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Development of a New Spectrophotometric Method for the Determination of Copper(II)

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Abstract

A new and highly sensitive spectrophotometric method has been developed for the determination of copper(II). **N**,**N**'-o-phenylene-bis(3-methoxysalicylideneimine) (H_2IF) was used as a new chromogenic reagent. The absorbance is measured at λ_{max} = 420 nm. Various factors influencing on the complex formation, such as, effect of pH, reagent concentration was studied. Under the optimum conditions, Beer's law was obeyed in the concentration range 3.18- 318 μg L^{-1} of copper(II). The interference of various ions has been studied and the experimental results are reported. The proposed method has been successfully applied for the determination of trace amount of copper(II) in food materials, pharmaceutical samples and water samples. The accuracy and feasibility of method was verified by AAS and the analysis of standard reference material SPS-WW2 (Waste water).

Keywords: Spectrophotometry, copper (II) determination, real sample analysis

1. Introduction

Copper is considered one of the most important heavy metals in the world. Copper is released into the environment from various sources such as industry and agriculture. Quantification of copper in different sources represents a challenging task for many researchers. Atomic absorption spectrometry [1,2], inductively coupled plasma emission spectrometry [3], inductively coupled plasma-mass spectroscopy [4] and electrochemical methods [5,8] are the most widely used methods for copper(II) determination.

These methods are fast and accurate for the determination of copper(II) ion but these techniques involve the use of expensive apparatus and require complicated operations. Other frequent disadvantages of these methods are time consuming, labor intensive and the use of large amounts of organic solvents and need for well-controlled experimental conditions.

However, spectrophotometric methods are often used for the determination of wide variety of analytes at trace levels in complex matrices. These methods involve inexpensive instruments and provide simplicity, versatility and high sensitivity when appropriate chromogenic reagents are available [9,14]. Specifically, many sensitive chromogenic reagents are reported for spectrophotometric copper determination. However, many metal ions are interfered in the determination procedure of copper(II) ion especially in complex matrices. Some chromogenic reagents require more equilibrium time or heating for full color development [12,21]. Hence, usage of new chromogenic reagents for fast, sensitive and selective spectrophotometric determination of copper(II) is still needed.

In the present work, a new reagent, **N**,**N**'-o-phenylene-bis(3-methoxysalicylideneimine) (H_2IF) was used for determination of copper(II) by spectrophotometry. This reagent can be suggested readily among one of selective spectrophotometric reagents and has a potential application for rapid, selective and sensitive detection of Cu(II) in aqueous media. The developed method is simple and allows highly accurate determination of copper(II) by measuring the absorption intensity of the complex at a distinct wavelength of 420 nm. The developed methodology was applied to the determination of copper(II) in complex samples, such as food materials and pharmaceutical samples.

2. Material and methods

2.1. Reagents and solutions

All over the study, analytical-reagent grade chemicals were used.

The solutions of metal salts were prepared with the relevant cations. 10^{-1} M stock solutions were prepared for each cation and then the dilute solutions ($1x10^{-2}$ to $1x10^{-9}$ M) were prepared one by one dilution of the stock solutions.

Acetate buffer solutions were prepared at pH range 2.20–5.60 by mixing appropriate proportions of sodium acetate solution (0.1 M) and acetic acid (0.2 M).

Certified materials C12X3500 and SPS-WW2 were supplied from MBH Analytical Ltd and LGC Group (UK).

2.2. Synthesis of H_2IF

0,305 g (2 mmol) o-vanillin and 0,108 g (1 mmol) o-phenylenediamine were refluxed in absolute methanol for 30 minutes and bright orange precipitate of the Schiff base was formed. Upon cooling the mixture, the precipitate was filtered, washed with cold ethanol and dried in air. Yield: 93%. Anal. Calc. C, 70.20; H, 5.36; N,7.44. Found: C, 69.21; H, 5.19; N 7.02. IR (KBr, cm-1): 3463 νas(OH); 3058-3011 νar(CH); 1623 ν(C=N); 1490 ν(C=C). 1H-NMR (Scheme 1, 400 MHz, ppm, CDCl3): 13.56 (m, 2H, (H6, O–H..N)) 8.66 (s, 2H, (H5, CH═N); 7.06-7.28 (m, 6H, aldehyde); 6.80-6.94 (m, 4H, diamine); 3.97 (s, 6H, methyl).
The structure of the ligand is given in Figure 1.

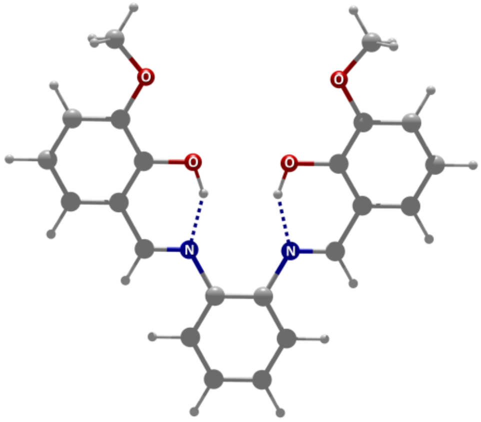

Figure 1. The structure of H_2IF

A $1x10^{-3}$ M solution of the H_2IF was prepared by dissolving a proper weight of reagent in 10.0 mL ethanol and then diluted with ethanol to 50 mL in a standard volumetric flask.

2.3. Apparatus

A Thermo Array Evolution UV–Vis spectrophotometer (USA) was used for the observation of the all absorption spectra.
A glass pH electrode (Schott) connected to a Jenway 3040 model Ion Analyzer was used for pH measurements of the buffer solutions.

2.4. Sample collection and treatments

2.4.1. Water samples

The water samples, taken from the different waste stream, were filtered over a 0.45 m filter from Millipore (Milford MA).

2.4.2. Food materials

A known weight of sample (0.5 g) was dissolved in 20.0 mL of aqua regia solution and evaporated up to moist dryness on a hot plate at a low temperature to avoid spurting. The residue was dissolved in 7 mL HClO4 and filtered through Whatmann filter paper No. 1. The obtained filtrate was diluted with water to 25 mL in a calibrated flask.

2.4.3. Pharmaceutical samples

Two commercially available pharmaceutical samples such as Supradyn and Decavit were selected for the analysis of copper(II). A known weight of sample was crushed and then heated in a furnace at 400 ^{o}C for 2 hours. The residue was dissolved in 5 mL HCl and filtered through Whatmann filter paper No. 1. The obtained filtrate was diluted with water to 100 mL in a calibrated flask.

2.5. Interferences and precision study

The general procedure was applied for interference studies. Different amounts of ions possibly present in analysed samples were added to the standart solution containing 31.8 μg L^{-1} Cu (II).

The repeatability of the method, replicate samples (n=3) containing Cu(II) 15.9 and 31.8 μg L^{-1}, respectively, were prepared and analyte contents were determined by proposed methodology.

3. Results and discussion

3.1. Spectral characteristics of the H_2IF and [Cu-IF] complex

H_2IF ligand form a stable square planar 1:1 complex adduct with Cu(II) ion. The complex is neutral since the ligand is deprotonated at donor hydroxyl groups upon binding to copper(II) ion. The complex is highly soluble in ethanol-water mixture. The proposed structure of the complex is depicted in Figure 2.

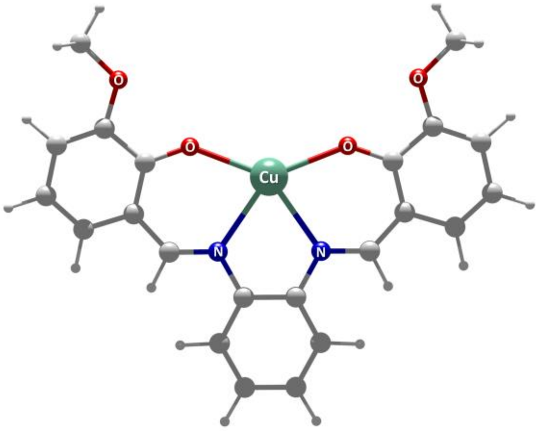

Figure 2. The structure of the [Cu-IF] complex

All metal ions react with H_2IF in aqueous medium to form complexes with different stoichiometry. The absorption profiles of free ligand and its complexes with Cu^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Mn^{2+}, and Cd^{2+} ions are superimposed and given in Figure.3.

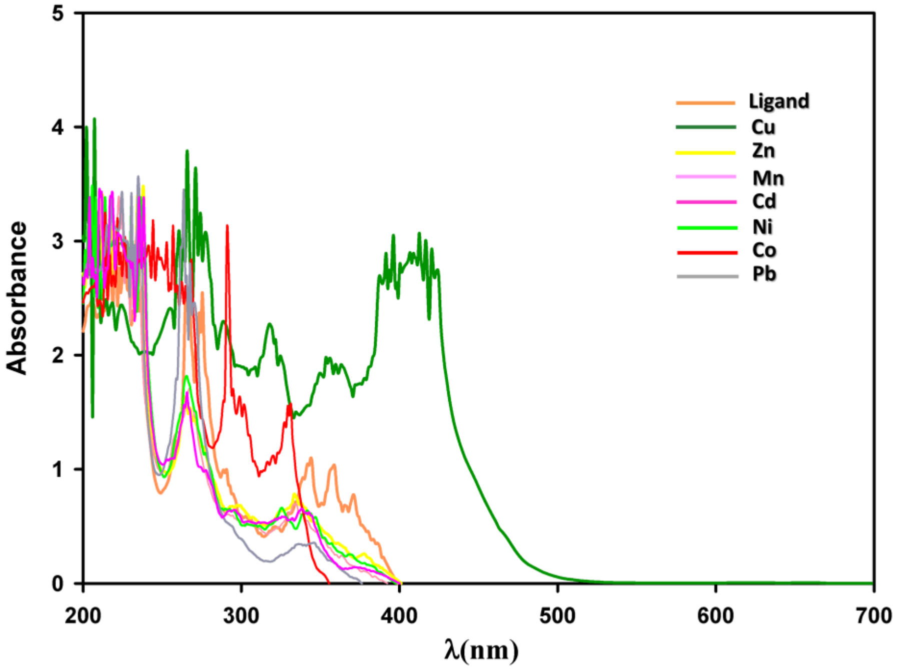

Figure 3. The absorption spectra of free ligand and its solutions with metal ions

H_2IF exhibits no absorption at 390 - 800 nm range. Once trace amounts of copper(II) ion were added to the IF solution, the colour of the solution immediately turned into light brown by forming a complex. The complex displays three distinct absorption maxima at 320, 354 and 420 nm that are otherwise absent in case of free ligand. The latter two maxima are not observed in upon addition of other ions as well. Especially the absorption band maximized at

420 nm and peaking apparently at 380-425 nm makes the determination of copper(II) reasonably straightforward since none of absorption relating to free ligand and to the adducts of other ions are observed within this range. These results clearly indicate that IF exhibits a high affinity towards copper(II) ion in aqueous solution. In addition, the reagent blanks had a negligible absorbance at 420 nm. These results suggested that a higher sensitivity could be achieved at 420 nm, which was selected for the following studies.

3.2. Optimization of the experimental parameter

The workable pH range, concentration of H_2IF, effect of time on the complex formation reaction between copper(II) and H_2IF, and effect of common interfering ions on the analysis of copper(II) were studied in detail.

For the optimization of the pH, several types of buffers, which pH values varies in the range 3.00 to 8.00, were prepared and used. Acetate buffer was used to as optimum buffer solution which gives highest absorbance at 420 nm. The pH values were varied in the range 3.50 to 5.50 as shown in Fig. 4. A pH of 4.50 was chosen for optimum value for maximum absorbance of the colored complex.

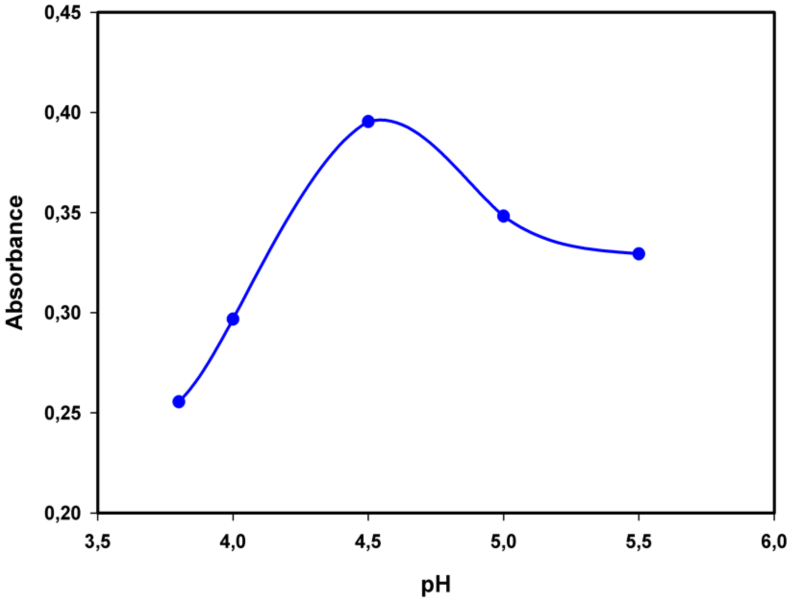

Figure 4. Dependence of the absorbances of [Cu–IF] complex on pH

The influence of the H_2IF concentration was studied in the range $1x\ 10^{-5}$ to $1\ x10^{-4}$ M. Increasing the chromogenic reagent concentration resulted in an increment in the absorbance of the complex. The maximum absorbance of the colored complex was found corresponded to $5\ x10^{-5}$ M H_2IF.

The effect of time on the complex formation reaction between copper(II) and H_2IF was also studied. Just in a minute, the solution color changed from light yellow to light brown upon addition of copper(II) to the H_2IF solution then the absorbance of the complex at 420 nm reached to maximum and did not increase more by the time.

The selectivity of the proposed method for copper(II) determination was evaluated with various common ions. A relative error of ± 5.0% was considered acceptable. About 1000-fold excess NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, $C1^-$, NO_3^-, SO_4^{2-}, 400-fold excess Co^{2+} and 40-fold excess Mn^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, did not interfere with determination of copper(II). Satisfactory tolerance was observed for inorganic compounds found in studied samples.

The calibration curve for determination of copper(II) was obtained under the optimized conditions. Table 1 shows experimental parameters, optimal values and quality analytical parameters for developed methodology. From the calibration curve, LOD (µg L^{-1}) and LOQ (µg L^{-1}) were calculated by three times the standard deviation of a blank solution divided by the slope value, and 10 times standard deviation of a blank solution divided by the slope value, respectively.

The calculated relative standard deviations (n=3) was 0.52 % and 0.72 % for a standard solution containing copper(II) 15.9 and 31.8 µg L^{-1} respectively.

Table 1. Experimental conditions and analytical parameters for copper(II) determination.

Parameters	Studied range	Optimal conditions
pH	3.0–8.0	4.50
Acetate buffer concentration	1.0×10^{-2}–1.0×10^{-1} mol L^{-1}	$1.65x10^{-2}$ mol L^{-1}
H_2IF concentration	$1.0x\ 10^{-5}$ – $1.0\ x10^{-4}$ mol L^{-1}	$5x\ 10^{-5}$ mol L^{-1}
LOD		0.16 µg L^{-1}
LOQ		0.56 µg L^{-1}
LOL		3.18- 318 µg L^{-1}
R^2		0.9926

3.3. Determination of the stoichiometry of the complex

Job method was applied for the determination of the stoichiometry of [Cu–IF] complex. Equimolar (2.5×10^{-4} mol L^{-1}) solutions of copper(II) and H_2IF was prepared and then copper(II) and ligand solutions were mixed in constantly ranging proportions and ensuring the total volume of metal and ligand constant at 4.0 mL. The absorbance values of the prepared solutions were measured at 420 nm at a constant pH value of 4.5. The changes of absorbance values are shown in Figure 5.

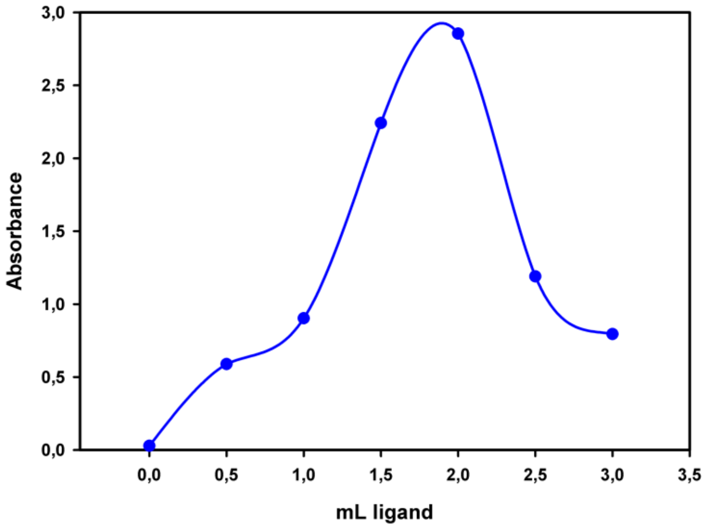

Figure 5. Job’s plot for the mixtures of H_2IF and copper(II) solutions

The maximum absorbance value was read at around 2 ml ligand volume as deduced from Figure. 5 and [Cu–IF] complex formation stoichiometry is proposed to be 1:1 proportion.

3.4. Application of the proposed work and its validation

The proposed method has been successfully applied for the determination of copper(II) in food materials, pharmaceutical samples and water samples. Calibration curve was used for determination of the actual contents of copper(II) in real samples. The results obtained for copper(II) content of pharmaceutical samples were also verified by AAS method. Also, t-test was applied. The AAS determination was applied on the same solution used for the spectrophotometric determination. The copper(II) concentrations in food materials, pharmaceutical samples and water samples were given in Table 2. The comparison of the results indicates good correlation between the recommended procedure and AAS method. There was also good correlation between the procedure and labelled values. Calculated t values for Supradyn and Decavit versus AAS method and label values, were found 1.15, 4.24 and 0.91, 0.85 respectively, which are lower than the critical value (t= 4.30 at % 95 confidence level).

Also, certified reference materials including alloy and water sample have been tested for the determination of Cu using the proposed method for testing validation of the present method. The calculated t values were found 0.06 and 1.65 respectively, for alloy and water samples, which are lower than the critical value (t= 4.30 at % 95 confidence level). The analytical data are incorporated in Table 2. This means that, a high degree of correlation was observed between the results obtained by our method and the actual Cu content.

These satisfied results indicated that the proposed method can be used for the fast and sensitive determination of copper(II) in food materials, pharmaceutical samples and water samples.

Table 2. The results obtained for the determination of copper ions in samples with proposed method

Samples	Cu ions (mg/g)^a				
	Proposed method	AAS measurement	Label Values	t value^1	t value^2
Supradyn	1.31±0.27	1.13±0.25	1.16	1.15	0.91
Decavit	1.73±0.18	1.29±0.19	1.64	4.24	0.85
Water 1	$1.42x10^{-3} \pm 3.51x10^{-5}$				
Water 2	$1.20x10^{-3} \pm 3.42x10^{-4}$				
Food 1	$5.32x10^{-4} \pm 2.89x10^{-4}$				
Food 2	$2.95x10^{-4} \pm 2.30x10^{-4}$				
C12X3500	20.00±5.24		25.00		1.65
SPS-WW2	1999.85±41.36		2000.00		0.06

^{a}Average of three determinations ± S:D:
t value^1 calculated versus AAS measurement
t value^2 calculated versus label values

Conclusions

In this work, a new simple, inexpensive, fast methodology for copper (II) quantification has been developed. Application and validation studies showed that copper(II) could be quantified correctly by using the proposed method. Experimental results have indicated that the reagent can be suggested readily among one of selective spectrophotometric reagents and has a potential application for rapid, selective and sensitive detection of Cu(II) in aqueous media. The obtained analytical parameters such as sensitivity, accuracy and selectivity show the proposed methodology as an alternative analytical tool, competitive with previously reported procedures [12-22] for the determination of copper(II) ions. Also, the reaction time of the developed spectrophotometric methods was found to be shortest one among reported procedures [12-22].

Acknowledgements

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