TÜBİTAK

Turkish Journal of Chemistry

http://journals.tubitak.gov.tr/chem/

Research Article

Turk J Chem
(2018) 42: 1045 – 1055
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doi:10.3906/kim-1712-40

A rapid and sensitive spectrofluorometric method for the determination of Au(III) based on fluorescence quenching of a 1,3,5-triphenyl-2-pyrazoline

Aysel BAŞOĞLU[1,*], **Ümmühan OCAK**[2], **Seda FANDAKLI**[3,4], **Nurettin YAYLI**[4]

[1]Department of Chemical and Chemical Processing Technologies, Vocational School, Gümüşhane University, Gümüşhane, Turkey

[2]Department of Chemistry, Faculty of Sciences, Karadeniz Technical University, Trabzon, Turkey

[3]Vocational School of Health Services, Avrasya University, Trabzon, Turkey

[4]Faculty of Pharmacy Sciences, Karadeniz Technical University, Trabzon, Turkey

Received: 18.12.2017 • **Accepted/Published Online:** 02.04.2018 • **Final Version:** 03.08.2018

Abstract: A simple, rapid, sensitive, and low-cost spectrofluorometric method was developed for the determination of Au(III) using 5-(2,3-dimethoxyphenyl)-3-(4-methoxyphenyl)-1-phenyl-4,5-dihydro-1H-pyrazole **(L)** in ethanol/water. The method is based on the change in the fluorescence intensity at 464 nm after excitation at 355 nm as a result of the reaction between the ligand and Au(III). The fluorescent emission of ligand at 464 nm decreased with the increasing of Au(III) concentration. The ligand concentration, pH effect, response time, and effect of foreign ions were determined. From the results of fluorescence titration experiments, it was found that the ligand (1×10^{-7} M) was selective and sensitive to Au(III) in EtOH-H_2O (1:1, v/v, phthalate buffer, pH 4.0). The calibration curve showed good linearity in the concentration range of 17.4–237.6 μg L^{-1} Au(III). The limits of detection and quantification were 5.2 and 17.4 μg L^{-1} Au(III) with a response time of 1 min, respectively. Satisfactory accuracy was obtained for standard reference material (CRM-SA-C Sandy Soil C). The proposed method was successfully applied to the determination of Au(III) in tap water, sea water, and stream water samples, and high levels of recovery were obtained.

Key words: Gold determination, spectrofluorometric analysis, fluorescence quenching, 1,3,5-triphenyl-2-pyrazoline

1. Introduction

Gold is one of the most interesting noble metals due to its important role in the fields of biology, environment, and industry, although it has low abundance in natural samples. For chemistry, gold has many applications in catalysis, sensing, nanoelectronics, and surface and synthetic chemistry.[1–3] The content of gold is about 4 ng g^{-1} in basic rocks, 1 ng g^{-1} in solids, 0.2 ng mL^{-1} in river water, and 0.05 ng mL^{-1} in sea water.[4–6] Due to the antiinflammatory properties of gold ions, they are often used as drugs in the treatment of diseases such as rheumatoid arthritis,[7] asthma,[8] tuberculosis,[8] malaria,[8] and cancer.[8]

Despite their interesting medicinal properties, gold ions such as gold chloride are highly reactive and potentially toxic to the human body as they cause important damage to the liver, kidneys, and peripheral nervous system.[9,10] Since gold ions are particularly known to strongly bind DNA/enzymes, they cause DNA cleavage and disruption of the nervous system.

*Correspondence: abasoglu@gumushane.edu.tr

Due to the low concentration of gold ions in environmental samples and their great importance, many reports exist on the analysis of trace amounts of gold ions in water and several matrixes. Therefore, various analytical techniques such as spectrophotometry,[11] atomic absorption spectrometry (AAS),[12] thermospray flame furnace atomic absorption spectrometry (TS-FF-AAS),[13] carbon slurry sampling graphite furnace atomic absorption spectrometry (GFAAS),[14] inductively coupled plasma atomic emission spectrometry (ICP-AES),[15] inductively coupled plasma mass spectrometry (ICP-MS),[16] and electrochemistry[17] have been reported for detecting the amount of gold ions. However, these methods are time-consuming, have interference problems, and require complicated and expensive instruments. The significance of analyses of trace amounts of metal ions by fluorescence spectroscopy has been increasing thanks to its intrinsic sensitivity, selectivity, and the ability for quick real-time scanning. Several gold ion-selective molecular sensors based on various fluorophore units including rhodamine,[18] BODIPY,[19] fluorescein,[20] coumarin,[21] and naphthalimide[22] dyes have been reported in the literature. These methods include the use of many chemicals, long complexation and extra processes,[21–23,24] time-consuming analysis,[25] and pretreatment before analysis.[26]

Pyrazolines are known to have high fluorescence quantum yields as nitrogen-containing five-membered heterocyclic fluorescent compounds. Beside having hole-transfer performance,[27] triphenyl pyrazoline derivatives have been approved as blue emitters.[28] Owing to their exciting moiety, pyrazoline derivatives possess a wide spectrum of biological activities such as antimicrobial, antinociceptive, antiamoebic, anticancer, antidepressant, antiinflammatory, antibacterial, and antitumor, as well as roles in analytical applications and dye and extraction metallurgy.[29–33] In addition, they are important due to their wide applications for the optical brightening of textile fibers, plastics, and paper.[34] Due to their wide range of uses, many studies on the synthesis of derivatives of such compounds and the examination of their absorbance and emission behaviors have been introduced in the literature. Among the other derivatives of pyrazoline, the most studied pyrazoline-type compounds are 1,3,5-triaryl-2-pyrazolines. A few studies of the effect of metal ions on the absorption and fluorescence properties of pyridylpyrazole derivatives have been reported.[35–37] According to our investigation, in the literature there are just a few reports of pyrazoline-based chemosensors utilized for determination of some ions (Zn(II), Al(III), Cu(II), Ni(II)),[38–45] except Au(III) ions. Pyrazoline derivatives utilized for ion-sensing applications as chemosensors have been far less studied compared to other applications.

In this report, (5-(2,3-dimethoxyphenyl)-3-(4-methoxyphenyl)-1-phenyl-4,5-dihydro-1H-pyrazole) (**L,** a 1,3,5-triphenyl-2-pyrazoline compound) was used as a fluorescence chemosensor for the detection of Au(III) by performing a spectrofluorometric method. This proposed method can be accomplished simply and quickly at a reasonable cost when checked against many methods in the literature. According to the investigations of references, this ligand has not been used for any analytical applications. In addition, a pyrazoline derivative compound was used for the first time in the determination of gold by a spectrofluorometric method in this study. The aim of this work is to suggest an alternative simple method for gold determination by investigating the reaction between **L** and Au(III).

2. Results and discussion

2.1. Fluorescence performance of ligand for sensing Au(III)

The fluorescence spectra of the ligand gave a maximum emission of 464 nm by exciting at 355 nm. The effects of various metal ions on the fluorescence intensity of the ligand were investigated by monitoring the fluorescent signal after adding Ag(I), Au(III), Zn(II), Mn(II), Hg(II), Cd(II), Ni(II), Bi(II), Pb(II), Co(II), Cu(II), Fe(III),

Sn(II), Pd(II), Li(I), Na(I), K(I), Tl(I), NH_4(I), Ba(II), Mg(II), Ca(II), Be(II), Al(III), Se(II), Sr(II), Sc(II), As(II), Sb(II), Y(III), Cr(III), Al(III), Sc(III), Tl(III), V(III), Sb(III), Bi(III), B(III), and Ti(IV) ions (5×10^{-6} M) to the ligand solutions (1×10^{-7} M) (Figure 1).

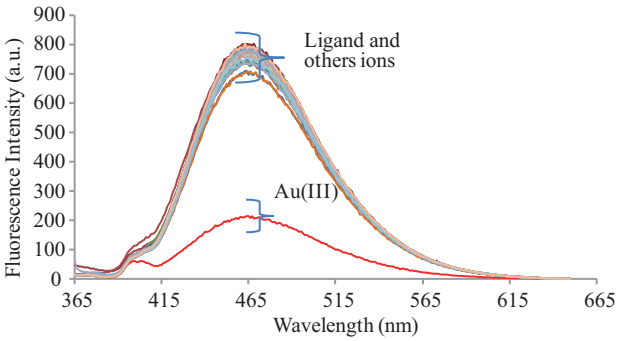

Figure 1. The effect of ions on the fluorescence spectra of the ligand in ethanol:water (1:1). [**L**] = 1.0×10^{-7} M. [Au(III)] = [Other ions] = 5.0×10^{-6} M. λ_{exc}: 355 nm.

The fluorescent signal of the ligand had no serious change in the presence of the abovementioned ions except for Au(III). Au(III) caused a significant decrease in fluorescence response of the ligand at 464 nm. Spectrofluorometric titrations were carried out between the ligand and Au(III) to examine the fluorescence quenching based on Au(III) ions (Figure 2).

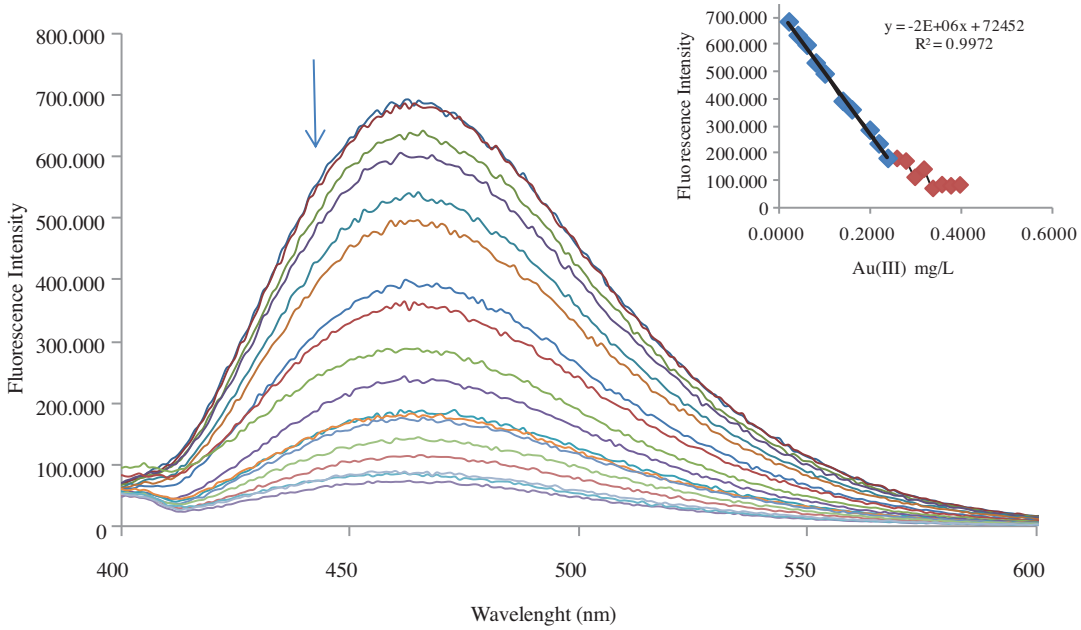

Figure 2. Fluorescence spectra (λ_{exe}: 355 nm, λ_{em}: 464 nm) for the spectrofluorimetric titration of ligand with Au(III) ions in ethanol-water (1:1). [**L**] = 1×10^{-7} M. [Au(III)] = 19.8–237.6 μg L^{-1}. Inset: The fluorescence intensity changes of ligand during the addition of 19.8–237.6 μg L^{-1} Au (III). λ_{em}: 464 nm.

2.2. pH effect

The study of the effect of pH on the fluorescence spectra of the free ligand and ligand-Au(III) solutions was conducted under different pH conditions (Supplementary Information, Figure S1). Ligand (1×10^{-7} M) and ligand-Au(III) (equal concentration, 1×10^{-7} M) systems show similar behaviors with pH changes. As can be seen from Figure S1, fluorescence intensity is low below pH 4, whereas the fluorescence intensity is higher and nearly constant between pH 4 and 8. The increase in fluorescence continues until pH 11 with slight fluctuations. The proposed method is based on the quenching of the ligand in the presence of Au(III) ions, so gold determination has been carried out in acidic media because of the high solubility of Au(III). pH 4.0 was selected as the optimum pH for further experiments.

2.3. Optimization of reagent concentration

The effect of ligand concentration on the determination of Au(III) was investigated in range of 1×10^{-6} to 1×10^{-8} M. The solution of the ligand was titrated with Au(III) and the values of fluorescence intensity of ligand-Au(III) solutions at 464 nm were plotted against the concentration of Au(III) to select the ligand concentration yielding the highest R^2 values. A ligand concentration of 1×10^{-7} M was used as an optimization reagent concentration because the highest R^2 value (0.9972) was obtained at this ligand concentration.

2.4. Selection of solvent for reagent

The use of ethanol, methanol, acetone, acetonitrile, dioxane, THF, DMSO, or DMF as a solvent did not affect the limit of detection of Au(III) as determined by spectrofluorometric titrations. Ethanol was selected as a solvent for the ligand and also provided high fluorescence intensity. It was more environmentally friendly and cheaper than the others, but the ligand was only partially soluble in ethanol at room temperature. Therefore, an appropriate amount of ligand was dissolved in 0.5 mL of DMSO and then ethanol was added to the ligand solution until a total volume of 25 mL.

2.5. Response time

To examine the effect of reaction time on the fluorescence intensity of the ligand, a 19.8 μg L^{-1} concentration of Au(III) was added to the ligand solution (1×10^{-7} M) in phthalate buffer of pH 4. The fluorescence intensity did not change much from 0 to 20 min with intervals of 1 min. The reaction of **L** with Au(III) was very rapid and it was suffice to wait 1 min before the measurement.

2.6. The complex composition and its stability

The addition of Au(III) caused a quenching in the absorption spectra of the ligand (1×10^{-5} M) in ethanol and water (1/1) at 355 nm. The molar ratio curve obtained by plotting a graph of absorbance of ligand vs. **[Au(III)]/[L]** at 355 nm showed the formation of a 1:2 (**Au(III):L)** complex of the ligand with Au(III). Additionally, a continuous variation Job plot confirmed the 1:2 stoichiometry of the **Au(III):L** complex by the fluorescence measurements with a total concentration of ([**L**] + [**Au(III)**] = 1.0×10^{-6} M) at λ_{em} 464 nm.

The conditional formation constants (log K $\pm$ standard deviation) of the ligand were calculated[46] to be 3.08 $\pm$ 0.02 and 3.10 $\pm$ 0.03 by using absorption and fluorescence measurements, respectively.

2.7. Interference effects

The effects of interfering metal ions on the determination of Au(III) ions were investigated at optimum detection conditions to evaluate the Au(III) ion selectivity of the ligand. In this investigation, the fluorescence intensities of the ligand solutions (0.1 μM) containing Au(III) ions (0.1 μM) and each of the interfering metal ions at different concentrations were measured and then checked with those of solutions of equivalent ligand and Au(III). Tolerable concentration ratios for foreign ions at relative error of $<5\%$ of analytical signals are given in Table S1 (Supplementary Information). This result suggests that the ligand could selectively bind the Au(III) ions in a real sample containing common coexisting ions.

2.8. Analytical performance

The determination of Au(III) in natural samples cannot be performed using external calibration due to the low accuracy. A modified standard addition method based on fluorescence quenching of the ligand by the effect of Au(III) ions was used under the optimized conditions (Table 1). Good linearity ($R^2 = 0.9972$) in range of 19.8–237.6 μg L^{-1} was obtained. The limits of detection (LOD = 3 $\times$ S_d / m) and quantification (LOQ = 10 $\times$ S_d / m) were calculated according to the IUPAC recommendations.[47] In these equations, S_d is the standard deviation of 11 replicate measurements of the blank response and m is the slope of the calibration line.

Table 1. Analytical performance data of the modified standard addition method for total gold determination.

Excitation wavelength (nm)	355
Emission wavelength (nm)	464
Limit of detection (LOD) (μg L^{-1})	5.2
Limit of quantification (LOQ) (μg L^{-1})	17.4
Linear range (μg L^{-1})	17.4–237.6
Optimum pH	4.0
Constant gold(III) concentration (μg L^{-1})	1000
Ligand concentration (mol L^{-1})	1.0×10^{-7}
Ligand volume (mL)	2.0
Total volume (mL)	4.0
Solvent	Ethanol:water (1:1)
Time before measurement	1–2 min
Correlation coefficient (R^2)	0.9972
Intraday precision (mean RSD%, n = 3, for CRM (CRM-SA-C Sandy Soil C) including 19.8 μg L^{-1} Au(III))	3.2

2.9. Analytical application to real samples

To evaluate the practical application of the proposed method, the analysis of Au(III) recovery from water samples was performed. Since water samples did not contain gold residues, the recovery study of spiked samples was carried out. At three different concentrations, Au(III) stock solution was spiked in stream water, tap water, and sea water samples. Under the optimized conditions, the samples were analyzed to detect Au(III) ions in

three replicates. The obtained results are showed in Table 2 for water samples. It was observed that Au(III) added to samples was accurately found with satisfactory recoveries. It was proved by the t-test that there were statistically no significant differences between the added and found values. Thus, the proposed method can be practically applied for Au(III) detection in real samples.

Table 2. Determination of Au(III) in real water samples with ligand (**L**).

Samples	Au^{3+} spiked (μg L^{-1})	Au^{3+} recovered mean^a ± SD^b	Recovery (%)	RSD^c (%)
Stream water	19.8	20.3 ± 0.7	101.6	3.4
	39.6	40.8 ± 0.2	103.1	4.4
	59.4	61.8 ± 0.2	102.4	3.7
Sea water	19.8	20.0 ± 0.6	100.0	3.0
	39.6	39.5 ± 0.5	99,7	1.2
	59.4	58.9 ± 0.2	99.2	2.9
Tap water	19.8	20.1 ± 0.1	100.5	4.2
	39.6	40.4 ± 0.1	102.0	3.0
	59.4	61.0 ± 0.2	102.7	3.3

^{a}n = 3, ^{b}SD = standard deviation, ^{c}RSD = relative standard deviation.

The accuracy of the proposed method was determined by analyzing standard reference material (CRM-SA-C Sandy Soil C) containing different concentrations of Au(III). Three replicates were carried out at each concentration (n = 3). The relative standard deviations were 3.2%, 3.8%, and 2.5% (n = 3) for the determination of 19.8, 39.5, and 58.9 μg L^{-1} Au(III), respectively. These results for CRM-SA-C Sandy Soil C were satisfactory. In addition, the statistical analysis of these obtained results for intraday and interday accuracy was carried out using the Student t-test, which showed that there was no significant difference between found and certified values.

The accuracy was also determined by analyzing spiked water samples (n = 3) on the same day (for intraday accuracy) and also on three consecutive days (for interday accuracy) at different concentrations of Au(III). Recovery results were calculated as recovery percentage for stream water, tap water, and sea water samples with RSD less than 5%.

2.10. Comparison with other methods

Table 3 compares the analytical and operational parameters of the proposed method with other methods for determination of gold in different samples reported in literature.[13,14,24,26,48–50] Lower detection limits for gold were calculated by some atomic methods or extraction methods.[14,26,30] However, in these methods, gold ions are extracted and coprecipitated because of their separation and preconcentration before the measurement. The pretreatments take a lot of time. Our method does not take much time in practice because it can be implemented. The used fluorescent sensor is a pyrazoline derivative compound. Pyrazolines are good compounds for the human body because of their biological activities. Therefore, it can be said that the reagent and also the solvent (ethanol) are environmentally friendly. Consequently, the proposed method is more advantageous than many others in the literature, because it is a simple, economical, rapid, and ecofriendly method.

It is of great importance to improve gold ion sensors to detect the amount of gold ions in real samples by spectrofluorometric methods. However, a few fluorescence chemosensors for gold have been reported. For

Table 3. Comparison of developed method for determination of Au(III) with some previously reported methods.

Reagent, method	Sample	pH	Linear working range (mg/L)	LOD (mg/L)	Ref.
A new thiol-ene based polymeric fluorescence sensor by photoinitiated polymerization of trimethylolpropane Tris(3-mercaptopropionate), 2-hydroxyethylacrylate, and 2,4,6-triallyloxy-1,3,5-triazine, SF*	Computer circuit board scraps	5.0	0.005–0.05	1.9	[48]
Ion-pairing reagent tetraheptylammonium bromide (THA^+Br^-) immobilized polyurethane foams sorbent in packed column, FAAS*	Waste water samples and anodic slime	3–4	0.0–0.020	0.00006	[49]
N-(4-{4[(Anilinocarbothioyl) amino] Benzyl}phenyl)-N-phenylthiourea, ETAAS*	Tap water, well water, dam water, and hair	2	0.02–40	0.0048	[24]
5-[(E)-(2,6-diaminopyridine-3-yl) diazenyl] 1,3,4-thiadiazole-2-thiol, DLLME*	Anode slime, catalytic converter, ore, and road sediment	5	0.0011–0.085	0.0004	[26]
Modified activated carbons, GFAAS*	Magmatic rocks samples	For A carbon in the pH range from 0.5 to 2 and for B carbon pH about 2	0.001–0.070	0.000004	[14]
Gold(III) and 5-(4-sulfophenylazo)-8-aminoquinoline, FI*	Ores and anode slimes	50 mL of 2 M acetic acid, 2 M sodium hydroxide being added to keep the pH constant	0–75	1.1	[51]
Nickel tubes and quartz tubes, TS-FF-AAS*	Homeopathic medicines	-	0.01–4	0.004	[13]
1,3,5-Triphenyl-2-pyrazoline compound (**L**) SF*	Tap, sea, and stream water samples	4	0.0156–0.2376	0.0052	Present work

*DLLME: dispersive liquid-liquid microextraction method, GFAAS: graphite furnace atomic absorption spectrometry, TS-FF-AAS: thermospray flame furnace atomic absorption spectrometry, FI: flow injection, SF: spectrofluorimetric, FASS: flame atomic absorption spectrometry, ETAAS: electrothermal atomic absorption spectrometry.

example, Do et al. prepared a latent apocoumarin fluorophore sensor for Au(III) in a protic solvent with the limit of detection of 64 μg L^{-1}.[51] Chinapang et al. developed two fluorescent sensors based on a ferrocenyl derivative, naphthalimide, for the analysis of Au(III) in aqueous media.[52] Under optimum conditions, the study had a detection limit of 95 μg L^{-1} for Au(III). In addition, a few fluorescence probes were successfully applied to bioimaging applications to monitor Au(III) metal ions in living organisms such as zebrafish.[53] Amjadi et al. successfully used fluorescent graphene quantum dots for the monitoring of Au(III) with a detection limit of 98.9 μg L^{-1} in water plasma samples.[54] Park et al. devised a colorimetric and fluorescent signaling of Au(III) (LOD, 21.8 μg L^{-1}) in aqueous acetonitrile.[55] The signaling was performed using a thiocumarin derivative in the presence of chelator N,N,N′,N′-tetrakis-(2-pyridylmethyl) ethylenediamine (TPEN) as a masking agent. In this proposed method, the detection limit was 5.2 μg L^{-1} for Au(III). The LOD was lower than those of the above reported studies. No masking agent or organic solvent was necessary in this study, but they were used in others.[55]

2.11. Conclusions

In this study, we report 1,3,5-triphenyl-2-pyrazoline as a fluorescence sensor for Au(III) ions. It showed selective and sensitive fluorescence response to Au(III) in EtOH-water. On the addition of Au(III), the fluorescence quenching of **L** showed a linear response over the Au(III) concentration in the range of 17.4–237.6 μg L^{-1}. The detection limit is 5.2 μg L^{-1} with a short response time of 1 min. A 1:1 binding stoichiometry of the **[L-Au(III)]** complex was obtained with good stability. Under optimized experimental conditions, **L** solution (1×10^{-7} M) in 1/1 (v/v) ethanol/water was buffered by phthalate buffer at pH 4.0. This sensor can successfully be used for determination of Au(III) in real water samples such as stream water, tap water, and sea water samples. The detection limit of the proposed method was considerably lower than those of other fluorescent sensor methods. The method is simple, sensitive, rapid, and cost-effective, and it can be applied without any solvent extraction or pretreatment of real water samples. The proposed method requires no toxic solvents and does not require the use of surfactants. The use of environmentally friendly ethanol as a cosolvent and the quick fluorescence response are its advantages. In addition, for the first time in a study, a pyrazoline derivative compound was used in the determination of gold by a spectrofluorometric method.

3. Experimental

3.1. Equipment and materials

Absorbance and fluorescence intensity were measured with a PerkinElmer UV–Vis spectrophotometer and a PTI spectrofluorometer (QM 2006 model), respectively. Fluorescence emission spectra were taken in the range of 370–650 nm with a slit width of 1.0 nm and with λ_{ex} = 355 nm. pH measurements were performed with a Jenway 3040 ion analyzer.

Standard solutions of metal ions (1×10^6 μg L^{-1}), buffer solutions (AVS Titrinorm, Merck Certipur), acid solutions, chemicals, and solvents were purchased from Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland) and were of analytical grade. The sandy soil standard (CRM-SA-C) was supplied by High-Purity Standards (USA). The digestion of CRM-SA-C was done by utilizing an ultrapure concentrated solution mixture of HNO_3, HCl, HF, and H_2O_2 in a CEM Mars 6 Microwave system. The starting compound (3-(2,3-dimethoxyphenyl)-1-(4-methoxyphenyl)prop-2-en-1-one) and the final product (5-(2,3-dimethoxyphenyl)-3-(4-

methoxyphenyl)-1-phenyl-4,5-dihydro-1H-pyrazole) (Figure 3) were synthesized according to previous reports.[56] An appropriate amount of this compound was dissolved in 25 mL of ethanol/DMSO (9.6:0.4) to prepare a 1.7 $\times$ 10^{-3} mol/L solution of this ligand and kept in refrigerator at 4 °C for 7 days.

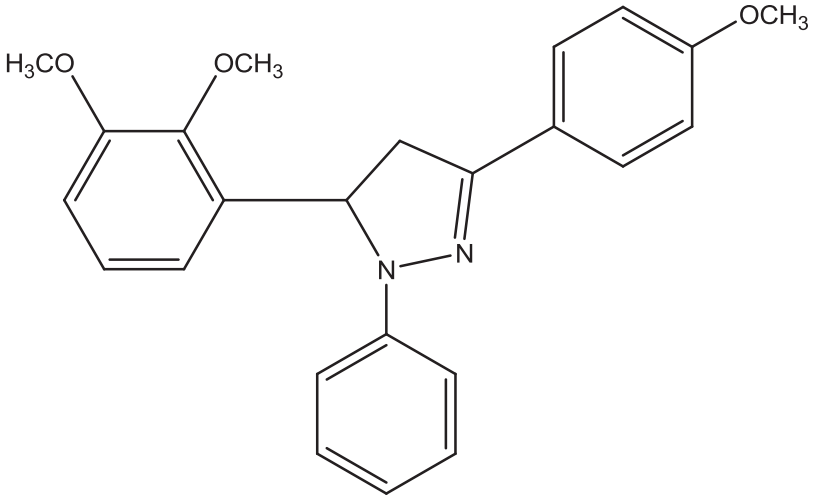

Figure 3. 1,3,5-Triphenyl-2-pyrazoline compound used as fluorescent ligand (**L**).

3.2. Samples

The stream water, tap water, and sea water samples were collected from Harşit River in Gümüşhane, the water supply of Gümüşhane, and the Black Sea at Trabzon, respectively. Real water samples were filtered through a 0.45-mm cellulose nitrate membrane.

The digestion of the sandy soil standard (0.5 g) was performed using 1.5 mL of nitric acid, 4.5 mL of hydrochloric acid, 1.0 mL of hydrofluoric acid, and 2.0 mL of hydrogen peroxide in a closed microwave digestion system. One can see the used digestion program in Table S2. After the microwave digestion process, the solution was filtered with a 0.45-mm cellulose nitrate membrane and evaporated. The final volume of sandy soil standard solution was adjust to 25 mL with deionized water.

3.3. Optimum conditions

Performance criteria such as solvent, concentration of ligand, effect of pH, and complexation time were optimized in the proposed method. Ethanol was determined as the solvent of the ligand. The pH of the solution changed the fluorescence intensities of the ligand. A series of experiments were applied by using a solution of ligand in aqueous buffers at various pH levels (using glycine buffer for pH 1.0; citrate buffer for pH 2.0, 3.0, 5.0, 6.0, 7.0; phthalate buffer for pH 4.0; borate buffer for pH 8.0). Investigations of the detection capacity of the sensor under different pH conditions were performed and then the optimal solution pH was determined. In the study, pH 4.0 was appropriate for detection of Au(III) with the ligand. The complexion reached maximum stability in 1 min.

3.4. Analytical method

The proposed method was carried out by using a modified standard addition method.[57,58] A constant amount of Au(III) (1000 μg L^{-1}), 2 mL of ligand (1 $\times$ 10^{-7} M), and an aliquot sample solution (19.8 μg L^{-1}) were

added to all tubes. The sample was not added to the first tube. Increasing amounts of Au(III) were sequentially added to the third and next tubes. The pH of the solutions was adjusted to 4.0 with phthalate buffer and the final volume was completed to 4 mL. Fluorescence spectra of all solutions were obtained at 464 nm by exciting at 355 nm. The concentration of Au(III) was calculated from Eq. (1):

$$C_x = (F_0 - F_{1)}/m, \tag{1}$$

where C_x is the gold concentration of the sample, F_0 is the fluorescence intensities of the first tube, F_1 is the fluorescence intensities of second tube, and m is the slope of the standard addition graph. Figure S2 (Supplementary Information) shows the standard addition graph, which was plotted to determine the gold content (19.8 μg L^{-1}) of tap water.

Acknowledgment

This study was supported by the Gümüşhane University Scientific Research Foundation (Project Number 15.A0118.02.01).

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Supplementary Information

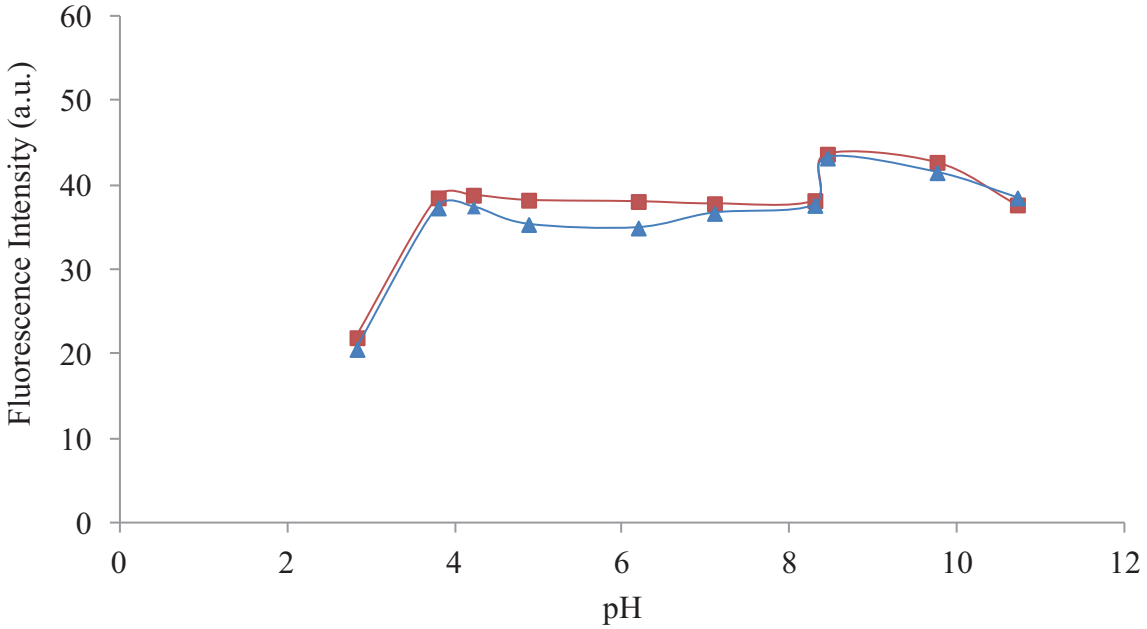

Figure S1. The effect of pH on the fluorescence intensity of **L** (1.0×10^{-7} M) (■) and [**Au(III)-L**] (equivalent, 1.0×10^{-7} M) (▲). λ_{em}: 464 nm.

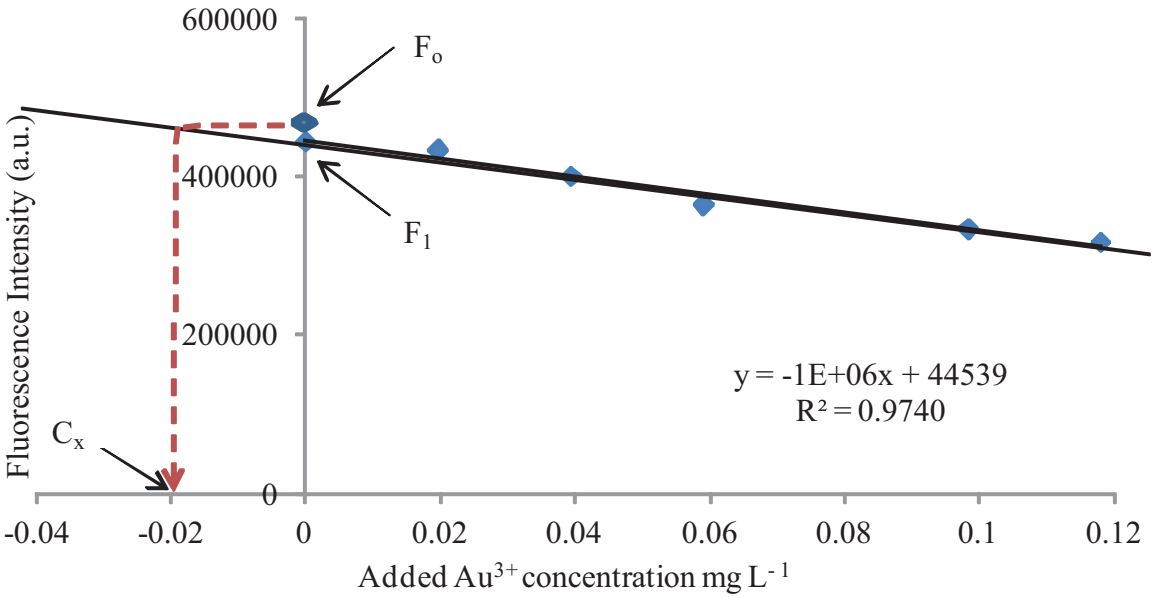

Figure S2. Standard addition graph for gold determination (19.8 μg L^{-1}) in tap water.

Table S1. Tolerance limits for foreign ions on the fluorescence intensity of the solution containing equivalent ligand and Au(III). Concentration = 1.0×10^{-7} M, pH 4.0.

Foreign ion	Tolerable concentration ratio (foreign ions/Au(III))	Tolerance limit (mg/L)
Ni(II)	5	0.0294
Sc(II)	7	0.0315
Sn(II)	7	0.0831
Cu(II)	7	0.0445
B(III)	10	0.0108
W(VI)	15	0.2758
Ti(IV)	15	0.0719
As(II)	15	0.1124
Sr(II)	15	0.1314
Co(II)	20	0.0295
Ca(II)	20	0.0802
Cd(II)	20	0.2248
Pd(II)	25	0.2660
Zn(II)	25	0.1634
Hg(II)	25	0.5015
Fe(III)	25	0.1675
Ag(I)	25	0.3236
Sb(III)	25	0.3044
Li(I)	25	0,0174
Na(I)	25	0.0575
K(I)	25	0,0977
Be(II)	25	0.0225
Mg(II)	25	0.0073
Ba(II)	25	0.3434
Cr(III)	25	0.1300
Al(III)	25	0.0675
Tl(I)	30	0.6131
Bi(III)	40	0.8359
Mo(VI)	40	0.3838
Y(III)	50	0.4445
V(III)	50	0.4797

Table S2. The digestion program of sandy soil standard (CRM-SA-C) in microwave system.[59]

Stage	Time (min)	Power (W)	Pressure (atm)	Temperature (°C)
1	6	250	45	160
2	6	400	45	180
3	6	650	45	220
4	6	250	45	220