

## Zero order and first Derivative Spectrophotometric Determination of pb(II) by Complex with N,N'-cyclohexane-1,2-diylidene-bis (4-methoxybenzoythydrazide) (CHMBH)

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طريقة الترتيب الصفري والمشتقة الاولى لتقدير الرصاص باستخدام التعقيد مع ن, ن- سايكلو هيكسان-1,2-دايلادين-ثنائي(4-ميثاكسي بنزو ثايدرازيد) (CHMBH)

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### الخلاصة

في هذه الدراسة طريقتان طيفيتان دقيقتان وبسيتان استخدمت لتقدير ايون الرصاص وذلك بتعقيده مع الليكند (CHMBH). وتم تقدير الرصاص بتطبيق طريقة الترتيب الصفري والمشتقة الاولى عند الطول الموجي 258 نانومتر, وبلغت الخطية لكلا الطريقتين 20-55 مغم/ لتر, حد الكشف وحد الكمية بلغت 0.33 و 1 مغم/ لتر لطريقة الترتيب الصفري وبلغت 1.438 و 4.360 مغم/ لتر لطريقة المشتقة الاولى بالتعاقب. وكانت الدقة عالية لكلا الطريقتين وبلغت 99.594 % لطريقة الترتيب الصفري و 100.496 % لطريقة المشتقة الاولى .  
الكلمات المفتاحية: ايون الرصاص, CHMBH, المشتقة الاولى, الترتيب الصفري, طريقة فاراغاس

### Abstract

In this work, two novel, accurate and reliable spectrophotometric methods have been developed for the determination of pb(II) ion by complexation with the ligand N,N'-cyclohexane-1,2-diylidene-bis(4-methoxybenzoythydrazide) (CHMBH).

In this study, pb(II) ion was determined by the application of Zero order and first Derivative Spectrophotometric by measuring the amplitude at 258 nm, The linearity ranges for both methods were found to be 20–55 mg/l, Limit of Detection and Quantitation were found to be 0.33 mg/l and 1 mg/l for zero order and 1.438 mg/l and 4.360 mg/l for first derivative method respectively.

Both methods have good accuracy found to be 99.594% and 100.497% respectively.

**Keyword:** pb(II), CHMBH, first derivative, Zero order, Varagas method

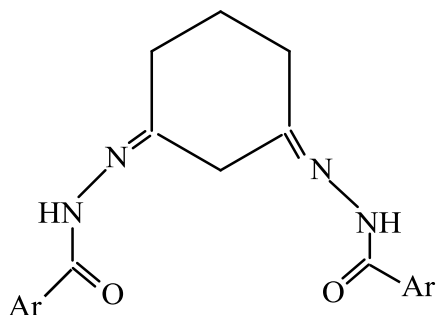
## Introduction

Lead is a toxic metal which can enter the body from lead-based paints and lead water pipes. also, other products pollutants contain lead metal are dangers to the health and environment such as petrol products, cosmetics and hair dyes[1,2].

Many methods were used to determination lead such as, solid phase extraction[3], cloud point extraction combined with flame atomic absorption[4], graphite furnace atomic absorption[5,6], spectrophotometric [7] and flame atomic absorption[8].

Most of their methods are expensive or low selectivity and sensitivity. Spectrophotometric and derivative spectrophotometric methods are simple, low cost and ecological friendly because not require extraction using organic solvent and also have respected accuracy and precision.

This study a novel simple, high sensitivity, low expensive spectrophotometric methods are determination of pb(II) ion by complexion with the ligand CHMBH (fig.1) in acetonitrile medium.



**Fig.1: the structure of the ligand N,N'-cyclohexane-1,2-diylidene-bis(4-methoxybenzoylhydrazide) (CHMBH)**

## Experimental

### Apparatus

- UV-Vis spectrophotometer, spectrophotometric(VARIAN UV-visible) with 1cm path quartz cells with software program

### Preparation of standard solutions of N,N'-cyclohexane-1,2-diylidene-bis(4-methoxybenzoylhydrazide) (CHMBH):

The ligand CHMBH was prepared as same in paper [9]. 100mg/l of CHMBH(M.Wt=408 mg/l) was prepared by dissolved 0.01 gm from this ligand with the solvent( CH<sub>3</sub>CN) and complete the volume to 100 ml with the same solvent. After that 20 ml from 100mg/l CHMBH solution was transferred into 100 ml volumetric flask and complete to the mark with CH<sub>3</sub>CN solvent to obtained the concentration equall to 20 mg/l.

### Preparation of standard solutions of pb(NO<sub>3</sub>)<sub>2</sub> (M.Wt=331.20)(BDH)

100mg/l was prepared by dissolving 0.01 gm of with CH<sub>3</sub>CN solvent then complete the volume to the 100 ml in volumetric flask.

**0.1 N of HCl:** was prepared by diluting of (1.54 ml) of HCl conc. which have (37% wt/wt) and diluted to (250 ml) in a volumetric flask by distilled water .

**0.1 N NaOH (Fluka):** was prepared by dissolving (0.4 gm) of NaOH in distilled water and diluted to (100 ml) in a volumetric flask with the same solvent.

#### Constructed of calibration curve:

5 ml of (20 mg/l) from the ligand CHMBH was transferred into a series of 20 ml volumetric flask, and then, an aliquot of 100 mg/l standard solution containing (4,5,6,7, 8,9,10 and 11ml) of  $\text{pb}(\text{NO}_3)_2$  was transferred into the series of 20 ml of volumetric flasks and 1 ml of 0.1 N of HCl was added and finally complete the volume to the mark with the solvent  $\text{CH}_3\text{CN}$ . After 5 min., the absorbance was measured at 258 nm against the  $\text{CH}_3\text{CN}$  as a blank.

#### Jobs method

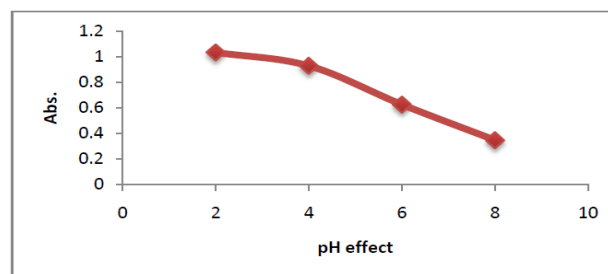
Different volumes (0.2, 0.4, 0.5, 0.6 and 0.8ml ) from the (20 mg/l) CHMBH ligand was added to the series of 20 ml volumetric flask, to each flask (0.8,0.6,0.5,0.4 and 0.2 ml) of 35mg/l (0.0001057 mol/l)  $\text{pb}(\text{NO}_3)_2$  and 1 ml (0.1N) HCl were added then complete the volume to the mark with the solvent  $\text{CH}_3\text{CN}$ .

## RESULTS AND DISCUSSION

#### The Effect of PH

The absorption spectra of the lead solution (II) with the ligand was studied using a pH meter device between (2-10). Fig. 2 that shown The solution of the complexes at the

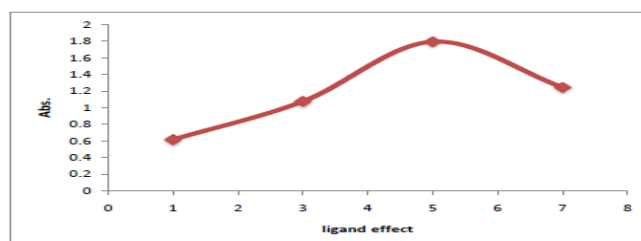
value of pH (2) Is suitable for the formation of the lead complex (II) Which has high stability .



**Fig. 2: the effect of pH on the pb(II)-CHMBH complex, 3ml of (50mg/l) pb(II), 5 ml of (20mg/l) CHMBH and 1ml of (0.1N) HCl or (0.1N) NaOH , at wavelength 258 nm.**

#### The effect of the Volume of ligand

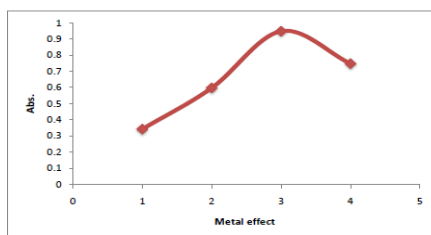
the volume of ligand CHMBH was investigated from 1 mL to 7 ml when the volume of ligand(CHMBH) was found 5 ml was the optimal condition an excessive amount of lead to remarkable decrease of signals as shown in fig.3.



**Fig. 3: the effect of ligand volume on the pb(II)- CHMBH complex, 3ml of (50mg/l) pb(II), (1-7) ml of (20mg/l) CHMBH and 1ml of (0.1N) HCl , at wavelength 258 nm.**

### The effect of the volume of metal

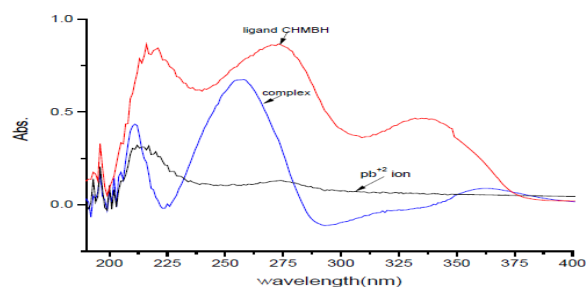
Fig. 4 is shown the absorption of the metal  $\text{pb}^{+2}$  with the ligand CHMBH was tracked to different quantities ranging from (1 – 4) ml of the  $\text{pb}^{+2}$  metal ion. It was observed that the volume (3) ml gives the highest absorption intensity after adding it to the ligand CHMBH and the complex remains stable .



**Fig. 4:** the effect of metal volume on the  $\text{pb(II)}$ - CHMBH complex, (1-4)ml of (50mg/l)  $\text{pb(II)}$ , 5 ml of (20mg/l) CHMBH and 1ml of (0.1N) HCl , at wavelength 258 nm.

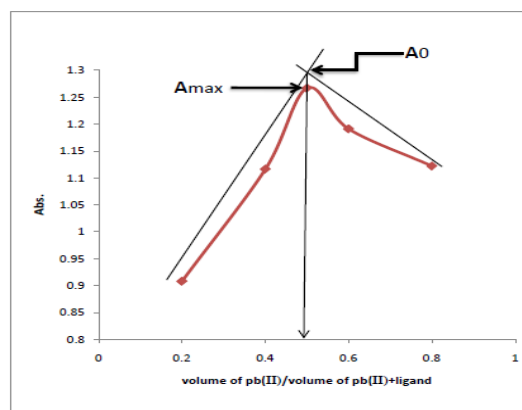
### Absorbance spectra

The complex of  $\text{Pb(II)}$ -CHMBH which showed a maxima peak at 258 nm against  $\text{CH}_3\text{CN}$  as a reagent blank fig.5



**Fig.5:** Absorption spectra of 35 (mg/l) of  $\text{pb(II)}$ , 50 (mg/l) of the ligand CHMBH and complex contained from 35 (mg/l) of  $\text{pb(II)}$  with 50 (mg/l) of the ligand CHMBH and 1 ml 0.1N HCl against reagent blank

The structure of the  $\text{pb(II)}$ -CHMBH complex was investigation by jobs method, the stoichiometry of the  $\text{pb(II)}$ -CHMBH complex in fig.6 that shown 1: 1  $\text{pb(II)}$  to the ligand CHMBH.



**Fig .6:** Job's plot for  $\text{pb(II)}$ -CHMBH complex

The stability constant  $K$  was calculated by using varagas method[10,11] as the following equation:

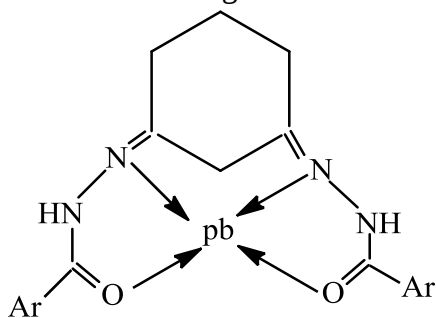
$$K = \frac{C - \frac{A\alpha}{\epsilon}}{n^n \left(\frac{A\alpha}{\epsilon}\right)^{n+1}} \dots (1)$$

Where,  $C$  = is a concentration of pb(II)(0.0001057mol/l) at stoichiometry point,  $\epsilon$  = is a molar absorptivity (8528.2 L/mol.cm),  $n$  = is the no. of ligand CHMBH (1) and  $A\alpha$  = is the absorbance of the part of dissociated constant of pb(II)-CHMBH complex(0.034),  $A\alpha$  was obtained by the following equations:

$$A_\alpha = A_0 - A_{\max} \dots (2)$$

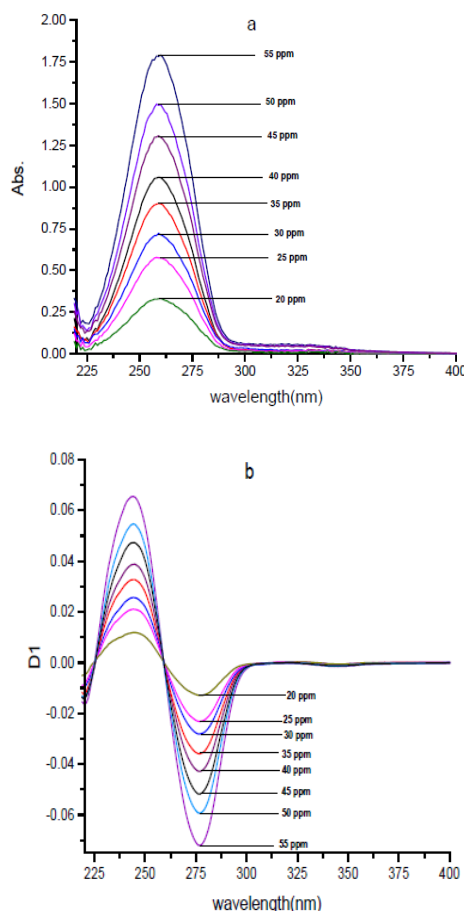
Where,  $A_0$  = is a theoretical absorbance value was obtained from jobs plot(1.30),  $A_{\max}$  = is a maximum absorbance at pb(II)-CHMBH complex(1.266).

the stability constant  $K$  is found to be(  $66.92965 \times 10^{+5}$  L/ mol), indicating that the pb(II)-CHMBH complex is stable, The possible structure of the complex might be written as the following :

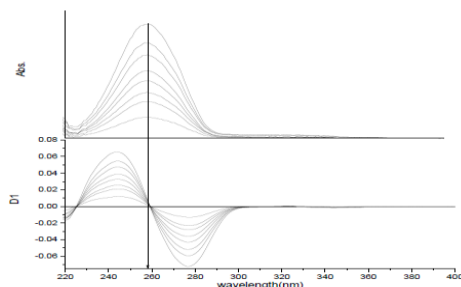


## Zero order and First derivative methods

Fig.(7a,b) is shown the zero order spectrum for the pb(II)-CHMBH complex and first derivative spectrum at concentration (20, 50 mg/ l), in this study, a first derivative are passes through the same wavelength as (258 nm)  $\lambda_{\max}$  of the zero order spectrum of the pb(II)-CHMBH complex as shown in fig.8.



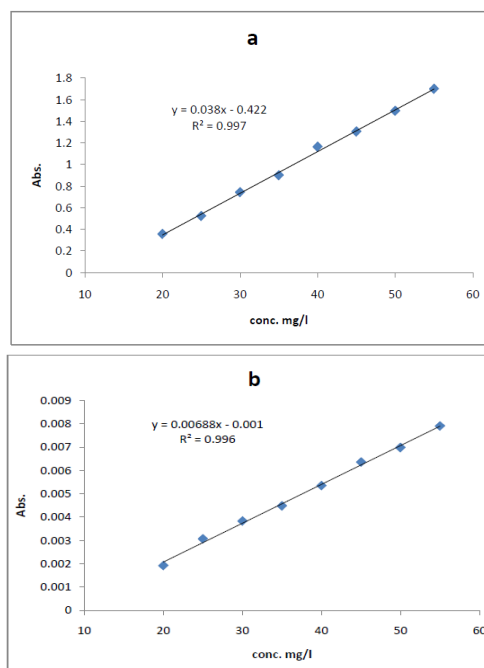
**Fig.7: spectrum of a- the zero order and b- the first derivative for the pb(II)-CHMBH complex**



**Fig.8: selected the wavelength 258 nm for first derivative method**

### Calibration curve

The calibration curves for the determination pb(II) by complexation with the ligand CHMBH were constructed by plotting the absorbance of standard solution vs. the concentration for the zero order method and first derivative method as shown in fig(9a,b)



**Fig.9: calibration curves for a- the zero order and b- the first derivative spectra of the pb(II)-CHMBH complex**

Under the experimental condition of this study, Molar absorptivity, Regression equation, Limit of detection and different analytical parameters are summarized in table 1.

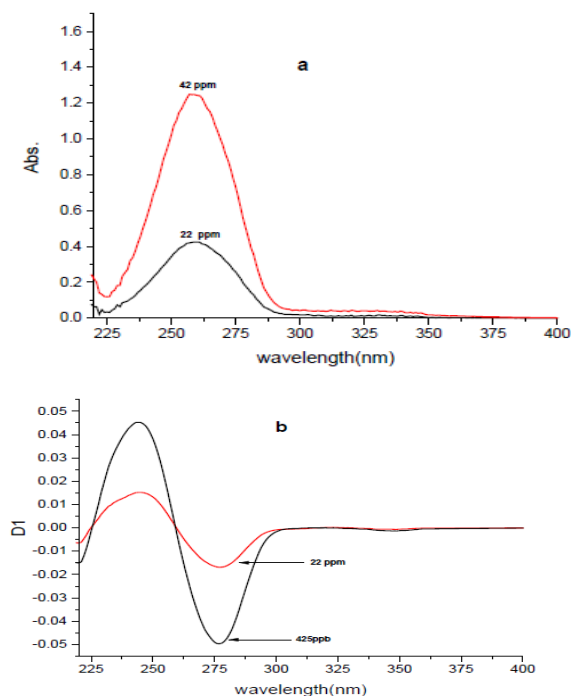
**Table(1): the analytical values of parameters and statistical treatment for the calibration curve.**

| Parameter                                | zero order method    | first derivative method |
|------------------------------------------|----------------------|-------------------------|
| Linearity mg/l <sup>1</sup>              | 20 - 55              | 20-55                   |
| Regression equation(y)                   | $Y = 0.038x - 0.422$ | $Y = 0.00688x - 0.001$  |
| Correlation of determination ( $r^2$ )   | 0.997                | 0.996                   |
| Slope (b)                                | 0.038                | 0.00688                 |
| Intercept (a)                            | -0.422               | -0.001                  |
| Conf. limit for slope $b \pm t_{sb}$     | $0.038 \pm 14.959$   | $0.00688 \pm 8.333$     |
| Conf. limit for Intercept $a \pm t_{sa}$ | $0.422 \pm 53.564$   | $0.001 \pm 43.281$      |
| Molar absorptivity $\epsilon$ (L/mol.cm) | 8528.8               | -                       |
| Sandell's sensitivity (mg/cm)            | 0.0388               | -                       |
| Limit of detection LOD (mg/l)            | 0.33                 | 1.438                   |
| Limit of quantification LOQ(mg/l)        | 1                    | 4.360                   |

LOD = limit of detection =  $3.3 \times \text{Sdb}/S$ , LOQ= limit of quantification =  $10 \times \text{Sdb}/S$ , Sdb=0.003= is the standard deviation of the solvent (distilled water as a blank) (n=3), S is the slop of the corresponding calibration curve.

### Accuracy and precision

The accuracy and precision was determination at two concentration levels (22 and 42 mg/l) of the zero order and first derivative methods for the pb(II)-CHMBH complex as shown in fig.(10a,b). each concentration were analyzing three times, the high percentage recoveries values and low standard deviation values, showing a good accuracy and precision are summarized in table 2



**Fig.10: a- the zero order and b- the first derivative spectra of two concentration 22 and 42 mg/l**

**Table (2): Accuracy of the zero order and first derivative methods for the pb(II)-CHMBH complex**

| methods                     | (taken)<br>mg/ml | (Found)<br>mg/ml | Rec.*%  | Average<br>of<br>Rec. % | RSD*%   |
|-----------------------------|------------------|------------------|---------|-------------------------|---------|
| <b>zero<br/>order</b>       | 22               | 21.810           | 99.136  | 99.594                  | 0.00226 |
|                             | 42               | 42.022           | 100.052 |                         | 0.00200 |
| <b>first<br/>derivative</b> | 22               | 22.130           | 100.590 | 100.497                 | 0.00021 |
|                             | 42               | 42.170           | 100.404 |                         | 0.00033 |

\*Average of three determined

The results of the two proposed methods in this study were shown a good agreement with reference methods in recoveries and relative standard deviation, the results are listed in table 3

**Table3: comparison the values of Recovery% and RSD% of the proposed methods with the references methods**

| Methods                                         | Recovery% | RSD%    | Ref.         |
|-------------------------------------------------|-----------|---------|--------------|
| graphite furnace atomic absorption spectrometry | 99.3      | 3.2     | [12]         |
| graphite furnace atomic absorption spectrometry | 109       | 4.61    | [13]         |
| Spectrophotometric method (second derivative)   | 96.6      | 4.02    | [14]         |
| graphite furnace atomic absorption spectrometry | 107.5     | -       | [2]          |
| Zero order method                               | 99.594    | 0.00226 | Present work |
| First derivative method                         | 100.497   | 0.00021 | Present work |

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