

Spectrophotometric and Selective Copper(II) Detection by Valine as an Optical Chemical Sensor

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الكشف الطيفي الفوتومتري والنحاس الانتقائي (II) بواسطة فالين كحساس كيميائي بصري

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Abstract:

Optical sensors have attracted significant scholarly attention for the detection of various metal ions, attributable to their superior selectivity, sensitivity, and rapid response capabilities. Among metal ions, copper(II) has emerged as a focal point of research due to its toxicological implications and prevalent utilization across diverse industrial applications. Recently, a multitude of optical chemical sensors exhibiting remarkable sensitivity and selectivity for copper(II) detection have been developed. This investigation employs a valine (Val) optical chemical sensor to quantify trace amounts of copper(II) via spectrophotometric techniques. Valine has demonstrated considerable efficacy as an optical chemical sensor for the detection of copper(II) ions in various aqueous matrices. resulting in a distinctly characterized Cu(II) complex exhibiting absorption maxima at 617 nm. Optical sensing demonstrated exceptional linearity between absorbance and Ni(II) concentration, with correlation coefficients (R^2) of 0.989 and limits of detection (LOD) quantified at 1×10^{-3} . (Val) has emerged as a highly effective reagent for the detection of Cu(II) ions across a variety of aqueous matrices, functioning proficiently as an optical chemical sensor.

Keywords: Solution structure; Optical chemical sensor; Spectrophotometric; Selective.

المخلص

جذبت أجهزة الاستشعار البصرية اهتماما كبيرا من الأكاديميين لاكتشاف أيونات المعادن المختلفة، ويرجع ذلك إلى انتقائيتها الفائقة وحساسيتها وقدراتها السريعة على الاستجابة. من بين أيونات المعادن، برز النحاس (II) كنقطة محورية للبحث بسبب آثاره السمية واستخدامه الواسع في تطبيقات صناعية متنوعة. مؤخرا، تم تطوير العديد من أجهزة الاستشعار الكيميائية البصرية التي تظهر حساسية وانتقائية ملحوظة للكشف عن النحاس (II). يستخدم هذا البحث حساس كيميائي بصري فالين (Val) لقياس كميات ضئيلة من النحاس (II) باستخدام تقنيات القياس الطيفية الضوئية. أظهر فالين فعالية كبيرة كحساس كيميائي بصري للكشف عن أيونات النحاس (II) في مصفوفات مائية مختلفة. مما أدى إلى مركب Cu(II) مميز يظهر أقصى امتصاص عند 617 نانومتر. أظهر الاستشعار البصري خطية استثنائية بين الامتصاص وتركيز Ni(II)، مع معاملات ارتباط (R^2) تبلغ 0.989 وحدود الكشف (LOD) تم قياسها عند 1×10^{-3} برز فالين (ك مادة فعالة للغاية للكشف عن أيونات Cu(II) عبر مجموعة متنوعة من المصفوفات المائية، وتعمل بكفاءة كمستشعر كيميائي بصري.

Introduction

Copper(II), being a transition metal endowed with distinctive optical characteristics, renders it particularly appealing for incorporation into optical chemical sensors. Over the years, extensive research endeavors have been dedicated to the advancement of copper(II)-based optical chemical sensors, driven by their intrinsic sensitivity and selectivity towards a variety of analytes. In the realm of environmental monitoring, optical sensors for copper(II) have been engineered to facilitate detection of this heavy metal ions and Other contaminants in aquatic environments. Furthermore, copper(II) sensors have been investigated for a range of applications within the biological and medical domains, encompassing the identification of proteins, enzymes, and deoxyribonucleic acid (DNA) [1].

Ultraviolet-visible absorption spectrophotometry (UV-Vis) constitutes a spectroscopic methodology employed to elucidate the structural characteristics of various metal species in solution [2,3]. This technique involves the examination of electronic transitions occurring between orbitals of disparate energy levels. Transition metal ions exhibit d-d absorption bands within the visible spectrum of electromagnetic radiation, alongside ligand-to-metal and metal-to-ligand charge transfer bands. Consequently, transition metal complexes frequently exhibit pronounced coloration [4]. These colors arise from electronic transitions between quantized energy levels, the spacing of which corresponds to the wavelengths of visible light. The variation in the spacing of energy levels is contingent upon the nature of the ligands involved, the geometric configuration of the complexes, and the oxidation state of the central metal ion. The electronic spectra of coordination complexes can provide significant insights pertaining to their bonding characteristics and structural configuration. [5,6].

The analysis of potentiometric data may facilitate a more accurate evaluation of the erroneous model. Conversely, the spectrophotometric data suggest the accurate model but yield a less precise assessment. The integration of both potentiometric and spectrophotometric data is crucial for the determination of stability constants and the delineation of the chemical model, respectively [7,8]. The quantification of heavy metals in environmental contexts is of considerable importance due to their deleterious effects on ecosystems, with human health being contingent upon the dosage and toxicity involved. Copper(II), akin to other heavy metals, is essential for biological processes; however, it simultaneously poses significant toxicity risks to various organisms, including algae, fungi, as well as numerous bacteria and viruses [9]. Copper has been implicated in inducing hepatic damage in pediatric populations. Contaminated drinking water may serve as a potential pathway for excessive copper exposure. A plethora of analytical methodologies has been proposed for the assessment of such contaminants for Cu(II) [10].

The application of immobilized reagents for the identification of copper has experienced a significant surge in contemporary research, particularly in the realm of chemical sensing via optical fiber sensors. The reagent is typically secured either through physical entrapment by adsorption, by electrostatic attraction, or through chemical binding to a dependable support structure. In recent times, numerous scholars have put forth proposals for optical sensors aimed at the detection of copper (II) ions. Bhalla et al [11]. introduced a fiber optic biosensor that utilizes immobilized bacterial cells for the detection of copper (II). This biosensor demonstrated a linear response across a concentration range of 0.05-50 ppm, achieving a detection limit of 0.02 ppm. A comparable methodology was documented by Trandafilović et al [12], who engineered a whole-cell optical biosensor for the monitoring of copper utilizing immobilized bacteria. This biosensor exhibited considerable sensitivity with a detection threshold of 1 μM . Additionally, another sensor employing surface-enhanced Raman spectroscopy (SERS) was developed for the detection of fabricated the sensor was synthesized through the deposition of gold nanoparticles onto a silicon wafer, followed by functionalization with a benzimidazole ligand. The sensor exhibited remarkable sensitivity towards copper(II), exhibiting a limit of detection quantified at 7.2 μM [13].

Numerous reagents immobilized on chitosan optical sensor developing film configurations, as well as probe-type sensors, have been documented in prior studies [14]. Rashd et al. In 2019, elucidated the efficacy of the immobilized 4(Dimethylamino)benzaldehyde (DABD) on chitosan film, serving as a reagent phase in the advancement of an optical reflectance sensor aimed at Cu(II) quantification [15]. In summary, optical chemical sensors present a highly promising avenue for the detection of copper(II) across a range of samples, characterized by elevated sensitivity and selectivity. Nevertheless, additional investigations are imperative to enhance the efficacy of the sensor and assess its practical usage in authentic environmental specimens.

This manuscript endeavors to critically examine the contemporary advancements in the fabrication of copper(II) optical sensors and their respective applications, concentrating on the fundamental sensing mechanisms and the pivotal design elements that influence their performance, including the ligand. Valine was meticulously engineered for the establishment of an optical sensing framework aimed

at the quantification of copper(II) in potable or wastewater. This ligand (Figure 1) encompasses one amine and one Carboxyl functional groups, which possess the potential to undergo deprotonation subsequent to the coordination with metal ions. [16].

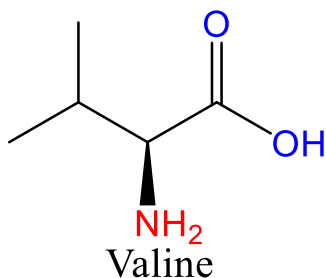


Figure 1: Chemical structure of Valine (Val).

Material and methods

All chemicals and reagents utilized were of analytical grade and were employed without additional purification. Valine was procured from Sigma-Aldrich, and its purity was corroborated through both chromatographic and potentiometric analyses. All other chemicals were acquired from Sigma and utilized without further purification. The stock solutions of metal ions were synthesized utilizing reagents of analytical grade, and their concentrations were verified through titrimetric analysis [17].

A. Measurements

The electronic spectra of the Cu(II) complexes were obtained utilizing a Hewlett-Packard 8452A Diode Array Spectrophotometer, calibrated to operate within the wavelength spectrum of 300 – 820 nm. All solutions were prepared immediately prior to use, employing deionised water as the solvent. The concentrations of both the ligand and the metal were maintained at 0.05 M. Experimental measurements were performed in aqueous medium across a pH spectrum of 3.22–7.74, utilizing 10 mm pathlength cuvettes within the 250–800 nm wavelength interval. An uncoordinated ligand served as the control blank.

B. Optimisation of Cu(II) Sensor Response

a) Preparation of Reagents for the Determination of Cu(II)

In the present investigation, a comprehensive array of chemicals and reagents was utilized, including copper(II) chloride dihydrate, L-Valine (L1), deionised water, ethanol, and phosphate buffer sourced from BDH or Aldrich. A standard Cu(II) solution with a molarity of 0.4 M was formulated by dissolving an appropriate quantity of 3.409 g in 50 mL of deionised water. A standard stock solution of 0.4 M was also prepared by dissolving the requisite amount of 2.343 g in 50 mL of deionised water..

b) Optimisation of the reaction condition between L¹ and Cu(II) ion

The optimization of the reaction conditions between L¹ and the Cu(II) ion was systematically evaluated by mixing identical concentrations of Cu(II). The solution comprised varying amounts of L-Valine L¹, with concentrations spanning from 10×10^{-3} to 0.25 M. Subsequently, all samples were subjected to analysis employing a UV-visible double-beam spectrophotometer for the assessment of absorption characteristics. The reproducibility of the sensor's response was systematically evaluated through the execution of seven independent experiments utilizing 0.15 M concentrations of Cu(II). The photostability of the sample was rigorously assessed. The concentration of L1 employed in this study was established at 0.15 M. This concentration was maintained for a duration of six hours, during which the absorption intensity was meticulously recorded at 30-minute intervals. The absorption spectrum of each mixture was recorded using a UV-visible spectrophotometer.

Results and discussion

The emergence of absorption peaks indicates the occurrence of electronic absorption transitions of the compounds recorded in a 0.15 M solution of deionised water for valine, Cu(II), and the Cu(II)-valine complex. The wavelength range corresponding to these absorption spectra spans from 200 to 800 nm. The UV-visible spectrum of valine, Cu(II), and the Cu(II)-valine complex exhibits three distinct bands associated with the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. The UV-visible spectra (Figure 2) reveal analogous absorption characteristics of the ligand, which are shifted towards lower wavelengths, accompanied by a pronounced increase in peak intensity attributable to the d-d transition, thereby confirming the formation of the complex.

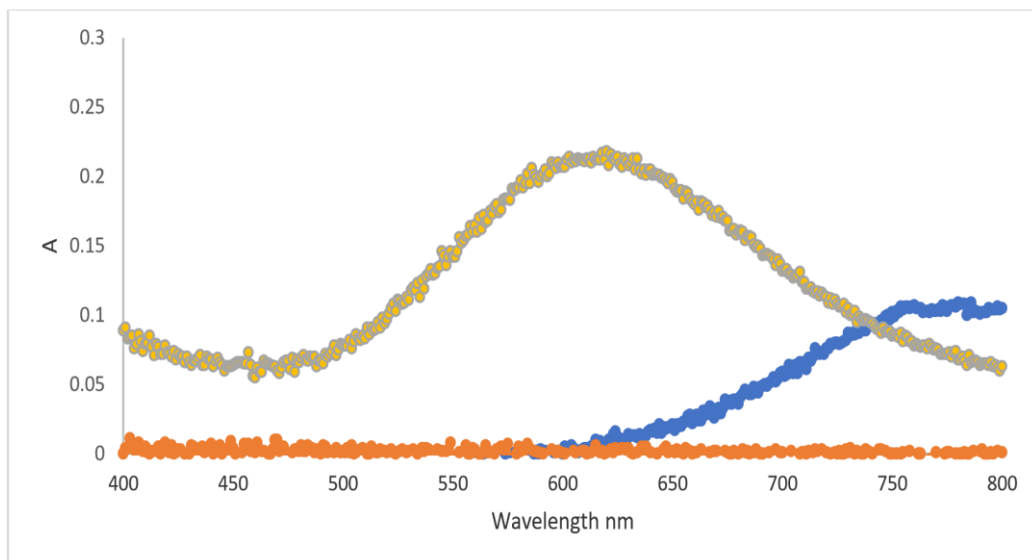


Fig. 2: The ultraviolet-visible (UV-Vis) absorption spectra were acquired for a 0.15 M solution of valine, a 0.15 M solution of Cu (II) ions, and a mixture of Cu (II) ions with valine.

The influence of pH was examined across various pH levels in a 0.25 M sodium hydroxide solution, as illustrated in Figure 2. pH constitutes a critical parameter during the synthesis of complexes due to its implications for the stability and longevity of the resultant product.¹ Absorbance values corresponding to pH were quantified at a wavelength range of 200-800 nm. At a pH of 11, the peak absorbance value recorded was 1.233. The optimal absorption intensity for the ligand valine was detected at a wavelength of 617 nm. At this specific wavelength, the absorbance measurements exhibited variability in accordance with different pH conditions. The influence of valine concentration on the formation of the The effect of pH was also studied at different pH values in a 0.25 M sodium hydroxide solution. (Figure 3). pH is an essential factor during the formation of complexes because of its relation to the stability and shelf life of the product.¹ The absorption values related to pH were measured at a wavelength of 200-800 nm. At a pH of 11, the highest value of absorption was 1.233. The maximum absorption intensity of the ligand valine was observed at a wavelength of 617 nm. At this wavelength, the absorbance readings varied with different pH levels.

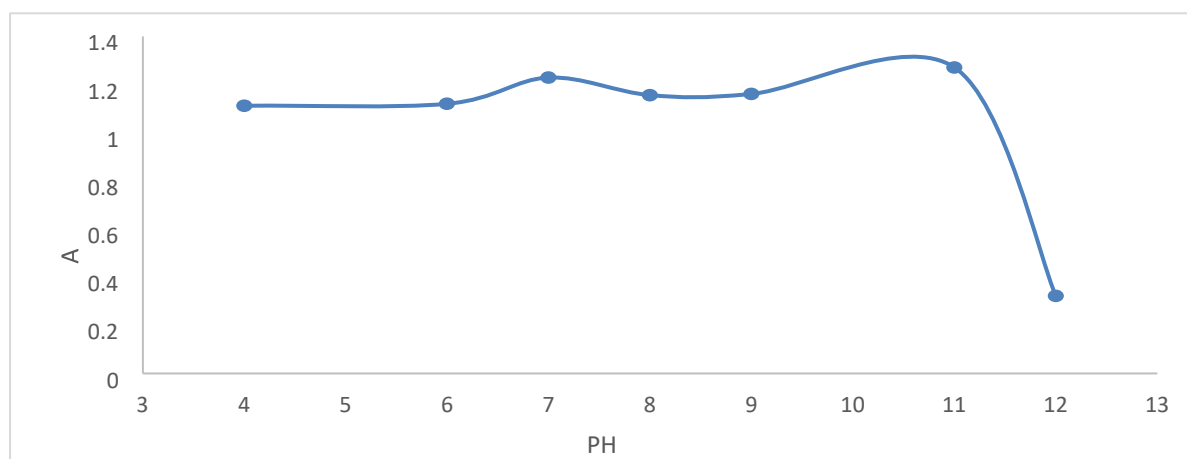


Figure 3: The effect of working pH on the absorbance of L-Valine upon reaction with 0.15 M Cu (II) solution.

The effect of valine concentration on Cu (II)- valine complex formation was studied by measuring absorbance at a fixed wavelength of 617 nm. The maximal absorbance of the Cu(II)-L-valine complex solution was observed at a reagent concentration of 0.15 M (Figure 4). The absorbance exhibited a proportional increase across the valine concentration spectrum ranging from 0.05 to 0.15 M. The initial investigation revealed a significant enhancement in the absorbance signal correlated with the increasing concentrations of valine. At elevated valine concentrations, the response gradually reached a state of stabilization and ultimately exhibited saturation at 0.15 M. The application of a higher valine

concentration facilitated a greater number of interactions between the valine ion and the Cu(II) ion present in the adjacent phase, thereby yielding a more pronounced absorbance signal. The absorbance signal eventually reached a plateau as nearly all valine binding sites became fully occupied by the Cu(II) ion.

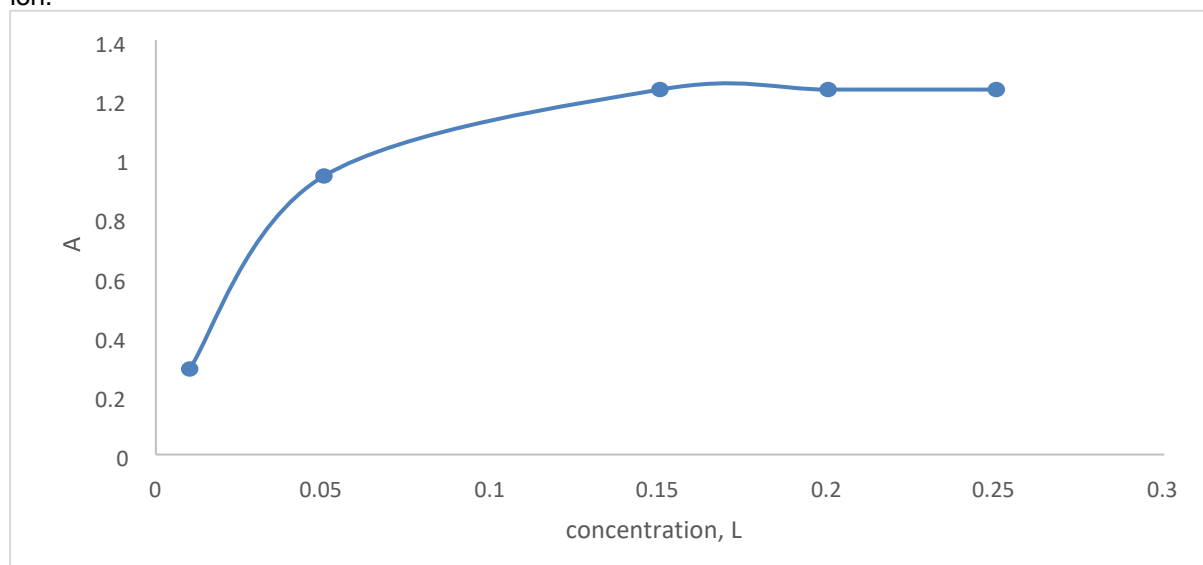


Figure 4: The impact of L-Valine concentration on the optical response of the Cu (II)-L-Valine complex was assessed while maintaining a constant copper (II) concentration of 0.15 M, utilizing a buffer solution at pH 11.

A study on the photostability of the valine solution was executed by subjecting the reagent to continuous illumination from a light source for a duration of 6 hours. A comparable investigation regarding photostability was documented by Ahmad & Yusof, [2] upon continuous exposure of gallochinin, immobilized within a chitosan membrane, to a light source for a duration of seven hours, this experimental procedure was instituted to investigate the potential occurrence of photodegradation or photobleaching of the chemical during the quantification of Cu (II) [1]. The reaction was carried out under controlled laboratory temperature and illumination conditions. A relative standard deviation (RSD) value of 0.5% was attained at the valine concentration of 0.15 M, which suggests that the reaction phase within the solution exhibited stability against light exposure.

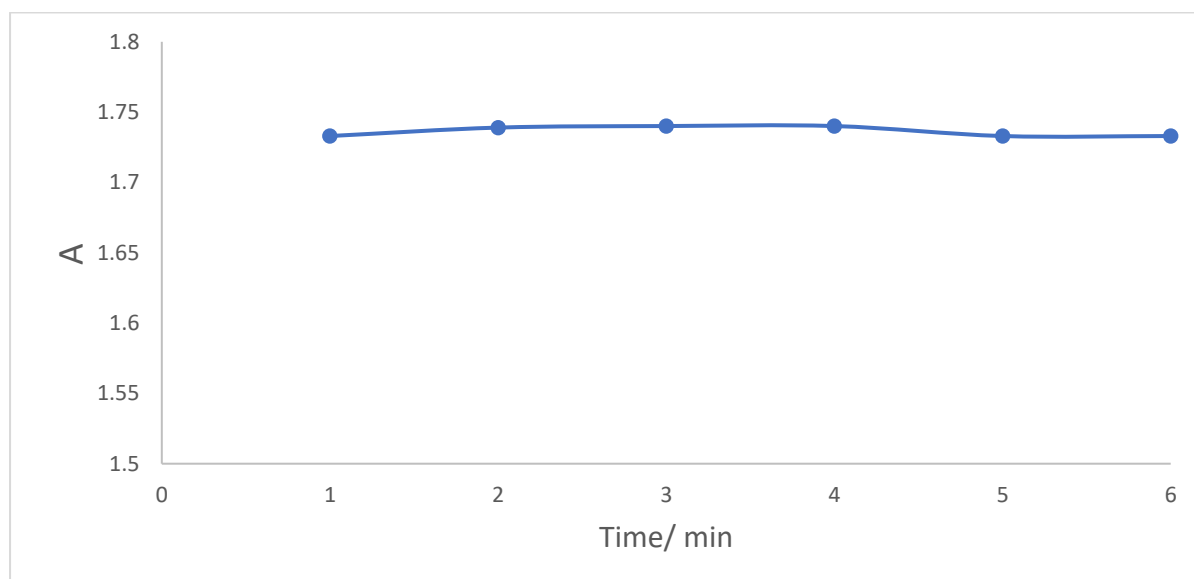


Figure 5: The photostability of the L_Valine with a concentration of 0.15 M against Time.

The reproducibility assessment (Fig. 6) regarding the solution's response was executed by acquiring seven measurements derived from distinct experimental batches, all containing an identical concentration of valine and Cu (II) (0.15 M). This procedure culminated in an RSD value of 2.7%. Prior

investigations on the copper fiber optic sensor utilizing sulfon black F (FSBF) immobilized on XAD-7 revealed an RSD value of 1%, and the reproducibility of the development is deemed satisfactory and significantly comparable to the existing literature [3]. It has been observed that the variability in sensor response is attributed to two principal sources: construction variability and operational variability. The former encompasses variations induced by factors such as matrix quantity, reagent concentration, particle dimensions, and sensor morphology, whereas the latter is attributable to discrepancies in analyte concentration. They deduced that the predominant source of non-uniformity in response is rooted in the sensor's construction rather than its operational conditions.

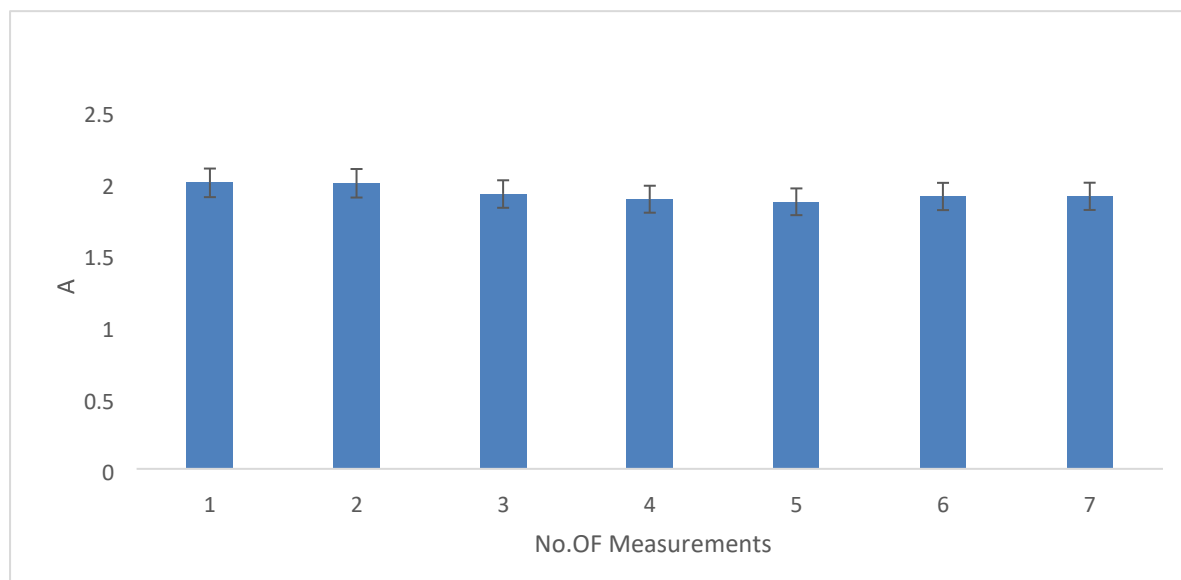
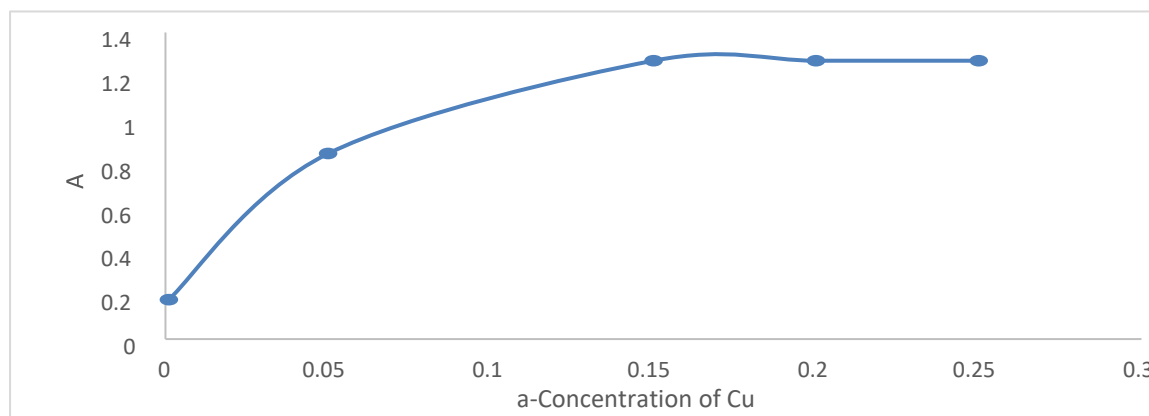
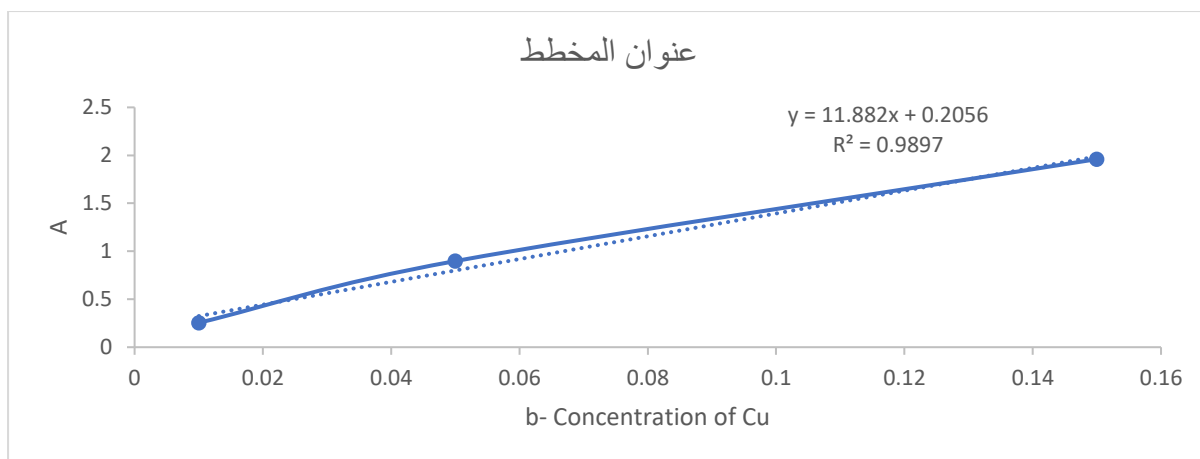


Figure. 6: The reproducibility of the reagent L_Valine 0.15 M Cu (II) analyte.

The response curve of the sensitive material is depicted in (Figure 7 a). The spectrophotometric signal exhibited a pronounced increase with escalating Cu (II) concentrations during the initial investigation, and the response gradually stabilized at elevated Cu (II) concentrations, ultimately reaching saturation at 0.15 M Cu(II). An augmented concentration of Cu (II) facilitated a greater number of reactions between the reactant and the analyte molecules present in the adjacent phase. Thus, an elevated signal was recorded. In these investigations, the concentration of valine was maintained at 0.15 M. The concentration of Cu (II) was varied within the range of 0.05 M to 0.15 M. A linear correlation was identified between the absorbance and the concentration of Cu(II) within the Cu(II) concentration spectrum of 0.001 M to 0.15 M. The relative absorbance exhibited a linear association ($R^2 = 0.98$) in the (Figure7 b). A nearly identical response curve was obtained when an amperometric glucose microsensor, predicated on glucose oxidase immobilized via a chitosan film on a Prussian blue substrate, was fabricated.



(a)



(b)

Figure 7: The response curve of the L_Valine at different concentrations of Cu (II) (a) and is the linear dynamic range of the Cu (II) concentration (b).

The presence of interference from various ions during the determination of Cu (II) was also scrutinized in this study. Figure 7 encapsulates the extent of interference quantified for several foreign ions, such as Co(II), and Ni (II), at a 1:1 molar ratio of Cu(II) to foreign ion. The curve illustrates that the acquired values of Ni (II) and Co (III) ions were close to each other.

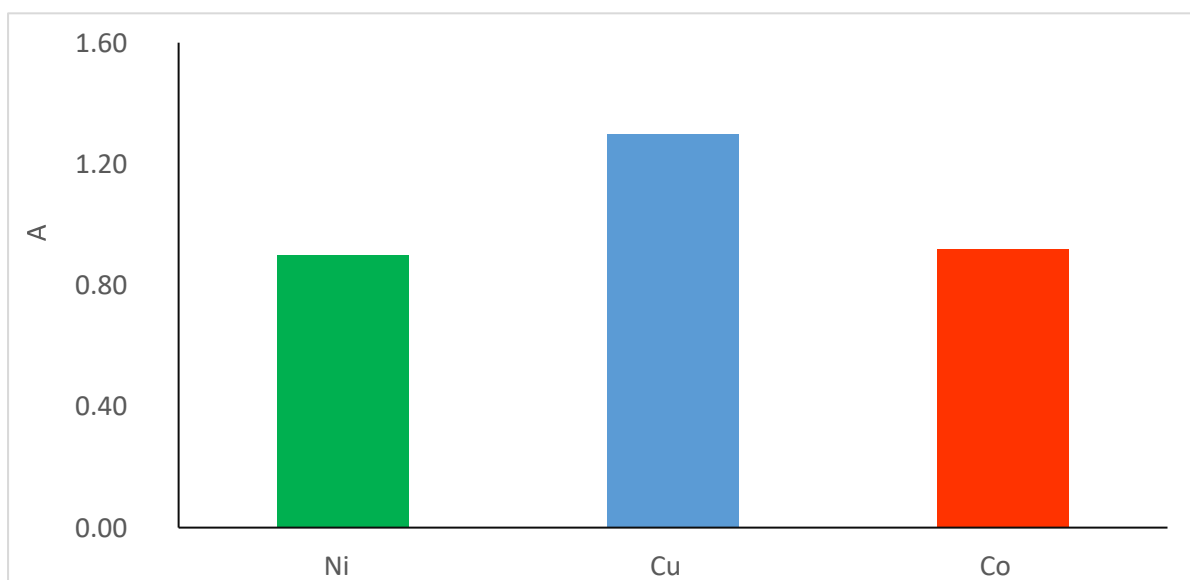


Figure 8: The degree of interference of the valine at a 1:1 molar ratio of Cu (II): foreign ion.

Conclusion

In conclusion, optical chemical sensors have shown excellent potential as a sensitive and selective copper (II) detection tool. Valine was observed to form various Cu(II) complexes in the solution, The colour intensity of the adduct increases proportionally with the increase in substrate concentration. The sensor has good photostability and reproducibility features. The solution used for operation is maintained at pH 11. The reproducibility study showed a good RSD value of 2.7%. The photostability test gave an RSD of 0.5% indicated no significant photobleaching upon exposure to ambient light, Ni(II), Co(II), and Cu(II) with their effect during Cu(II) determination was also examined in this work; the result showed these ions did not interfere during Cu (II) detection by using Valine.

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