

# Synthesis of 2-[4-Antipyriylazo] Orcinol as a New Sensitive Reagent for Determination of Cu (II) in Fly ash by Spectrophotometric Method

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**Abstract--** A spectrophotometric method was developed for the determination of Cu(II). The method was based on the formation of Fe (II), Ni(II) 2-[(4-antipyl azo)]orcinol (APAO) complex. The complex has been characterized by spectroscopic methods such as UV-Visible, FT-IR, molar conductivity measurements, melting points. The maximum absorbance of complex is at 474 nm with molar absorptivity of  $(0.55 \times 10^4) \text{ L.mol}^{-1}.\text{cm}^{-1}$  of Cu(II). Mole ratio of the complex which is formed between Cu(II) with APAO is 1:1 which was calculated by both the mole ratio and continuous variation methods. The absorbance of the complex obeys Beer's law in the concentration range of  $(0.1-3.0) \mu\text{g.ml}$  for Cu(II). The stability constant of the complex under optimized conditions and at room temperature was  $(0.13 \times 10^7) \text{ L.mol}^{-1}$  for Cu(II). This procedure can be carried out in the presence of many cations and anions in the presence or absence of the masking agents. The method was successfully applied to the determination of Cu(II) ion in analytical and fly ash samples.

**Index Term-** 2-(4-antipyriylazo) orcinol, Copper (II) determination, spectrophotometry.

## INTRODUCTION

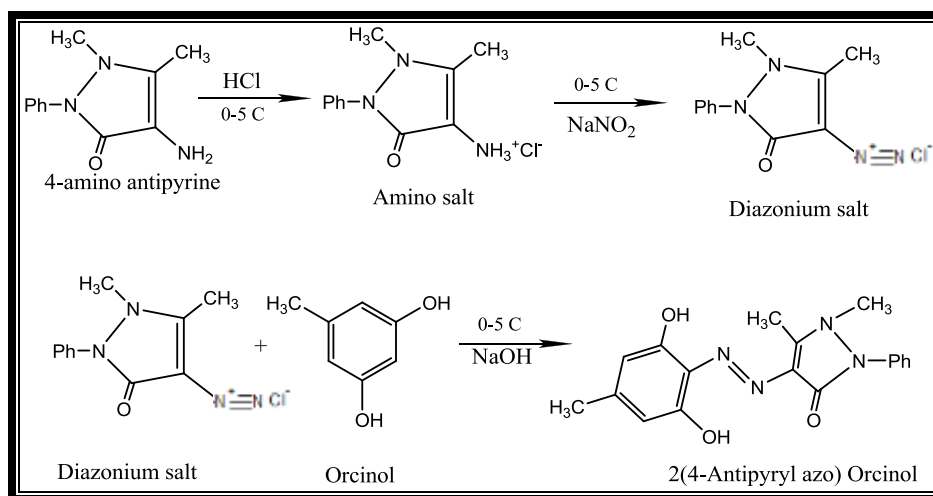
Pyrazolones are versatile heterocyclic, which have very important application in both chemistry and biology due to the great flexibility and diverse structural aspects, a wide range of pyrazolones have been synthesized and their complexation behavior studied [1-5]. Moreover, pyrazolones attached to a

sulphanilamido moiety through an azo linkage have been reported to exhibit biological activity [6]. It is known that pyrazolone azo compounds are widely used because of their very good chelogenic characteristics. The activity of pyrazolone azo is thought to be due to their power of chelation with traces of metal ions present in biological systems [7-12]. Determination of Copper (II) by various methods has been developed. Many of these methods require complicated and expensive instruments, therefore, development of Copper (II) in different samples seems desirable [13-15]. The aim of the present work is to develop an easy, rapid method for the determination of copper (II). The method is based on the reaction of 2-[(4-antipyl azo)]orcinol (APAO), which forms coloured complexes which form a coloured complex with Cu(II) ion.

## EXPERIMENTAL

### I/ Preparation of the reagent (APAO)

The reagent was prepared by coupling Orcinol with diazotized 4-amino antipyrine in alkaline alcoholic solution. A diazonium solution was prepared by taking 1 g from 4-amino antipyrine in 25 ml of ethanol and concentrated hydrochloric acid with 6 ml of distilled water and adding sodium nitrite solution drop wise at  $(0-5 \text{ C}^0)$ . Orcinol 1 g was dissolved in 25 ml of ethanol and 30 ml of sodium hydroxide were added at  $(0-5 \text{ C}^0)$ . The mixture was left to stand overnight. The precipitate was filtered off and recrystallized from ethanol [16]. Schem 1.



### II/Preparation of Cupper (II) complex

The complex was prepared by stoichiometric amount from ligand in 100 mL of ethanol then added drop wise with stirring to a stoichiometric amount 1:1 for Cupper salt in 100 ml distilled water. The solid product thus formed off, washed with ethanol and dried.

### Apparatus

spectrophotometric measurement were made with *UV – visible T80 double beam spectrophotometer* using 1.00 cm glass cells . Vibrational spectra were recorded on *Test scan Shimadzu FT.IR 8000 series* . Measurements of pH were made using Inolab *pH – meter WTW 720* equipped with a glass – saturated calomel combined electrode Melting points of both ligand and complex were obtained with an electrothermal melting point apparatus 9300. Conductivity was measured in DMSO ( $10^{-3}$ ) solution with an Inolab conductivity model -WTW 720

### Reagents

All chemicals used were of analytical grades

### Cupper (II) stock solution ( $100 \mu\text{g} \cdot \text{ml}^{-1}$ )

prepared by dissolving 0.042 g of Cupper chloride in 200 ml of distilled water , working standard of Cu (II) solutions were prepared by simple dilution of the appropriate volume of the standard Cu (II) solution ( $100 \mu\text{g} \cdot \text{ml}^{-1}$ ) with distilled water .

### 2(4antipyryl azo)Orcinol (1 mM )

0.067 g of reagent was dissolved in 200 ml of ethanol .

### Foreign ion solutions ( $10 \mu\text{g} \cdot \text{ml}^{-1}$ )

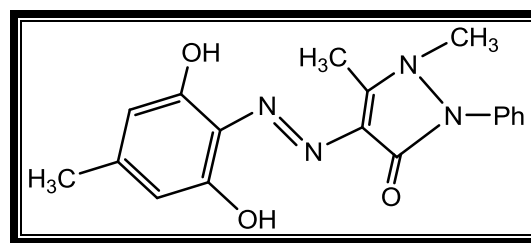
These solutions were prepared by dissolved an amount of the compound in distilled water completing the volume in a volumetric flask .

### General Procedure

In to a series of 10 ml calibrated flask, transfer increasing volumes of Cu(II) working solution 10 ppm to cover the range of calibration curve, add 3 ml of 1mM of (APAO) solution and pH was adjusted to 8.0. The complexes formed were solubilized in water and diluted up to 10 ml in a standard flask . The absorbance of the resulting solution was measured at the respective absorption maxima against a reagent blank prepared under similar condition but Cu(II) no .

### RESULTS AND DISCUSSION

Properties of (APAO) and its metal chelate APAO is a tridentate with coordination of azo group nitrogen , hydroxyl group and carbonyl group ; it has the following structure :



Structure of APAO

Owing to the large conjugated system, the compound showed excellent chelating ability to form inner metal chelates. APAO and its metal chelates can be easily solubilized in an aqueous solution.

### Spectra

The results of this investigation indicated that the reactions of Cu(II) with 2(4-pyrazolonazo) orcinol yields highly soluble colored complexes which can be utilized as a suitable assay procedure for determination of Cu(II). The electronic absorption of APAO and its complex in ethanol have been recorded in the wavelength range (190 – 800) nm. This colored complex has a maximum absorption at 474 nm for Cu(II), the blank at this wavelength shows zero absorbance Fig 1,

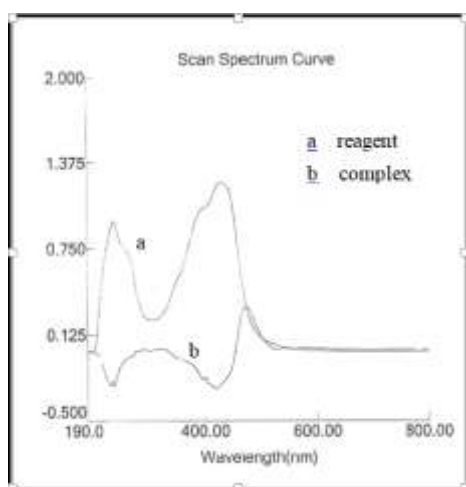


Fig. 1. Absorption spectra of [Cu (II) + APAO] treated as described under procedure and against a reagent blank and reagent blank against ethanol.

The effect of various parameters on the absorbance intensity of the formed products were studied and the reaction conditions were optimized.

To establish the optimum condition (stability of the product from the reaction of Copper (II) ion with the azo reagent, minimum blank value and relatively rapid reaction rate), the effect of pH (4.0-10.0) was studied. Only pH 8.0 and 6.0 was found to be optimum for Cu(II). Acid and alkaline results in low sensitivity and was not stable for Cu(II). pH change on the electronic absorption spectra of the complex was studied by adding a small amount of 0.05 M HCl and 0.05 M of NaOH. The UV-Visible spectra of complex gives the band centered at 474 nm for Cu(II). The bands appearing in the range of 240-311 nm for Cu (II) is attributed to  $\pi \rightarrow \pi^*$  transition. The other band observed in the region of 474 nm is attributed to  $n \rightarrow \pi^*$  electronic transition [17-19] for Cu(II) Fig.2 Table I.

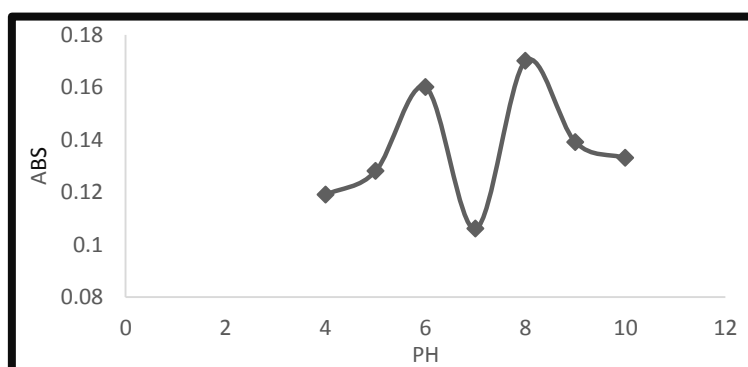


Fig .2. Effect of pH on complex Cu-APAO

Table I  
Analytical characteristics of Cu-APAO complex .

Characteristic	Co (II) – complex
Absorption maximum (nm)	474
Beer's law range (ppm)	(0.1– 3.0)
pH range	(6.0,8.0)
Sandell's sensitivity $\mu\text{g} \cdot \text{cm}^{-2}$	0.011
Molar absorptivity ( $\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ )	$0.55 \times 10^4$
Melting point for reagent	$(233 - 235)^\circ\text{C}$
Melting point for Cu (II) – complex	$(238.5 - 240.5)^\circ\text{C}$

#### Effect of (APAO) concentration

Various concentration of 2-(4'-antipyryl azo) Orcinol was added to fixed concentration of Cu (II) .3 ml of

1 mM (APAO) solution was sufficient and gave minimum blank value was increased causing a decrease in the absorbance of the sample. Therefore 3 ml of 1 mM of APAO was used in all subsequent experiment Fig. 3 .

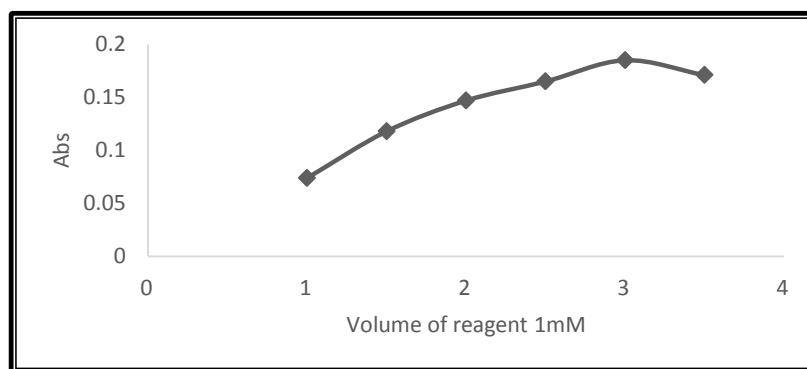


Fig. 3. Effect of APAO concentration

### Effect of reaction time

The colour intensity reached a maximum after the Cu (II) has been reached immediately with APAO and became stable after one minute , therefore one minute development

time was selected as optimum in the general procedure . The colour obtained was stable for a least 24 hours Fig 4.

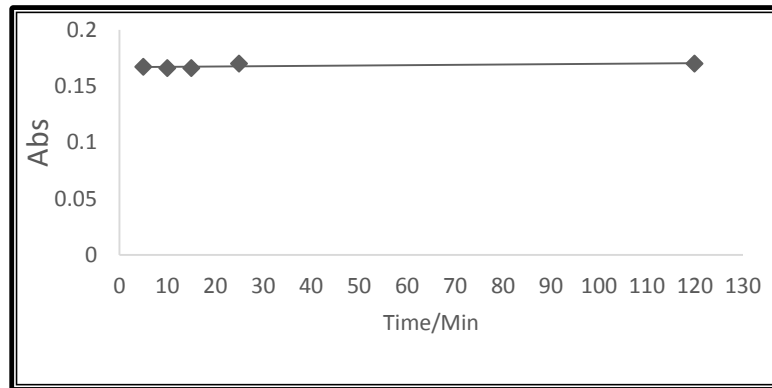


Fig. 4. Effect of time on complex of Cu[APAO]Cl

### Effect of temperature

The effect of temperature on the colour intensity of the product was studied . In practice , the same absorbance was obtained when the colour was developed at (10 – 60) C°, but when the volumetric flask were placed in a water –

bath at 70 C° a loss in colour intensity and stability were observed , therefore it is recommended that the colour reaction should be carried out at room temperature for complex Fig 5 .

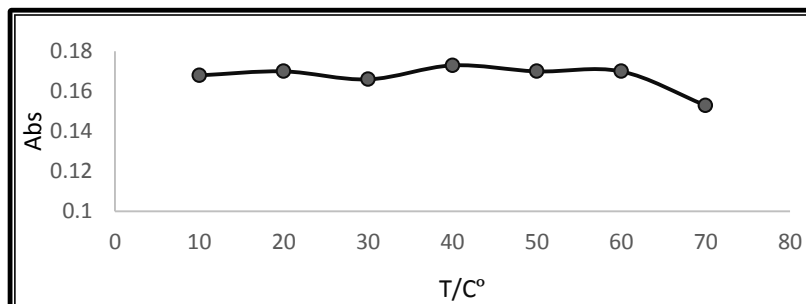


Fig.5. Effect of temperatures on complex Cu[APAO]Cl

### Order of addition of reagents

To obtain the optimum results, the order of addition of materials should be followed as give by the procedure, otherwise a loss in stability are observed.

stable for 24 hrs , the method can be applied to large series of samples . The molar absorptivity and sandell' sensitivity are given in Table.I .

### Calibration graph

At optimum conations ,a linear calibration graphs for Cu(II) was obtained ,that Beers law is obeyed over the concentration range of (0.1-3.0 ppm) with a correlation coefficient (  $R^2 = 0.9959$  ) .Since the coloured complex is

### Composition of the complex

The composition of complex was studied in the excess of reagent solution by the mole-ratio and Job s' methods [20,21] Fig 6,7 . A break at a 1:1 (M:L) mole ratio suggested the formation of complex where M= Cu(II) and L= APAO under the given condition.

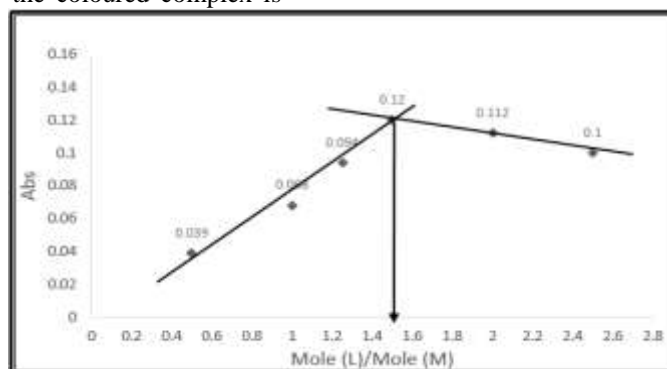


Fig 6. Mole-ratio method for Cu[APAO] complex

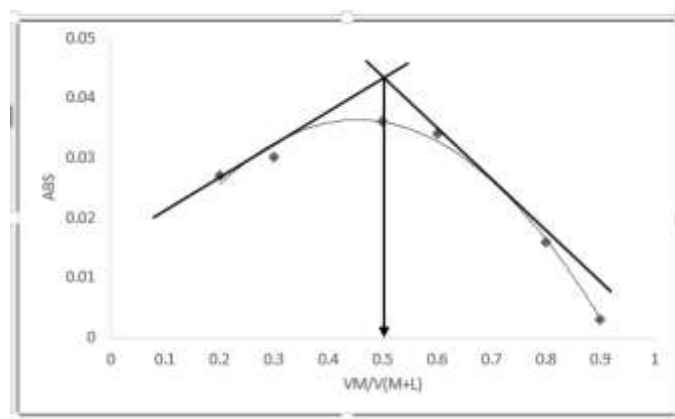


Fig. 7. Job's method for Cu[APAO] complex

### Conductivity measurements

The solubility of the complexes in dimethylsulfoxide and ethanol permitted the molar conductivity of  $10^{-3}$  M solution at 25 °C and by comparison, the electrolytic nature for complex. The low values of the molar conductance data listed in Table II indicate that the complex is electrolytes.

Table II  
Conductivity values of complex

Complex	Molar conductivity, S. mole <sup>-1</sup> .m <sup>2</sup> DMSO	Molar conductivity, S mole <sup>-1</sup> . m <sup>2</sup> Ethanol
[ Cu(APAO ) (H <sub>2</sub> O) Cl <sub>2</sub>	63.7	86.9

### Interferences

The effect of diverse ions in the determination metal ion was studied. To test of diverse ions were determined by the general procedure, in the presence of their respective foreign ions. The metal ion can be determined in the presence of a 10 or more fold excess of cation and anion Table. III. In the experiment, a certain amount of standard Cu (II) solution, coexisting ion solution and masking agent (or absence of masking agent) were added. It is found some of studied ions interfere seriously. However, their interferences are masked efficiently by addition 1.0ml or excess of 0.1 Mof Na<sub>2</sub>HPO<sub>4</sub>,Oxalic Acid, Thiourea.

Table III  
Effect of foreign ions

Seq.	foreign ions	Conc.µg/ml	E%
1-	Hg <sup>2+</sup>	100	-9.93
2-	Co <sup>2+</sup>	100	-1.13
3-	Pt <sup>2+</sup>	100	-8.0
4-	Fe <sup>3+</sup>	100	-98.7
5-	Zn <sup>2+</sup>	100	34.1
6-	Pd <sup>2+</sup>	100	85.0
7-	V <sup>5+</sup>	100	-40.9
8-	Ni <sup>2+</sup>	100	-68.3
9-	So <sub>4</sub> <sup>2-</sup>	100	26.0
10-	Br <sup>1-</sup>	100	12.4
11-	Cl <sup>1-</sup>	100	-46.5
12-	I <sup>1-</sup>	100	-24.8
13-	S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>	100	34.1

### FT.IR of reagent and it's complex

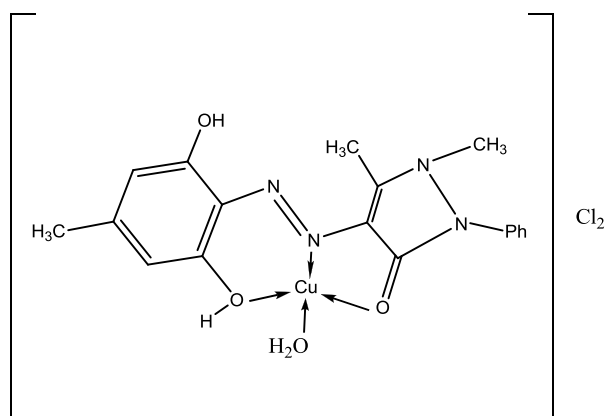
The FT.IR of the free ligand and it's metal chelate were carried out in the (400-4000) cm<sup>-1</sup>range .The IR bands of the (APAO) and its Cu (II) complex with their probable assignment are given in Table. IV . The IR spectrum of ligand shows a broad band at 3435 cm<sup>-1</sup>, which can be attributed to the OH group. However, the  $\nu(\text{N}=\text{N})$  stretching band in the free ligand is observed at 1506 cm<sup>-1</sup>. This band is shifted to lower with low intensity at 1444 cm<sup>-1</sup> frequency value upon complexation suggesting chelation via the (M-N)[22]. The IR spectrum of the ligand revealed a sharp band at 1693cm<sup>-1</sup> due to  $\nu(\text{C}=\text{O})$  of pyrazoleazo. This band is shifted to lower with low intensity at 1687 cm<sup>-1</sup> upon complexation [23,24]. The bonding of oxygen to the metal ion is provided by the occurrence of band at 505 cm<sup>-1</sup> as the result of  $\nu(\text{M}-\text{O})$ [25,26].

Table IV  
Selected FT.IR data of (APAO) and it's complex with Cu (II)

Compound	$\nu$ (OH)	$\nu$ (C-H) arom.	$\nu$ (N=N)	$\nu$ (C=O)	$\nu$ (M-O)	$\nu$ (M-N)
HL	3435	3090	1506	1693	-	-
[Cu(APAO)] H <sub>2</sub> O	3412	3050	1444	1687	505	420

S: sharp ; m: medium ; w: weak

On the basis of the FT.IR, stoichiometric, and elemental analysis molar conductivity data the structure of complex can be suggested as the following :-.



Structure of Complex

### Applications

#### 1-Determination of Copper (II) in practical samples

To determine the accuracy and precision of the method, Copper (II) was determined at two different

Table VI  
Determination of Cu(II) in fly ash sample

Sample.	Con.of sample µg / g	*R.S.D%	Re .%
Fly ash	1.63	0.42	99.52

\*For five determination

### REFERENCES

- [1] E. . Paul, L . Jean, and R. Paquin, *Can. J. Chem.*, vol. 31, 1025–1039, 1953.
- [2] S. Sugiura, O. Ohtani, K. Izumi, T. Kitamildo, H. Asa, K. Kato, M. Hori, and H. Fujimura, *J. Med. Chem.*, vol. 20, . 80, 1977.
- [3] A. Farghaly and A. Behit, *Arch. Pharm (Weinheim)*, vol. 333, 7–53, 2000.
- [4] S. Manfredini, R. Bazzanini, P. Baraldi, M. Bonora, M. Marangoni, D. Simoni, A. Pani, F. Scintu, E. Pinna, L. Pisana, and P. Lacolla, *Anticancer. Drugs*, vol. 11, no. 3, 194–204, 1996.
- [5] A. Farghaly, F. Soliman, M. Elsemary, and A. Rostom, *pharmazie*, vol. 56, no. 1, 18–32, 2001.
- [6] S. Nigram, G. Saharia, and H. Sharma, *Indian Chem.*, vol. 60, 583, 1983.
- [7] K. Yogesh, N. Rathis, S. Mayur, B. Shipra, and C. Sumitra, *J. Serb. Chem. Soc.*, vol. 12, no. 69, 991–998, 2004.
- [8] H. J.Mohammed, A. Y. Mohee, and A. Header, *E. J. Chem.*8(S1),.426-433, 2011.
- [9] H.J . Mohammed, M .H.Shaimaa, *Inte.J.Eng &Tech-IJENS*,14,No 2,102-111,2014.
- [10] H.J . Mohammed, M .Walla, *Inte.J.Civil &Envi-IJENS*,13,No 6,102-111,2013.
- [11] H.J . Mohammed, A.A.Masar, *Chem .Sci.Trans*,3(3),102-111,2014
- [12] Y. Altun, F. Köseoğlu, H. Demirelli, I. Yilmaz, A. Çukurovali, and N. Kavak, *J. Braz. Chem. Soc.*, vol. 20, 299–308, 2009.
- [13] A. Malik, K. Kaul, B. Lark, W. Faubeel, and A. Rao, *Turk. J. Chem.*, vol. 25, 99–105, 2001.
- [14] T. Stasys, K. Rolandas, and K. Aivaras, *J. Anal. Chem.*, vol. 15, no. 4, 49–52, 2004.
- [15] T. Kelle, V. Anu, V. Merike, M. Urmas, P. Keddy, T. Rando, and L. Tuuli, *Proc. Est. Acad. Sci. Chem.*, vol. 3, no. 56, 122–133, 2007.
- [16] M. Farukawa and S. Shibata :, *Anal.Chim .Acta* ,,140 ,301 ,1982.
- [17] V.Kaur, A.K. Malik and N. Verma :*Anal. Lett*, 40,12, 2360-2373, 2007.
- [18] J. Chasemi, S.H. Kiaee, A.Abdolmaleki and A.Semnaui :*Acta .Chim.Slov* , 55,184-189,2008.
- [19] R.L.DeSauza and M. Tubina : *J. Braz .Chem .Soc* , 16,5, 1068-1073, 2005.
- [20] A.E. Haervy and D.L. Manning, :*J.Am.Chem.Soc.*,72,4488 ,1950.
- [21] W.C.Vosburgh and G.R.Cooper,:*J.Am.Chem.Soc.*,63,437 ,1941.
- [22] X.Li ,Y. Wu , D. Gu and F.Gan , *Dyes and Pigments*, 86,182-189, 2010.
- [23] G.Pandey andK.K.Narng ,*SyntReasInorgMetrog Chem.*, 34, 291,2004.
- [24] Z.M.Zaki ,*SpectrochimActa* , 56(10), 1917-1923,2000.
- [25] D. Boryana ,B.Karima , I.ElisaventaandA.Freddy ,*Canadian J Anal Sci.*, 49(6),346-352 ,2004.
- [26] T. Stasys ,K.Roland and K.Aivaras , *CHEMIJA* , 15(4),49-52, 2004.
- [27] A.K.Malik , K.N.Kaul, B.S.Lark, W.Faubel, A.L.J .Rao ; *Turk.J.Chem*, 25,99-105, 2001.

concentrations with different interferences ions and masked these ions by using masking reagent . The results are shown in Table. V , indicate that satisfactory precision and accuracy could be attained with proposed method.

Table V  
Determination of Cu (II) in synthetic samples

Amount taken of Cu (II) p.p.m	Recovery%	*RSD%
1.0	99.38	1.30
3.0	98.80	0.94

\*For five determinations

#### 2-Determination of Copper (II) in fly ash samples .

10 g of fly ash dissolved in beaker by 5 ml of concentrated HNO<sub>3</sub> and diluted to 25 ml by distilled water and then evaporated to dryness. The residue was dissolved in distilled water and translated to volumetric flask with capacity 100 ml and then the sample ready for UV-Visible spectrophotometric analysis [27].