

## Full Paper

### Studies on complexation equilibria between copper(II) and some new schiff bases derived from 3-hydrazino-6-methyl[1,2,4]triazine-5(4H)one

Magda S. Saleh , Ahmed H. Osman, Sanaa M. Mahmoud

Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt

Email: [magdamssaleh@yahoo.com](mailto:magdamssaleh@yahoo.com)

---

Article history : Received: 27/6/2015 ; Revised :29/8/201 ; Accepted:10/9/2015;  
Available Online : 24/11/2015 ;

---

#### Abstract

Complexation equilibria between Cu(II) and new bidentate and tridentate Schiff bases derived from the condensation of 3-hydrazino-6-methyl-[1,2,4]triazine-5(4H)one and aromatic aldehyde derivatives have been studied by zero-order absorption spectrophotometry in ethanol-water solution (50% v/v) at I= 0.1 M (NaClO<sub>4</sub>) and 25°C. The composition, equilibrium constants of the complexation reactions and overall formation constants of the resultant complexes have been determined and species of the complexes have been clarified. The values of the formation constants are correlated with the sum of the ionization constants of the ligands. A new direct spectrophotometric method for the determination of trace amounts of copper is proposed based on the reaction between Cu(II) and Schiff base derived from *p*-N,N-dimethyl amino benzaldehyde (HDBe) at pH 6.0. The absorption maximum, molar absorptivity, and calibration sensitivity of 1:2 [Cu(DBe)<sub>2</sub>] complex are 392 nm, 2.88x10<sup>4</sup> L mol<sup>-1</sup> cm<sup>-1</sup> and 0.36 ml μg<sup>-1</sup> respectively. The use of second-derivative spectrophotometry eliminates the interference of iron and enables the quantitative determination of Cu(II) in the range 0.15-1.0 ppm with a relative standard deviation of 0.5%. The proposed method has been successfully applied determination of copper in various synthetic samples and in fresh water samples with average percentage recoveries of 99.675±0.045 and 98.95±0.002 respectively.

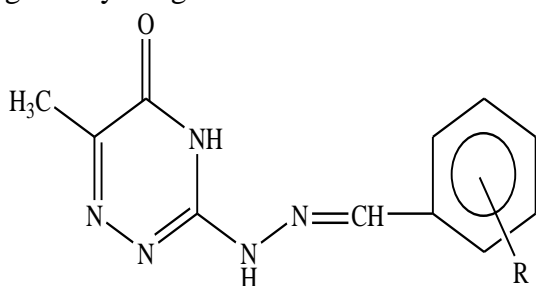
**Keywords:** Copper (II), complexation equilibria, Schiff bases derived from 3-hydrazino-6-methyl[1,2,4]triazine-5(4H)one.

#### 1. Introduction

It has been observed that substituted hydrazones with azomethines >C = N-N< groups are of considerable biological importance, as they show antimicrobial

activities [1]. Substituted hydrazones have been widely used as reagents for the spectrophotometric determination of various transition metal ions [1-13]. In earlier works [14,15] five new hydrazones which consist of

3-hydrazino-6-methyl[1,2,4]triazine-5(4H)one and various aromatic aldehydes such as benzaldehyde, *p*-methoxy, *p*-N,N-dimethyl-amino, *o*-nitro and *o*-hydroxybenzaldehyde were synthesized in order to develop highly sensitive and selective reagents for metals. Recently [14] we reported synthesis and characterization of some copper chelates with the above mentioned five hydrazones. A survey of the literature reveals that no work has been done on the solution equilibria of Cu(II) chelates with the Schiff bases under investigation. Based on preliminary results of the reactivity of these compounds towards copper(II) [15], the above mentioned Schiff bases were chosen for detailed spectrophotometric equilibrium study in 50% v/v ethanol-water medium at 25°C and ionic strength 0.1 M (NaClO<sub>4</sub>). The work was aimed at establishing the equilibria which exist in solution and at determining the basic characteristics of the complexes formed. The optimum conditions favouring the direct spectrophotometric determination of trace levels of copper using HDBe have been investigated. Second derivative spectrophotometry was used to improve the sensitivity and selectivity. The proposed method was applied successfully to the determination of Cu(II) in various synthetic samples and in fresh water samples. The structure of the Schiff bases is given by the general formula.



No.	R	Notation
1	H	HBe
2	<i>p</i> -OCH <sub>3</sub>	HMBE
3	<i>p</i> -N(CH <sub>3</sub> ) <sub>2</sub>	HDBE
4	<i>o</i> -NO <sub>2</sub>	HNBe
5	<i>o</i> -OH	H <sub>2</sub> Sal

<http://www.aun.edu.eg>

## 2. Experimental

### 2.1. Chemicals

All chemicals were of analytical reagent grade and deionized water (or pure ethanol) was used for preparation of solutions. The Schiff bases included in the present investigation were prepared by condensation of purified 3-hydrazino-6-methyl[1,2,4]triazine-5(4H)one [16] with the necessary amount of benzaldehyde derivative according to our previous paper [14]. All chemicals were of analytical reagent grade and deionized water (or pure ethanol) was used for preparation of solutions. A stock solutions of the Schiff bases ( $1 \times 10^{-3}$  mol L<sup>-1</sup>) were prepared by dissolving accurately weighed amount of the purified reagents in pure ethanol. A  $1 \times 10^{-3}$  mol L<sup>-1</sup> stock solution of Cu(II) acetate was prepared by dissolving the required amount of Analar product in deionized water and standardized by EDTA [17]. A carbonate-free NaOH solution was standardized with potassium hydrogen phthalate. The acidity of investigated solutions was adjusted by addition of either dilute perchloric acid or sodium hydroxide solution. Solutions of diverse ions used for interference studies were prepared using Analar products of nitrate, acetate or chlorides of the metal ions and potassium or sodium salts of the anions to be tested. Acetate buffer, 1.0 mol L<sup>-1</sup> of pH = 6.0 was prepared as recommended [18]. It was used for pH adjustment in the standard procedure and in the interference experiments. All measurements were made in 50% (v/v) ethanol-water medium at 25°C. The ionic strength was kept constant at  $I = 0.1$  M NaClO<sub>4</sub>.

### 2.2. Instruments

Absorption measurements ( $D^0$ ) were recorded on a Perkin Elmer, Lambda 35 UV/Vis spectrophotometer using 1 cm matched quartz cells and slit width 2 nm. The second derivative ( $D^2$ ) conditions:  $\Delta\lambda = 10$  nm, scan rate = 480 nm/min. Normal or derivative spectra of Cu(II) - Schiff bases complexes were measured against a reagent blank, similarly prepared but containing no metal ion. pH measurements were made with Jenway 3040 ion analyser-

E-mail: president@aun.edu.eg

pH meter, equipped with Jenway 924005 combined glass electrode. The pH-meter was calibrated before use with standard buffer solution of pH 4.0±0.01 and 7.00±0.01.

### 2.3. Standard procedures

#### 2.3.1 Calibration curve at D°

Calibration curve at D° was obtained from the standard solution (19.06 µg/ml) by transferring aliquot volumes containing up to 95.3 µg/25 ml of Cu(II), 10 ml of 3.0x10<sup>-4</sup> mol L<sup>-1</sup> ethanolic solution of HDBe, 2.5 ml pure ethanol, 2.5 ml of 1.0 mol L<sup>-1</sup> acetate buffer adjusted to pH 6.0 were added. The resulting solution was completed to 25 ml with deionized water and the absorbance was measured at 392 nm against a reagent blank similarly prepared but containing no Cu(II).

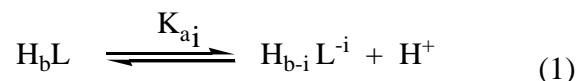
#### 2.3.2 Calibration curve at D<sup>2</sup>

Calibration curve at D<sup>2</sup> was constructed from the working standard solution (9.53 µg/ml) by transferring a volume of solution containing 3.75-82.5 µg of Cu(II), 10 ml of 3x10<sup>-4</sup> mol L<sup>-1</sup> ethanolic HDBe solution, 2.5 ml acetate buffer of pH 6.0, 2.5 ml of pure ethanol to a 25 ml standard flask and diluted to the mark with deionized water. After mixing well the D<sup>2</sup> spectra was recorded in the range 370-460 nm against a reagent blank and the amplitude of the trough was measured at λ 394.7 nm.

## 3. Results and Discussion

### 3.1. Acid Dissociation Constants of Schiff Bases

As is apparent from their structure, the five Schiff bases studied in this work exist in solution in any of the following forms depending upon the acidity or pH:



Where H<sub>b</sub>L represents the neutral species of the Schiff bases, b denotes the number of their dissociable protons (b = 1 for all compounds except H<sub>2</sub>Sal, b = 2) and K<sub>ai</sub>

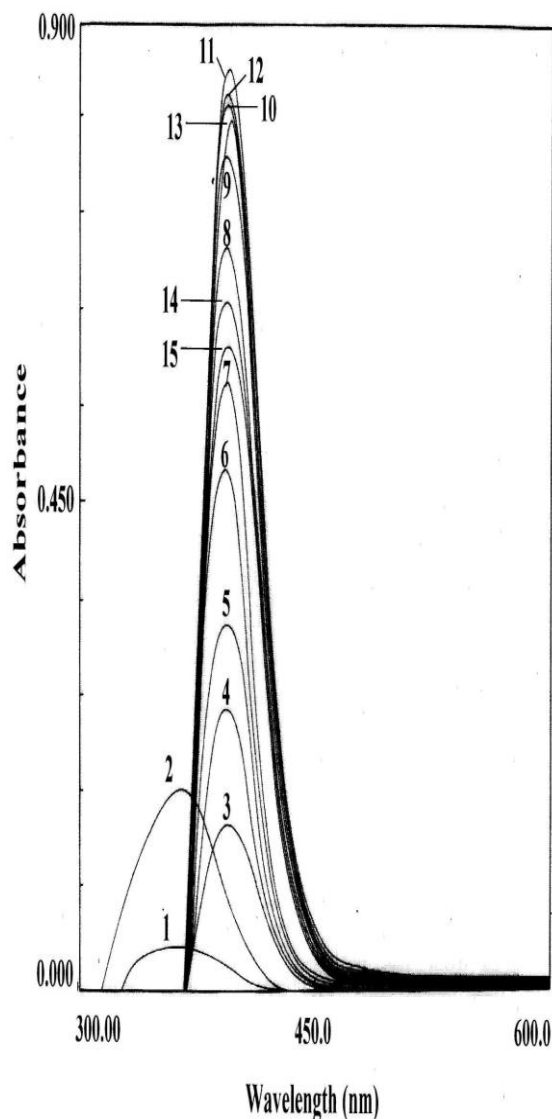
is the acid dissociation constant. The pK<sub>ai</sub> values of the Schiff bases, which were already determined in earlier work [15] are necessary for the calculation of the formation constants and are summarized in Table 1. Where K<sub>a1</sub> of the first four compounds may be assigned to the deprotonation from the heterocyclic amido group. The values of K<sub>a1</sub> and K<sub>a2</sub> of H<sub>2</sub>Sal correspond to the deprotonation from the hydroxyl and heterocyclic amido group respectively are also given.

**Table 1:** Mean pK<sub>ai</sub> values for investigated Schiff bases in ethanol/water solution (50% v/v), I = 0.1 mol L<sup>-1</sup> (NaClO<sub>4</sub>) at 25±0.1°C (reference 15).

Compound	pK <sub>a1</sub>	pK <sub>a2</sub>
HBe	9.8155 ±0.012	—
HMBE	10.0655 ±0.021	—
HDBE	10.265 ±0.013	—
HNBe	9.515 ±0.023	—
H <sub>2</sub> Sal	9.415 ±0.01	11.99 ±0.012

### 3.2. Effect of pH on Complexation and Absorption Spectra of Complexes

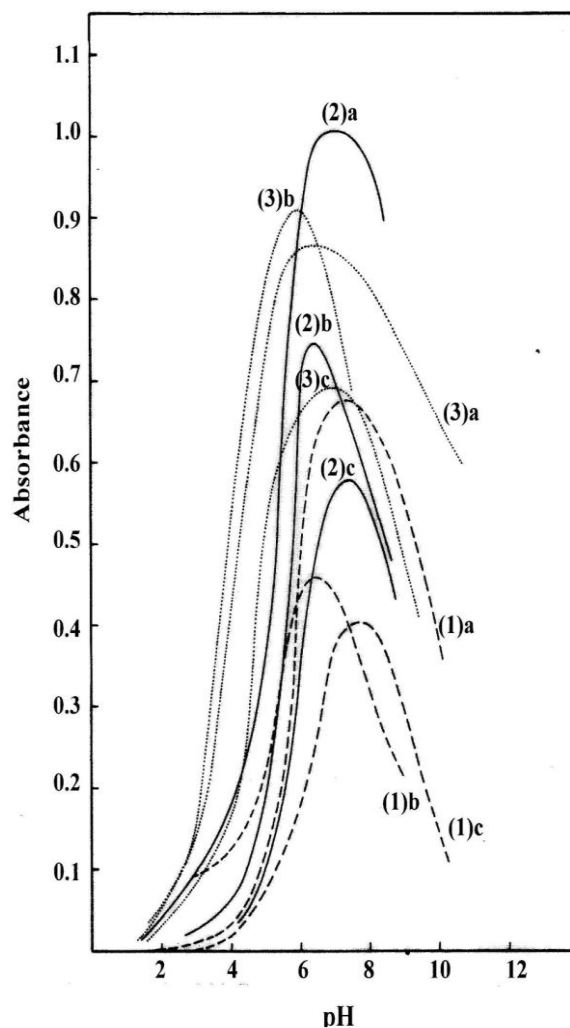
The reaction of Cu(II) with the bidentate ligands HBe, HMBE, HDBE or HNBe were studied in 50% (v/v) ethanol-water medium at 25°C and I = 0.1 M (NaClO<sub>4</sub>) in the pH range 1.5-10.5. Complexation reactions were investigated at different pH values in equimolar solutions and in solutions containing an excess of one component. The solution spectra reflect the formation of at least two complex species in the pH range 2.5-7.0 depending on the pH of the reaction mixture and the concentration of components. The absorption spectra of C<sub>M</sub>/C<sub>L</sub> = 1 and C<sub>L</sub>/C<sub>M</sub> > 1 solution at various pH values are analogous and exhibit maximum absorption at the same wavelength. The absorbance vs. pH graphs for the above solutions indicate the existence of only one chelate equilibrium in the pH range 5.5-7.5 (cf. Figs. 1,2 and 3).



**Fig. 1 :** Zero-order, ( $D^0$ ) absorption spectra of Cu(II)-HDBe complex,  $C_L = 0.9 \times 10^{-4}$  M,  $C_M = 2.25 \times 10^{-5}$  M and pH: (1) 1.65; (2) 2.53; (3) 3.09; (4) 3.5; (5) 3.82; (6) 4.21; (7) 4.5; (8) 5.0; (9) 5.5; (10) 6.0; (11) 7.70; (12) 7.85; (13) 8.15; (14) 10.1; (15) 10.7.

Effect of pH on the complexation of copper(II) with the tridentate  $H_2Sal$  was also studied in the pH range 0.5-10.5. The solution spectra were recorded at several  $C_M/C_L$  ratios. The spectra of all solutions at various pH values are analogous and exhibit an absorption band with  $\lambda_{max} = 376$  nm. The

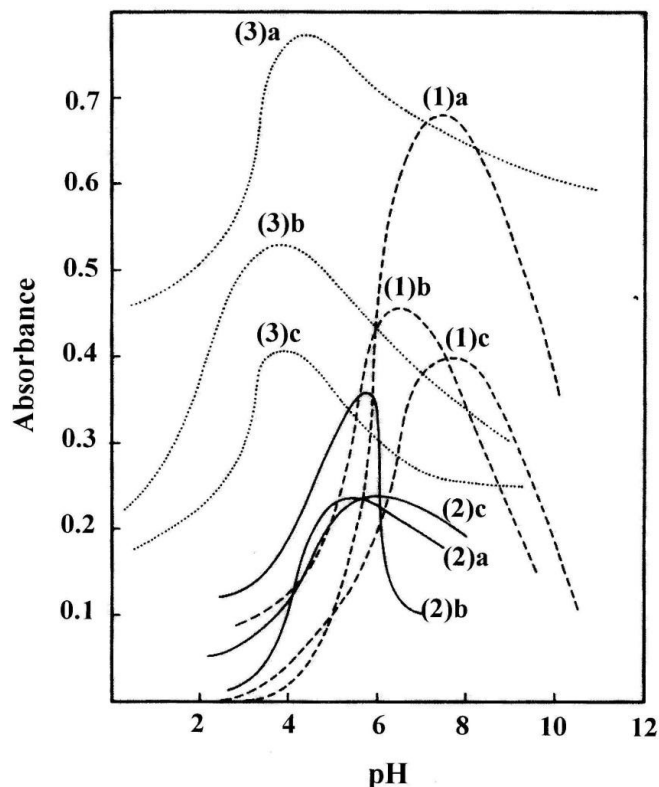
<http://www.aun.edu.eg>



**Fig. 2:** Graphs of absorbance versus pH for Cu(II)-Schif base systems (p- substituted) (1) Cu(II)-HBe (a)  $\lambda = 340$  nm;  $C_L = 2 \times 10^{-4}$  M,  $C_M = 5 \times 10^{-5}$  M; (b)  $\lambda = 336$  nm;  $C_L = 5 \times 10^{-5}$  M,  $C_M = 2 \times 10^{-4}$  M; (c)  $\lambda = 340$  nm;  $C_L = C_M = 5 \times 10^{-5}$  M; (2) Cu-HMBe (a)  $\lambda = 348$  nm;  $C_L = 2 \times 10^{-4}$  M,  $C_M = 5 \times 10^{-5}$  M; (b)  $\lambda = 346$  nm;  $C_L = 5 \times 10^{-5}$  M,  $C_M = 2 \times 10^{-4}$  M; (c)  $\lambda = 348$  nm;  $C_L = C_M = 5 \times 10^{-5}$  M; (3) Cu-HDBe (a)  $\lambda = 392$  nm;  $C_L = 0.9 \times 10^{-4}$  M,  $C_M = 2.25 \times 10^{-5}$  M; (b)  $\lambda = 390$  nm;  $C_L = 3 \times 10^{-5}$  M,  $C_M = 1.2 \times 10^{-4}$  M; (c)  $\lambda = 392$  nm;  $C_L = C_M = 3 \times 10^{-5}$  M.

absorbance vs. pH graph, for the above solutions indicate the existence of only one chelate equilibrium in the pH range 4.0-4.5 (Fig. 3). The results are summarized in Table 2 along with the complex compositions determined by the continuous variation method [19].

E-mail: president@ aun.edu.eg



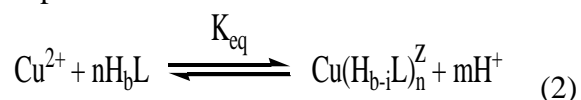
**Fig. 3:** Graphs of absorbance versus pH for Cu(II)-Schiff base systems (o- substituted) (1) Cu(II)-HBe (a)  $\lambda = 340$  nm;  $C_L = 2 \times 10^{-4}$  M,  $C_M = 5 \times 10^{-5}$  M; (b)  $\lambda = 336$  nm;  $C_L = 5 \times 10^{-5}$  M,  $C_M = 2 \times 10^{-4}$  M; (c)  $\lambda = 340$  nm;  $C_L = C_M = 5 \times 10^{-5}$  M; (2) Cu-HNBe (a)  $\lambda = 398$  nm;  $C_L = 4 \times 10^{-4}$  M,  $C_M = 1 \times 10^{-4}$  M; (b)  $\lambda = 393$  nm;  $C_L = 2 \times 10^{-4}$  M,  $C_M = 8 \times 10^{-4}$  M; (c)  $\lambda = 397$  nm;  $C_L = C_M = 2 \times 10^{-4}$  M; (3) Cu-H<sub>2</sub>Sal (a)  $\lambda = 376$  nm;  $C_L = 2 \times 10^{-4}$  M,  $C_M = 5 \times 10^{-5}$  M; (b)  $\lambda = 376$  nm;  $C_L = 5 \times 10^{-5}$  M,  $C_M = 2 \times 10^{-4}$  M; (c)  $\lambda = 376$  nm;  $C_L = C_M = 5 \times 10^{-5}$  M.

**Table 2:** Optimal ranges for complexation and characteristics of Complexes

Complex	[L]/[M] ratio	Optimal pH range	$\lambda_{\max}$ Schiff base nm	$\lambda_{\max}$ complex	Molar Absorptivity $Lmol^{-1} cm^{-1}$	Compositon (M : L)
Cu(II)-HBe	1	7.0-7.5	299	340	$1.36 \times 10^4$	1:2
	4	7.0-7.5		340	$1.36 \times 10^4$	1:2
	1/4	6.0-6.5		336	$0.920 \times 10^4$	1:1
Cu-HMBe	1	7.0-7.5	313	348	$2.0 \times 10^4$	1:2
	4	7.0-7.5		348	$2.0 \times 10^4$	1:2
	1/4	6.0-6.5		346	$1.5 \times 10^4$	1:1
Cu-HDBe	1	5.5-6.5	345	392	$2.88 \times 10^4$	1:2
	4	5.5-6.5		392	$2.88 \times 10^4$	1:2
	1/4	5.5-6.0		390	$3.03 \times 10^4$	1:1
Cu-HNBe	1	5.0-6.0	290	397	$0.24 \times 10^4$	1:2
	4	5.0-6.0		398	$0.24 \times 10^4$	1:2
	1/4	5.0-5.5		393	$0.18 \times 10^4$	1:1
Cu-H <sub>2</sub> Sal	1	4.0-4.5	231	376	$1.06 \times 10^4$	1:1
	4	4.0-4.5		376	$1.06 \times 10^4$	1:1
	1/4	4.0-4.5		376	$1.06 \times 10^4$	1:1

### 3.2.1 Complexation Equilibria

The absorbance-pH graphs for solutions with various [L]/[M] ratio were interpreted by direct graphical and logarithmic analysis [20,21] using the earlier derived slope-intercept transformations of the equilibrium constants of the assumed complex for conditions under which a single equilibrium predominates and for selected wavelength. In general, the complexation equilibrium between the specified Schiff base (bidentate or tridentate) and copper ion may be expressed as



Where  $z = ni - m$  and  $K_{\text{eq}}$  is the equilibrium constants. If the initial concentration of the ligand,  $C_L$ , is much higher than that of the metal ion  $C_M$ , equation (3) can be obtained.

$$K_{\text{eq}} = \frac{x[\text{H}^+]^m}{(C_M - x)(C_L - nx)^n} \quad (3)$$

Where  $x$  is the equilibrium concentration of the complex formed. On the other hand, as the system obeys Beer's law additively over the wavelength range of interest, equation (4) can be deduced.

$$A = \varepsilon_L (C_L - nx) + \varepsilon_C x \quad (4)$$

Where  $\varepsilon_L$  and  $\varepsilon_C$  are molar absorptivities of the ligand and the complex at a specified wavelength, respectively, and  $A$  is the absorbance of the solution containing the copper ion and the ligand. When the absorbance of the solution is measured against a reagent blank, from equation (3) and (4), equation (5) can finally be obtained.

$$\frac{C_M}{A} = \frac{1}{\varepsilon_C} + \frac{[\text{H}^+]^m}{\varepsilon_C C_L^n K_{\text{eq}}} \quad (5)$$

Equation (5) means that either the plot of  $C_M/A$  versus  $1/C_L^n$  at constant values of  $C_M$  and  $[\text{H}^+]$  or the plot of  $C_M/A$  versus  $[\text{H}^+]^m$  at constant values of  $C_M$  and  $C_L$  should give

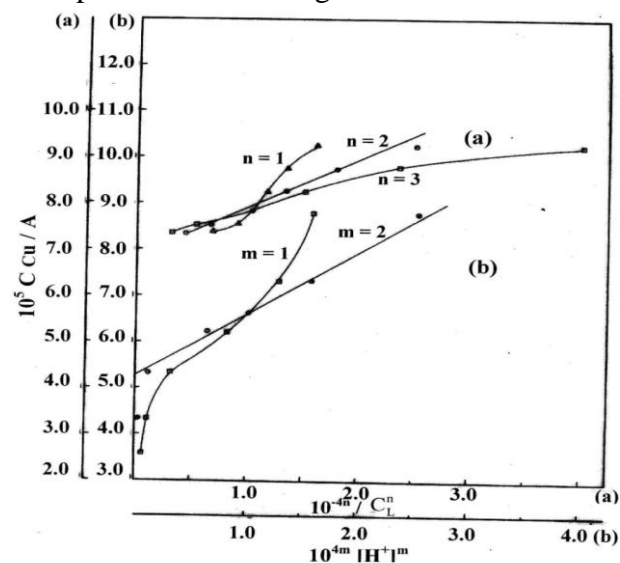
a straight line, provided that the values of  $n$  and/or  $m$  were correctly assumed. The values of  $K_{\text{eq}}$  can be calculated from the slope of either line. The overall stability constant  $B_n$  of the complex formed can be calculated from the values of  $K_{\text{eq}}$  and  $K_{a_i}$  as follows.

$$B_n = K_{\text{eq}} / K_{a_i}^m \quad (\text{Cu-bidentate ligand}) \quad (6)$$

$$B_1 = K_{\text{eq}} / K_{a_1} \cdot K_{a_2} \quad (\text{Cu-tridentate ligand}) \quad (7)$$

### 3.2.2 Copper (II) Complexes with the Bidentate Ligands

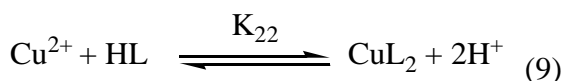
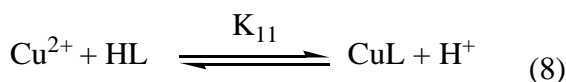
Copper(II) forms 1:2 (metal : ligand) complexes with HBe, HMBe, HDBe or HNBe in solutions with excess ligands or equimolar solutions in the pH range 5.5-7.5 as described already. Since each Schiff base exists as one species under the experimental conditions adopted, plots of  $C_{\text{Cu}}/A$  vs.  $1/C_L^n$  and  $C_{\text{Cu}}/A$  vs.  $[\text{H}^+]^m$  based on equation (5) were prepared for each copper-bidentate ligand system. Both plots give straight lines when it was assumed  $n = 2$  and  $m = 2$  in every system. An example of each plot is shown in Fig. 4.



**Figure 4a.** Plots of  $C_{\text{Cu}}/A$  versus  $1/C_L^n$  for the formation of the Cu(II)- HDBe complex.  $C_{\text{Cu}}$ ,  $5 \times 10^{-5}$  M; pH, 6.0; I, 0.1 mol/L ( $\text{NaClO}_4$ );  $\lambda$ , 396 nm; at  $25 \pm 0.1^\circ\text{C}$ . . Plots of  $C_{\text{Cu}}/A$  versus  $[\text{H}^+]^m$  for the formation of the Cu(II)- HDBe complex.  $C_{\text{Cu}}$ ,  $2.25 \times 10^{-5}$  M,  $C_L$ ,  $0.9 \times 10^{-4}$  M. Other condition are the same as for (a).

**b.** Plots of  $CCu/A$  versus  $[\text{H}^+]^m$  for the formation of the Cu(II)- HDBe complex.  $C_{\text{Cu}}$ ,  $2.25 \times 10^{-5}$  M,  $C_L$ ,  $0.9 \times 10^{-4}$  M. Other condition are the same as for (a).

By considering values of the dissociation constants of bidentate Schiff bases under our experimental conditions, it can be concluded that the neutral form is the prevalent ligand species in the pH range of complexation. The following equilibria were considered during direct and logarithmic analysis of the A-pH graphs.



The ascending region of A-pH graphs in solutions with excess metal ions in the pH range 2.5-6.5 was also analysed using Eq. (10) and assuming equilibrium (8) with  $n = m = 1$ .

$$\text{Log} [\Delta A / (\varepsilon_1 C_L - \Delta A)] = \text{pH} + \text{log } C_M + \text{log } K_{11}$$

For equimolar solutions Eq. (11) is valid for equilibrium (9) in the pH range 3.0-7.5.

$$\text{Log} [\Delta A / (\varepsilon_2 C_L - 2\Delta A)^2] = 2\text{pH} + \text{log } K_{22} + \text{log} (C_M - A/\varepsilon_2) - \text{log } \varepsilon_2 \quad (11)$$

The existence of this complex equilibrium is proved in solutions with excess ligand in the same pH range as evidenced by the analysis of the rising portion of the A-pH graphs. Logarithmic analysis according to Eq. (12) indicated the splitting of two protons and the formation of  $\text{CuL}_2$  complex species according to equilibrium (9).

$$\text{Log} [\Delta A / (\varepsilon_2 C_M - \Delta A)] = \text{log } K_{22} + 2\text{pH} + \text{log} \left( C_L - \frac{2\Delta A}{\varepsilon_2} \right)^2 \quad (12)$$

All the absorbance - pH graphs at various wavelengths and concentrations of components have a descending branch within the pH range 8.0-10.5 which is due to the hydrolysis of the complexed ligands. The calculated values of equilibrium ( $\text{log } K_{nm}$ ) and stability constants ( $\text{log } B_n$ ) of Cu(II)-bidentate ligand complexes are given in Table 3.

**Table 3:** Equilibrium constants, overall formation constants and species of complexes. Dependence of  $\text{log } B_1$  and  $\text{log } B_2$  of Cu-Schiff bases complexes on  $\Sigma \text{p}K_{a1}$

System	$\Sigma \text{p}K_{a1}$	Species of complex	$\text{Log } K_{nm}$	$\text{Log } B_1$	$\text{Log } B_2$
Cu(II)-HBe	9.816	$\text{CuL}_2^a$	-0.82		18.692 <sup>d</sup>
		$\text{CuL}_2^b$	-0.784		18.712 <sup>d</sup>
		$\text{CuL}^c$	-1.102	8.654 <sup>e</sup>	
Cu-HMBe	10.066	$\text{CuL}_2^a$	-0.95		19.1115 <sup>d</sup>
		$\text{CuL}_2^b$	-1.102		18.9595 <sup>d</sup>
		$\text{CuL}^c$	-1.201	8.8297 <sup>e</sup>	
Cu-HDBe	10.265	$\text{CuL}_2^a$	+0.479		20.939 <sup>d</sup>
		$\text{CuL}_2^b$	+0.542		21.002 <sup>d</sup>
		$\text{CuL}^c$	+0.521	10.751 <sup>e</sup>	
Cu-HNBe	9.515	$\text{CuL}_2^a$	-0.422		18.668 <sup>d</sup>
		$\text{CuL}_2^b$	-0.305		18.5835 <sup>d</sup>
		$\text{CuL}^c$	-1.004	8.44 <sup>e</sup>	
Cu-H <sub>2</sub> Sal	21.405	$\text{CuL}^a$	-0.575	20.69 <sup>f</sup>	
		$\text{CuL}^b$	-0.850	20.419 <sup>f</sup>	
		$\text{CuL}^c$	-0.601	20.668 <sup>f</sup>	
Slope (p)				0.867	0.778
Intercept c				-0.2	11.2

a) From the A vs pH graphs for solutions  $C_L = C_M$ .

b) From the A vs pH graphs for solutions  $C_L / C_M = 4$ .

c) From the A vs pH graphs for solutions  $C_M / C_L = 4$ .

d)  $\text{Log } B_2 = \text{Log } K_{22} + 2 \text{p}K_a$ .

e)  $\text{Log } B_1 = \text{log } K_{11} + \text{p}K_a$ .

f)  $\text{Log } B_1 = \text{log } K_{12} + \text{p}K_{a1} + \text{p}K_{a2}$ .

### 3.2.3 Copper Complex with the Tridentate Ligand ( $\text{H}_2\text{Sal}$ )

Copper(II) reacts with  $\text{H}_2\text{Sal}$  forming 1:1 complex with all  $[\text{M}]/[\text{L}]$  concentration ratios. As neutral molecule of  $\text{H}_2\text{Sal}$  exist in weakly acidic solutions where 1:1 complex is formed, plot of  $C_{\text{Cu}}/A$  vs.  $1/C_L^n$  and  $\text{Cu}/A$  vs.  $[\text{H}^+]^m$  based on equation (5) were prepared for each  $[\text{M}]/[\text{L}]$  concentration ratio. These plots gave straight lines when it was assumed  $n = 1$  and  $m = 2$  in every ratio. For solutions containing various concentrations of components, the graphical-logarithmic analysis of the A-pH graphs in the pH range 1.0-4.0, using the appropriate equations (10-12) yields the best fit for equilibrium (13) and the formation of  $\text{CuL}$  complex species.

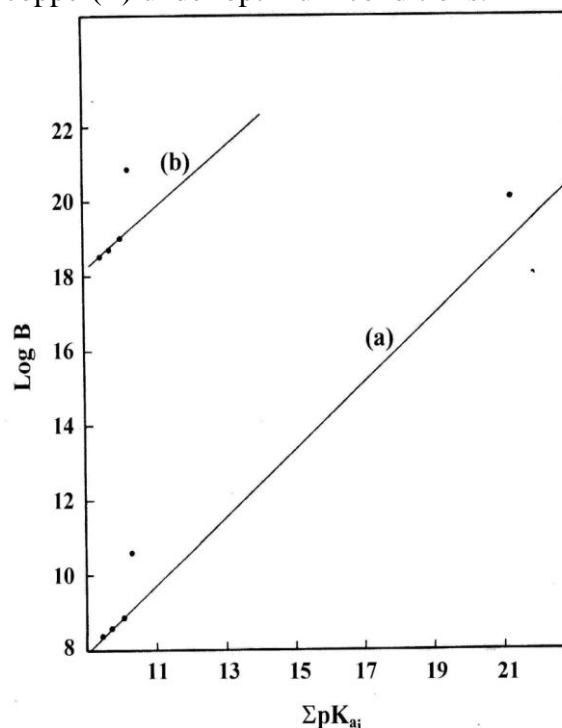


The calculated values of  $\text{log } K_{12}$  and  $\text{log } B_i$  are given in Table 3.

### 3.2.4 Log B - $\sum pK_{a_i}$ Relationship

The relation between the sum of the ionization constants of investigated Schiff bases and the stability constants ( $\log B_1$  or  $\log B_2$ ) of their complexes with copper(II) ion are represented graphically in Fig. 5. There is a linear relation between  $\sum pK_{a_i}$  of the reactive ligands and  $\log B_1$  of their complexes. Therefore, Schiff base with higher  $\sum pK_{a_i}$  are expected to form more stable complexes. The results are treated statistically using the least square method [22]. The regression of the lines may be represented as  $\log B_1 = C_1 + \rho_1 \sum pK_{a_i}$  or  $\log B_2 = C_2 + \rho_2 \sum pK_{a_i}$ , where the values of C and  $\rho$  are given in Table 3. The plots have correlation coefficient of 0.93 for  $\log B_1$  and 0.85 for  $\log B_2$  of Cu(II) complexes. Such values indicate the dependence of the stability constants of the complexes on  $\sum pK_{a_i}$  of the ligand. This favours the assumption that the reaction between the metal ions and the Schiff bases proceeds through proton elimination (eqs. 8,9,13). From Fig. 5 it is clear that H<sub>2</sub>Sal has the highest affinity for chelation with copper ions among the investigated Schiff bases. This is attributed to the presence of an additional coordinating site (phenolic OH group). On the other hand HNBe was found to have the lowest ability for chelation. This can be explained by the presence of the *o*-NO<sub>2</sub> group which has a strong electron withdrawing effect [15] resulting in a decrease in electron density on the heterocyclic amido nitrogen atom and hence in a decrease of stability constant of the formed complex. It is also evident from Fig. 5 that Cu-HDBe complex has abnormal high stability ( $\log B_2$ ). This is because of electron donating *p*-N(CH<sub>3</sub>)<sub>2</sub> group which intensify electron density on azomethin nitrogen atom. In general the values of  $\log B_1$  and  $\log B_2$  reflect the affinities of the investigated Schiff bases for chelation with copper ions and are comparable with those reported for some nitrogen-containing Schiff

bases [23]. This affinity may be attributed to the simple structure of the investigated ligands and consequently little steric hindrance in the formed 1:1 and 1:2 complexes. According to the results of this work, the formation of Cu(DBe)<sub>2</sub> complex which possesses the greatest stability and the highest molar absorptivity was undertaken as a suitable base for the spectrophotometric determination of copper(II) under optimum conditions.



**Figure 5a:**  $\log B_1$  of Cu(II)-complexes with Schiff bases (1-5) vs.  $\sum pK_{a_i}$  of ligands.

**b:**  $\log B_2$  of Cu(II)-complexes with Schiff bases (1-4) vs.  $\sum pK_{a_i}$  of ligands.

### 3.3. Calibration Graphs and Statistical Treatment of Results

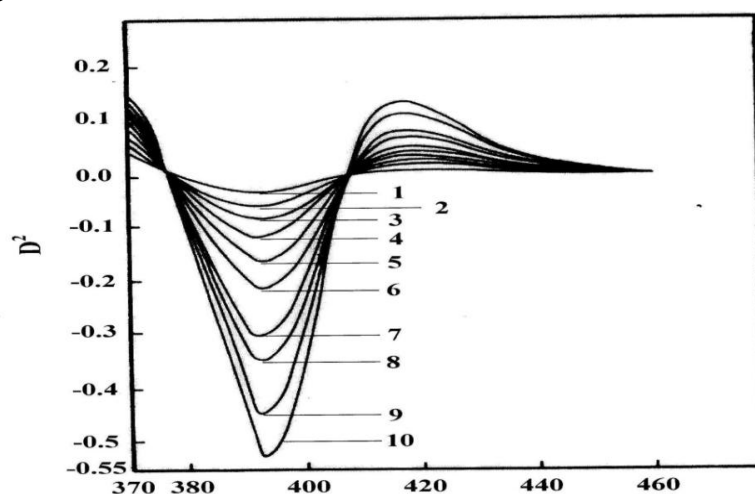
Zero-order ( $D^0$ ). In the normal photometric method, Beer's law was obeyed in the copper concentration range 0.3-3.06  $\mu\text{g ml}^{-1}$ . The molar absorptivity at  $\lambda = 392 \text{ nm}$  was  $2.88 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ . A Ringbom plot showed that the optimum copper range for accurate determination was 0.457-3.02  $\mu\text{g ml}^{-1}$ . Second order ( $D^2$ ). In an attempt to increase the sensitivity of the procedure and eliminate any interferences, we investigated the different derivatives orders. We conducted a large number of preliminary tests to select the more convenient order of the derivative and



working range. Standardization of derivative spectrophotometry [24] requires establishment of optimum instrumental conditions such as derivative order, ordinate axis, differential wavelength, and scan speed. Second order ( $D^2$ ) mode proved to be maximal. The ordinate axis was  $+0.2 - -0.55$  absorbance  $\text{nm}^{-2}$ . The differential wavelength used was 10 nm, which gives the lowest S/N ratio. Figure 6 shows  $D^2$  modes for determination of Cu(II) as  $[\text{Cu}(\text{DBe})_2]$  complex over the range of 370-460 nm. The linearity of the amplitude of the trough ( $D^2A$ ) to the concentration of copper at  $\lambda$  394.7 nm was rectilinear over the range 0.15-1.05  $\mu\text{g ml}^{-1}$ . The sensitivity of the method can be reported as calibration sensitivity [25]  $S_c$  (i.e. the slope of the calibration curve) and the analytical sensitivity [26]  $S_A = S_c/S_D$  where  $S_D$  is the standard deviation of the signal at a particular concentration. Thus  $S_A$  is inversely related to the ability to distinguish a concentration difference, therefore the inverse relationship  $1/S_A$  is also given. The high values of correlation coefficient and intercepts on the Y- axis (close to zero) indicate the good linearity of calibration graphs and the conformity of Beer's law. The statistical parameters for calibration graphs and other details about the precision of the method are given in Table 4.

### 3.4. Interference Study

The effect of potentially interfering ions on the determination of copper at the 1.0  $\mu\text{g ml}^{-1}$  level was examined over wide range of concentrations, by the ordinary photometric method. Those species which interfered seriously in the ordinary photometric method were also examined by the second derivative approach for solutions containing 10  $\mu\text{g}$  copper per 25 ml. The tolerance criterion was a deviation of the absorbance values or derivative amplitude by more than  $\pm 2\%$  from the value expected for copper alone. The determination of copper as  $[\text{Cu}(\text{DBe})_2]$  complex was possible in presence of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ag}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{MoO}_4^{2-}$ ,  $\text{Al}^{3+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{F}^-$ ,  $\text{ZrO}_2^+$ ,  $\text{CNS}^-$ , acetate (50 fold) and  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$  (20 fold). The interference from the presence of  $\text{Fe}^{3+}$ , up to (5 fold) 0.05 mg could be eliminated by adding potassium fluoride ( $\sim 100$  fold excess) as masking agent. From the investigated ions  $\text{Hg}^{2+}$  interfered seriously, even when present in amount of 0.05 mg. Use of the second derivative methods improves the tolerance for  $\text{Fe}^{3+}$  and  $\text{Hg}^{2+}$  ions. Under the present experimental conditions, it was observed that Cu(II) could not be determined in presence of  $\text{CN}^-$  and EDTA, accordingly the above reagent could not be used as masking agents.



**Figure 6.** Second-order absorption spectra ( $D^2$ ) of Cu(II)-HDBE complex.  $[\text{L}] = 1.2 \times 10^{-4}$  M; pH = 6.0 (acetate buffer);  $[\text{Cu}^{2+}] = 1, 0.15; 2, 0.381; 3, 0.58; 4, 0.762; 5, 1.05; 6, 1.64; 7, 2.12; 8, 2.606; 9, 3.00; 10, 3.30$  ppm.

**Table 4:** Statistical analysis of spectrophotometric determination of Cu(II) with HDBe.

Method	$\lambda_{(nm)}$	Linear dynamic range ( $\mu\text{g/ml}$ )	Percentage recovery	Regression equation	Correlation coefficient (r)	n	RSD	$S_c$ ml/ $\mu\text{g}$	$1/S_A$ ng/ml
Photometric (zero order ( $D^0$ ))	392	0.3-3.06	99.88	$D^0A = 0.36 C_0 + 0.0032$	0.995	6	0.6	0.36	16.6
Second Derivative $D^2$	395	0.15-1.0	100.0	$D^2A = 0.145 C_2 + 0.001$	0.997	6	0.5	0.145	13.69

**Table 5:** Determination of copper in various synthetic samples using second-derivative spectrophotometry.

Sample	Synthetic mixture composition <sup>(a)</sup>	Amount found <sup>(b)</sup>	Recovery (%)	Standard deviation	Coefficient of variation (%)
1	Cu (10), Pb (500), Al (500), Co	9.96	99.6	0.05	0.502
2	Cu (10), Mg (500), Zn (500), Ni	9.95	99.5	0.06	0.603
3	Cu (10), Mn (500), Zn (500), Co	9.97	99.7	0.04	0.401
4	Cu (10), Pb (500), Al (500), Cd	9.99	99.9	0.03	0.300

<sup>(a)</sup> Numbers of parentheses are microgram amounts of the metals.

<sup>(b)</sup> Average of five determinations.

### 3.5.Applications

#### 3.5.1 Determination of Copper (II) in Synthetic Mixtures

The proposed method was applied to the determination of copper (10  $\mu\text{g}/25$  ml) in various synthetic mixtures containing lead, nickel, cobalt, zinc, iron, manganese, aluminium, magnesium and cadmium. The results are shown in Table 5.

**Table 6:** Results of determination of total copper in fresh water samples using second-derivative spectrophotometry.

Sample	Copper found <sup>(c)</sup> , ppm		Recovery%
	Proposed method	Atomic absorption, ppm	
Tap water <sup>(a)</sup>	$0.235 \pm 0.002$	$0.2394 \pm 0.002$	98.2
Natural water <sup>(b)</sup> (Baraka)	$0.064 \pm 0.001$	$0.0642 \pm 0.001$	99.7

a) Assiut University Chemistry Dept. Labs, sample taken = 5.0 ml/25 ml.

b) Sample taken = 10.0 ml/25 ml.

c) Average of four determinations.

#### 3.5.2.Determination of Copper (II) in Fresh Water

The proposed method was applied to the determination of the total copper in tap-water and natural water (Baraka) samples (0.6 mg of potassium fluoride was added as masking reagent). By applying standard addition methods, five or ten millilitre portions of the samples were analysed for copper without preconcentration process. The results shown in Table 6 are in good agreement with each other and with those obtained by atomic absorption spectrometry.

#### 3.6. Comparison of HDBe with Other Spectrophotometric Reagents

Table 7 summarizes the spectral characteristics of some of the reported methods for the determination of Cu(II). A careful comparison between the proposed method and reported methods showed that our method has the advantages of high sensitivity ( $2.88 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) and high stability in solution ( $\log \beta_2=21.0$ ).

**Table 7:** Comparison of the sensitivities of various spectrophotometric reagents for Cu(II).

Method <sup>(a)</sup>	Solvent	Acidity range	$\lambda_{\max}$ , nm	$\epsilon$ , L mol <sup>-1</sup> cm <sup>-1</sup>	Determination range	Ref.
HYP A	EtOH/H <sub>2</sub> O	pH= 5.5, M:L (1:1)	335	1.42x10 <sup>4</sup>	1.8-10.45 ppm	27
ETC	aqu.	pH= 8.5	420	1.1x10 <sup>4</sup>	0-4.4 ppm	28
HTPA	aqu.	pH= 6.4-6.9, M:L (1:2)	402	7.037x10 <sup>3</sup>		29
naph.	EtOH/H <sub>2</sub> O		330	1.84x10 <sup>4</sup>	up to 4.5 ppm	30
BTAEB	EtOH/H <sub>2</sub> O	pH= 2.5- 6.3, M:L (1:1)	655	7.94x10 <sup>4</sup>	0-24 µg/ 25 ml	31
HDBe	EtOH/H <sub>2</sub> O	pH= 5.5-6.5, M:L (1:2)	395	2.88x10 <sup>4</sup>	0.15-1.0 ppm	this work

HYP A = 3-hydroxypicolinic acid; ETC = diethyl-dithiocarbamate; HTPA = 3-hydroxy-3-m-tolyl-1-p-sulphonatophenyl triazene; naph. = 5,8-dihydroxy-1,4-naphthoquinone; BTAEB = 2-(6-methyl benzothiazolyl)azo 5-diethylamino-benzoic acid

#### 4. Conclusions

From the results of the five studied Schiff bases HDBe is considered the most useful ligand for spectrophotometric determination of copper(II) because the [Cu(DBe)<sub>2</sub>] complex has abnormal high stability (log B<sub>2</sub>) which reflect its high affinity for chelation with copper(II) ions. The structure of the complex is square planar<sup>(14)</sup> and the chelate formation takes place via the hydrazino nitrogen and heterocyclic amido nitrogen. The proposed method for determination of micrograms of copper is rapid, selective and has excellent colour stability. This procedure indicates reasonable sensitivity at second derivative (D<sup>2</sup>) where about (0.2 µg/ml) was determined accurately. In terms of selectivity, the proposed method was found to be superior to most of the established methods reported for spectrophotometric determination of copper. Furthermore it gives reproducible results for spectrophotometric determination of copper in fresh water samples and in various synthetic samples.

#### References

- [1] P.Jain, R.P. Singh, Talanta 29(1982) 77.  
 [2] B.A. El-Shetary, M.S. Abdel-Moez, S.

Stefan, G. El-Inany. (1988) J. Serb. Chem. Soc. 53(1988) 679.

[3] I. Hajime, Y. Mitsuru, O. Tsugikatsu, j.) Talanta 39(1992) 1181.

[4] M.Yamamoto, K.Uesugi, H. Nishioka,.; T.Kumagai, T.Nagahiro, Kenkyu Hokoku-Himeji Kogyo Daigaku Kogakubu 47(1994), 1.

[5] S.S.G.Kawatkar, R.V. Nimbalkar, J. Indian Counc. Chem. 10(1994) 40.

[6] T.Nakanishi, Anal. Sci. Technol 8 (1995) 469.

[7] D.G.Themelis, G.A. Zachariadis, J.A. Stratis, . Analyst 120(1995) 1593.

[8] N.Koprivanac, Z. Grabaric, S. Papic, B.S. Grabtaric, B.S., G. Acamovic- Dokovic, Monatsh. Fur Chem. 126(1995) 23.

[9] C. Jiang, B. Tang, C.Wang, X. Zhang, Analyst 121(1996) 317.

[10] S.G.Kawatkar, R.V. Nimbalkar, . J. Indian Chem. Soc. 73(1996) 371.

[11] S.Sharma, Rameshwar, J.R. Mehta, Indian J. Chem., Sect. A. 35A (1996) 76.

[12] S.G.Kawatkar, R.V. Nimbalkar, J. Indian Chem. Soc. 74(1997) 69.

[13] N.Y.Sreedhar, K. Samatha, . Proc. Natl. Acad. Sci., India, Sect. A 69 (1999) 287.

[14] A.H.Osman, M.S.Saleh, S.M.Mahmoud, Synth. React. Inorg. Met.-Org. Chem. 34(2004) 1069.

[15] A.H.Osman, M.S. Saleh, S.M. Mahmoud,

- Bull. Fac. Sci., Assiut Univ. 33(2004)33.
- [16] A.A.Geies, A.A.Abdel-Hafez, A.M.Kamal El-Dean, Z.A.Hozien, Bull. Fac. Sci., Assiut Univ. 22(1993)37.
- [17] A.I.Vogel, Textbook of Quantitative Inorganic Analysis, ELBS-Longman, London(1985)
- [18] H.T.S.Britton, . Hydrogen Ions, Chapman and Hall, London(1952).
- [19] P.Job, Ann. Chem. 9(1928) 113.
- [20] L.Sommer,M. Langova, CRC, Crit. Rev. Anal. Chem. 19(1988)225.
- [21]K.A. Idriss, M.M. Seleim, M.S. Saleh, M.S.Abu-Bakr,H. Sedaira, Analyst 113(1988) 1643.
- [22] H.H.Jaffe, Chem. Rev. 53(1953)191.
- [23]N. Koprivanac, Z. Grabaric, S. Papic, B.S.Grabaric, G. Acamovie- Dokovie, Monatsh. Fur Chem. 126(1995) 23.
- [24]P. Levillain, S.Fombeydie, Analyst 14(1986) 1.
- [25] Spectrochim. Acta , 33(1978) 242.
- [26]J. Mandel, R.D. Stichler, . J. Res. Natl. Bur. Stand. 53(1954) 155.
- [27]K.A. Idriss, M.S. Saleh, H.A. Azab, E.Y.Hashem, Bull Polish Academy Sci. Chem. 34(1995)67.
- [28] L.Ying, F.Lijuan, L. Jingfeng, G. Ridi, Guangdong Weiliang Yuansu Kexue 6(1999)64.
- [29] K.Sharma, U. Maroo, R.S. Chauhan, A.K.Goswami, Purohit Orient. J. Chem. 15(1999) 177.
- [30] W.Palkawong-na-ayuthaya, K. Grudpan, Talanta 53(2000) 579.
- [31]F. Xuezhong, Z. Chunhua, Yejin Fenxi 18(1998)49.