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Spectrophotometric determination of zinc using N-(2-(2-amino-5-nitrophenyl) diazenyl)ethyl)naphthalen-1-amine

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ABSTRACT

Zinc(II) ion was determined by spectrophotometry using ´´N-(2-(2-amino-5-nitrophenyl)diazenyl)ethyl)naphthalen-1-amine as a reagent. The absorbance of the zinc complex was measured at 468 nm to quantify the complex under optimal conditions. The mole ratio was used to study the stoichiometric composition of the zinc complex, considering that the M:L ratio in any complex is equal to 1:1. Results indicated that the complex was stable for 60 min following the preparation experiments. Beer's law was obeyed within the concentration range of 0.653–6.538 µg/mL, with a correlation coefficient (R^2) of 0.9997. The molar absorptivity was 8740 L/mol·cm at 468 nm, with LOD of 0.096 µg/mL, LOQ of 0.291 µg/mL, Sandell's sensitivity of 0.011 µg/cm², recovery percentage ranging from 98.48% to 100%, and error percentage from −1.75% to 0.25%. Precision was assessed using intra-day analyses of multiple samples, yielding an RSD% between 0.031 and 0.127.

Introduction

Azo compounds are recognized as the most extensively produced dyes in chemistry today, with their significance having escalated in recent years [1]. Ligands, antioxidants, complexes, polymers, dyes, bioactive compounds, and other biological components have been prepared widely using the basic materials of Azo [2]. These compounds are characterized by the functional group (-N=N-) linking two symmetric or asymmetric identical or non-azo alkyl or aryl radicals [3]. The azo group (-N=N-), which is responsible for color, and auxochromes (which intensify color), which are electron-withdrawing or -donating groups (such as -NH_2, -COOH, -SO_3H, and -OH), are both present in the molecular structure of dye [4]. Azo compounds are diazine (HN=NH) derivatives in which both hydrogen (H) atoms are substituted with azobenzene, hydrocarbyl, or diphenyldiazene groups [5].

The phenyl and naphthyl rings are linked by one to three azo bonds, which can be substituted by chloro, amino, nitro, or hydroxyl groups [6]. Traditionally, these compounds are synthesized by diazo-coupling the appropriate active methylene molecule with diazonium salt [7]. The history of synthesis can be divided into two key periods: the pre-aniline era, which extended up to 1856, and the post-aniline era, which began after 1856 and continues to the present along with its applications. The former period had a limited range of colors because of its reliance on plants and animals [8]. Approximately 65% of azo dyes are used as food additives [9]. Zinc-based complexes have been extensively utilized in medical applications, including antimicrobial, antibiofilm, antioxidant, and other diverse uses [10]. Additionally, many zinc complexes have demonstrated efficacy in the treatment of skin diseases when incorporated into medicinal formulations, and they play a significant role in various catalytic reactions [11]. Recently, Schiff base metal complexes have demonstrated remarkable efficacy as chelating ligands in

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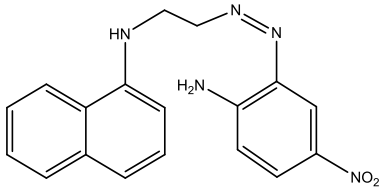
synthetic chemistry because of their simple use in synthesis, structural diversity, and extensive utilization in biological and industrial applications [12]. Thus, researchers have been focusing on zinc complexes derived from Schiff bases [13].

The study aimed to use N-(2-(2-amino-5-nitrophenyl) diazenyl) ethyl) naphthalen-1-amine for the facile and sensitive determination of zinc(II) complexes at a reduced cost, as shown in Figure 1.



N-(2-(2-Amino-5-nitrophenyl)diazenyl)ethyl)naphthalen-1-amine

Figure 1. Chemical structure of N-(2-(2-amino-5-nitrophenyl) diazenyl) ethyl) naphthalen-1-amine.

Materials and Methods

Reagent and instruments

The highest purity for analytical reagents and solutions was used to prepare all reagents and complexes.

The following apparatuses were used in the study: pH-meter (InoLab, WTW, 135i, Germany) and UV-vis spectrophotometer (Shimadzu UV-160A).

Preparation of standard solutions

Zn(II) stock solution was prepared by dissolving 0.0272 g of $ZnCl_2$ salt in 200 mL of water to prepare Zn(II) solution (1.0×10^{-3} M) [14]. N-(2-(2-Amino-5-nitrophenyl) diazenyl) ethyl) naphthalene-1-amine (A 1.0×10^{-3} M; 0.067 g) with molecular weight (335 g/mol) was dissolved in ethanol (200 mL) to prepare the complex solution. Phosphate buffers with pH ranging from 2.0 to 11.0 were prepared using 0.1 M KH_2PO_4, 1 M H_3PO_4, or 0.1 M NaOH.

Results and Discussion

Absorption spectra of the ligand and complex

The absorption spectra of the reagent and zinc complex are shown in Figures 2 and 3. The reagent solution spectrum had an absorption maximum of λmax=509 nm, whereas the zinc(II) complex had an absorption maximum of λmax=468 nm.

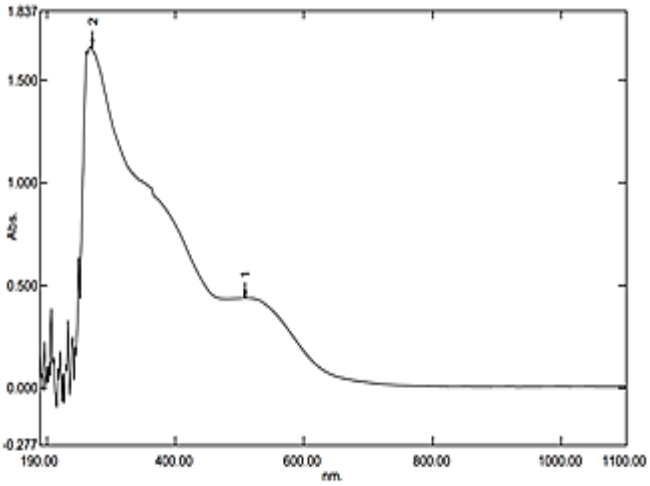


Figure 2. Absorption spectra of the Azo reagent.

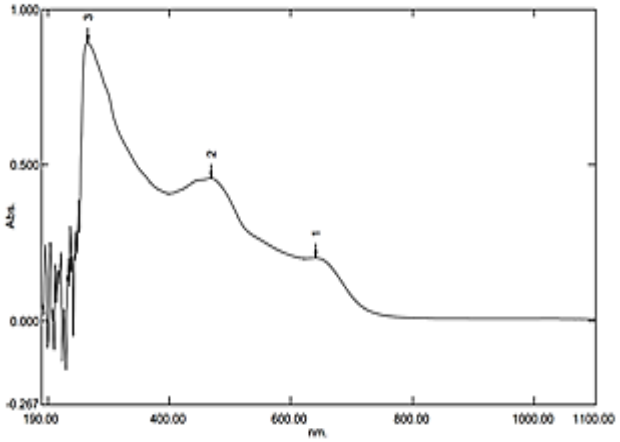


Figure 3. Absorption spectra of the zinc complex with Azo reagent

Effect of PH

The effect of pH on Zn(II) complexation was studied at pH 2–11. About 1.0 mL of 1.0×10^{-3} M ligand was mixed with 1.0 mL of 1.0×10^{-3} M Zn(II) in 10 mL flasks and diluted to 10 mL with phosphate buffers, and absorbance was measured at 468 nm. The pH with the highest absorbance was chosen, specifically pH 11, as shown in Figure 4.

Stability of Zn(II) complex with time

The stability of the zinc complex between N-(2-(2-amino-5-nitrophenyl)diazenyl)ethyl) naphthalene-1-amine and Zn(II) was assessed via spectrophotometry at λmax = 468 nm and pH 11 for 1 h. The results were recorded every 5 min.

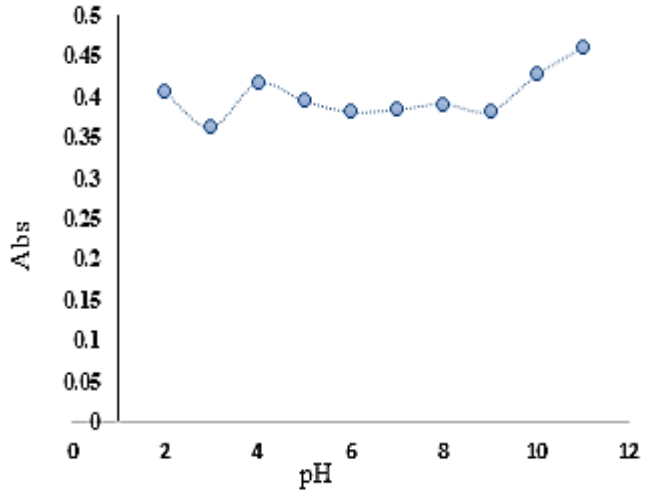


Figure 4. Effect of pH on the absorbance of the zinc(II) complex

The results showed that the complex reached its stable absorbance values within 60 min and maintained them for 24 h, enhancing the method's reliability and application for numerous samples. The results are shown in Figure 5.

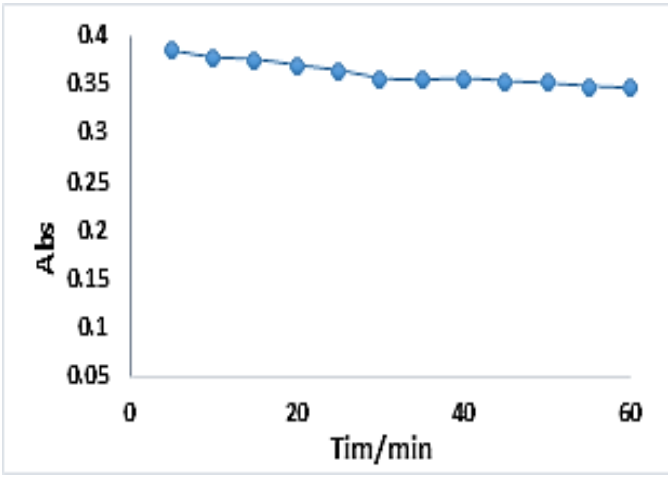


Figure 5. Effect of time on the absorbance of the zinc(II) complex

Molar ratio method

The ligand-to-metal ratio was determined using molar ratios by adjusting the amounts of Zn(II) and N-(2-(2-amino-5-nitrophenyl) diazenyl) ethyl) naphthalen-1-amine. The mixture's absorbance was recorded at 468 nm under pH 11 (Table 1). The optimal ratio was found to be 1:1 [15, 16], as shown in Figure 6.

Table 1. Mole ratio and absorbance values

VM : VL 1×10^{-3} M	Absorption
1: 0.25	0.073
1: 0.50	0.15
1: 0.75	0.211
1: 1.00	0.305
1: 1.25	0.33
1: 1.50	0.435
1:1.75	0.51
1: 2.00	0.617

*Absorbance was measured under λmax=468 nm

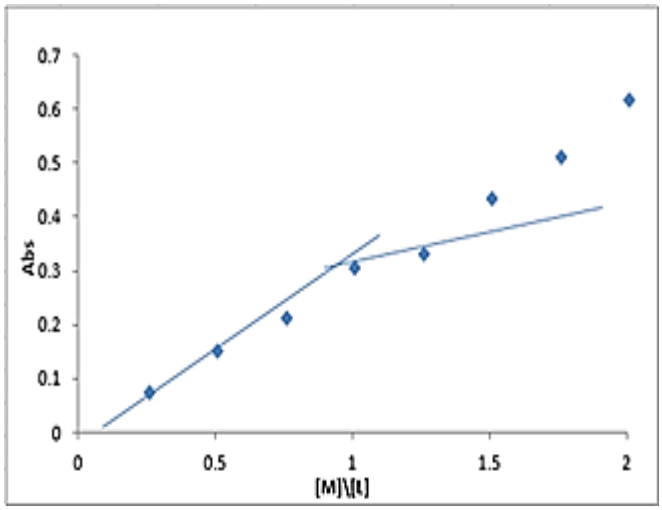


Figure 6. Mole ratio method for the Zn:L complex

Calibration Curve

About 1.0 mL of 1.0×10^{-3} M N-(2-(2-amino-5-nitrophenyl)diazenyl)ethyl)naphthalen-1-amine was added to 10 mL volumetric flasks, each containing 0.1–1.0 mL of 1.0×10^{-3} M Zn(II). The solutions were then diluted to 10 mL with phosphate buffer at pH 11. After 120 min, the absorbance was determined, and the results were recorded at 468 nm. All data were plotted against Zn(II) using different concentrations (expressed in micrograms per milliliter), as indicated in Figure 7.

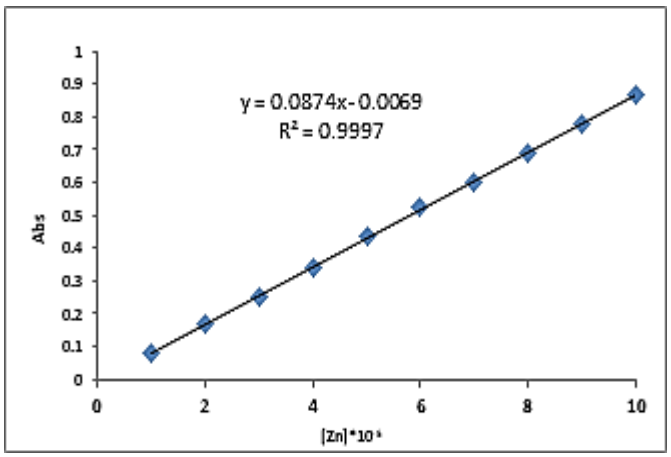


Figure 7. Standard calibration curve of zinc ion

Accuracy and precision

Three synthetic Zn(II) samples were used and analyzed to test repeatability using concentrations across the method's linear range. Each sample was measured five times per day (intra-day). Results, expressed as RSD% values to denote precision, are shown in Table 2.

Sensitivity

Sandell's sensitivity, limit of detection (LOD), and limit of quantification (LOQ) were used as indicators to determine and evaluate the method's sensitivity [17, 18]. The calibration graph for the synthesized Zn(II)-N-(2-(2-amino-5-nitrophenyl) diazenyl) ethyl)naphthalen-1-amine system was plotted, and the values are presented in Table 3.

Table 2. Accuracy and precision for Zn(II)

[] *10^{-5}	Amount µg/mL	Result µg/mL	SD	Rec%	RSD%	Er%
1	2	1.99	0.022	99.942	1.101	-0.5
2	4	3.93	0.015	98.483	0.389	-1.75
3	8	8.02	0.022	100	0.273	0.25

***(Rec) recovery, (SD) standard deviation, (RSD) relative standard deviation, and (Er) error.**

Spectral characteristics of the proposed method

Following Beer's law, the synthesized complex was characterized within a concentration range of 0.653–6.538 µg/mL under a molar absorptivity (468 nm) of 8740 $L \cdot mol^{-1} \cdot cm^{-1}$. Linearity was confirmed by a high correlation coefficient (R^2 = 0.9997). The method exhibited sensitivity, with low LOD (0.096 µg/mL), LOQ (0.291 µg/mL), and Sandell's sensitivity (0.011 $\mu g \cdot cm^{-2}$). The method demonstrated exceptional accuracy (98.48%–100% recovery and %Er of −1.75% to 0.25%) and precision, with small RSD% values (0.031%–0.127%). These results indicated superior repeatability with good reproducibility (Table 3).

Table 3. Analytical parameters of the synthesized complex

Parameter	Value
λmax nm	468
Beer's Law (µg/ mL) limit	0.653–6.538
MA (L/mol·cm)	8740
LOD (µg/mL)	0.096
LOQ (µg/mL)	0.291
pH	11
SL ($mL \cdot \mu g^{-1} \cdot cm^{-1}$)	0.0874
Intercept	-0.0069
CC (r^2)	0.9997
Sandell's ($\mu g/cm^2$)	0.011
% RSD	0.031–0.127
% Recovery	98.48%–100%
% Er	(-1.75)%–0.25%

*ML: molar absorptivity, LOD: limit of detection, LOQ: limit of quantification, SL: slope, CC: correlation coefficient.

Conclusions

The spectrophotometric method using N-(2-(2-amino-5-nitrophenyl) diazenyl) ethyl) naphthalen-1-amine for the determination of zinc(II) ions was successful. The 1:1 complex was measured at 468 nm and remained stable for 120 min. The method adhered to Beer's law in 0.653–6.538 µg/mL, with a molar absorptivity of 8740 L/mol·cm. Sensitivity, accuracy (98.48%–100% recovery), and precision (RSD% 0.031–0.127) were confirmed, indicating reliability for Zn(II) analysis.

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التقدير الطيفي للزنك باستخدام N-(2-(2-Amino-5-nitrophenyl) diazenyl)ethyl)naphthalen-1-amine

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الخلاصة:

تم تقدير أيون الزنك الثنائي طيفياً باستخدام الكاشف 2–(2– امينو–5–نايترو فينيل) ثنائي زينيل) اثيل) نفثالين–1– امين . تم قياس الامتصاصية للناتج الملون لمركب الزنك عند طول موجي 468 nm لتحديد كمية المركب تحت الظروف المثلى .تمت دراسة التركيب الكيميائي للمعقد بواسطة النسبة المولية، وقد أظهرت النتائج أن نسبة M:L في المعقد تساوي 1:1. بقي معقد الزنك ثابتاً ومستقراً بعد تحضيره حتى60 دقيقة. كذلك اعطى علاقة خطية والذي يخضع لقانون لامبرت_بير عند التراكيز µg/mL (0.653–6.53) وبمعامل ارتباط 0.9997 ، الامتصاصية المولارية 8740 L/mol·cm .تم حساب حد الكشف 0.096 µg/mL والحد الكمي 0.291 µg/mL ، وحساسية ساندل 0.011 µg/cm² ، وكانت النسبة المئوية للاستيعادية (98.48 %(100%–%) ونسبة الخطأ بين (0.25%–%(1.75–)% وتم تقييم الدقة من خلال إجراء تحليلات لعدة عينات في نفس اليوم وقد أظهرت النتائج أن نسبة الانحراف المعياري النسبي تتراوح بين (0.127–0.031)%.

كلمات مفتاحية: قاعدة شف، معقدات الزنك، التحديد الطيفي، اصباغ الآزو