Journal of Fluorescence (2019) 29:921–931
https://doi.org/10.1007/s10895-019-02404-1

ORIGINAL ARTICLE

4-Quinolone-Carboxamide and Carbothioamide Compounds as Fluorescent Sensors. New Fluorimetric Methods for Cu^{2+} and Fe^{3+} Determination in Tap Water and Soil

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Received: 8 February 2019 / Accepted: 10 June 2019 / Published online: 4 July 2019

Abstract

Ion sensor properties of the carboxamide and carbothioamide compounds carrying 4-quinolone group were investigated by means of emission spectrometry in methanol-water (1:1). The compounds were selectively complexed with Cu^{2+}, Pd^{2+}, and Fe^{3+} among many metal ions. The complex stoichiometry and the stability constant were determined by fluorimetric measurements. The carboxamide compound having phenyl group (**QPO**) showed sensitivity for Fe^{3+} ion with a linear range between 0.1 and 0.7 mg/L. The new method was applied in the determination of iron in the spiked tap water samples and the sandy-soil reference material. A modified standard addition method was used to remove the matrix effect. Limit of detection was 0.03 mg/L for the Fe^{3+} determination method. The carboxamide compound with benzyl group (**QBO**) showed sensitivity for Cu^{2+} ion with linear range 0–0.4 mg/L. There was no matrix effect for copper determination in the spiked tap water samples. The detection limit of the method for Cu^{2+} ion was 0.05 mg/L. The quantification limits of the methods were low enough to determine iron and copper amount in drinking water samples according to EPA.

Keywords Carboxamides · Carbothioamide · Quinolone · Cu^{2+} · Fe^{3+} · Fluorescence method · Complex stability constant

Introduction

Metals are indispensable components of natural life [1]. Also, most of the metals are essential for the human body. For example, studies on the investigation of iron metabolism are still in progress [2]. Another important metal involved in metabolism is copper. Copper, which is involved in the synthesis of collagen, is also an important element for the human. It is found in the structure of proteins to produce some enzymes [3, 4]. As a result, both them has a very important role in metabolism. However, the amount that should be found in the body is also limited. Their deficiencies or excesses cause serious health problems [5–7]. Therefore, there is always a need to develop method for the detection and detection of metals in biological or environmental samples.

Fluoroionophore compounds have been used in the development of selective and sensitive analytical methods for metal ions. The ionophore part complexes selectively with target ion and it provides the selectivity of the method. The fluorophore part signals the complexation between ion and ionophore part through the fluorescence properties [8]. The high fluorescence property of fluorophore group results in the highly sensitive analytical method. Therefore, the fluoroionophore comprising an appropriate ionophore and an effective fluorophore can be used to selectively and sensitively determine the target ion. From this point of view, many

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Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10895-019-02404-1) contains supplementary material, which is available to authorized users.

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fluoroionophore compounds synthesized for metal determination are available in the literature [9–12].

Quinolones are a class of antibiotic compounds that can be isolated from natural products. However, the term quinolone is commonly used for quinolonecarboxylic acids or 4-quinolones. They are also a group of synthetic antibacterial compounds and contain the 4-oxo-1,4-dihydroquinoline (4-quinolone) skeleton. Studies on the biological activities of many compounds based on the quinolone skeleton are available in the literature [13–15]. However, studies on the fluorescence properties of these compounds are limited in the literature [14, 16]. For example, norfloxacin, which has an antibacterial effect in the treatment of urinary tract infections, has been shown to emit strong blue light when stimulated at 350 nm, and these complexes have been reported to be used as a blue-light-emitting diode [16]. The number of analytical studies based on the measurement of the fluorescence properties of compounds containing the 4-quinolone structure is also very limited. For example, a 6-methoxy-4-quinolone compound has been reported to exhibit strong fluorescence with high stoke shift in pH 2 to pH 11 and to be a stable compound that is not sensitive to heat and radiation [17]. In the same study, it has been shown that a similar compound can also be used as a fluorescent labeling reagent for the chromatographic separation of certain carboxylic acids [17]. In another study, it was reported that the 7-hydroxy-4-quinolone derivative compound had pH-dependent and low fluorescence properties and was proposed as Calcein Blue-type metal-fluorescent indicator [18].

A review paper related to the interaction of 4-quinolone class compounds with metal ions and their antibacterial activity has been reported by Turel [19]. In this study, the effects of metal ions on the biological activity of 4-quinolones are described. The structure of metal-quinolone complexes formed with metals such as magnesium, calcium, cobalt, iron, nickel, copper, silver, zinc, cadmium, depending on the substituents in the structure of quinolones are discussed [19]. Despite the fluorescence characteristic expected from the structure of the quinolone compounds, a proposed analytical method based on the change in fluorescence intensity with metal complexation was not included in the literature.

Although the complexation properties of carboxamide [20–26] and carbothioamide compounds [27–31] are well known, they have not yet been proposed as analytical reagents in the literature. Several hydrazine carbothioamide compounds including 4-quinolone structure are found in the proposed positions in the literature [32, 33]. Synthesis of these compounds and their biological properties has been reported [32, 33]. No further studies are available on this type of compounds.

In the present study, ion sensor properties of two new carboxamide compounds and a group of structurally similar compounds were investigated to show their usability as analytical reagents. The fluorophore group in the investigated compounds is the substituted 4-quinolone group. This group has a conjugated π electron system, which provides high fluorescence properties. The ionophore parts in these compounds are hydrazine carboxamide and hydrazine carbothioamide groups. It is well known that hydrazine carboxamide groups complex selectively with such as Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Mn^{2+}, and Zn^{2+} while hydrazine carbothioamide groups complex with the softer metal ions such as Pd^{2+}, Hg^{2+} and Cd^{2+} [27–31]. Therefore, it is thought that the compounds investigated can exhibition sensor properties and can be used as fluorescent sensors for these cations. Moreover, the new determination method for the target metal ion will have an extra advantage because fluorimetric methods are cheaper and simpler than the commonly used atomic methods for metal determination.

Experimental

Chemicals and Materials

In fluorometric measurements, methanol was used (Merck, spectrometric grade). All chemicals for synthesis were provided from Merck. 1000 mg L^{-1} of standard solutions of all of the cations (Merck) were used to prepare working solutions. The tap water sample was used from KTU campus in Trabzon. It was diluted in a ratio of 1/5 before the analysis. Sandy-soil standard reference material, CRM-SA-C, was purchased from High-Purity Standards, Inc.

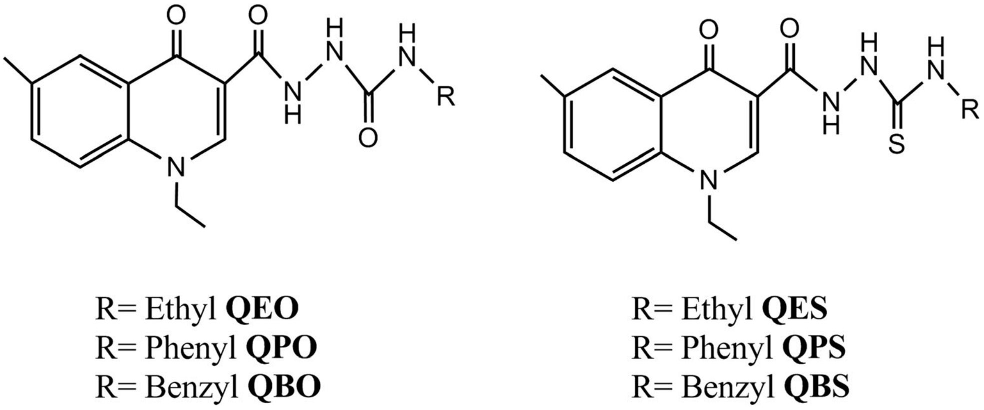
Apparatus

Analytic Jena Specord 210 spectrophotometer was used to record the absorption spectra of the solutions. A spectrofluorimeter (PTI, QM-4/2006) was used for all of the fluorescence measurements. Deionized water was obtained by a Sartorius Milli-Q system (arium® 611UV).

Measurements

Methanolic solutions of the ligands were used in the fluorometric measurements. Emission spectra of the ligands in methanol containing 10 M equivalents of Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Ag^{+},

Scheme 1 The structure of the carboxamides and carbothioamides carrying 4-quinolone group



Au^{3+}, Ti^{4+}, Tl^{+}, W^{6+}, Y^{3+}, Sn^{2+}, and Pd^{2+} were measured by using 1-cm quartz cell. The excitation wavelength was 320 nm for all ligands. Fluorescence emission spectra were recorded in the range of 325–650 nm with the slit width 1.0 nm.

The molar-ratio method was used to predict the stoichiometry of the complexes by using the data of fluorometric titrations. The known method in the literature was applied to calculate the stability constants [34].

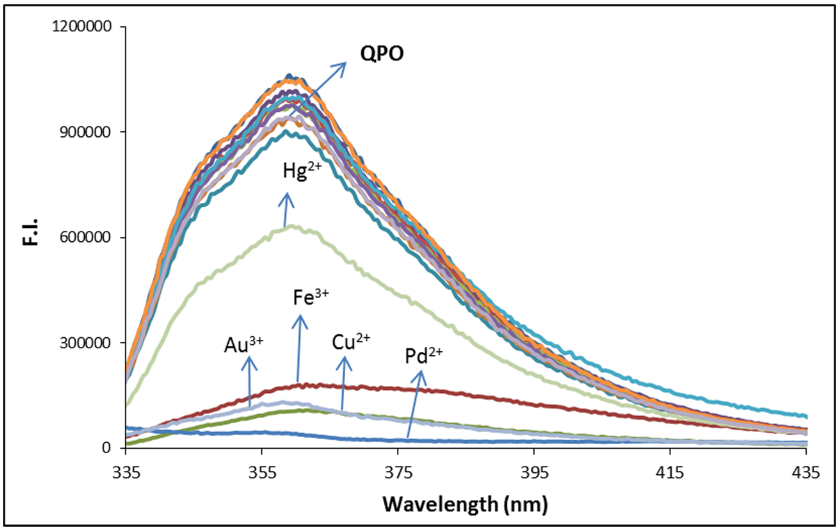
A kind of standard addition method [35–37] was used to determine Fe^{3+} in the spiked tap water sample and the sand-soil reference material with **QPO**. An external calibration graph was enough for the determination of Cu^{2+} in the spiked tap water sample with **QBO**. A known digestion procedure was used for the sandy-soil reference material in a closed microwave system [37].

Synthesis of the Ligands

The compounds used in this study were prepared according to the method in the literature [38]. 1- (7-Chloro-1-ethyl-6-fluoro-4-oxo-1,4-dihydroquinoline-3-carbonyl) -4-etilsemikarbazid (**QEO**) and 4-Benzyl-1-(7-chloro-1-ethyl-6-fluoro-4-oxo-1,4-dihydroquinoline-3-carbonyl) semicarbazide (**QBO**) are new compounds and they synthesized from the reaction ethyl isocyanate and benzyl isocyanates with 1-etil-6-metil-4-okso-1,4-dihidrokinolin-3-karbohidrazid according to the previous method [38].

QBO: FTIR (ν_{max}, cm^{-1}): 3327 (NH), 3039 (Ar-CH), 2920 (aliphatic-CH), 1668 (C=O), 1605 (C=O). ^{1}H-NMR (DMSO-d_6, δ ppm): 1.35 (t, 3H, CH_3, $J=$ 16.0 Hz), 4.47–4.52 (m, 2H, CH_2), 4.71 (d, 2H, CH_2, $J=8.0$ Hz), Ar-H: [7.29 (d, 5H, $J=4.0$ Hz), 7.67 (t,

Fig. 1 The effect of cations on the fluorescence spectra of **QPO**. **QPO** concentration = 5.0 × 10^{-5} M. Ion concentration = 5.0×10^{-4} M



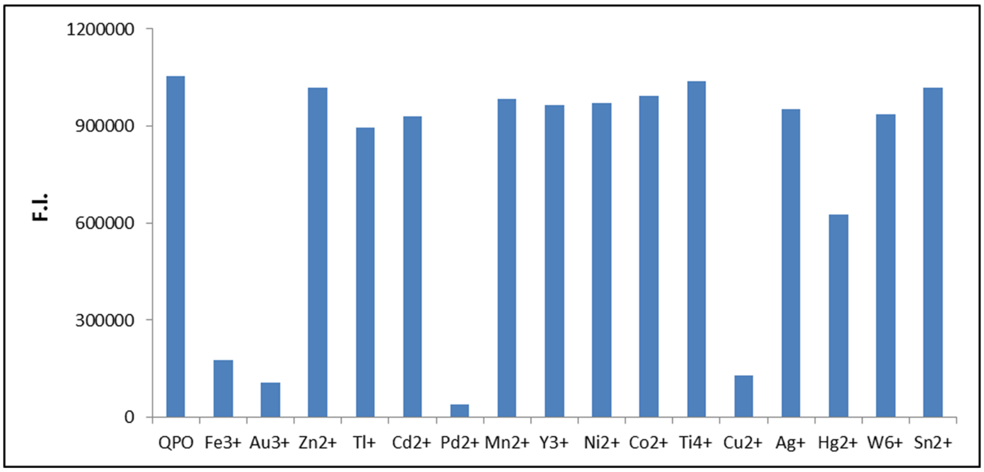


Fig. 2 The effect of cations on the fluorescence spectra of **QPO** at 360 nm. **QPO** concentration = 5.0×10^{-5} M. Ion concentration = 5.0×10^{-4} M

1H, $J = 12.0$ Hz), 7.80 (d, 1H, $J = 8.0$ Hz)], 8.13 (s, 1H, quinolone-CH), 8.86 (s, 3H, NH).^{13}C-NMR (DMSO-d_6, δ ppm): 15.12 (CH_3), 21.03 (CH_3), 47.26 (CH_2), 48.73 (CH_2), Ar-C: [117.82 (CH), 126.12 (CH), 127.05 (CH), 127.51 (C), 127.53 (2CH), 128.51 (2CH), 135.01 (CH), 135.46 (C), 137.08 (C)], 110.57 (quinolone-C3), 147.75 (quinolone-C2), 159.42 (C=O), 162.85 (C=O), 175.31 (quinolone-C4). EI MS m/z (%): 380.99 ($[M+2]^+$, 19), 273.81 (58), 132.89 (100).

QEO: FTIR (ν_{max}, cm^{-1}): 3245 (NH), 3033 (Ar-CH), 2980 (aliphatic-CH), 1662 (C=O), 1604 (C=O). ^{1}H-NMR (DMSO-d_6, δ ppm): 0.99 (t, 3H, CH_3, $J = 16.0$ Hz), 1.36 (t, 3H, CH_3, $J = 12.0$ Hz), 3.04 (s, 2H, CH_2), 4.45–4.50 (m, 2H, CH_2) Ar-H: [7.78 (d, 1H, $J = 8.0$ Hz), 8.11 (s, 1H)], 8.81 (s, 1H, quinolone-CH), 11.21 (s, 3H, NH).^{13}C-NMR (DMSO-d_6, δ ppm): 15.04 (CH_3), 15.95 (CH_3), 21.02 (CH_3), 34.53 (CH_2), 48.71 (CH_2), Ar-C: [117.74 (CH), 126.07 (CH), 127.54 (C), 134.87 (CH), 135.28 (C), 137.09 (C)], 110.57 (quinolone-C3), 147.63 (CH), 158.06 (C=O), 164.49 (C=O), 175.28 (quinolone-C4). EI MS m/z (%): 316.86 ($[M]^+$, 18), 338.99 ($[M\text{-}1+Na]^+$, 100). The spectra were given in Supporting Information.

Results and Discussion

The Effect of Ions on the Fluorescence Spectra and Complexation

The effects of cations on the fluorescence spectra of the ligands were investigated in methanol-water (1:1). The changes in the fluorescence spectra and selectivity data were given in Supporting Information. As seen from Figs. S1-S8, Hg^{2+}, Fe^{3+}, Cu^{2+}, Pd^{2+}, and Au^{3+} ions cause pronounced quenching in the fluorescence spectra of **QPS**, **QBS**, **QES** and **QEO** ligands. However, the selectivity is not high for these metal ions in case of

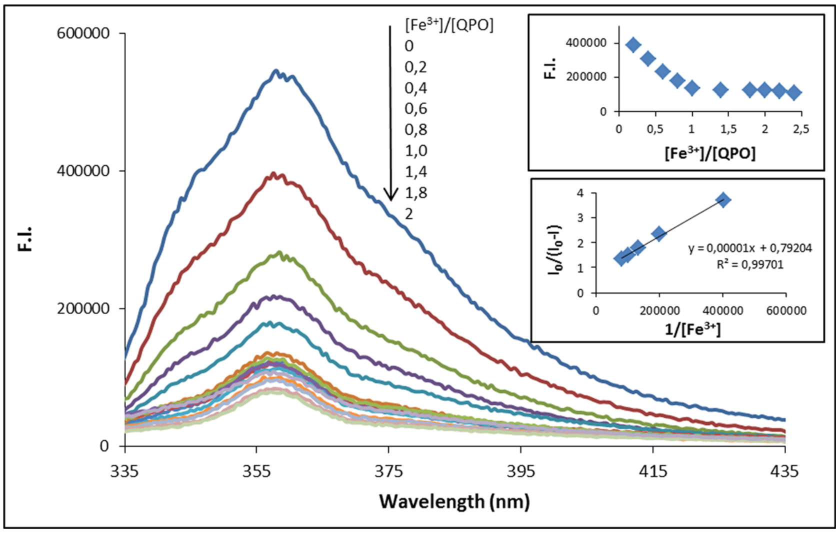


Fig. 3 Change in the fluorescence spectra of **QPO** with Fe^{3+} concentration. Inset: Molar ratio plot (above). The graph for calculation of stability constant (below). Measurements were carried out at 360 nm. **QPO** concentration = 5.0×10^{-5} M

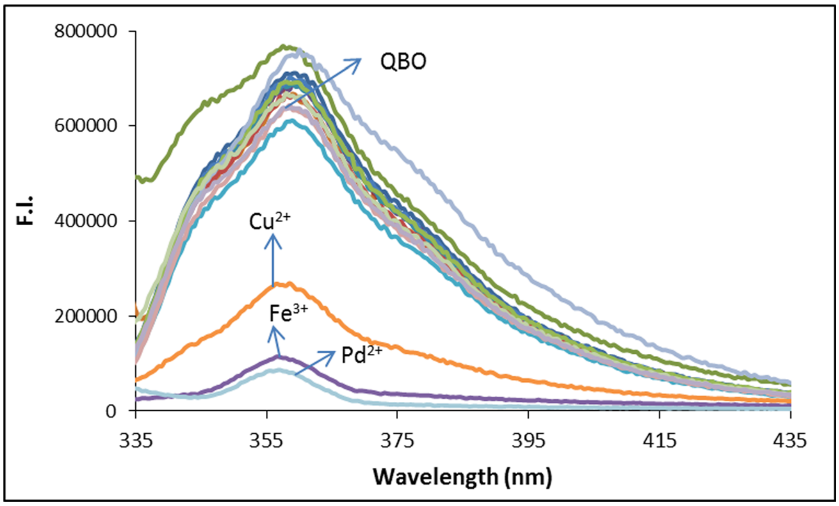


Fig. 4 The effect of cations on the fluorescence spectra of **QBO**. **QBO** concentration = 6.3 × 10^{-6} M. Ion concentration = 6.3 × 10^{-5} M

the three carbothioamide ligands and the carboxamide compound, **QEO** (Scheme 1).

Figure 1 shows the effect of cations on the fluorescence spectra of the carboxamide compound carrying phenyl group, **QPO**. As seen from Fig. 1, there is considerable quenching on the fluorescence spectra of **QPO** with Au^{3+}, Fe^{3+}, Cu^{2+} and Pd^{2+} among the investigated cations. However, many cations did not cause any changes in the fluorescence spectra. Figure 2 shows the changes in the fluorescence intensity of **QPO** with ions at 360 nm. As seen from Fig. 2, **QPO** shows selectivity for Au^{3+}, Fe^{3+}, Cu^{2+} and Pd^{2+} among the tested ions.

Fluorimetric titrations were performed with Au^{3+}, Fe^{3+}, Cu^{2+}, and Pd^{2+} by using **QPO** to study the interaction between the ligand and the metal cation. The stable 1:1 complex was predicted with the only Fe^{3+} among those metal ions. Figure 3 shows the regular fluorescence quenching with increasing Fe^{3+} concentration. The molar ratio plot was given above inset in Fig. 3. From this plot, it is clear that the composition of Fe^{3+}-**QPO** complex is 1:1. The stability constant of the complex was calculated from the equation of the line according to the known method [34]. The below inset in Fig. 3 shows the graph of $I_0/(I_0\text{-}I)/I_0$ versus $1/[Fe^{3+}]$ to calculate the complex stability constant. Log K value was 4.90 for Fe^{3+}-**QPO** complex according to this equation.

Figure 4 shows the effect of cations on the fluorescence spectra of the carboxamide compound with a benzyl group, **QBO**. As different from that of **QPO**, **QBO** shows selectivity for Fe^{3+}, Cu^{2+}, and Pd^{2+} (Fig. 5). The other cations did not cause any changes in the fluorescence intensity of **QBO** at 360 nm (Fig. 5).

For Fe^{3+}, Cu^{2+} and Pd^{2+} ions, fluorimetric titrations were performed with **QBO** to disclose metal-ligand interaction. As different from those of **QPO**, it is predicted that the carboxamide compound with benzyl group

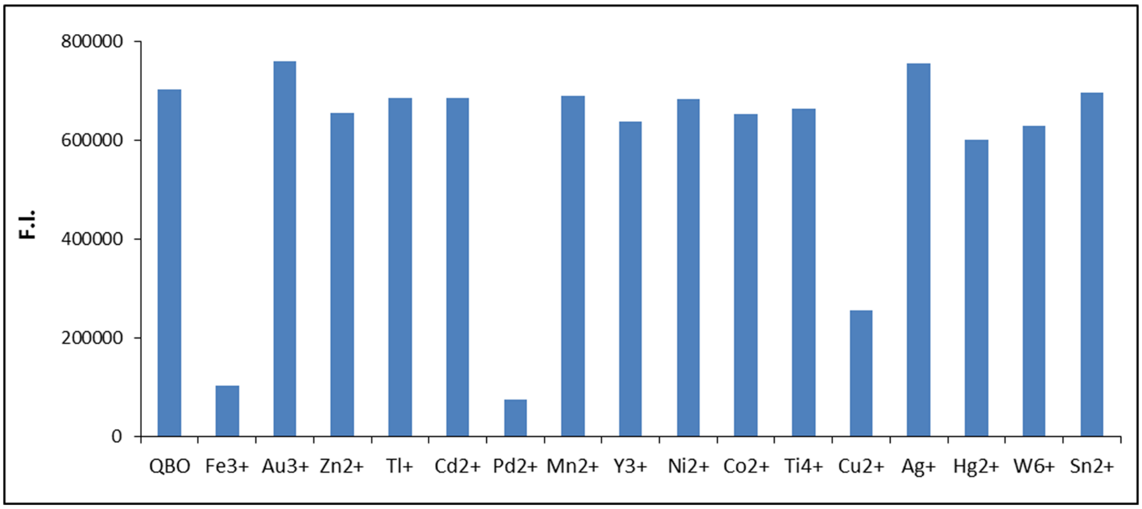


Fig. 5 The effect of cations on the fluorescence spectra of **QBO** at 360 nm. **QBO** concentration = 6.3 × 10^{-6} M. Ion concentration = 6.3 × 10^{-5} M

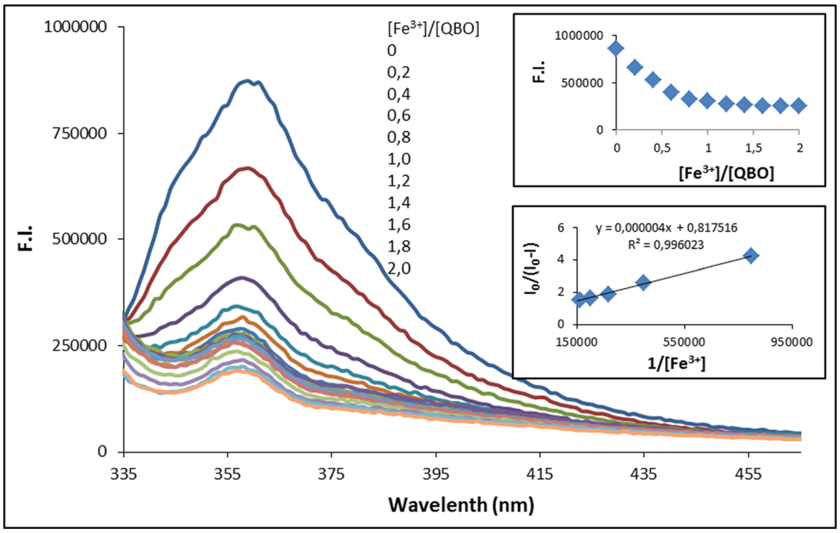


Fig. 6 Change in the fluorescence spectra of **QBO** with Fe^{3+} concentration. Inset: Molar ratio plot (above). The graph for calculation of stability constant (below). Measurements were carried out at 360 nm. **QBO** concentration = 6.3×10^{-6} M

QBO forms the stable 1:1 complex for the three cations. Figure 6 shows the regular fluorescence quenching with increasing Fe^{3+} concentration in case of **QBO**. The molar ratio plot was given above inset in Fig. 6. From this plot, it is clear that the composition of Fe^{3+}-**QBO** complex is 1:1. The stability constant of the complex was calculated from the equation of the line in the inset graph (below) in Fig. 6. Log K value was 5.31 for Fe^{3+}-**QBO** complex according to this equation.

Figures 7 and 8 show fluorimetric titration results for **QBO** with Cu^{2+} and Pd^{2+} ions, respectively. As seen from Figs. 7 and 8, **QBO** forms the stable 1:1 complex with these ions. Interestingly, **QEO** compound carrying ethyl group form a stable 1:1 complex with only Pd^{2+} ion (Fig. 9).

Table 1 indicates the stability constant of the 1:1 complex with the ligands. As can be seen from Table 1, the carbothioamide compounds form a stable 1:1 complex with only the Fe^{3+} from the tested ions. The most stable complex of these compounds is the ethyl group bearing, **QES**. Log K value is calculated as 5.15 for Fe^{3+}-**QES** complex. The **QPO** compound carrying the phenyl group between carboxamide compounds also shows similar behavior. It was determined

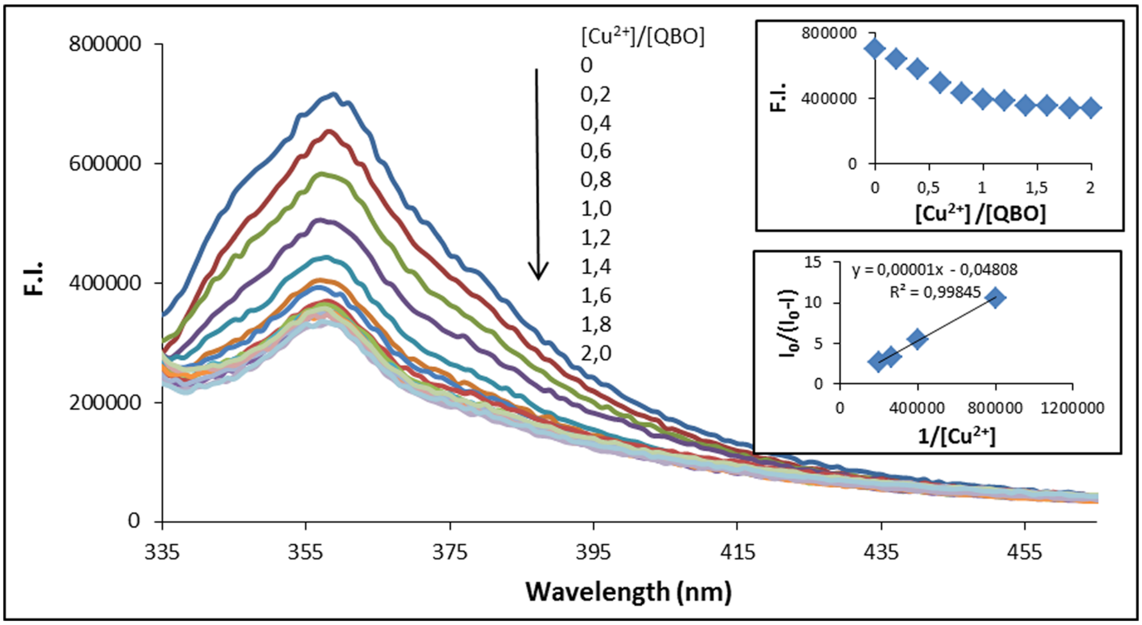


Fig. 7 Change in the fluorescence spectra of **QBO** with Cu^{2+} concentration. Inset: Molar ratio plot (above). The graph for calculation of stability constant (below). Measurements were carried out at 360 nm. **QBO** concentration = 6.3×10^{-6} M

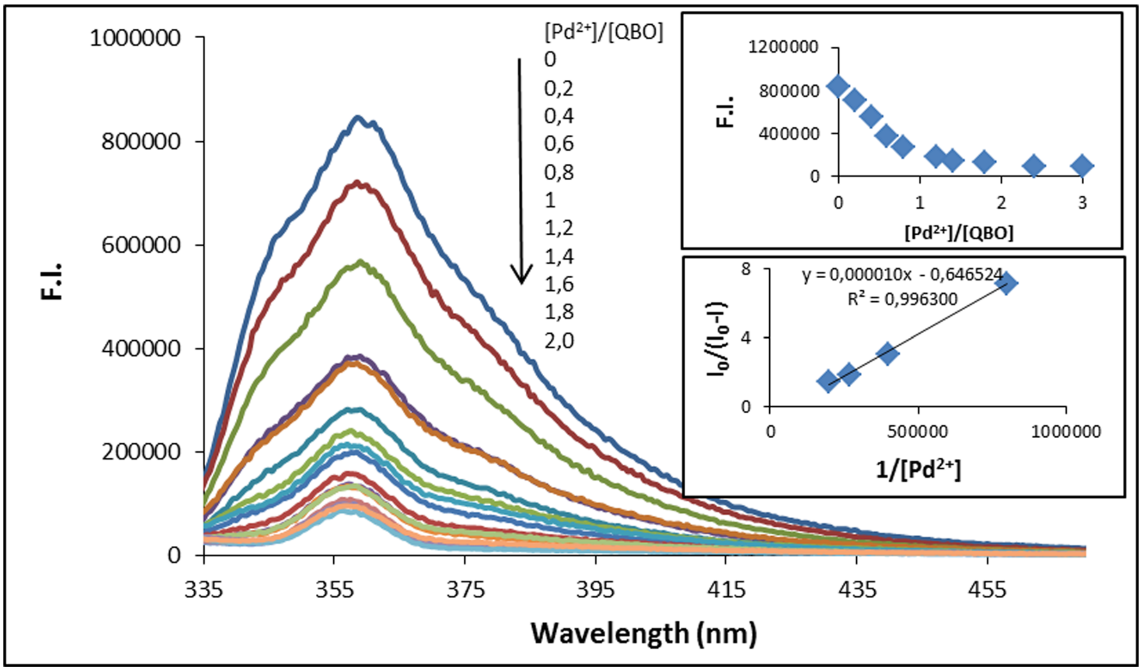


Fig. 8 Change in the fluorescence spectra of **QBO** with Pd^{2+} concentration. Inset: Molar ratio plot (above). The graph for calculation of stability constant (below). Measurements were carried out at 360 nm. **QBO** concentration = 6.3×10^{-6} M

that only the Fe^{3+} ion formed a stable complex with **QPO**. The stability constant with 4.90 is closer to that of **QBS**. The behavior of carboxamide compounds carrying benzyl and ethyl group is more interesting. Of these compounds, the compound with benzyl group gives a stable complex with the three ions, whereas the ethyl group-bearing carboxamide compound **QEO** only forms a stable complex with Pd^{2+}. The Pd^{2+} complex of **QEO** is also the most stable of the six compounds examined. Log K value is calculated as 5.83 for Pd^{2+}-**QEO** complex. These results indicate that the oxygen and sulfur donor atoms in the main structure of

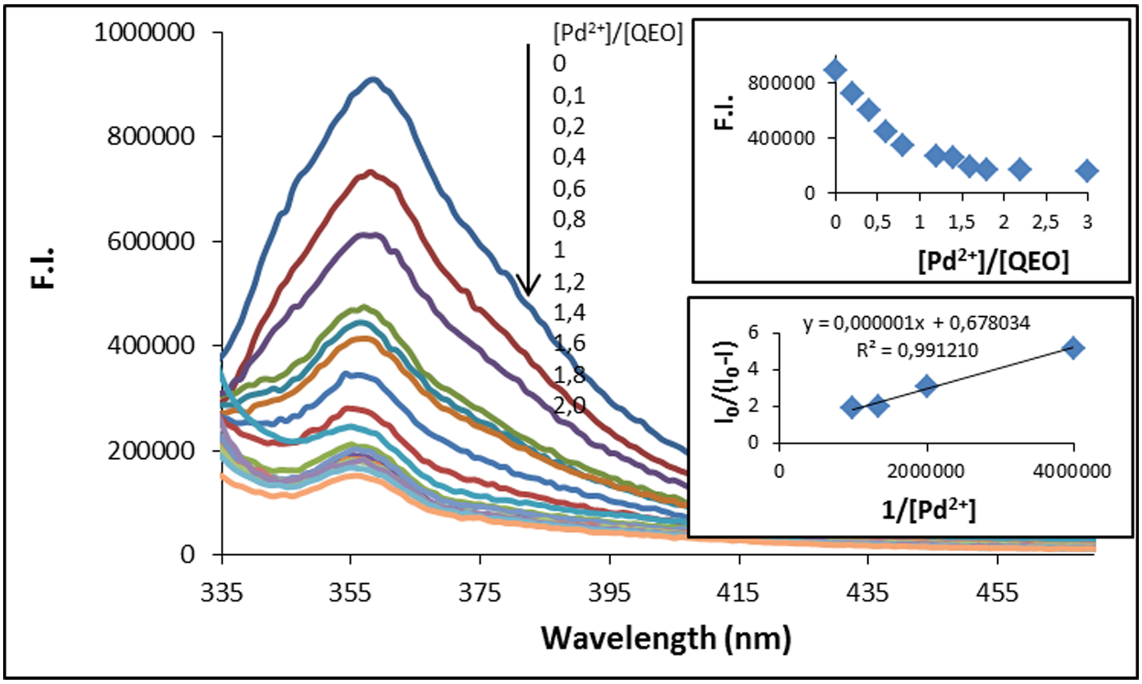


Fig. 9 Change in the fluorescence spectra of **QEO** with Pd^{2+} concentration. Inset: Molar ratio plot (above). The graph for calculation of stability constant (below). Measurements were carried out at 360 nm. **QEO** concentration = 1.3×10^{-5} M

Table 1 The stability constants of 1:1 complex of ligands in methanol-water (1:1)

Ligand	Complex stability constant (Log K)		
	Fe^{3+}	Cu^{2+}	Pd^{2+}
QFS	4.96 ± 0.22	–	–
QBS	4.89 ± 0.15	–	–
QES	5.15 ± 0.19	–	–
QPO	4.90 ± 0.36	–	–
QBO	5.31 ± 0.11	3.68 ± 0.25	4.81 ± 0.29
QEO	–	–	5.83 ± 0.21

the ligands and the alkyl substituents in the end groups are effective in complex formation.

Analytical Studies

All compounds were tested to use as a fluorescent sensor. Although the three carbothioamide compounds complex with Fe^{3+} selectively, they could not be used as a fluorescent reagent in iron determination. However, a suitable calibration graph from the titration data with the carboxamide compound, **QPO**, was formed to determine Fe^{3+} ion (Fig. 10). There was good correlation constant with $R^2 = 0.9848$. Beer Law's deviation was observed after 0.7 mg/L. Therefore, **QPO** was tested as an analytical ligand to determine Fe^{3+} ion. It is detected that **QPO** is a suitable ligand to determine Fe^{3+} ion in tap water and soil samples.

The Proposed Method for Fe^{3+} Determination

A constant amount of Fe^{3+} (0.05 mg/L), 2 mL of **QPO** (1.3×10^{-5} M), and an aliquot sample solution (0.1 mg/L) was added to all tubes, except for the first tube. Increasing Fe^{3+} amounts were added to the third and next tubes before final volumes in all tubes were completed to 4 mL with deionized water. Fluorescence intensity of all solutions was measured at 360 nm by exciting at 320 nm. The Fe^{3+} concentration was calculated from Eq. 1

Table 2 Analytical criteria of the proposed method for Fe^{3+} determination with **QPO**

Excitation wavelength (nm)	320
Emission wavelegth (nm)	360
Detection limit (LOD) (mg/L)	0.03
Quantification limit (LOQ) (mg/L)	0.10
Linear range (mg/L)	0.1–0.7
Constant Fe^{3+} concentration (mg/L)	0.05
Ligand concentration (mol/L)	1.3×10^{-5} M
Ligand volume (mL)	2
Total volume (mL)	4
Solvent	methanol:water (1:1)
Waiting time before measurement	1–2 min.
The correlation coefficient (R^2)	0.9848

$$C_x = (I - I_0)/m \quad (1)$$

C_x is the Fe^{3+} concentration of the sample in the tubes, I and I_0 are the fluorescence intensities of the first and second tubes, respectively, in Eq. 1. m represents the slope of the standard addition graph. The difference between I and I_0 corresponds to the Fe^{3+} concentration of the sample.

The Method Validation for Fe^{3+} Determination

A linear response of the fluorescence intensity as a function of Fe^{3+} concentration at 360 nm was observed from 0.1 mg/L to 0.7 mg/L with linearly dependent coefficient $R^2 = 0.9848$ (Fig. 10). The LOD ($3xS_d/m$) and LOQ ($9xS_d/m$) were determined by the standard deviation of eleven measurements of the blank response (S_d) and the slope of the calibration line (m) according to the IUPAC recommendations. The LOD and LOQ values were 0.03 mg/L and 0.10 mg/L, respectively. The accuracy of the method was showed by recovery measurements. A kind of standard addition method was used to determine Fe^{3+} concentration in tap water samples (0.1 mg/L, Fig. S9). The recovery rate was above 96.6%. Also, standard reference material was analyzed to show the suitability in the determination of iron content in soil samples. The results obtained with the proposed method were not different from the reference value as statistically according to the t-student test. The intra-day and inter-day precision were calculated by analyzing three spiked tap water samples. The precision, expressed as relative standard deviation (RSD%), was calculated as 3.32 for the intra-day measurements. Inter-day precision was found as 3.52. In the measurements made for the standard soil-sand reference material for the same concentration, it was found that the RSD% was 1.69 and 2.94 in inter and intra-day precision measurements, respectively. The analytical performance data for the proposed method under the optimized conditions are given in Table 2. The results showed that the method can be used for the determination of iron amount in water and soil samples.

The Proposed Method for Cu^{2+} Determination

An external calibration graph was used to determine Cu^{2+} in a tap water sample with **QBO** (6.3×10^{-6} M). To prepare the calibration solutions, the standard Cu^{2+}

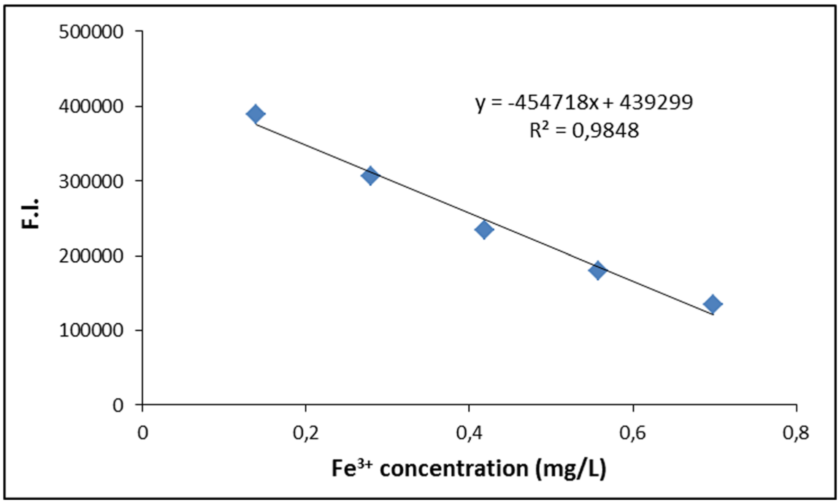


Fig. 10 Change in the fluorescence intensity of **QPO** with Fe^{3+} concentration. **QPO** concentration = 5.0×10^{-5} M

solution was diluted appropriately with deionized water to give concentrations between 0 and 0.4 mg/L. Fig. S10 shows the calibration plot in the determination of Cu^{2+} (0.1 mg/L) in a spiked tap water sample.

The Method Validation for Cu^{2+} Determination

A linear response of the fluorescence intensity as a function of Cu^{2+} concentration at 360 nm was observed from 0 mg/L to 0.4 mg/L with linearly dependent coefficient $R^2 = 0.9929$ (Fig. 11). LOD and LOQ values were determined in a similar way as in iron determination. These values were 0.05 mg/L and 0.15 m/L, respectively. The accuracy of the method was shown by spiking-recovery measurements. An external calibration graph was enough to determine Cu^{2+} concentration in tap water samples (0.16 mg/L). The recovery rate was calculated at 96.5%. The intra-day and inter-day precision were determined by analyzing three spiked tap water samples. It was found that the %RSD was 2.00 and 2.80 in inter and intra-day precision measurements, respectively. The analytical performance data for Cu^{2+} determination are given in Table 3. The results showed that the method can be used for the determination of copper in water samples.

Conclusions

Ion sensor properties of a series of hydrazine carboxamide and hydrazine carbothioamide compounds carrying 4-quinolone group were investigated in methanol: water (1:1) media. The compounds have high fluorescence intensity that allows examination of the metal-ligand interaction. Fluorimetric titrations with metal ions disclosed the 1:1 (M:L) complex composition for the ligands. The carbothioamide compounds were complexed selectively with Fe^{3+} ion among a variety of

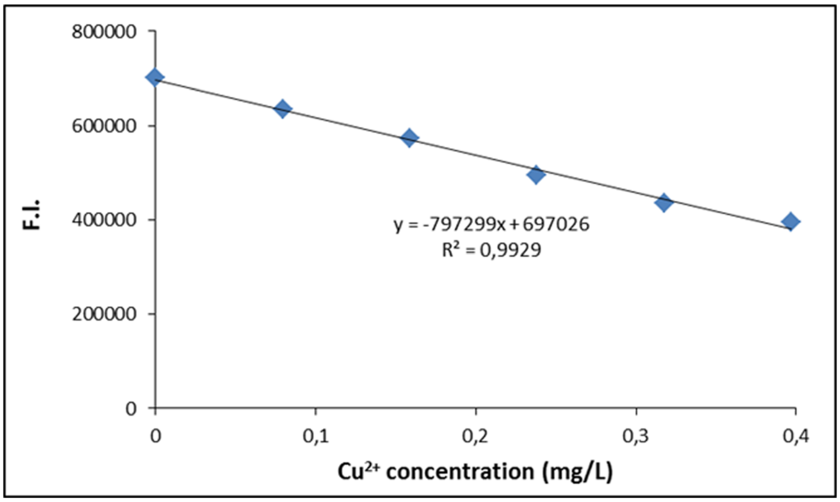


Fig. 11 Change in the fluorescence intensity of **QBO** with Cu^{2+} concentration. **QBO** concentration = 6.3×10^{-6} M

Table 3 Analytical criteria of the proposed method for Cu^{2+} determination with **QBO**

Excitation wavelength (nm)	320
Emission wavelegth (nm)	360
Detection limit (LOD) (mg/L)	0.05
Quantification limit (LOQ) (mg/L)	0.15
Linear range (mg/L)	0–0.4
Constant Cu^{2+} concentration (mg/L)	0.05
Ligand concentration (mol/L)	6.3×10^{-6} M
Ligand volume (mL)	2
Total volume (mL)	4
Solvent	methanol:water (1:1)
Waiting time before measurement	1–2 min.
The correlation coefficient (R^2)	0.9929

metal ions. However, only the carboxamide compound carrying phenyl group **(QPO)** as fluorescent chemosensor could be used to determine Fe^{3+} ion in real samples. A kind of standard addition method was used to remove the matrix effect for iron determination with **QPO**. Also, the carboxamide compound carrying benzyl group (**QBO**) was used as a fluorescent sensor to determine Cu^{2+} ion in tap water. An external calibration procedure was enough to determine copper with **QBO**. The proposed methods are relatively economical, time-saving and simpler compared to convenient metal determination methods.

Acknowledgements This work was supported by The Scientific and Technological Research Council of Turkey (TUBITAK, project no: 117Z552).

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