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Using Gold Nanoparticles for Ultra trace Spectrophotometry Determination of Tolyltriazole in Aqueous Media

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Abstract

In this study, the detection limit sensitivity to the level of $\mu g\ L^{-1}$ was achieved. For this, by applying AuNPs signal fluctuations of high sensitivity was carefully monitored so that they become measureable with highest possible precision. The proposed method is capable of determining TTA over a range of 10-100 μgL^{-1} with a limit of detection 5 $\mu g\ L^{-1}$. The relative standard deviation of the method was 3% and 1.5%. The obtained preliminary results from this study proved to be effectively successful in determination of TTA in water. A comparison between the proposed method and the previously published methods for TTA determination has also been made for the first time.

Keywords: Gold nanoparticles; Spectrophotometry; Tolyltriazole; Determination

Introduction

One of the most frequently used chemicals that are also used as a corrosion inhibitor in industries to protect copper and copper alloys from corrosion is Tolytriazole. It has been reported [1] that this chemical has also a positive impact on a series of engineering materials such as steel, gray iron, cadmium and nickel as well as applicable in industrial units and systems such as, but not limited to, cooling water systems, industrial water treatment, industrial lubricants dishwashing tablets, metal detergents and polishing, coolants, metal packaging and antifogging agent [2]. Contrary to its advantages, TTA has been reported [3] to have downsides such as toxicity and not easily bio-deteriorated.

Therefore, there is a need to provide methods for the precise measurement of its very low amounts. There have been a variety of methods that have been applied to determine diazoles some of which Mercaptobenzothiazole (MBT) [4], Benzotiazole (BT) [5], Benzotriazole (BTA) [6] and also ultraviolet Spectrophotometry [7], Anodic chronopotentiometry [8], Amperometric titration [9], and High Performance Liquid Chromatography (HPLC) [10,11]. But the above mentioned methods have high, expensive and often time-consuming costs. One of the most rapidly growing areas of science and technology in recent years has been Nano-technology that has also been successful in drawing the attention of researcher's worldwide [12]. Among metals nanostructures features, their optical properties have been the main focus of methods such as Localized Surface Plasmon Resonance (LSPR).

LSPR relies on the overall oscillation of electrons that may appear in the spectrum may be featured as visible to near-UV region [13,14]. It is in this respect that study of these particles and their characterization has become a pivotal research area in materials science research [15]. Gold Nanoparticles (AuNPs) have very interesting features among which the Surface Plasmon resonance (SPR) and/or Resonance Rayleigh Scattering (RRS) can be highlighted. These two methods have different applications in many fields of research [16-18]. The followings have made gold nanoparticles (AuNPs) a new class of probes:

1. Their unique surface plasmon
2. Their optical properties [19].

In this research we found that spectrophotometry is a very applicable and useful method to determine TTA because of its simplicity, low cost, safety, easy, and sensitivity. In addition, this method has proved to be also very useful as it does not require extraction and further preparations. The main methodology applied was by using AuNPs as inhibitor to characterize TTA-AuNPs intensity of aggregated particles. Figure 1 shows structured TTA and Scheme 1 shows the aggregated structure of AuNPs nanoparticles when they react with nitrogen groups of 2TTA. The reaction leads in to an increase in the size of nanoparticles and also enhancement of the visibility intensity.
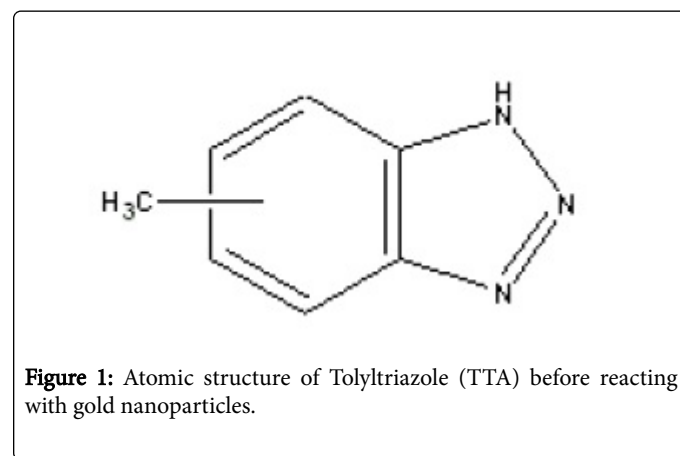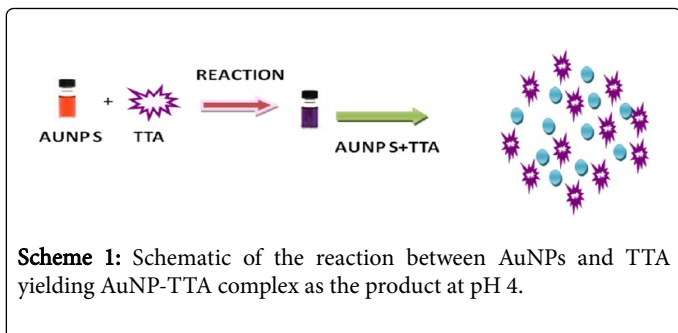

Figure 1: Atomic structure of Tolyltriazole (TTA) before reacting with gold nanoparticles.

Scheme 1: Schematic of the reaction between AuNPs and TTA yielding AuNP-TTA complex as the product at pH 4.

Experimental Procedure

The chemicals of analytical grade were used throughout this study without further purification. All chemicals were purchased from Merck (Merck, Darmstadt, Germany) and double distilled water was used throughout. A stock solution of 1000 mg/L of Tolyltriazole was prepared by dissolving 0.100 g of the Tolyltriazole in acetone and diluting to 100 mL in a volumetric flask. More diluted solutions were prepared daily using this stock solution.

Absorption studies were carried out using a UV–Vis spectrophotometer model Genesis10s (Miltonroy, American). The pH was measured using an Inolab wtw720 (Germany). Transmission Electron Microscopy (TEM) images AuNPs were recorded using a Zeiss - EM10C-100 KV (Germany).

Experimental procedure to prepare gold nanoparticles

As the reducing agents, we used gold nanoparticles, trisodium citrate theater supposed to facilitate synthesizing procedure [20]. The first step for preparation was bringing 100 mL of 50 mM $HAuCl_4$ solution to boiling. Then, 3 mL of a 1% trisodium citrate solution was added quickly to the solution. After 5 min at the same temperature, the color of solution changed from light yellow to gray, and finally became deep red (Figure 2). After the color change, the reaction continued for an additional 5 min and then the solution was let cool down to room temperature while being stirred to be later stored at 4°C.

Figure 2: Procedure for changing the color of gold nanoparticles by adding TTA.
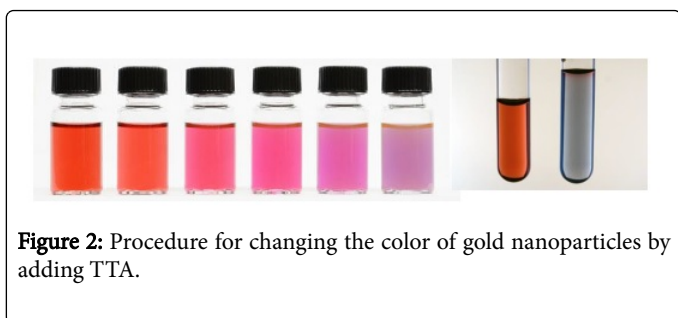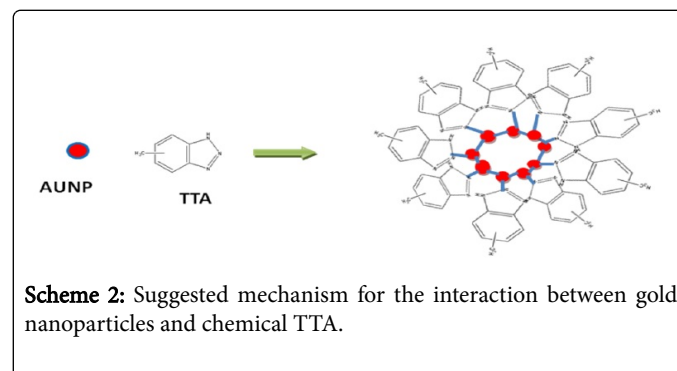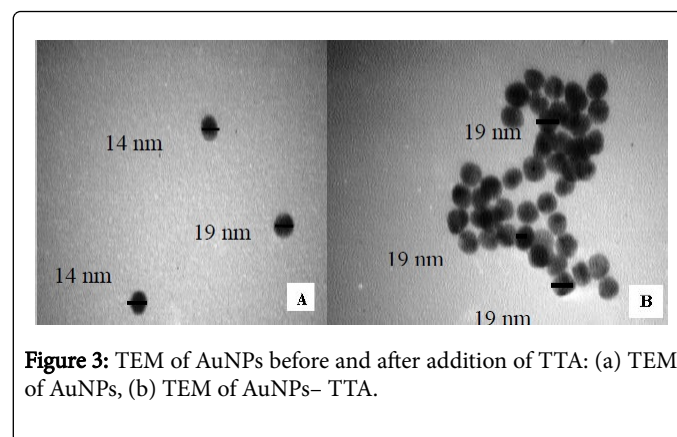
General Procedure

In this procedure, 1 mL prepared AuNPs solution (50 µM), 1 mL of acetate buffer (pH=3.5) and different concentrations of tolyltriazole were added to 10 mL volumetric flasks and diluted with double distilled water. The solution was shaken and a portion was transferred to a 1 cm Spectrophotometry cell to record absorbance spectrum. The same procedure was done on blank without the presence of tolyltriazole.

Real samples analysis

Different standard amounts of TTA were spiked into 100 mL samples of cooling as well as drinking water at Ramin power plant (Water samples were taken from the Ramin power plant and Ahwaz drinking water). After standing for 24 h in refrigerator, the samples were filtered by a piece of filter paper) where the TTA content in each sample was determined blue at optimum conditions. Each test was repeated at least two times for consistency of the results. TTA content of different water samples and their recovered counterparts were subjected to further investigation.

Results and Discussion

It is well known that citrate is capable of reducing and as stabiliser of $AuCl_{4-}$ to AuNPs at ambient temperature. The AuNPs obtained, which were highly dispersed (effectively considered as single particles) in the red coloured solution by citrate on their surfaces. The morphologies of the nanoparticles were observed using TEM (Figure 3). However plasmon absorption spectrum of AuNPs shows a single peak at 620 nm only. The presence of Tolytriazole 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 Tolytriazole with gold (Scheme 2).

Figure 3: TEM of AuNPs before and after addition of TTA: (a) TEM of AuNPs, (b) TEM of AuNPs– TTA.

Scheme 2: Suggested mechanism for the interaction between gold nanoparticles and chemical TTA.

TEM analysis

The structural characteristics such as shape and size of AuNPs and AuNPs–TTA and also aggregation phenomenon were investigated by TEM analysis (Figure 4). The AuNPs nanoparticles shapes are distorted spherical, with an average size range of 12-15 nm as shown by TEM

image (Figure 3a). Upon the addition of TTA, AuNPs aggregated due to the presence of substance with groups S and N (Figure 3b).

Effect of pH

Solution pH is a crucial factor to determine Tolytriazole in this method. Based on this, we measures pH of the system's absorbance over pH range of 3 to 6. The dilute HNO_3 and NaOH solutions (0.01 mol L^{-1}) were used to adjust the pH of the solutions. As can be seen from the Figure 3, the pH is maxima in 4. It is well-known that AuNPs are negatively charged [21,22]. Therefore, it is reasonable that the connection between AuNPs and TTA occurs at a lower pH as a consequence of AuNPs neutralization (Figure 4).
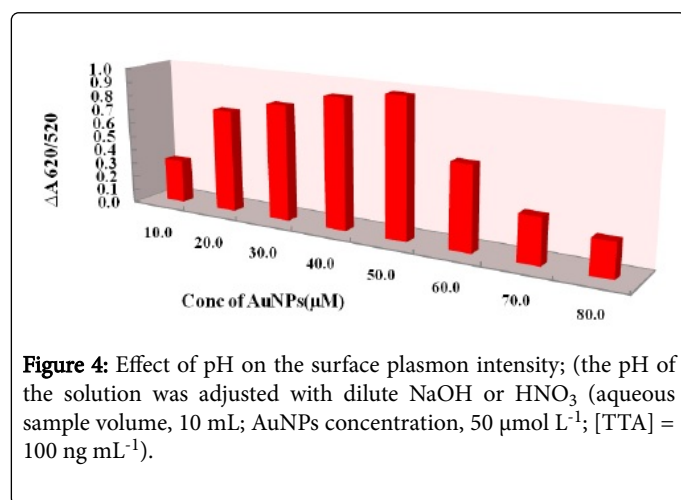

Figure 4: Effect of pH on the surface plasmon intensity; (the pH of the solution was adjusted with dilute NaOH or HNO_3 (aqueous sample volume, 10 mL; AuNPs concentration, 50 μmol L^{-1}; [TTA] = 100 ng mL^{-1}).

In order to choose the optimal buffer, three buffers (i.e., format, acetate and oxalate buffer) were investigated that acetate buffer was the best (Figure 5). Furthermore, 1.0 mL of acetate buffer was selected as optimum (Figure 5).
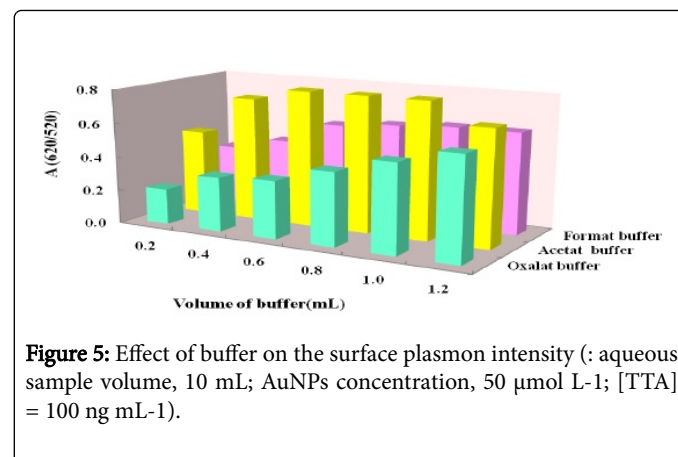

Figure 5: Effect of buffer on the surface plasmon intensity (: aqueous sample volume, 10 mL; AuNPs concentration, 50 μmol L-1; [TTA] = 100 ng mL-1).

Effect of AuNPs concentration

The AuNPs concentration has an important role in the sensitivity of the method. In this section, different amount of AuNPs solution were used to study the absorption spectra. As shown in Figure 6 A620/A520 ratio was increased by increasing the amount of AuNPs. Therefore, 50 μM of AuNPs concentration was selected as the optimum amount (Figure 6).
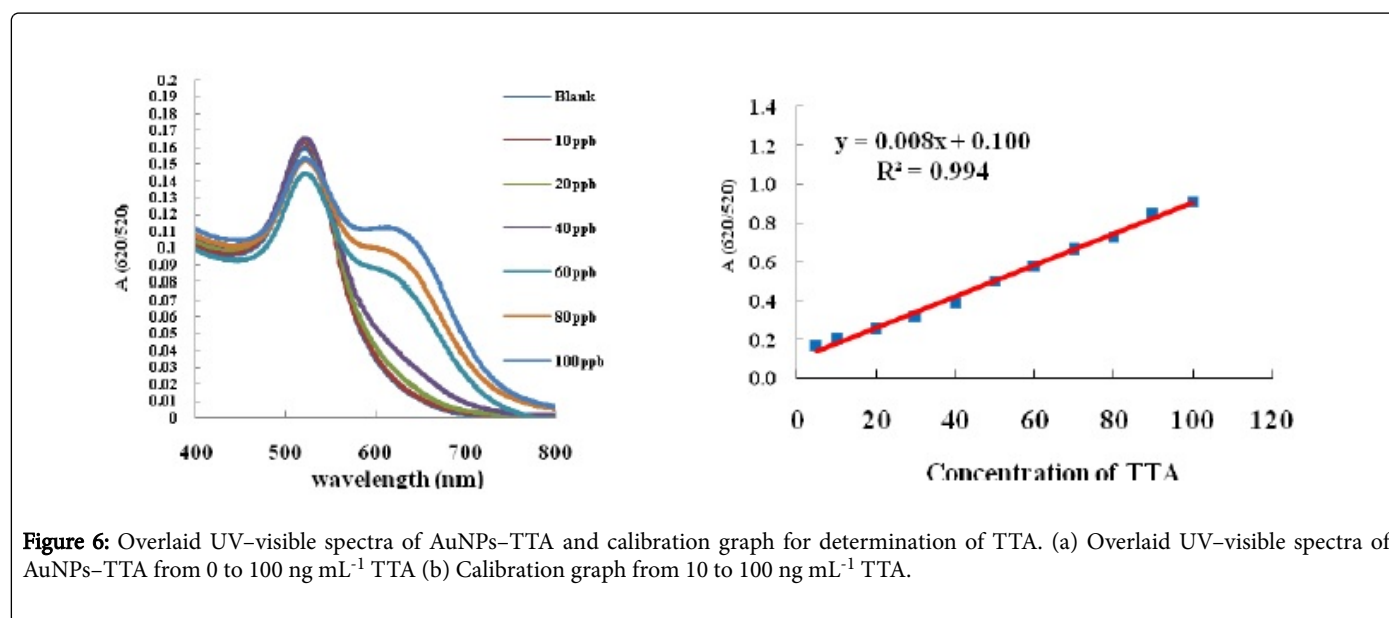

Figure 6: Overlaid UV–visible spectra of AuNPs–TTA and calibration graph for determination of TTA. (a) Overlaid UV–visible spectra of AuNPs–TTA from 0 to 100 ng mL^{-1} TTA (b) Calibration graph from 10 to 100 ng mL^{-1} TTA.

Effect of time

The effect of interaction time on absorption spectra was investigated in the range of 1-10 min. No significant variation was observed in the absorption spectra in all cases studied. This means that the interaction of TTA and AuNPs does not require time and is very fast.

Effect of ionic strength

High concentrations of electrolytes usually affect Surface Plasmon Resonance (SPR) processes. In order to study the electrolyte effect, the experiments were carried out by adding different salts such as NaCl, KCl, and K_2SO_4. The results indicate that the addition of up to 100 mM of NaCl, K_2SO_4 and 10 mM of KCl did not have any significant effects on the A620/A520 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 A620/A520 ratio was decreased. However, it is possible that electrolytes could change the surface of nanoparticles (Parham et al., 2015 and Farkhari et al., 2016). So that in the high concentration of electrolytes, interaction between TTA and nanoparticles decreased and thus aggregation decreased.

Effect of interfering substances the possible

Among what we studied were also the interaction between anions and cations on TTA direction. To perform these studies, various ions were introduced into the solution that contained 100 ng mL^{-1} of TTA and then applying the general procedure. The following criteria were defined as the tolerance limit. The maximum concentration of potentially interfering ions that would create ± 5% error in the determination of TTA. Based on the obtained results as tabulated in Table 1 the method we have developed in our studies appears to be relatively selective for determination of TTA.

Interference	Concentration of interfering ion (µg L^{-1})	Tolerance limits [X]/TTA
Na$^+$, K$^+$, Cl$^-$, NO^{-3}, CO3^{2-}, SO4^{2-}	100	1000
Hg^{2+}	5	50
Ag$^+$, Fe^{2+}, Fe$^+$	2	20
Ca^{2+}, Ba^{2+}, Zn^{2+}	1	10

Table 1: Limit of tolerance foreign ions on determination of TTA.

Analytical application

Calibration graphs and detection limits: Under the optimum conditions calibration graph was constructed by plotting ΔA values as a function of the TTA concentration. The calibration graph was linear (in the range of 10-100 ng mL^{-1}) of TTA with regression equation y=0.008x+0.100 and correlation coefficient (r=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 µg L^{-1}. The precision of the method was evaluated by performing eight replicate measurements of solutions containing 20.00 and 80.00 µg L^{-1} of TTA and the Relative Standard Deviations (RSDs) for these determinations were 3% and 1.5%, respectively (Figure 6).

Determination of TTA in water samples: In order to test the validity of the method, the developed procedure was applied for determination of TTA in real water samples. Recovery tests were used to examine the reliability and accuracy of the method. The results showed that by applying our proposed method it is possible to determine TTA content in all water samples with acceptable precision (Table 2). Amounts of TTA were added (10 µg L^{-1} and 20 µg L^{-1}) and were determined by the aforementioned procedure.

Sample	TTA added (µg L^{-1})	TTA Found a (µg L^{-1})	% Recovery
Ahwaz drinking water	-	6.2 ± 0.05	-
	20	27 ± 0.06	103
	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	99

Table 2: Analytical results of the determination of TTA content and recovery test of TTA in water samples with the proposed method (n=5).

The proposed method was successfully applied for the determination of TTA in water. A comparison between the proposed method and the previously published methods for TTA determination is shown in (Table 3). In the future, we are planning to investigate more on the possible other reactions that may be involved in making our approach of these qualifications.

Number	Method	Linear range (ng mL^{-1})	Detection limited (ng mL^{-1})	RSD (%)	Real sample
1	(SPME-GC– QqQMS)	1-100	0.07	1.5	Tap water
2	(SPME-GC– QqQMS)	0.05-3	0.001	7	River
3	DLLME	5.3-533.9	0.5	1	Water
4	SPE/LC-MS/MS	-	0.05-0.1	<4	Water
5	SPE-GC/MS	0.1	120-1100		Ground water
6	SPE/LC–MS	-	0.003	5 (0.2)	Drinking water
7	Spectrophotometry	1-100	1	1.5 (80)	Drinking, industrial Tap water

Table 3: Analytical results of the determination of TTA content and recovery test of TTA in water samples with the proposed method (n=5).

Conclusions

To measure the residual TTA content at Ramin power plant cooling water and Ahwaz drinking water, we applied Plasmon Resonance Absorption (PRA) on gold nanoparticles surfaces. These nanoparticles were produced by reduction of HAuCl$_4$ through Trisodium Citrate

application. At the beginning the produced nanoparticles were red in color, later to change into blue. It was observed that by adding TTA in an acidic environment, PRA of these nanoparticles was highly reduced. We believe that TTA must have been instrumental in inducing this effect via formation of AuNPs bond. Our method has try capability to quantify TTA assessment by measuring PRA of the gold particles.

Overall, what we found under carefully designed and monitored laboratory conditions are the followings:

1. This method is quite straightforward and simple
2. No Extraction preparations are required
3. Using Transmission Electron Microscopy (TEM) shape and size of AuNPs and AuNPs-TTA were also measured.

The present approach can be used for the determination of TTA in the range of 10-100 $\mu g \ L^{-1}$ with a limit of detection 5 $\mu g \ L^{-1}$.

Acknowledgements

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