

SPECTROSCOPIC DETERMINATION OF COBALT(II) ION BY USING AZO DYE OF TRIAZOLE DERIVATIVES

Yasser J. Majid*, Wassan B. Ali and Sahar R. Fadhel

Department of Chemistry, College of Sciences, University of Diyala, Iraq

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ABSTRACT. Highly efficient azo-day triazole derivatives carrying a π bond and OH electron donor groups have been designed, synthesized, and evaluated as colorimetric chemosensors for detecting metal ions in environmental samples, which was further supported by the functional theory studies and UV-Vis spectrophotometric experiment. The 4-amino-5-(2-((2,3-dimethylphenyl)amino)phenyl)-4H-1,2,4-triazole-3-thiol was directed to react with 3-nitrophenol during a diazotization type reaction to form an azo-day 4-(3-(2-((2,3-dimethylphenyl) amino)phenyl)-5-mercapto-4H-1,2,4-triazol-4-yl)diazenyl)-3-nitrophenol (Y), which have been confirmed by FTIR, ^1H NMR, and could also be easily used for the detection metal ions. Compound (Y) exhibited a rapid quantitative method for the detection of Co(II) at λ_{max} (532 nm) in an aqueous solution. The current study introduces a facile, low cost, more specific and selective chemosensor for detecting trace amounts of cobalt ions.

KEY WORDS: Mefenamic acid, Azo dye, Cobalt(II), Spectroscopy

INTRODUCTION

Metals and their possible uses are now fundamental to every aspect of human existence. A growing field of study in inorganic chemistry, water analysis, environmental measurements, and medical laboratories is the qualitative and quantitative determination of metal ions in biological and environmental samples [1-9]. Cobalt and ferrous ions have been the subject of much research because of the biological functions they possess. Vitamin B12, which is needed for the enzymatic breakdown of DNA, lipids, carbohydrates, and certain amino acids, contains cobalt as one of its primary components [10]. Overconcentration of cobalt ions can cause asthma, allergies, rhinitis, dermatitis, and vasodilation in humans, whereas a shortage of cobalt causes hemological and neurological diseases [11-13]. According to the World Health Organisation, there is a decreased risk of $40 \mu\text{gL}^{-1}$ due to cobalt poisoning in drinking water [14]. Hence, a selective and very accurate chemosensor for monitoring low quantities of cobalt ions is essential in environmental and biological sciences. Atomic absorption spectroscopy is one routine method for detecting Co(II) [15], plasma emission spectroscopy [16], voltammetry [17]. These procedures necessitate costly, intricate, time-consuming, and specialised machinery. Therefore, our goal is to create new synthetic chemosensors that can easily measure Co(II) in different samples. The development of chemosensors based on ortho-amino derivatives of heterocyclic compounds has made use of three distinct methods. Ortho substituted azobenzene is first treated with electron-donating groups, such as alkyl or amine groups. Utilising this technique in conjunction with solution-based trace metal ions helps expedite the oxidative cyclization reaction [18]. The inner ligand technique, a potent tool for activating C-H bonds to form C-C bonds, is related with the second approach [19, 20]. Thirdly, *o*-azophenyl-based molecular probes can have multifunctional groups attached to them, for example Si-O groups, which break the Si-O bond when exposed to a strong anion [18]. Motivated by the aforementioned three methods and our past collaboration on the development and assessment of metal ions sensors [21-24], novel colorimetric chemosensors were developed in this work using 4-amino-5-(2-((2,3-dimethylphenyl)amino)phenyl) Co(II) assay and

*Corresponding authors. E-mail: seichemms2209@uodiyala.edu.iq

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identification using 4H-1,2,4-triazole-3-thiol. Therefore, we found that triazole scaffolds containing azo-dye chromophores enhance a visual colorimetric response. There is a good chance that these structures will chelate with metal ions because of the diaza and hydroxyl groups that are nearby.

EXPERIMENTAL

Apparatus

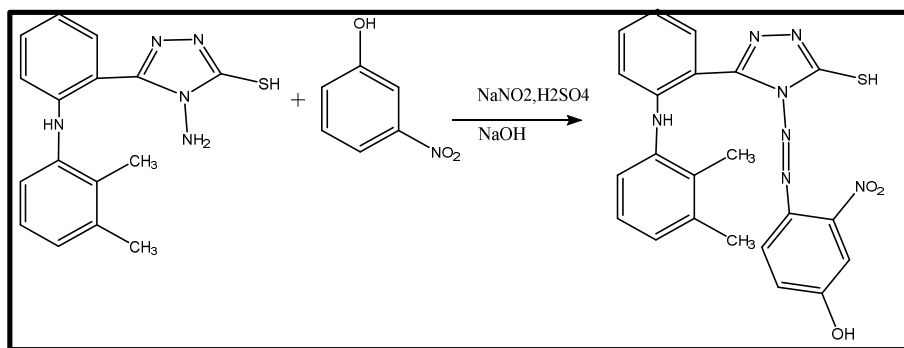
Infrared spectra of the prepared compounds were recorded on (KBr) disc by using (FTIR). spectrophotometer Perkin Elmer Speactrum-65/Germany. Double beam UV-Vis spectrophotometer equipped with 1cm quartz cell, JASCOV-650, Japan, ^1H NMR the spectra was recorded on a Bruker 400 MHz spectrometer at Central Lab.

Materials and methods

Chemicals were sourced from BDH and Panreac and were of analytical reagent quality. Samara, Iraq's State Company for Drug Industries and Medical Appliances (SDI) generously supplied the mefenamic acid standard powder. Tap water sample (drinking water system in June, Baquba, Diyala), river water (Diyala River, Baquba, Diyala), and industrial wastewater from the Diyala Electrical Industry Company (industrial wastewater from Electrical manufacturing factory), juice bottles in the local markets in Baquba.

Synthesis of compounds [Y]

0.007 moles of 4-amino-5-(2-((2,3-dimethylphenyl)amino)phenyl)-4H-1,2,4-triazole-3-thiol [Y1] was dissolved in mixture of (2 mL H_2SO_4 , 10 mL ethanol and 10 mL distilled water) and placed in an ice bath 0-5 $^\circ\text{C}$. Then we dissolved 0.07 moles of NaNO_2 in 5 mL of distilled water and placed in ice. Then added NaNO_2 to the first solution gradually and left in the ice bath for 15 min. 3 g of NaOH was dissolved in 27 mL of distilled water and added 3-nitrophenol with a number of moles of 0.007 mol and placed in an ice bath and then added this solution to the first prepared solution gradually while maintaining the temperature of the ice bath 0-5 $^\circ\text{C}$ and continued stirring for 30 min or more and then leave it to filter [25]. The final product was filtered and recrystallized from an appropriate solvent after cooling to room temperature. Maximum product at 149 $^\circ\text{C}$: 2.7 g at 60%. Scheme 1 illustrates the typical response to [Y] synthesis.



Scheme 1. Synthesis of compounds [Y].

Reagent working solution (0.0026 M). A 0.0279 g of the 4-((3-(2-((2,3-dimethylphenyl)amino)phenyl)-5-mercapto-4H-1,2,4-triazol-4-yl)diazanyl)-3-nitrophenol was dissolved in 25 mL of distilled water.

Cobalt standard solution (1000 mg/L). Cobalt standard solution (1000 mg/L) was prepared by dissolving (0.4936 g) from $(\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$ in 100 mL distilled water.

Determination of λ_{max} of Co(II) complex

The main test for the reaction was to combine 1 mL of standard Co(II) ion solution with 1.0 mL of 4-((3-(2-((2,3-dimethylphenyl)amino)phenyl)-5-mercapto-4H-1,2,4-triazol-4-yl)diazanyl)-3-nitrophenol (Y) (0.0026 M) in a 10-mL volumetric flask. The mixture was gently shaken until it took on a dark yellow colour. Distilled water was added to dilute the content to the mark. Then, the entire UV-VIS range of (200 - 1100) nm was scanned against the blank. The λ_{max} was determined to be 532 nm based on the spectra that was acquired.

General recommended procedure for calibration

The following steps were taken in a series of 10 mL volumetric flasks: 1.0 mL aliquots of Co(II) standard solution containing (10-500) ppm were transferred to each flask, and 2 mL of (0.0026) M reagent solution was added to each flask. Following 10 min, the contents were diluted with distilled water to the specified level and allowed to stand for another 10 min. The absorbance at 532 nm was then measured in comparison to the reagent blank.

RESULTS AND DISCUSSION

Infrared spectroscopy and ^1H NMR spectroscopy verified the chemical structure of substance Y. The band at $(3425) \text{ cm}^{-1}$ for (NH) is shown in the FTIR Figure 1, and the absorption band of OH overlaps with (-NH). Due to (C-H) aromatic, an absorption band was seen at 3078 cm^{-1} . A good indicator of the creation of this compound was the presence of an absorption band at (1594) due to the nitrogen-hydrogen bond in the azo compound, and an aliphatic (C-H) bond at $(2921, 2842) \text{ cm}^{-1}$, which was attributed to the triazole ring. There was also a stretching vibration of (NO_2) at $(1527 \text{ and } 1318) \text{ cm}^{-1}$, and a frequency at $(1574 \text{ and } 1491) \text{ cm}^{-1}$ was associated with the (C=C) group.

Figure (2), ^1H NMR spectrum of compound (Y) in δ ppm: shows a singlet signal at (9.63) ppm for (1H, SH), singlet signal at (8.29) ppm due to (1H, NH), multiplet signals between (7.22-6.60) specified to ten protons of aromatic ring, while as singlet signal at (5.13) due to (1H,OH), and the signal at (2.20-2.16) ppm due to (6H, $2 \times \text{CH}_3$).

Spectrophotometric determination of Co(II) ion with the reagent [Y]

Studies absorption spectra at primary test

The UV-Visible spectrum of the synthesized reagent (0.0026 M) (Y) after dissolving in 0.01 M H_2SO_4 , the spectrum shows two main maximum absorption peaks. The first at wavelength of λ_{max} at 239 nm is due to transitions $(\pi-\pi^*)$ in imidazole ring [26] and the second peak at λ_{max} of 280 nm due to the transition of $(\pi-\pi^*)$ type in the benzene ring [27]. To limited λ_{max} for complex of Co(II) with (Y), 1 mL aqueous solution contain 20 μg of Co(II) then add 1 mL of (0.0026 M) (Y) and mixed well, the spectrum was as in Figure 3 shows λ_{max} at 532 nm is the wavelength for maximum absorbance of complex against reagent blank.

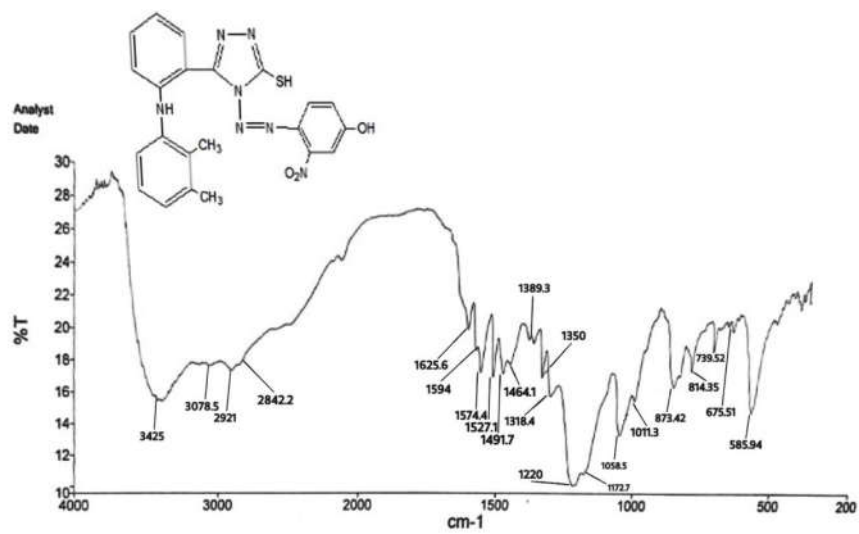
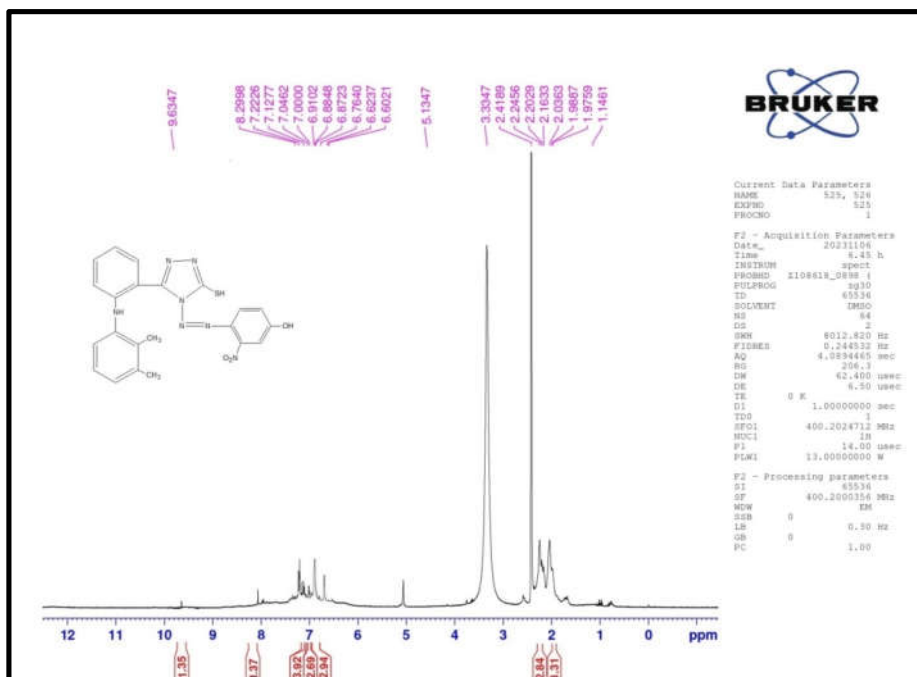


Figure 1. FTIR spectrum of compound (Y).

Figure 2. ^1H NMR spectrum of compound (Y).

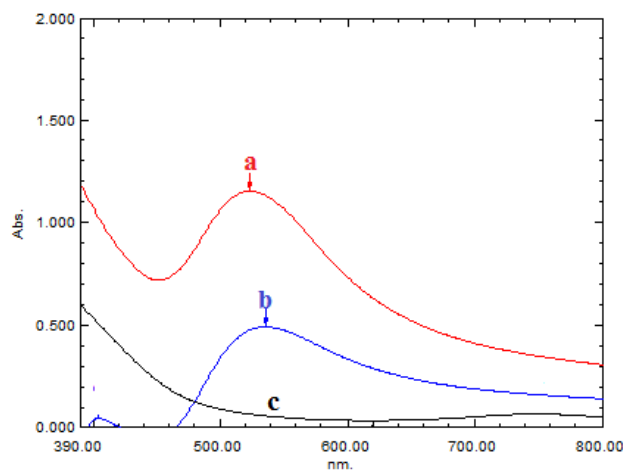


Figure 3. Absorption spectra of: (a) $20 \mu\text{g.mL}^{-1}$ Co(II) against reagent blank under optimum conditions, (b) $20 \mu\text{g.mL}^{-1}$ Co(II) against reagent blank under primary test conditions, and (c) blank solution against distilled water.

Optimization of reaction variables

We varied each parameter independently while keeping the others constant in order to conduct a systematic analysis of their influence on colour product development. Reagent volume (Y), reaction duration (RT), temperature (T), and product stability are all factors to consider.

Effect of reagent solution volume

In order to verify the effect of reagent size on the formation of the complex Co(II) with reagent (Y), different sizes of reagent were used, ranging from (0.5-3) mL, the absorbance was seen to reach its peak at 2.0 mL of (0.0026) M (Y), after which it slightly dropped. At lower volumes of the π -acceptor reagent, the intensity of the absorbance was unaffected.

Impact of reaction time coupling

When a constant concentration of Co(II) $20 \mu\text{g.mL}^{-1}$ was reacted with reagent (Y), the impact of reaction time on the formation of the colored complex was investigated. The measurement of absorbance was done at various intervals, from immediately to after a 25 min waiting time. The reaction was finished in 10 min.

Effect of temperature

Here, we looked at how temperature affected the formation complex. By conducting a series of reactions at different temperatures that ranged (10-50) °C. The given results show that the absorbance attains a maximum colour at temperature 25 °C. The absorption values then decrease with increasing temperature the reason may be due to a decrease in stability or as a result of its disintegration at high temperatures [28].

The stability

We let the reaction to continue for different amounts of time It ranged between (0-60) min to see how time affected the product's development. The general recommended approach indicated that 10 minutes was the optimal duration, and the generated colour stayed stable for 60 min at room temperature. This stability period is enough to enable for numerous measurements to be performed consecutively.

Calibration curve of Co(II)

A calibration curve for the determination of the quantity of Co(II) in aqueous solution, using proposed method. The procedure involves adding 2 mL of reagent (Y) to 1 mL of water-based solution containing Co(II) ions ranging from 10.0-500 μg , and then measuring the absorbance at 532 nm λ_{max} . A look at Figure 4 shows the outcomes (7). The expressions, $(3.3 \text{ SD})/S$ for the limit of detection (LOD) and $(10 \text{ SD})/S$ for the limit of quantitation (LOQ), were used to determine the minimum concentration that could be determined with acceptable precision and accuracy [29] and the lowest concentration that could be reliably detected but not necessarily quantified, respectively. Here, "SD" stands for the standard deviation of the blank [30] and "S" is the slope of the calibration line. The computations and results were as follows of the regression equation ($y = 0.0236x + 0.7187$), correlation coefficient R^2 (0.9988), molar absorptivity (the ability of a material to absorb light of a specific wavelength) [31] (23906.8) $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$, Sandell's sensitivity [32] (0.0423) $\mu\text{g}\cdot\text{cm}^{-2}$, and limits of detection (LOD) (0.0372) $\mu\text{g}\cdot\text{mL}^{-1}$ and quantification (LOQ) (0.2091) $\mu\text{g}\cdot\text{mL}^{-1}$.

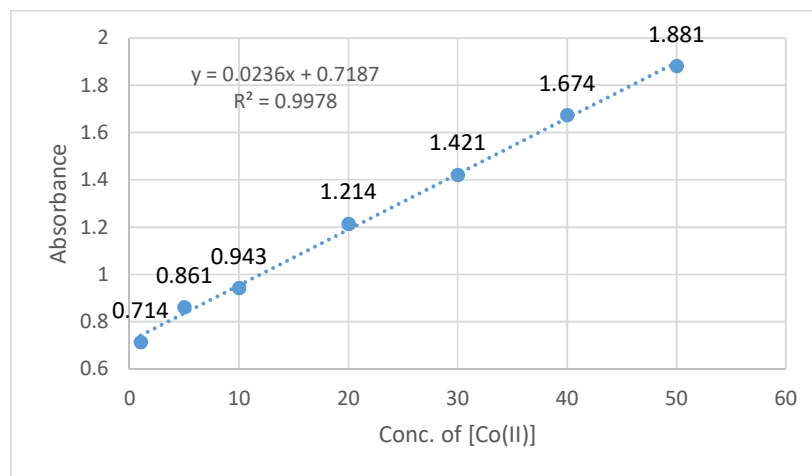
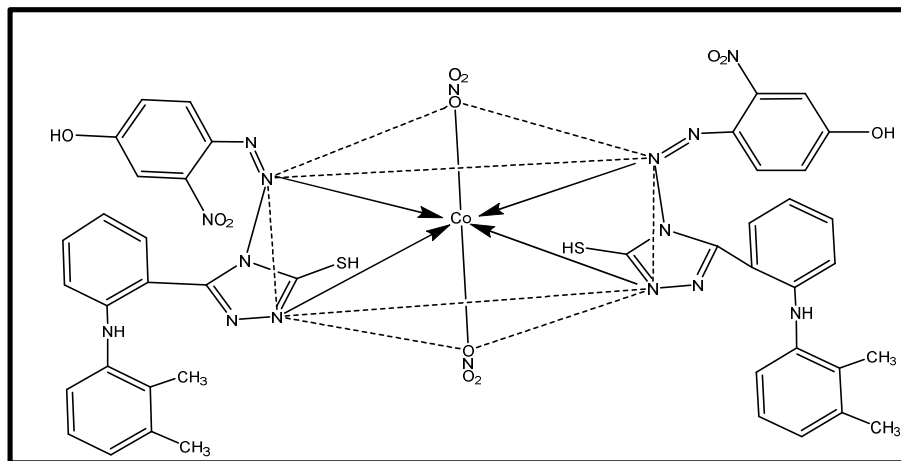


Figure 4. Calibration curve for Co(II) ion.

Stoichiometric ratio determination

To calculate the Co(II) drug-Y reagent ratio, Job's continuous variation methods and molar ratio [33] are used. The result indicate that Co(II) ions and reagent interact equimolarly; the two straight lines overlap at 1:2 [Co(II)]:[Y].



Scheme 2. The suggested format for the prepared complex.

*The effect of interference and masking agents**Interference effect*

To estimate the effect of the presence of cations as interferers when estimating the cobalt ion, a number of cations were chosen to determine the extent of their influence on the absorption of the cobalt ion, as shown in Table 1. A number of anions were also chosen to study their effect on cobalt ion estimation. The results of the study appear in Table 2.

Table 1. Examination of cations interference for Co(II) determination by proposed method.

Cations	Chemical formula	25 µg/mL		50 µg/mL	
		Valuable absorption after adding cations	Relative error E%	Valuable absorption after adding cations	Relative error E%
-	-	1.214	-	1.214	-
Cu(II)	Cu(NO ₃) ₂ ·4H ₂ O	0.593	-51.15	0.765	-36.99
Ag(I)	AgNO ₃	0.661	-45.55	0.702	-36.99
Pb(II)	Pb(NO ₃) ₂	0.751	-38.14	0.910	-25.04
Mg(II)	Mg(NO ₃) ₂ ·4H ₂ O	0.682	-43.82	0.772	-36.41

Table 2. Evaluation of anions interference for the determination of Co(II) by propose method.

Anions	Chemical formula	25 µg/mL		50 µg/mL	
		Valuable absorption after adding anions	Relative error E%	Valuable Absorption after adding anions	Relative error E%
-	-	1.214	-	1.214	-
SO ₄ ²⁻	K ₂ SO ₄	0.638	-47.45	0.485	-50.05
Br ⁻	KBr	0.892	-26.52	0.836	-31.14
SCN ⁻	KSCN	0.748	-38.39	0.556	-54.20
CN ⁻	KCN	0.921	-24.14	0.859	-29.24

Masking agent

A method was proposed to remove the effect of interference, and based on that, four masking agents were chosen to determine the extent of the effect of the competition process between them and the reagent on the reaction. 1 mL of a masking agent was added to remove the ions causing the interference and block them. Masking agents were used at a concentration of (0.1 M) and the absorption results of (20 µg/mL Co(II)) without masking agent it was (1.214), with thiourea it was (0.673), with ascorbic acid it was (0.492), with Na₂EDTA it was (0.980) and with KCl it was (1.186). The results showed that potassium chloride can be used as a masking agent when measuring cobalt ions better than other agents that cause the complex to dissociate.

Application

In clean polyethylene bottles, following samples were taken: tap water sample (drinking water system in June, Baquba, Diyala), river water (Diyala River, Baquba, Diyala), and industrial wastewater from the Diyala Electrical Industry Company (industrial wastewater from Electrical Manufacturing Factory), juice bottles in the local markets in Baquba. With the exception of the tap water, they were passed through a filter and kept in the fridge at 4 °C. Finally, 100 mL of each sample was used to measure the amount of studied ions present in these samples by following the proposed method. 1mL and 2 mL are taken from each sample, and the method of work is applied to it, and the absorption is measured for Co(II) ion separately at λ_{max} . With optimal conditions were used to form the Co(II) complex. The process was repeated three times. The results are shown in the Table 3.

Table 3. Measurement of absorbance of ion Co(II) in samples.

Determination of Co(II) ion				
Samples	Sample volume (mL)	Added (µg/mL)	Found* (µg/mL)	**Recovery (%)
Tap drinking water	1	-	0.000	-
		10	10.002	100.02
	2	-	0.000	-
		10	10.008	100.08
Diyala River	1	-	0.037	-
		10	10.049	100.49
	2	-	0.153	-
		10	11.028	110.28
Industrial wastewater	1	-	0.071	-
		10	10.073	100.73
	2	-	0.148	-
		10	10.196	101.96
Juice	1	-	0.000	-
		10	10.013	100.13
	2	-	0.000	-
		10	10.003	100.03

*Measuring three replicate.

In order to assess the practicality of the suggested approach to Co(II) ion measurement in water samples. The method was used to measure the concentration of cobalt ions in various samples taken from Baquba, Diyala, Iraq, including water from the tap, river water, industrial wastewater from the Diyala Electrical Industry Company, and juice from local markets. All of these samples were collected in June and kept in the refrigerator until they were ready to be used,

without any pretreatment. The purpose of the non-spiking analysis was to confirm the presence of the investigated ion and to quantify it in a range of real-world water samples. Table 3 displays the data showing that the investigated ion was not present in the juice and tap water samples, but was present in significantly higher concentrations in the water from the Diyala river and the industrial effluent from the enterprise. To the actual samples, we added a 10 mg/mL concentration of the examined ion's standard ionic solution in the correct volume. The established approach was found to be both applicable and accurate for quantifying the stated ion in the analyzed real samples, as the computed relative recovery values (RR%) ranged from 100.02 to 110.28%, demonstrating the absence of a substantial matrix effect.

CONCLUSION

As a result of our work, we have developed novel azo compounds, one of which is triazole that can detect cobalt ions. Based on the results of the FTIR and ^1H NMR experiments, the bond between the (Y) and Co(II) ions is indeed real. Compound Y has demonstrated to be the best choice to donate electrons due to its low ionisation potential (I) values. Among these materials, chemosensors Y demonstrated a strong optical colorimetric response when tested for the presence of the Co(II) ion in water. Using a straightforward and cost-effective manner, the new chemical sensor Y has proven to be highly sensitive and selective for Co(II) at a maximum of 532 nm.

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