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# USE OF SPECTROPHOTOMETRIC METHOD AND FLOW INJECTION TECHNIQUES FOR DETERMINING COPPER (II) BY 2-(4-BROMO 2,6-DIMETHYL PHENYL) AZO 4,5-DIPHENYL-1-IMIDAZOL)

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## ABSTRACT

This research includes use of an organic reagent 2-(4-bromo 2,6-dimethyl phenyl) azo 4,5-diphenyl-1-imidazol) for determination of Cu(II) ion by spectrophotometric method. After determining the optimum conditions of the complex reaction such as pH value, reagent concentration and the results were 8.0 and $10.0 \times 10^{-4}$ M, respectively and the temperature and equilibrium time of complex determination too. The stoichiometry of complex was determined by methods (mole ratio and Job method) and it was (2:1) (reagent : ion). Then calibration graph was prepared. The linearity ($7 \times 10^{-5} - 10^{-6}$ M) sensitivity 5261.2 and detection limit of Cu(II) complex was found by depend on the calibration graph. The effect of foreign ions was studied and suitable the masking agents were found for each. The new reagent was used for determination Cu(II) ion in new design of flow injection system (FIA). Various parameters, physical and chemical, affecting the determination have been investigated such as flow rate, reaction coil, volume reagent, volume sample pH and reagent concentration. The results were 14 mL/min, 15 cm, 0.253 mL, 0.253 mL, 8, $5 \times 10^{-5}$ M, respectively then preparation the calibration graph in FIA system and the average of dispersion coefficient determined reliability were studied. The results were compared between two methods (spectrophotometric method and FIA method).

**Key words**: Copper ion, Flow injection, Determination.

## INTRODUCTION

Flow injection technique is characterized by its simplicity, speed, and lack of cost as it is based on the use of trace amounts of reagent[1], high symmetry in the analysis process in a way automatic or semi-automatic, highly efficient, fast distinct and sensitive to chemical analyses. The number of modeling is large and limits of detection are low-lying[2]. The total content of copper in the Earth's crust is relatively small (about 0.01%) and rarely increase the percentage of copper in the raw materials to 1.2%. Copper ore sore Alchalkws at $Cu_2S$ and Alkoprit $Cu_2O$ and ten copper ores with the installation of a complex with other metals such as zinc, lead, nickel, molybdenum, gold and other of precious items[3]. Copper is one of the most important key elements in biological systems[4], for example, contain blood serum of humans of

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0.7-1.4 ppm Cu[5]. Copper deficiency in food is a cause for a wide range of pathological disorders such as congestive growth, and these disorders naturally depends on the type, age, gender, the environment, as well as on the level of copper deficiency, or the continuation of a shortage. On the other hand, eating a large amount of copper, consistently leads to the accumulation of this element, especially in the liver and is usually followed by the accumulation of copper in the liver to the liberation into the blood; thereby, creating a hemolytic and occurrence of Janudice. For humans, it may be the main source of copper poisoning is the inhalation of industrial waste in addition to other sources as large amounts of copper may enter to the human body by the use of food (food saved or dyed)[6-8].

Several analytical techniques have been monitored for the determination of copper(II) in different matrices. They include spectrophotometry[9,10], chemiluminescence[11] atomic absorption spectrometry[12]. Inductive coupled plasma-atomic emission spectrometry, neutron activation analysis[13,14] and flow injection analysis[15]. Copper is an industrially important metal and it is used in coin making, wire making, medicine, alloys, fashioning metal products, transportation industry and thermal conductance[16]. On the other hand, toxic role of the metal ion is well recognized. Copper is available in nature in a free state in the form of sulfides, chlorides and carbonates. Copper is utilized in electric industries and in industrially useful alloys. Copper is also a vital dietary nutrient, although only small amounts of the metal are needed for well-being[17]. It has a high electrical and thermal conductivity. Copper is available in nature in a free state in the form of sulfides, chlorides and carbonates. Copper is utilized in electric industries and in manufacture of industrially useful alloys[18-21].

## EXPERIMENTAL

### Apparatus

Analytical balance sensitive Denver Instrument, Spectrophotometer Labomeding single beam, USA, and a spectrophotometer Shimadzu UV-1700 spectrophotometer, recorder pen Siemens C 1032, hitter thermal Ardeas 51, peristaltic pump Germany, Ismatic, home made reaction coil with radius of 0.5 mm, homemade valves, pipes load of Teflon, flow cell volume of 450 μL.

### The materials

All chemicals used were analytical materials of high purity.

### Preparation of solutions

1. Preparation of solution of 0.001 M organic reagent by dissolving 0.0433 g of reagent in 25 mL distilled water and then transferring the solution to volumetric flask 100 mL.
2. Preparation of 0.1 M of copper salt by dissolving 1.7054 g of salt in 25 mL distilled water and then transfering the solution to volumetric flask 100 mL.
3. Preparation of 0.2 M of sodium carbonate by dissolving 2.118 g of salt in 25 mL distilled water and then transferring the solution to volumetric flask 100 mL.
4. Preparation of 0.2 M of hydrochloric acid by diluting from concentrated reagent (S.G.; 1.8 and purity; 36-37.5%). After preparation, the solution was standardized with carbonate solution.

# RESULTS AND DISCUSSION

## Determination of copper by the use of new organic reagent by the visible-ultraviolet spectroscopy

### Determination of the wavelength for maximum absorption

Ultraviolet visible spectroscopy was use to determine the optimum conditions for the complex formation and the result are shown in Fig. 1. From this study, 522 nm was found as max wave length of complex.

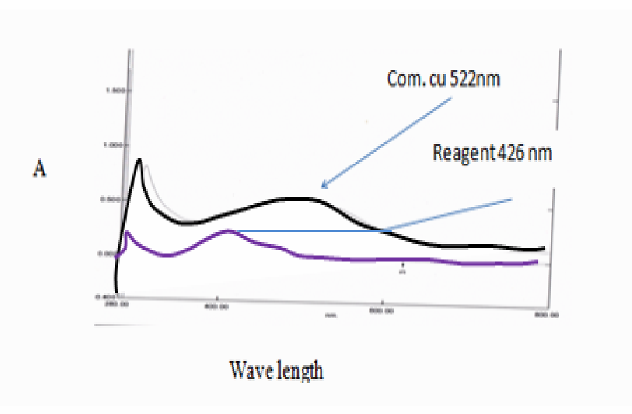

**Fig. 1: UV-vis spectroscopy for copper complex and reagent**

### Optimum condition of complexation

### Effect the pH

After preparation, the suitable buffer from sodium carbonate and HCl was used to adjust the pH value. The formation of the complex was studied in the different pH medium from (4-10) to determine the ideal pH for complexation. The best pH was 8.0 (Fig. 2).

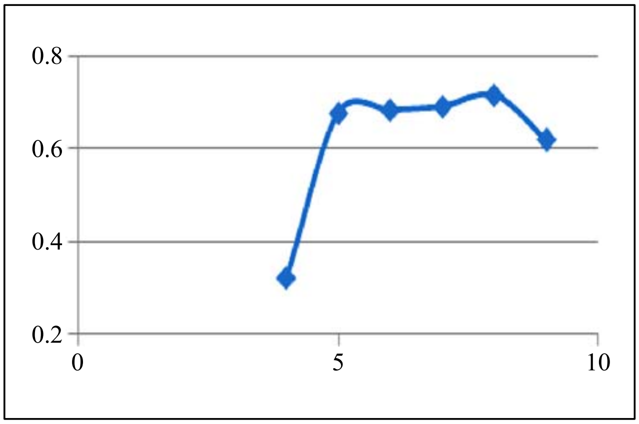

**Fig. 2: The effect of pH**

### Effect of the reagent concentration

The use of different concentrations of reagent in the range ($5.0 \times 10^{-6} - 1.0 \times 10^{-3}$ M) was made (Fig. 3), where the optimum concentration was found to be $1.0 \times 10^{-4}$ M.

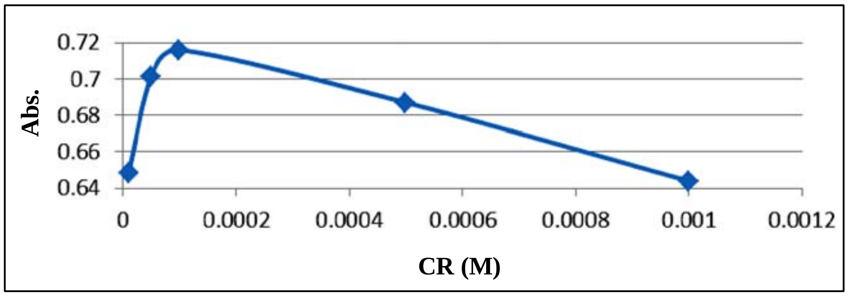

**Fig. 3: The effect of reagent concentration**

## Effect of the volume of metal ion

The complex was prepared by mixing 2 mL of 1.0 × $10^{-4}$ M of the reagent with different volume of 5 × $10^{-5}$ M of the metal ion when the pH = 8 (Fig. 4). The ideal volume for complexation 2 mL of metal ion and 2 mL of reagent, where the ratio was 2 : 2.

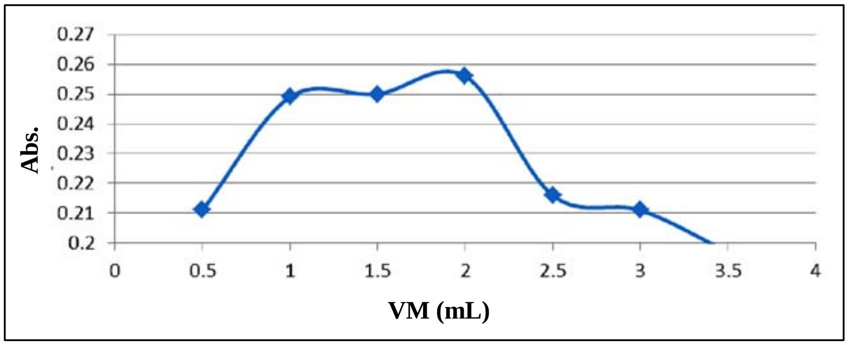

**Fig. 4: Effect of metal ion volume**

## Effect of the time

To determine stability complex, a study was conducted and it was found that the complex was stable during 1440 minutes (Fig. 5).

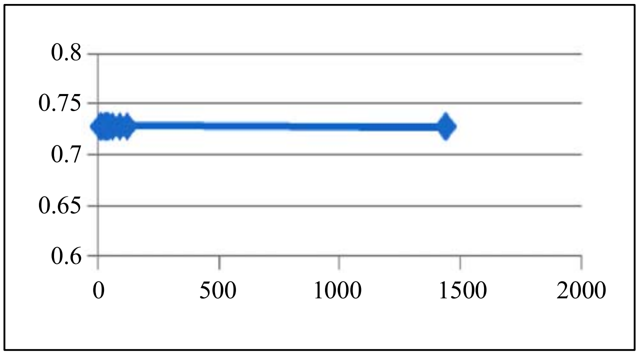

**Fig. 5: Stability with time**

## Effect of temperature

Complex was prepared in different temperatures of (5-60°C) (Fig. 6). It was found that a stable complex was obtained (0-50°C) and it begins to dissociate above 50°C (Fig. 6).

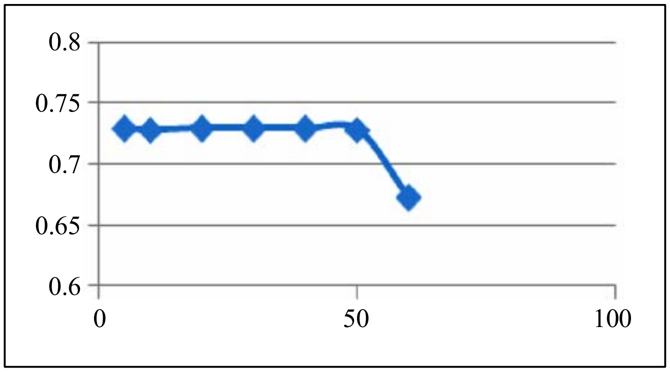

**Fig. 6: Stability with temperature**

## F-Study effect stoichiometric of complex formation

Equivalent studied have been using a complex method of mole ratio and job methods. The result shown that complex ratio was 1:2 (Fig. 7 and 8).

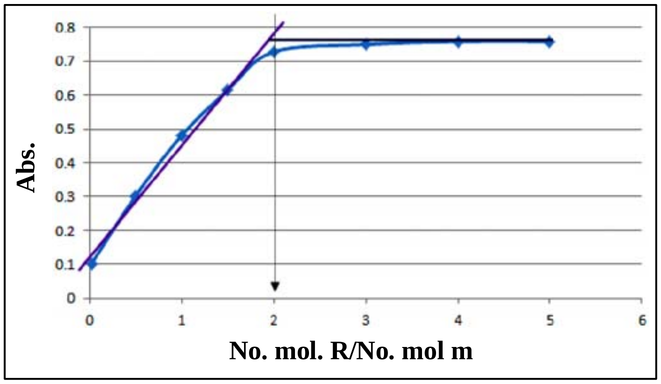

**Fig. 7: Mole ratio**

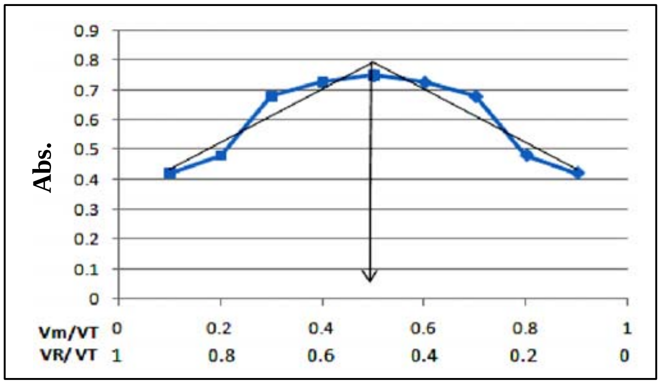

**Fig. 8: Job method**

## Preparation of the calibration graph

Calibration graph was prepared at the optimum conditions of complexation by changing the metal ion concentration (Fig. 9).

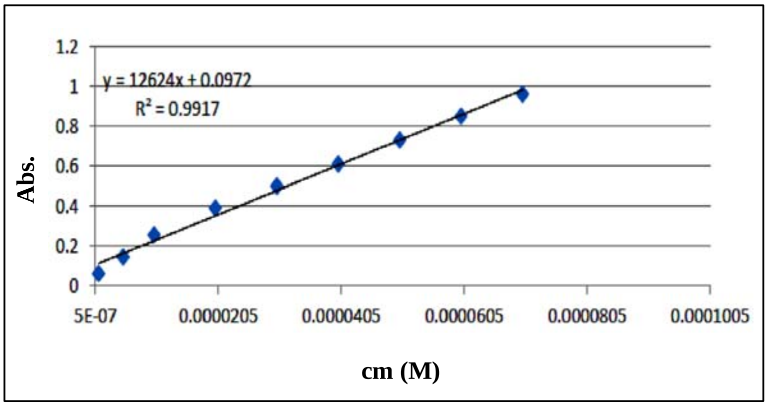

**Fig. 9: Calibration graph of copper ion**

From calibration graph, characteristies were determined in the following Table 1.

**Table 1: The characteristics of the calibration graph**

| Linearity | Correlation coefficient | Detection limit practically | Slope |
|---|---|---|---|
| $1.0 \times 10^{-7} - 7 \times 10^{-4}$ M | 0.9886 | $10^{-8}$M | 1266.7 |

## Interference

Effect of different foreign ions with copper in the composition of the copper complex was studied at wavelength 522 nm. The greatest absorption of the copper complex was 0.729, when the the ideal concentration of copper ion in the complex was $5.0 \times 10^{-4}$ M. Foreign cations ($Na^+$. $K^+$.$Co^{2+}$. $Ni^{2+}$ and $Ba^{2+}$) do not interfere with the formation of copper complex, and the other ions interfere with formation of complex and the results are shown in Table 2.

**Table 2: foreign cations**

| S. No. | Name | Conc. (M) | Interference | Treatment with masking |
|---|---|---|---|---|
| 1 | $Cd^{2+}$ | $5 \times 10^{-4}$ | -0.042 | One drop of iodine from 0.1 M |
| | | $5 \times 10^{-3}$ | -0.095 | Two drops of iodine from 0.1 M |
| 2 | $Hg^{2+}$ | $5 \times 10^{-4}$ | -0.191 | Two drops of iodine from 0.1 M |
| | | $5 \times 10^{-3}$ | -0.297 | Three drops of iodine from 0.1 M |
| 3 | $Fe^{3+}$ | $5 \times 10^{-4}$ | -0.11 | One drop of iodine from 0.1 M |
| | | $5 \times 10^{-3}$ | -0.17 | Two drops of iodine from 0.1 M |
| 4 | $Pb^{2+}$ | $5 \times 10^{-4}$ | -0.12 | One drop of iodine from 0.1 M |
| | | $5 \times 10^{-3}$ | -0.312 | Two drops of iodine from 0.1 M |
| 5 | $Mn^{2+}$ | $5 \times 10^{-4}$ | -0.073 | One drop of 0.1 M of oxalates |
| | | $5 \times 10^{-3}$ | -0.121 | Two drops of 0.1M of oxalates |

**Table 3: The characteristics of the calibration curve**

| Linearity | Correlation coefficient | Detection limit practically | Slop |
|---|---|---|---|
| $2.0 \times 10^{-4} - 9.0 \times 10^{-4}$ | 0.9947 | $10^{-7}$ | 59524 |

### Determination of copper ion (II) by using new organic reagent in flow injection technique

System was designed to determine copper by flow injection after the wavelength of the complex was measured.

### Determine of optimum conditions

A study was conducted to determine the chemical and physical optimal complexation.

### Study of chemical variables

### Effect of reagent concentration

A study was made to determine the ideal concentration of reagent needed for the complexation. The ideal concentration was $10^{-5}$ M; After this concentration, the beak begin distorting (Fig. 10).

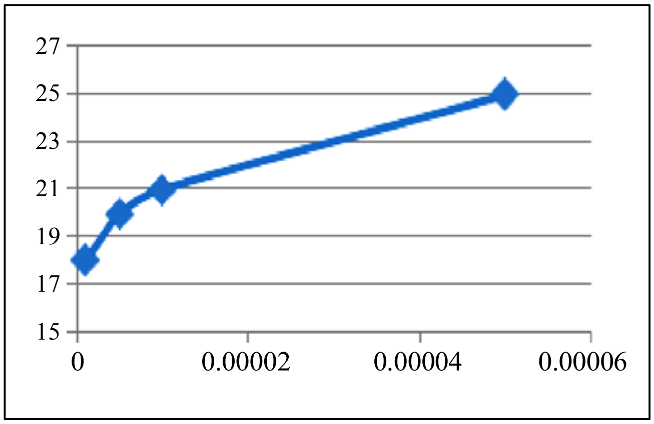

**Fig. 10: Effect of reagent concentration**

### Effect of pH

The suitable buffer used was sodium carbonate and HCl. The formation of the complex was observed in the different of pH from 4.0-10.0. The optimum pH was 8 (Fig. 11).

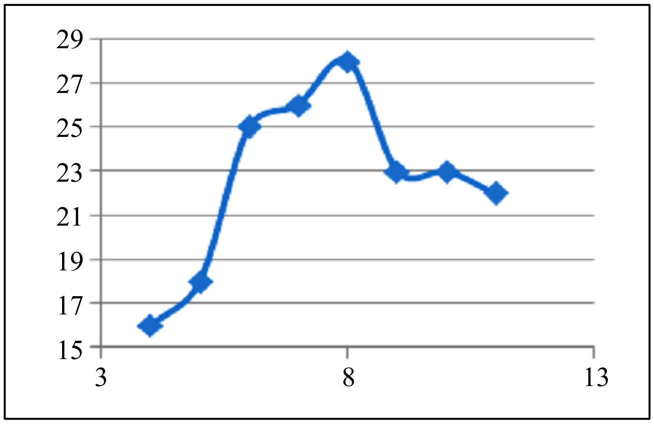

**Fig. 11: Effect of pH**

## Physical variables

### Effect of flow rate

The effect of flow rate was studied by using different flow rates, which extend from 4.0-16.0 mL/min. The ideal flow rate of the carrier was 13.5 mL/min (Fig. 12). It has the optimum flow rate to obtain the best peak height.

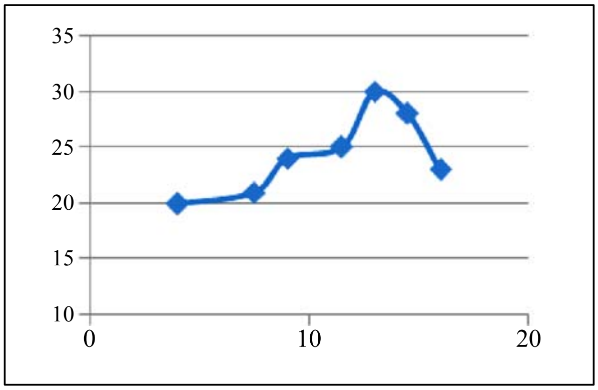

**Fig. 12: Effect of flow rate**

### Effect of reaction coil length

By changing the reaction coil length from 0-70 cm, it has been shown that the sensitivity of method increases with the length of reaction coil (15 cm) (Fig. 13).

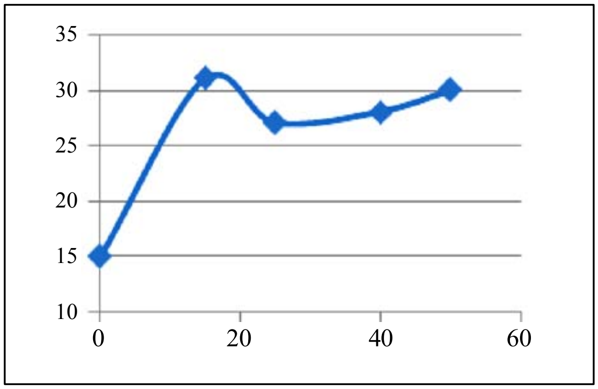

**Fig. 13: Effect of reaction coil length**

### Effect of volume of the reagent

A set of injected volume of reagent was used ranging from 108.5-275.5 µL by changing the length of reagent loop. The optimum volume of reagent was 235 µL (Fig. 14).

### Effect of volume of copper ion

The effect of sample volume (copper ion) was examined in the range from 108.5-275.5 µL by changing the length of ion. It was observed that the ideal volume of metal was 235 µL (Fig. 15) while at larger volumes than 235 µL will decrease this response.

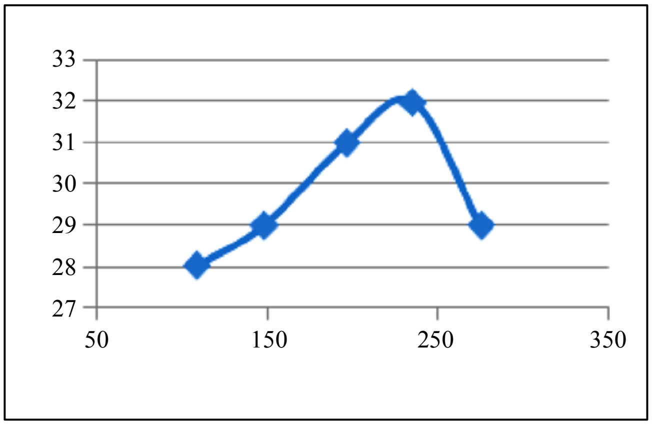

**Fig. 14: Effect of volume of reagent**

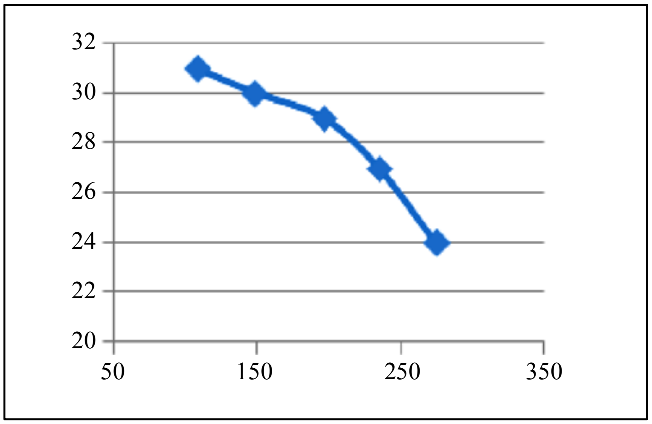

**Fig. 15: Effect of volume of copper ion**

## Preparation of calibration graph

A series of sample ion solutions of the range ($2.0 \times 10^{-4} - 9.0 \times 10^{-4}$ M) were prepared from stock solution under the optimum condition. The typical response is shown in Fig. 16.

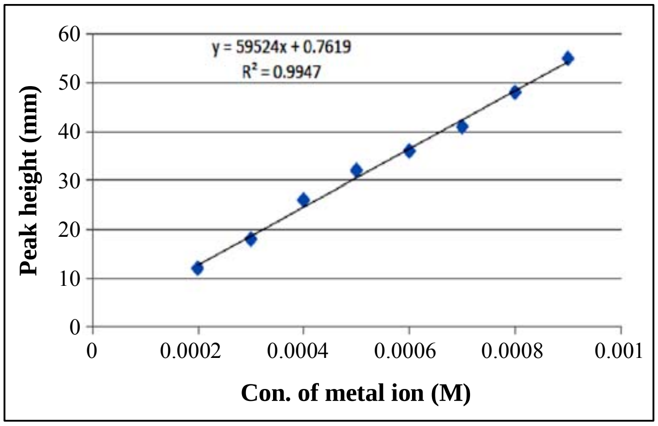

**Fig. 16: Calibration graph**

## Reproducibility

To study the precision of FTA unit, the reproducibility in results was observed by repeating the experiment ten times for $5.0 \times 10^{-4}$ M copper ions and the results are reported in Table 4.

**Table 4: Reproducibility**

| S. No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | mean | SD | RSD% |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Average peak height | 32 | 32 | 31.5 | 32 | 32 | 31.5 | 32 | 32 | 32 | 32 | 31.9 | 0.352 | 1.105 |

## Dispersion

The dispersion coefficient of low concentration of copper ion were studied and the results are shown in Table 5.

**Table 5: Dispersion coefficient of FIA unit**

| Copper ion concentration M | Response in (mm) | | Dispersion (D) |
|---|---|---|---|
| | $H^o$ | $H_{max}$ | $D = \frac{H^\circ}{H_{max}}$ |
| $5 \times 10^{-4}$ | **33.5** | **32** | 1.0475 |
| $4 \times 10^{-4}$ | 28 | 26 | 1.1888 |

## Interference

The composition of the copper complex at wavelength 522 nm was studied with interfering elements. The peak height of the copper complex was 32 mm when the concentration of copper in the complex was $5.0 \times 10^{-4}$ M interfering cations ($Na^+$. $K^+$. $Co^{2+}$. $Ni^{2+}$. $Ba^+$). These ions did not interfere with the formation of copper complex while the other cation interference with the results (Table 6).

**Table 6: interference**

| S. No. | Name | Conc. (M) | Interference | Treatment with masking |
|---|---|---|---|---|
| 1 | $Cu^{2+}$ | $5 \times 10^{-4}$ | 32 | **With out interference** |
| 2 | $Cd^{2+}$ | $5 \times 10^{-4}$ | 31 | One drop of iodine from 0.1 M |
| | | $5 \times 10^{-3}$ | 26 | Two drops of iodine from 0.1 M |
| 3 | $Hg^{2+}$ | $5 \times 10^{-4}$ | 28 | Two drops of iodine from 0.1 M |
| | | $5 \times 10^{-3}$ | 27.5 | Three drops of iodine from 0.1 M |
| 4 | $Fe^{3+}$ | $5 \times 10^{-4}$ | 30 | One drop of iodine from 0.1 M |
| | | $5 \times 10^{-3}$ | 24 | Two drops of iodine from 0.1 M |
| 5 | $Pb^{2+}$ | $5 \times 10^{-4}$ | 30 | One drop of iodine from 0.1 M |
| | | $5 \times 10^{-3}$ | 28 | Two drops of iodine from 0.1 M |
| 6 | $Mn^{2+}$ | $5 \times 10^{-4}$ | 31 | One drop of 0.1 M of oxalates |
| | | $5 \times 10^{-3}$ | 29 | Two drops of 0.1 M of oxalates |

**Table 7: Applications**

| Sample | Take | Found by uv-vis spectrum | Found value by flow injaction |
|---|---|---|---|
| Milk Diallak | $5 \times 10^{-4}$ M | $4.85 \times 10^{-4}$ M | $4.9 \times 10^{-4}$ M |
| Drug feramera | $5 \times 10^{-4}$ M | $4.9 \times 10^{-4}$ M | $4.95 \times 10^{-4}$ M |
| Aqueous solution | $2 \times 10^{-4}$ M | $2.0 \times 10^{-4}$ M | $2.0 \times 10^{-4}$ M |

Interference by some anions was found, but bromide, oxalate and acetate did not interfere with the formation of copper complex.

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