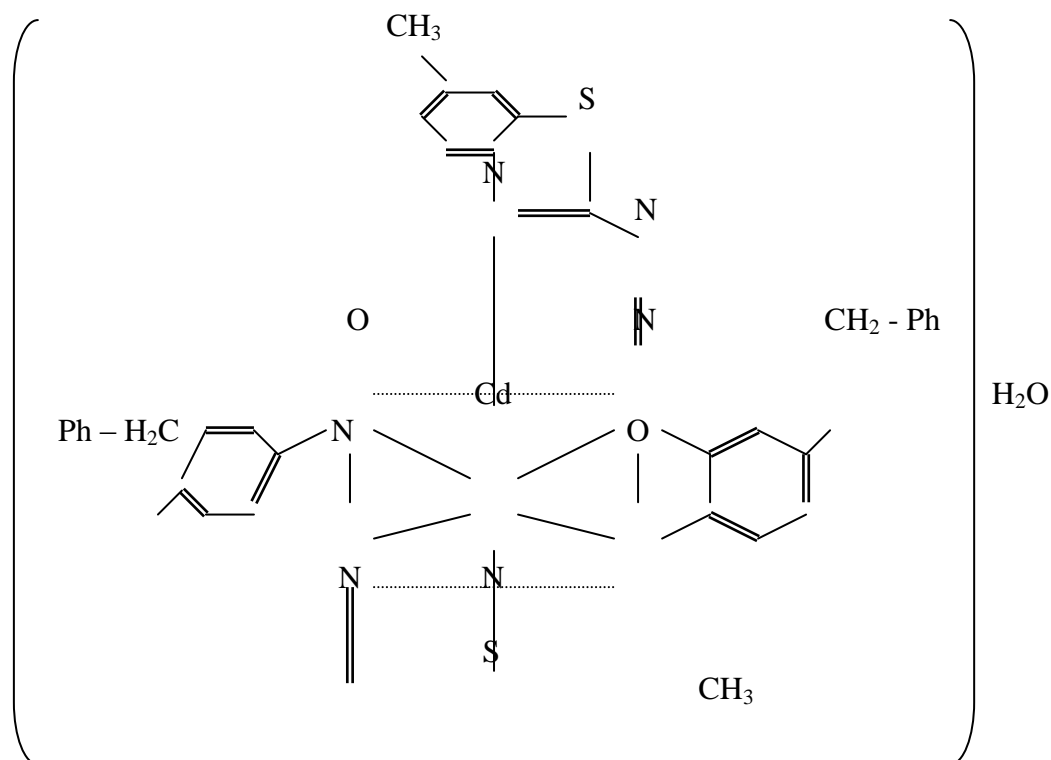
The influence of PH on the  $\text{Cd ( II )} - ( 6 - \text{MeBTABP} )$  complex is studied to find out the optimum PH range for cadmium determination . Where the maximum absorbance obtained at PH of 6 was adopted . Fig . ( 3 ) shows the relationship between absorbance of complex and PH in the rang 3 – 9 , where at  $\text{PH} < 6$  a decreases in absorbance was absorbed due to competition between the hydrogen ion and cadmium ( II ) cation , with the increase of the hydrogen ion concentration the competition leads to a less favorable complex formation .

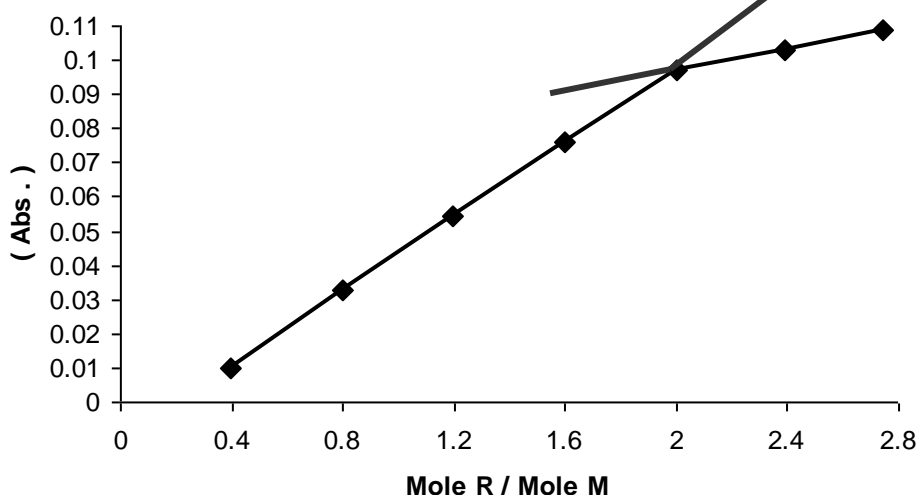
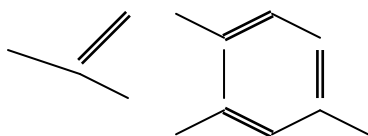


**Fig . 4 : Effect of PH on the absorbance of cadmium complex**  
 $\text{Cd ( II )} = 15 \mu\text{g} \cdot \text{m}^{-1}$

### Composition of Cd ( II ) - ( 6 – MeBTABP ) complex

The metal : ligand ratio in the complex was found to be 1 : 2 , using molar conductivity method <sup>(8)</sup> and the mole ratio method <sup>(9)</sup> ( fig . 4 ) , and the stability constant was found to be  $73 \times 10^{10} \text{ L}^2 \cdot \text{mol}^{-2}$  . The reagent ( 6 – MeBTABP ) react with Cd ( II ) to form the complex , which probably has the following structure :





### Beer's law and sensitivity

The Cd ( II ) – ( 6 – MeBTABP ) complex followed Beer's law over the concentration range  $1 - 20 \mu\text{g} \cdot \text{ml}^{-1}$  of cadmium , and it has molar absorptivity  $1056 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$  and Sandell sensitivity  $0.0045 \mu\text{g} \text{ cm}^{-2}$  .

### Precision Accuracy

To assess the precision and accuracy of the method , determinations are carried out for a set of seven measurements of  $15 \mu\text{g} \cdot \text{ml}^{-1}$  of cadmium ( II ) , under optimum conditions . Calculations reveal that the relative standard deviation was 1.6 % . The recovery and Erel % for the complex solution containing  $10 \mu\text{g} \cdot \text{ml}^{-1}$  of cd ( II ) were found to be 101.1 % , and 1.1 % respectively . The detection limit was found to be



$0.7 \mu\text{g} \cdot \text{m}^{-1}$  . These values indicate that this method has the highest accuracy and precision .

#### Interference studies

To study the effect of various metal ions on the determination of Cd ( II )  $20 \mu\text{g} \cdot \text{m}^{-1}$  with ( 6 – MeBTABP ) , the selectivity various masking agents are examined <sup>(10)</sup> . The results are shown in Table 1 .

**Table 1 : Effect masking agents**

$\text{Cd}^{2+} \mu\text{g} \cdot \text{ml}^{-1}$	Masking agent ( 2 ) ml , [ 0.01 ] M	Absorbance
20	Complex with any addition	0.091
20	Oxalic acid	0.090
20	Citric acid	0.088
20	Tarataric acid	0.090
20	Ascorbic acid	0.089
20	1 , 10 – phenathroline	0.065
20	Sodium floride	0.072

The results indicate that 1 , 10 – phenathroline and sodium floride cased masking for cadmium , while other masking agents have no or little effects on the absorbance . There for these use as masking agents suitable for eliminating the effect of the interfering ions are given in Table 2 .

**Table 2 : Effect of foreign ions**

Foreign ion	Form added	Amount added / $\mu\text{g} \cdot \text{ml}^{-1}$	Error %
$\text{Zn}^{2+}$	$\text{ZnCl}_2$	10	1.5
$\text{Ni}^{2+}$	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	10	-0.5
$\text{Co}^{2+}$	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	10	-2
$\text{Cu}^{2+}$	$\text{CuSO}_4$	10	0.8
$\text{Fe}^{2+}$	$\text{FeSO}_4$	10	-1.2
$\text{Fe}^{3+}$	$\text{FeCl}_3$	10	0.9

## Conclusion

The method using ( 6 – MeBTABP ) as spectrophotometric reagent to determine cadmium is selective , rapid and simple . The Cd - ( 6 – MeBTABP ) complex is stable and the determination sensitivity is comparable to other analytical methods , and the method involves less sophisticated instrumentation .

## References

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