

Research Article

A Fluorimetric Method Based on an Imidazole Compound for Cu^{2+} Determination in Tap Water

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Ion sensor properties of 4-(1-(4-hydroxy-3-methoxybenzyl)-1H-benzo[d]imidazol-2-yl)-2-methoxyphenol (**L**) in acetonitrile-water (1:1) were evaluated by fluorescence spectrometry. Pronounced quenching in the fluorescence spectra of the ligand was only observed for the Cu^{2+} ion among many metal ions. Linear fluorescence responses of the ligand at 360 nm as the function of the Cu^{2+} concentration were used for the determination of the Cu^{2+} ion in spiked tap water samples. Recovery values (R%) were satisfactory, and relative standard deviation (RSD%) was below 5.00 in intraday and interday measurements. Detection and quantification limits were 0.28 and 0.84 $\mu\text{g/L}$, respectively. The assay based on external calibration only took a few minutes.

1. Introduction

Benzimidazole compounds are obtained as a result of the reactions between diamine compounds and aldehyde compounds. In fact, the formation of the Schiff bases is expected from the reactions between such compounds. However, sometimes the reaction proceeds to a further step, and the cyclization of the formed diimine compound results in benzimidazole compounds. Many benzimidazole derivative compounds synthesized in this manner have been reported in the literature [1–8]. Sometimes a catalyst is used in the synthesis of benzimidazole compounds [1, 4–6]. Acidification was effective in the formation of the cyclization [2, 3].

Benzimidazole compounds have generally been investigated for their biological activity and have been reported to be potent compounds with high biological activity [9–15]. The structural properties of these compounds also make them fluorescent compounds. However, there are a limited number of studies on the fluorescence properties of benzimidazole compounds [16–21]. There are studies reporting that benzimidazole derivative compounds interact selectively with metal ions [18–20]. Benzimidazole derivatives which are proposed as fluorescent sensors for iodide and phosphate ions are mentioned [19, 21]. According

to our knowledge, some fluorescent sensors based on benzimidazole derivatives to detect the Cu^{2+} ion in water were proposed in the literature [18, 22–24]. However, there are no methods based on fluorescent benzimidazole compounds used in the determination of Cu^{2+} in real samples.

In this work, a Cu^{2+} determination method based on measuring the fluorescence of the benzimidazole derivative compound is proposed. Therefore, it is desirable to draw attention to the ion sensor properties of benzimidazole derivative compounds as fluorescent compounds. The ligand used has high fluorescence property. It has been shown that it can be used as an analytical reagent in the determination of sensitive Cu^{2+} . The synthesis of the compound is simple and economical. The usage of an inexpensive and sensitive fluorescence method is advantageous compared to existing expensive and laborious Cu^{2+} detection methods. In addition, the proposed method has been applied to tap water samples, and it has been desired to demonstrate practical availability.

2. Experimental

2.1. Chemicals and Apparatus. For synthesis, *o*-phenylenediamine, *p*-vanillin, and methanol were obtained from Merck and used directly. Spectrometric-grade acetonitrile as

the solvent of ligand was used in fluorescence measurements and was purchased from Merck. Standard metal solutions of 1000 mg/L (Merck) were used to prepare the working solutions. The stock solution was used to prepare working solutions. The absorbance spectra of the ligand were recorded by using an Analytik Jena Specord 210 spectrophotometer. The fluorescence spectra were recorded with a PTI QM-4 spectrofluorimeter.

2.2. Synthesis of the Ligand. The ligand (L) (Figure 1) was prepared according to the modified version of the report in the literature [25]. For this, *o*-phenylenediamine (1 mmol) and aldehyde (2 mmol) were refluxed in ethanol for 10 h. The progress of the reaction was monitored by thin layer chromatography (petroleum ether: ethanol: benzene; 1:1:1). After the completion of the reaction, the solution was concentrated under reduced pressure to obtain the crude product, which was recrystallized from ethanol to attain the pure product. The characterization data such as ¹H-NMR, IR spectra, and the melting point of the solid compound were consistent with the literature [25, 26].

Mp 189–190°C; ¹H NMR (DMSO-*d*₆, 200 MHz): δ 3.61 (s, 3H, OCH₃), 3.69 (s, 3H, OCH₃), 5.42 (s, 2H), 6.32–6.37 (m, 1H, ArH), 6.62–6.67 (m, 2H, ArH), 6.87–6.91 (d, 1H, ArH), 7.14–7.24 (m, 4H), 7.42–7.48 (m, 1H, ArH), 7.61–7.67 (m, 1H, ArH), 9.00 (s, 1H, OH), and 9.57 (s, 1H, OH); ¹³C NMR (DMSO-*d*₆, 50 MHz): δ 47.19 (NCH₂), 55.31 (OCH₃), 110.51 (ArCH), 110.76 (ArCH), 112.84 (ArCH), 115.42 (ArCH), 118.38 (ArCH), 118.71 (ArCH), 120.97 (ArCH), 121.81 (ArCH), 121.91 (ArCH), 127.73 (ArC), 135.90 (ArC), 142.48 (ArC), 145.72 (ArC), 147.47 (ArC), 147.57 (ArC), 148.08 (ArC), and 153.44 (ArC); FT-IR (KBr, cm⁻¹): 1662.5 and 3400.4; ESI-MS (*m/z*): 377.07 [M+1]⁺. Anal. calcd. for C₂₂H₂₀N₂O₄: C, 70.19; H, 5.37; and N, 7.44. Found: C, 70.05; H, 5.48; and N, 7.59.

2.3. Absorbance and Fluorescence Measurements. Absorption and emission spectra of the free ligand were measured in acetonitrile: water (1:1). The ligand concentrations were 2.6×10^{-5} and 2.0×10^{-7} M for absorption and fluorescence measurements, respectively. The effect of excess metal ions on the fluorescence spectra was investigated in acetonitrile: water (1:1). Pd²⁺, Sc³⁺, Sr²⁺, Ag⁺, Bi³⁺, Co²⁺, Cd²⁺, Ni²⁺, Cr³⁺, Zn²⁺, K⁺, Ca²⁺, Fe³⁺, Be²⁺, Li⁺, Mn²⁺, Al³⁺, Mg²⁺, Na⁺, and Cu²⁺ ions and 1 cm quartz cell were used in these measurements. The ligand was excited by 300 nm to record the fluorescence spectra.

Spectrofluorimetric titrations with the Cu²⁺ ion were performed at constant ligand concentration and varying metal concentration. The Cu²⁺ concentration range was between 0 and 30 μg/L. The ligand concentration was 2.0×10^{-7} M.

2.4. The Proposed Method to Determine the Cu²⁺ Ion. Measurements were made in acetonitrile and water (1:1) using an equal volume of ligand solution and water sample. An external calibration graph based on the change in

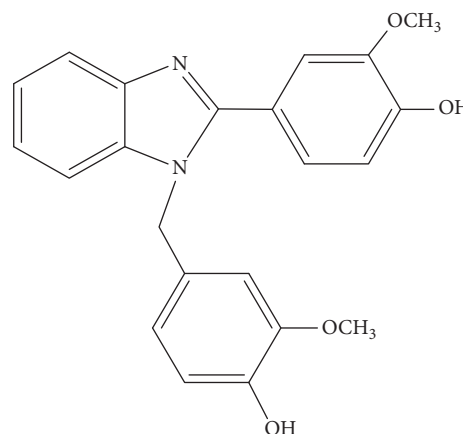


FIGURE 1: The benzimidazole compound (L) used in this study.

fluorescence intensity of the ligand with increasing metal ion concentration was used to determine the Cu²⁺ ion in the spiked tap water. KTU campus water (Trabzon, Turkey) was used as a tap water sample.

2.5. Determination of Metal-Ligand Interaction. The metal-ligand complex formation in the system was determined with the molar ratio method by means of fluorescence measurements. For this, the molar ratio graph was plotted by the data of the spectrofluorimetric titration of the Cu²⁺ ion with the ligand. The composition of the CuL complex was determined from the extrapolation of two curves with different slopes. The complex stability constant was calculated according to the method in the literature [27].

3. Results and Discussion

3.1. Absorption and Emission of the Ligand. The absorption and emission spectra of the ligand were determined in acetonitrile: water (1:1). In Figure 2, the absorption and fluorescence spectrum of the ligand was shown. As seen from Figure 2, there is an absorption band resulting from the $n \rightarrow n^*$ transition about 285 nm in the absorption spectra. When the ligand was excited with 300 nm, the maximum emission was observed at 360 nm in the fluorescence spectra (Figure 2).

The effect of 10 equivalent excess of metal ions on the fluorescence spectra of the ligand in acetonitrile: water (1:1) was investigated. In Figure 3, the effect of metal ions on the fluorescence spectra was shown. There were no significant changes on the fluorescence spectra of the ligand with the influence of ions such as Pd²⁺, Sc³⁺, Sr²⁺, Ag⁺, Bi³⁺, Co²⁺, Cd²⁺, Ni²⁺, Cr³⁺, Zn²⁺, K⁺, Ca²⁺, Fe³⁺, Be²⁺, Li⁺, Mn²⁺, Al³⁺, Mg²⁺, and Na⁺. However, the Cu²⁺ ion causes an effective fluorescence quenching. Figure 4 shows the fluorescence intensity at 360 nm of the free ligand and the ligand solution containing metal ions. As seen from Figure 4, the ligand shows selectivity for the Cu²⁺ ion over the other metal ions. This result is consistent with the outcome in the literature. It is known from the literature that benzimidazole and Schiff base compounds show selectivity for Cu²⁺ due to donor

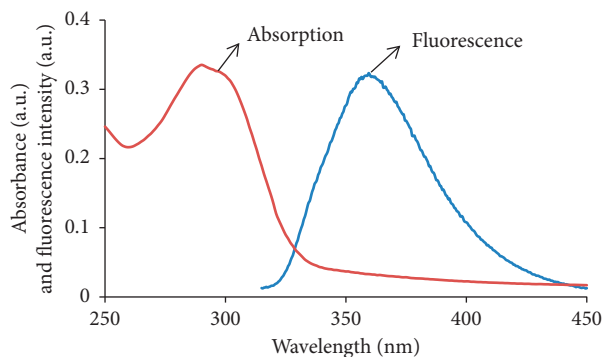


FIGURE 2: UV absorption and emission spectra of the ligand in acetonitrile-water (1:1). Ligand concentrations are 2.6×10^{-5} M and 2.0×10^{-7} M for absorption and emission spectra, respectively. The excitation wavelength is 300 nm.

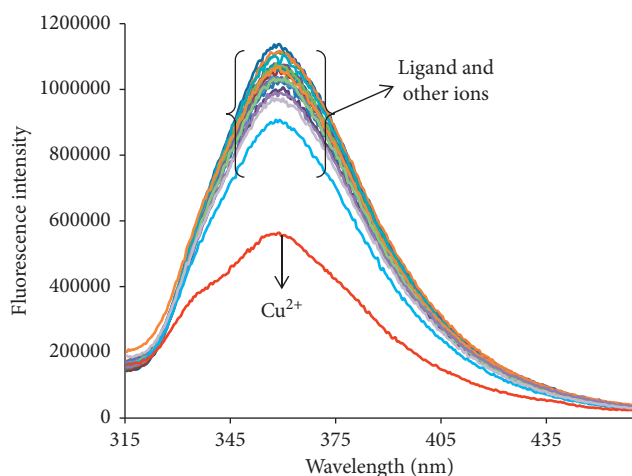


FIGURE 3: The effect of metal ions on fluorescence spectra of L in acetonitrile-water (1:1). L: 2.0×10^{-7} M; metal ion: 2.0×10^{-6} M.

groups such as C=N and OH groups in their structure [22, 28].

3.2. Complexation between Cu^{2+} and the Ligand. To investigate the interaction between Cu^{2+} and the ligand, spectrofluorimetric titrations were carried out. Figure 5 shows the change in the fluorescence spectra of the ligand with the increasing Cu^{2+} concentration in acetonitrile-water (1:1) media. As seen in Figure 5, there is regular fluorescence quenching in all spectra, while Cu^{2+} concentration increases. From the fluorescence quenching at 360 nm, the molar ratio graph was plotted. As seen from Figure 5 inset, the CuL complex composition is 1:1.

From the spectrofluorimetric titration data, the change in $I_0/(I_0-I)$ versus $1/[\text{Cu}^{2+}]$ is plotted to determine the stability constant of the CuL complex (Figure 6). From the intercept divided to the slope, the complex stability constant is calculated. The log K value is found as $\log K = 5.51$ in the mentioned conditions.

3.3. The Determination Method for the Cu^{2+} Ion. A linear concentration range between 0 and $15.2 \mu\text{g/L}$ was found for

the spectrofluorimetric determination of Cu^{2+} ions in a standard solution with the ligand. A calibration graph in this range was used to determine Cu^{2+} in spiked water samples. The R% values were satisfactory in the Cu^{2+} determination of the samples by external calibration; namely, there is no matrix effect in copper determination with the proposed method.

Figure 7 shows the change in the fluorescence intensity of the ligand with increasing Cu^{2+} ion concentration. The calibration graph was obtained from the fluorescence quenching of the ligand at 360 nm. Figure 7 inset shows the linear range. The deviation from Beer's law was seen after $15.2 \mu\text{g/L}$. The correlation coefficient R^2 was 0.9842.

3.4. The Method Validation. The analytical performance data of the Cu^{2+} determination method are given in Table 1. The limit of detection (LOD) and limit of quantification (LOQ) values were calculated as 3 s/m and LOQ (9 s/m), respectively, by the standard deviation (s) of the blank response for eleven measurements and the slope of the calibration line (m) according to the IUPAC recommendations. The LOD and LOQ values were found to be 0.28 and $0.84 \mu\text{g/L}$, respectively. The method accuracy was showed by spiking recovery measurements. In these measurements, the Cu^{2+} concentration in the spiked tap water samples was $5.1 \mu\text{g/L}$. The R% was between 96.1 and 102.0, as seen in Table 2. The method precision was established by analyzing a series of spiked tap water samples intraday and interday. The number of repeated measurements is three in the precision experiments, and the corresponding results are given in Table 2. Relative standard deviation (RSD%) was used to express the method precision. RSD% value was calculated as 3.63 and 5.00 for the intraday and interday measurements, respectively.

3.5. Comparison with Other Methods. It is reported in the literature that metals are generally determined by atomic methods [29, 30]. However, the atomic methods require the usage of expensive instruments and suffer from matrix effects and extraction process before the measurements [29]. Moreover, the appropriate detection limits can be achieved by time-consuming preconcentration procedures [30]. Methods based on measurements of fluorescence intensity of a fluorophore are much cheaper and simpler. Also, detection limits comparable to the atomic methods can be obtained by these methods under optimum conditions. The LOD values of some methods proposed for the fluorimetric Cu^{2+} determination in tap water are summarized in Table 3 [31–47]. Most of the recommended methods, as seen in Table 3, are based on the use of nonenvironmentally friendly nanostructures containing heavy metals such as gold, copper, cadmium, and iron. The preparation and characterization of such materials are also complicated and expensive. In this study, the fluorescence of a simple imidazole compound is used to develop a fast method in order to determine Cu^{2+} in tap water. Moreover, the limit of detection of the proposed Cu^{2+} determination method is lower than most

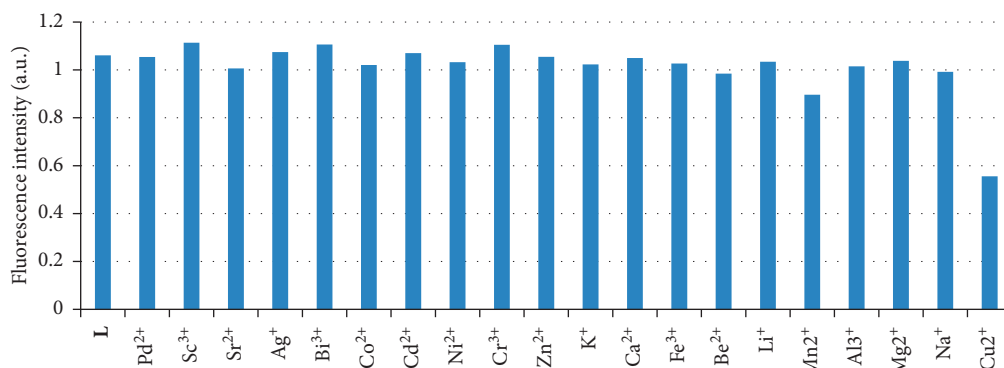


FIGURE 4: The fluorescence intensity at 360 nm of L with the metal ions. L: 2.0×10^{-7} M; metal ion: 2.0×10^{-6} M.

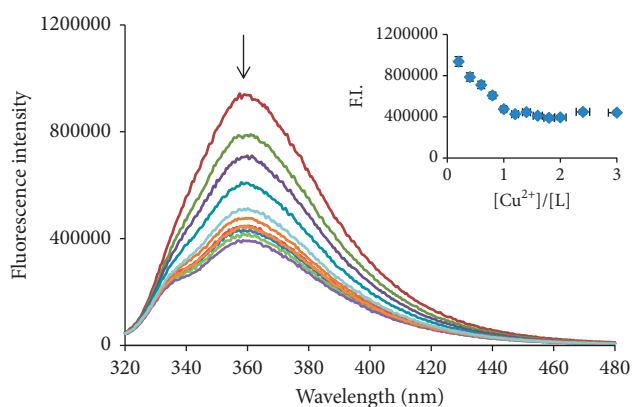


FIGURE 5: The change in the fluorescence spectra of L with the increasing Cu^{2+} ion concentration (from 0 to $30 \mu\text{g/L}$) in acetonitrile-water (1:1). Inset: the molar ratio graph plotted from the change in the fluorescence at 360 nm. L: 2.0×10^{-7} M.

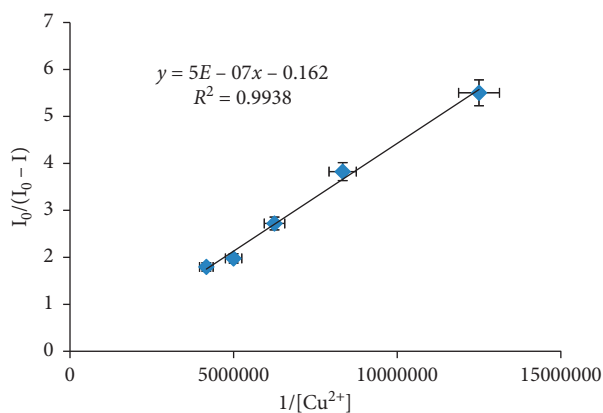


FIGURE 6: The change in $I_0/(I_0-I)$ versus $1/[\text{Cu}^{2+}]$ to determine the complex stability constant.

of the methods proposed in Table 3. Unlike most methods in the literature, the measurement process is only a few minutes.

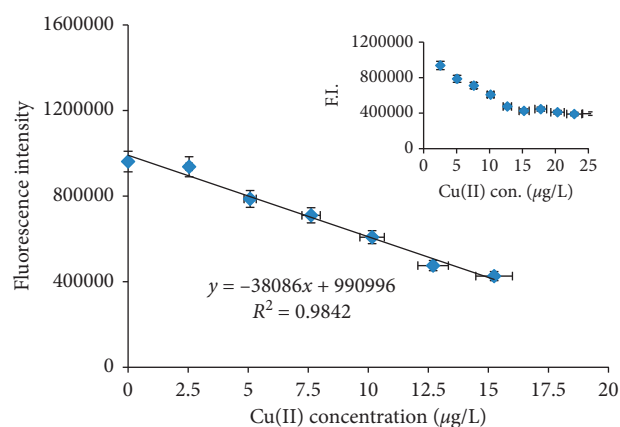


FIGURE 7: The change in the fluorescence intensity with the increasing Cu^{2+} concentration at 360 nm in acetonitrile-water (1:1). L: 2.0×10^{-7} M. Inset: deviation from Beer's law after $15 \mu\text{g/L}$ of Cu^{2+} concentration.

TABLE 1: Analytical performance data for the Cu^{2+} determination method.

Wavelength (nm)	360
Limit of detection ($\mu\text{g/L}$)	0.28
Limit of quantification ($\mu\text{g/L}$)	0.84
Linear range ($\mu\text{g/L}$)	0–15.2
Ligand concentration (M)	2.0×10^{-7}
Ligand volume (mL)	2.0
Total volume (mL)	4.0
Solvent	Acetonitrile : water (1:1)
Waiting time	1-2 min
Correlation coefficient (R^2)	0.9842

TABLE 2: Analytical performance data for the Cu^{2+} determination method.

Added (mg/L)	Found (mg/L) \pm RSD (%)	R (%)
5.1	4.9 ± 3.1	96.1
5.1	5.2 ± 0.7	102.0
5.1	5.2 ± 0.4	102.0

TABLE 3: Detection limits of fluorimetric Cu²⁺ determination methods in tap water.

Reagent	LOD	Reference
Schiff base	0.1 nM	[30]
N-CQDs	0.09 μM	[31]
PVA/CdS QDs	0.12 nM	[32]
CA-CdS QDs	9.2 × 10 ⁻⁹ M	[33]
Coordination polymer	3.0 μM	[34]
Fe ₃ O ₄ @SiO ₂ -NH ₂ -morin	7.5 nM	[35]
DPA-capped CdTeQDs	0.4 × 10 ⁻⁹ M	[36]
AuNCs	0.33 nM	[37]
AuNCs	0.9 μM	[38]
CuNCs core/shell NPs	1.3 ppm	[39]
CuNPs	5.6 μM	[40]
CdTeQDs	1.55 × 10 ⁻⁸ M	[41]
CdSe/ZnSQDs	0.14 nM	[42]
Fe ₃ O ₄ -MOFs	0.1 nM	[43]
Fe ₃ O ₄ @SiO ₂	6 nM	[44]
Porous silicon NPs	0.1 μM	[45]
SrF ₂ nanocrystals	2 nM	[46]
Imidazole compound	0.28 μg/L	This study

4. Conclusions

p-Vanillin derivative benzimidazole compound (L) was proposed as highly selective and sensitive fluorescence sensors for Cu²⁺ detection. The fluorescence quenching of L at 360 nm with increasing metal ion concentration provides Cu²⁺ determination in tap water. LOQ value of the proposed method is better than most of the literature and is much under the legal limits in tap water. According to EPA, the maximum contaminant level goal for copper in primary drinking water is 1.3 mg/L. Moreover, using an external calibration graph is enough to determine Cu²⁺ ions in tap water. The proposed method is very simple and has high sensitivity and selectivity to determine copper in tap water.

Data Availability

All data generated or analyzed during this study are included within this published article.

Conflicts of Interest

The author declares that there are no conflicts of interest.

Authors' Contributions

Zafer Ocak carried out all the studies.

Supplementary Materials

A fluorimetric method based on an imidazole compound for Cu²⁺ determination in tap water. Fig. S1: FTIR spectra of the ligand. Fig. S2: ¹H NMR spectra of the ligand. Fig. S3: ¹³C NMR (APT) spectra of the ligand. Fig. S4: mass spectra of the ligand. (*Supplementary Materials*)

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