A Simple, Selective, and Fast Colorimetric Assay Using Gold Nanoparticles for Trace Determination of Tolyltriazole in Aqueous Media

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ABSTRACT: *In this study, a simple and fast colorimetric assay based on the aggregation of gold nanoparticles (AuNPs) was achieved for the determination of µg/L of tolyl triazole (TTA). The aggregation of AuNPs is due to the high affinity between gold surface and nitrogen atoms of TTA and intermolecular bonding formation between TTA molecules. The plasmon peak of AuNPs at 520 nm was decreased with the formation of a band about 620 nm owing to the aggregation phenomenon. The effective parameters on the peak shift such as ionic strength, pH of the sample, and AuNPs concentration was investigated. The proposed method is capable of determining TTA over a concentration range of 10-100 µg/L with a limit of detection of 5.0 µg L⁻¹ based on the absorbance ratio at 620 nm to 520 nm. The relative standard deviation of the method was 3.0% and 1.5% for 20 and 80 µg/L, respectively. A comparison between the outlined method and the previously published methods for TTA determination has also been made. The obtained results from this study proved to be effectively successful in the determination of TTA in water.*

KEYWORDS: *Gold nanoparticles; Colorimetric assay; Tolyltriazole; Aggregation; Determination.*

INTRODUCTION

Gold nanoparticles (AuNPs) are the most remarkable class of metal NPs with numerous applications in optics, catalysts and biology [1]. Nowadays, an increasing interest in colorimetric sensors has emerged which provides easy and also reliable on-site real-time detection without a need for complex instruments, thus colorimetric sensors with high sensitivity and selectivity are highly desirable [2]. AuNPs are known as an important class of probes due to their suitable features such as strong size- and distance-dependent optical characteristics, high extinction coefficient and actually convenient surface modification. Hence, the investigation of functional AuNPs have been developed in diverse critical areas, including separation science [3], catalytic applications, nanomedicines, biosensors and cell imaging [4]. One of the most surprising characteristics of AuNPs is their ability to show the localized surface plasmon resonance (LSPR) [5]. Indeed, localized surface plasmon resonance is the collective oscillations of metal nanoparticles' conduction electrons which are excited by an electromagnetic field [6]. LSPR is basically due to the size, shape and composition of the nanoparticles, moreover, because of the existing interparticles distance and the dielectric constant of the surrounding medium [5]. AuNPs absorb visible light since

the coherent oscillations of conduction band electrons occurs on the nanoparticle surface [7]. The shift of surface plasmon band to longer wavelengths due to the interaction of the nanoparticles with some target molecules causes the transformation of AuNPs from the dispersion to aggregation state, which usually results in a distinct color change [8]. Numerous sensing techniques based on AuNPs aggregation have been reported in a variety of detection strategies [9-14].

Cu containing alloys are widely utilized in industrial water utilities including heat exchangers, water treatment plants, pipelines and condensers, etc. due to its remarkable and thermal conductivities, appropriate mechanical workability and resistance to chemical and atmospheric factors [15,16]. However, copper in strong aggressive media with high salinity which contain high concentration of chloride ions is susceptible of corrosion. Employment of an appropriate dose of a proper corrosion inhibitor in such aggressive media is crucial for protecting metals and alloys [15]. The inhibitors contain polar moieties, double bonds or various hetero-atoms such as sulfur, nitrogen, and oxygen, which interact with metal surface through p π - d π bond. Azoles known as effective corrosion inhibitors in diverse environments are structurally polar organic derivatives containing nitrogen atoms with free lone pairs of electrons [17]. Tolyltriazole (TTA, Fig. 1) has been recognized as one of the effective copper corrosion inhibitors in neutral and acid media containing chloride ions. Tolyltriazole acts by the chemisorbtion of the surface copper atoms through sharing the lone-pair electrons of its nitrogen atoms [18]. Although heterocyclic molecules, e.g. benzotriazole and tolyltriazole are widely consumed as corrosion inhibitor agents, they possess some disadvantages, including toxicity and a low degree of biodegradation [19]. Several methods have been developed to estimate TTA such as liquid chromatography [20], Liquid chromatography tandem mass spectrometry (LC-MS/MS) [21], and so on. These methods need sophisticated and expensive instruments [22]. Unlike mentioned methods, colorimetry is simple, rapid, available, and cost-effective method [23]. This technique is based on determining the concentration of the desired component using measuring the absorption wavelength [24].

In this work, a simple and highly sensitive colorimetric method was developed for trace detection of TTA based on the aggregation size-dependent optical property of
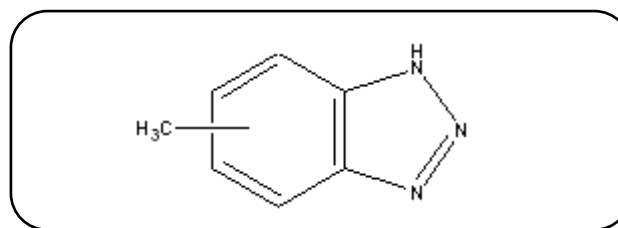

Fig. 1: Chemical structure of tolyltriazole.

citrate capped AuNPs, via utilizing the affinity characteristics of the nitrogen moieties of this analyte towards the surface of the AuNPs (Scheme 1). The effects of various parameters, such as AuNPs concentration, pH of the sample, and salt addition to the sample solution have been investigated to find the optimized condition, with highest sensitivity and selectivity.

EXPERIMENTAL SECTION

All chemicals (TTA, $HAuCl_4$, trisodium citrate, NaOH, HNO_3, sodium acetate, acetic acid, sodium oxalate, sodium format, oxalic acid, formic acid, KCl, NaCl and K_2SO_4, deionized (DI) water, acetone) were of analytical grade, purchased from Merck (Merck, Darmstadt, Germany) and used without further purification. A stock solution of TTA (1000 mg/L) was prepared by dissolving 0.100 g of the Tolyltriazole in acetone and diluting to 100 mL in a volumetric flask. The diluted solutions were prepared daily using this stock solution and DI water.

Absorption studies were carried out using a UV-Vis spectrophotometer model Genesis10s (Miltonroy, USA) with a one cm glass quartz. The pH of the sample was measured using an Inolab model wtw720 pH meter (Germany). Transmission Electron Microscopy (TEM) micrographs were recorded using a Zeiss instrument model EM10C - 100 KV (Germany).

Synthesis of gold nanoparticles

Herein, trisodium citrate was used as a reducing reagent to produce citrate-capped AuNPs [18]. At the first step, 100 mL $HAuCl_4$ solution (50 nM) was refluxed up to boiling. Thereafter, 3.0 mL 1.0 w/v% trisodium citrate solution was quickly added to the Au(III) solution. After 5.0 min refluxing, the color of solution changed from light yellow to gray, and finally became deep red. After the color change, the reaction continued for an additional of 5.0 min and then the solution was to let cool down to room temperature while being stirred to be lated stored at 4 °C [25].
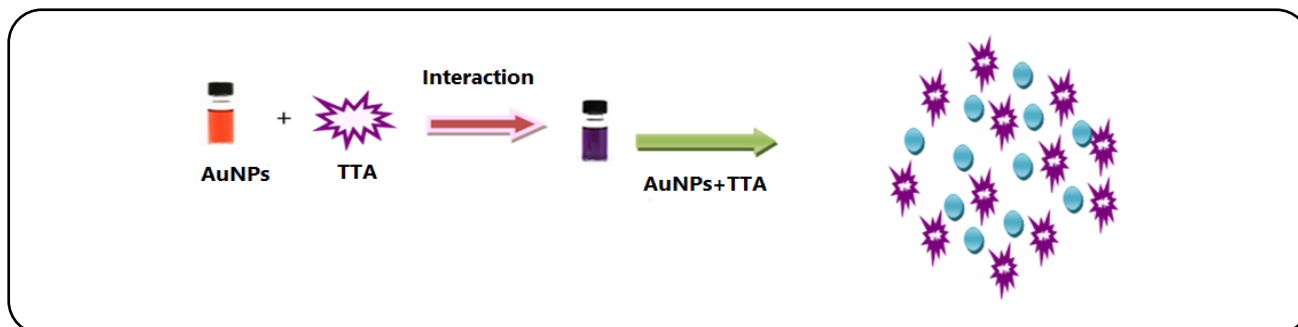
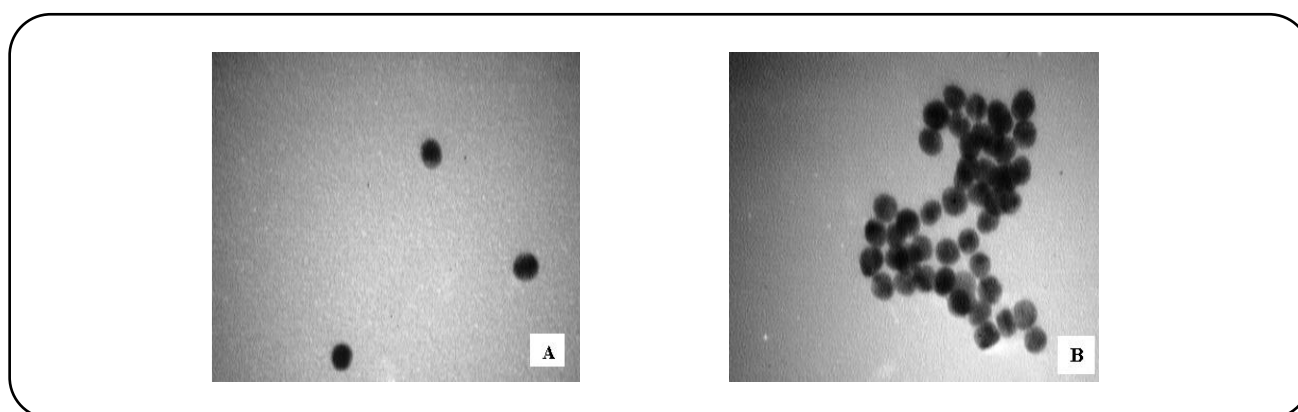***Scheme 1: Schematic of the interaction between AuNPs and TTA yielding AuNP-TTA complex as the product at pH=4.***

Fig. 2: TEM of AuNPs before and after addition of TTA: (a) TEM of AuNPs, (b) TEM of AuNPs– TTA.

General Procedure

To determine TTA, 1.0 mL prepared Au NPs solution (50 nM) 1.0 mL of acetate buffer (pH=4) and different concentrations of tolyltriazole were added to 10 mL volumetric flasks and diluted with double distilled water. Afterwards, the solution was shaken and a portion was transferred to the 1.0 cm quartz cell to record absorbance spectrum. The same procedure was accomplished on blank without the presence of tolyltriazole.

### RESULTS AND DISCUSSION

Characterization

It is well known that citrate is capable to reduce $AuCl_4^-$ to AuNPs at ambient temperature as well as a stabilizer for these nanoparticles. The citrate-coated AuNPs are highly dispersible (effectively considered as single particles) in the red coloured solution. The morphologies of the nanoparticles were explored using TEM (Fig. 2). However plasmon absorption spectrum of AuNPs shows a single peak at 620 nm only. The presence of TTA during AuNPs formation has effective influence on the plasmon resonance absorbance which leads to decrease in its

intensity. This effect can be due to interaction of nitrogen atoms of TTA with gold (Scheme 2). In the presence of substances with groups S or N, AuNPs are aggregated and the color of the solution changes to blue [26,27].

The structural characteristics such as shape and size of AuNPs and AuNPs–TTA and also aggregation phenomenon were investigated by TEM analysis (Fig. 2). The AuNPs shapes are distorted spherical, with an average size range of 12-15 nm as shown by TEM image (Fig. 2a). Upon the addition of TTA, AuNPs aggregated due to the presence of substance with groups S and N (Fig. 2b).

Effect of pH

The pH of solution is a significant parameter owing to the presence of ionizable moieties of TTA. In this context, the pH of sample solution was varied in the range of 3-6 using diluted HNO_3 and NaOH solutions (0.01 mol/L As illustrated in Fig. 3, the highest aggregation response (A_{620}/A_{520}) was achieved at pH=4. It is well-known that AuNPs are negatively charged [28]. Therefore, it is reasonable that the interaction between gold NPs
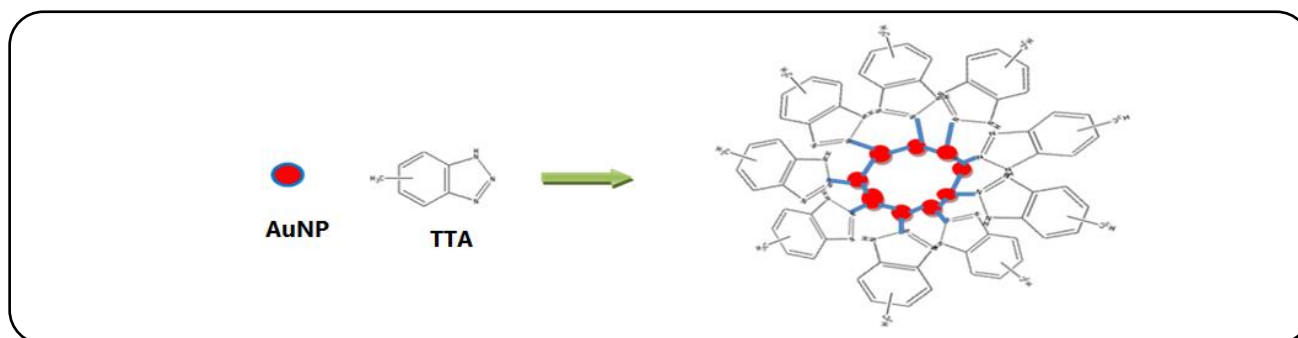
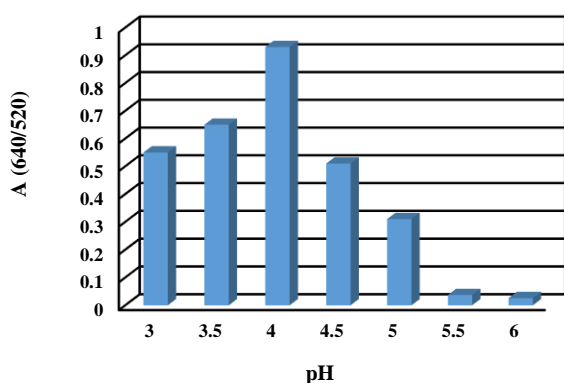*Scheme 2: Suggested mechanism for the interaction between gold nanoparticles and chemical TTA.*

Fig. 3: Effect of pH on the surface plasmon intensity; (the pH of the solution was adjusted with dilute NaOH or HNO₃ (aqueous sample volume, 10 mL; AuNPs concentration, 50 nM; [TTA] = 100 ng/mL).

Fig. 4: Effect of buffer on the surface plasmon intensity (: aqueous sample volume, 10 mL; AuNPs concentration, 50 nM; [TTA] = 100 ng/mL).

and the analyte molecules could occur at a lower pH as a consequence of AuNPs neutralization. (Fig. 3)

In order to choose the optimal buffer, three buffers (i.e., format, acetate and oxalate buffer) were investigated and the results revealed that acetate buffer led to the highest aggregation performance (Fig. 4). Thereby, 1.0 mL of acetate buffer with pH= 4.0 was selected as optimum. (Fig. 4)

Effect of Au NPs concentration

The AuNPs concentration has an important role in the sensitivity of the method. In this regards, to further optimize the sensitivity and selectivity of the method, the effect of the AuNPs concentration was explored on the aggregation process. Accordingly, different amount of AuNPs solutions were used to study the aggregation performance. As shown in Fig. 5 A_{620}/A_{520} ratio was increased by increasing the AuNPs concentration. Nevertheless, higher concentrations of AuNPs led
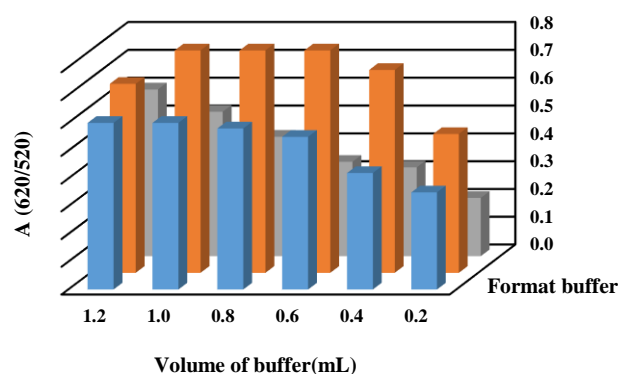
to the limited linear range. Thereby, 50 nM of AuNPs concentration was selected as the optimum amount (Fig. 5).

Effect of interaction time

2 ml of AuNPs solution, 2 ml of acetate buffer with pH=4, and 2 mL of TTA solution were added to a 10 mL volumetric flask and the volume was made up to the mark. Then, the absorption changes were studied at different times (1-14 min). The results showed that time had no effect on absorption.

Effect of ionic strength

The electrolytes usually affect surface plasmon resonance (SPR) processes based on the fact that can be related to the ability of strong electrolytes to expedite the aroused electrical double-layer [29]. In order to study the effect of ionic strength, the experiments were carried out by adding different salts such as NaCl, KCl, and K_2SO_4 to the sample solution. The results indicated that the addition

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Table 1: Effect of potentially interfering ions on TTA determination.

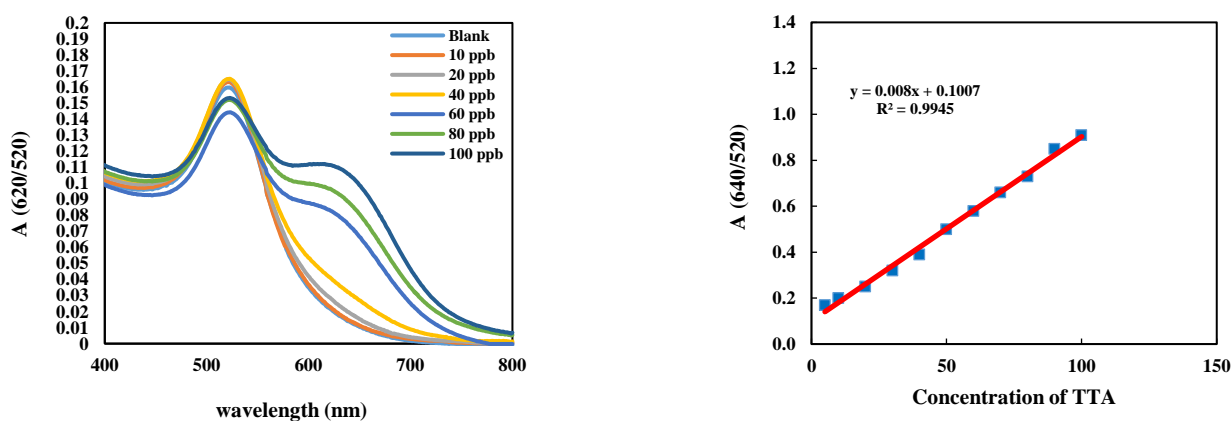| Interference	Concentration of interfering ion (mg/L)	Tolerance limits [X]/TTA
Na^+, K^+, Cl^-, NO_3^-, CO_3^{2-}, SO_4^{2-}	100	1000
Hg^{2+}	5	50
Ag^+, Fe^{2+}, Fe^{3+}	2	20
Cd^{2+}, Ba^{2+}, Zn^{2+}	1	10

Fig. 5: Overlaid UV–visible spectra of Au NPs-TTA mixture and calibration graph for determination of TTA. (a) Overlaid UV–visible spectra of AuNPs–TTA from 0 to 100 ng/mL TTA (b) Calibration graph from 10 to 100 ng/mL TTA.

of up to 100 mM of NaCl, K_2SO_4 and 10 mM KCl did not have any significant effects on the A_{620}/A_{520} ratio. In the high concentration of electrolytes, it was observed that the color of the sample solution is close to the color of blank solution and the A_{620}/A_{520} ratio was decreased. However, it is possible that electrolytes could change the surface of nanoparticles [27]. Thereby, in the high concentration of electrolytes, interaction between TTA and nanoparticles decreased and thus aggregation decreased.

Effect of potentially interfering species

Coexisting species may affect selectivity and sensitivity of TTA determination, so the effect of various species on the aggregation performance was explored under the optimum conditions. To perform these studies, various ions were introduced into the solution that contained 100 ng/mL TTA and then the aggregation ratio was measured using general procedure. The maximum concentration of potentially interfering ions that would create ±5% error in the determination of TTA was considered as interference. As summarized in Table 1, the method has high selectivity toward TTA even at the high concentration of these species.

Analytical application

Under the optimum conditions, calibration graph was constructed by plotting ΔA values as a function of the TTA concentration (Fig. 5). The calibration graph was linear in the range of 10-100 ng/mL with regression equation of $y = 0.008 X + 0.100$ and correlation determination (r^2) of 0.994. The limit of detection (LOD) based on the average blank signal plus three times its standard deviation ($n = 10$) was found to be 5.0 µg/L. The precision of the method was evaluated by performing eight replicate measurements of solutions containing 20 and 80 µg/L TTA and the Relative Standard Deviation (RSD) for these determinations were 3% and 1.5%, respectively.

Determination of TTA in water samples

In order to test the applicability of the method, the developed procedure was employed for determination of TTA in real water samples. Recovery tests were used to examine the reliability and accuracy of the method, and different amounts of TTA were spiked into 100 mL samples water samples. The water samples were taken from the Ramin power plant and Ahwaz drinking water (Ahwaz, Iran). TTA is used to prevent corrosion of copper

Table 2: Analytical results of the TTA determination in water samples (n = 5).

Sample	TTA added (µgL)	TTA Found [a] (µg/L)	Recovery (%)
Ahwaz drinking water	-	6.2±0.05	-
	20	27±0.06	104
	50	54.8±0.06	97
Ramin power plant cooling water	-	68.5±0.09	-
	20	92.6±0.06	105
	50	117.5±0.07	98

pipes and it is added to the cooling water of the Ramin power plant. So, it was chosen for this study. The sampling path was the cooling water that the container of sampling was filled with water and tested. After standing for 24 h in the refrigerator, the samples were filtered by a piece of filter paper and TTA content in each sample was determined under the optimum conditions. Each test was repeated five times for consistency of the results. The results showed that by applying the proposed method it is possible to determine TTA content in real water samples with acceptable precision (Table 2).

Comparison of the performance of the developed method with the other methods

A comparison between the proposed method and the previously published methods for TTA determination is shown in Table 3. As depicted in this table, the new method has a very good precision and acceptable LOD and linearity in comparison to the other reported methods. Besides, he most significant advantage of the current method is its simple and general instrumentation that is available in all laboratories.

CONCLUSIONS

In this study, a simple, selective and fast colorimetric assay based on the aggregation of gold nanoparticles (AuNPs) was achieved for determination of µg/L of tolyltriazole (TTA). The aggregation of Au NPs is due to the high affinity between gold surface and nitrogen atoms of TTA and intermolecular bonding formation between TTA molecules. The most significant features of the new method are rapidity, simplicity, excellent precision, and sensitivity. Overall, what we found under carefully designed and monitored laboratory conditions are the followings:

1) This method is quite straight forward and simple,

2) No Extraction preparations are required

3) The present approach can be used for the determination of TTA in the range of 10-100 µg/L with a limit of detection 5 µg/L.

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