Talanta 129 (2014) 227–232

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

A sensitive and selective colorimetric method for detection of copper ions based on anti-aggregation of unmodified gold nanoparticles

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ARTICLE INFO

Article history:
Received 31 January 2014
Received in revised form
15 May 2014
Accepted 16 May 2014
Available online 27 May 2014

Keywords:
Gold nanoparticle
Anti-aggregation
Copper ions
Colorimetric detection

ABSTRACT

A highly sensitive and selective colorimetric method for detection of copper ions, based on anti-aggregation of D-penicillamine (D-PC) induced aggregated gold nanoparticles (AuNPs) was developed. Copper ions can hinder the aggregation of AuNPs induced by D-PC, through formation of mixed-valence complex with D-PC that is a selective copper chelator. In the presence of a fixed amount of D-PC, the aggregation of AuNPs decreases with increasing concentrations of Cu^{2+} along with a color change from blue to red in AuNPs solution and an increase in the absorption ratio (A_{520}/A_{650}). Under the optimum experimental conditions (pH 7, [AuNPs] $=3.0$ nmol L^{-1} and [NaCl]$=25$ mmol L^{-1}), a linear calibration curve for Cu^{2+} was obtained within the range of 0.05–1.85 μmol L^{-1} with a limit of detection ($3S_b$) of 30 nmol L^{-1}. Excellent selectivity toward Cu^{2+} was observed among various metal ions due to a specific complex formation between Cu^{2+} and D-PC. The proposed method has been successfully applied for the detection of Cu^{2+} in various real samples.

1. Introduction

In recent years, the detection of heavy metal ions has become a serious subject, due to their toxic effects on environmental and biological systems [1]. Among these metals, detection of copper ions is crucial because of mass consumer electronics production and the increasing rate of copper usage [2]. Although this metal (copper) as an important transition metal in human bodies [3] plays essential functions in biological systems, such as energy generation, dioxygen and enzyme activation [4,5], excessive amounts of Cu^{2+} in human and animal bodies, influence their nephric and nervous systems, consequently, leading to neural diseases like Alzheimer' s disease, Menkes and Wilson disease. According to this fact, the U.S Environmental Protection Agency (EPA) has reported the permissible limit of copper ions in drinking water lower than 1.3 ppm (20 μmol L^{-1}). Thus, detecting copper ions at this level or less is of great importance [6]. Some traditional analytical techniques used for determination of trace level of copper ions are based on electrochemical, voltammetry [7,8], inductively coupled plasma mass spectrometry (ICP-MS) [9] and atomic absorption spectrometry (AAS) [10,11]. These methods require not only complicated and expensive instruments, but they need sample preparation and long analysis time as well. Therefore, the development of a sensitive, rapid and inexpensive method for copper ion detection is essential and inevitable.

As a fast and simple technique, colorimetric sensors can be considered as promising candidates for this purpose [12]. They efficiently determine the presence of an analyte and produce results that are observable by the naked eye, rather than requiring sophisticated instrumentation. Gold nanoparticles-based colorimetric assays have recently gained much interest due to their simplicity and high order of magnitude extinction coefficients ($\sim 3\times10^{11}$ mol^{-1} L cm^{-1}) of AuNPs. Their strong extinction band appears when the incident photon frequency is in resonance with the collective excitation of the conduction electrons. This phenomena is known as the surface plasmon resonance (SPR) which depends on the size, shape, and inter-particle spacing of the gold nanoparticles, as well as their dielectric properties and those of their local environment [13–15]. The colorimetric sensing platform based on plasmonic nanoparticles, specially gold and silver nanoparticles, has been developed for the detection of alkali and alkaline earth metal ions [16], heavy metal ions [17–22], anions [23], amino acids [24,25], proteins [26,27], small molecules [28,29], oligonucleotides [30,31], and cancerous cells [32]. Compared to the large number of sensors based on the aggregation of AuNPs, a very few number of colorimetric sensors have been developed based on their anti-aggregation, though the latter

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http://dx.doi.org/10.1016/j.talanta.2014.05.022
0039-9140/

provides more selective probes and reduces false positive signals [33]. In corresponding systems, an aggregation agent initially induces the aggregation of AuNPs by changing their inter-particle distance; further, the target analyte deactivates the aggregation agent due to the high binding affinity among them, thus preventing the aggregation of AuNPs [34–40].

Recently, we have reported a method for the determination of a thiol-containing chelator drug, D-Penicillamine, which induces the aggregation process of citrate-capped gold nanoparticles due to the hydrogen bonding or electrostatic interaction between adsorbed D-PC molecules. As a result of aggregation, the intensity of surface plasmon resonance band of AuNPs around 520 nm decreases, along with the appearance of a new peak at a longer wavelength [41]. In this study, a highly selective colorimetric probe for Cu^{2+} detection based on anti-aggregation of AuNPs, through complexation between Cu^{2+} and an aggregation agent (D-penicillamine), has been developed.

2. Experimental

2.1. Apparatus

Water used for the preparation of all samples was purified with cartridges from Millipore (Direct-Q3) to a resistivity of 18.2 MΩ. The UV–vis absorbance spectra were recorded on a PerkinElmer (Lambda25) spectrophotometer with a 1.0 cm glass cell. Measurements of pH were made with a Denver Instrument Model of 270 pH meter equipped with a Metrohm glass electrode. A Philips (Pye Unicam) model SP9 atomic absorption spectrometer, equipped with deuterium lamp background correction and iron and copper hollow cathode lamps as radiation source, was used for obtaining AAS data.

2.2. Reagents

All chemicals were of analytical reagent grade and were used without further purification. All solutions were prepared using deionized water (18.2 MΩ). Hydrogen tetrachloroaurate ($HAuCl_4 \cdot 3H_2O$, 99.9%), Trisodium citrate, 3-Mercapto-D-valin (D-Penicillamine), $Cu(NO_3)_2$ and NaCl were purchased from Merck.

2.3. Preparation of AuNPs

Citrate-capped AuNPs were synthesized by the classical Turkevich method [42]. Briefly, 45 mL solution containing 1.0 mmol L^{-1} of $HAuCl_4$ was prepared and heated under reflux. At boiling point, 5 mL of 38.8 mmol L^{-1} trisodium citrate was added to this solution under vigorous stirring and the mixture was heated under reflux for an additional 30 min during which the color changed to deep red, proving the formation of AuNPs with the desired size (~13-nm). The surface plasmon resonance (SPR) wavelength of citrate-capped AuNPs emerged at 520 nm. The solution was set aside to cool to room temperature and was stored at 4 °C for further utilization. The particle concentration at the resulted solution was estimated to be 15 nM, according to Beer's law, and the extinction coefficient (ε) of about 13 nm AuNPs at 520 nm [43].

2.4. Determination of copper ions

Initially, different concentrations of Cu^{2+} were mixed with 2 mL of 0.02 mol L^{-1} D-penicillamine in a 10 mL volumetric flask and were incubated for 15 min in order to allow the formation of the complex between Cu^{2+} and D-PC. Different concentrations of the above solution were then added to a solution containing 2 mL of synthesized AuNPs, 250 µl of 1.0 mol L^{-1} NaCl, 50 µL of 0.01 mol L^{-1} NaOH (for adjusting pH at 7) and an appropriate amount of Milli-Q water to reach a final volume of 10 mL. Finally, this solution was transferred into a 1 cm spectrophotometric cell to record its absorbance.

3. Results and discussion

D-penicillamine (Scheme 1A) is a thiol-containing drug, showing a high affinity towards the surface of AuNPs through its thiol function. Subsequently, it is able to induce the aggregation of citrate-capped AuNPs via hydrogen bonding or electrostatic interaction among its amino acid groups. Thus, in the presence of D-PC, these interactions lead to the aggregation of citrate-capped colloidal AuNPs and accordingly, the intensity of surface plasmon resonance band of AuNPs around 520 nm decreases, along with the formation of a new band at 650 nm. D-PC is used as a pharmacological chelating agent for treating diseases such as Rheumatoid, Arthritis, and Wilson diseases. This drug can react strongly with copper ions and form different complexes with both Cu (I) and Cu (II) with different stoichiometries [44–46]. In the presence of D-PC, Cu(II) is partially reduced to Cu(I) which can form a mixed-valence complex such as $[Cu(II)_6Cu(I)_8(\text{D-penicillamine})_{12}Cl]^{5-}$ or $[Cu(I)_n(\text{D-PC})_{n+1}]^{-}$ through the thiol group (Scheme 1B) [47,48]. Therefore, in the presence of Cu^{2+}, D-PC prefers to coordinate with Cu^{2+} rather than acting as an aggregation agent for AuNPs, thus inhibiting the aggregation of AuNPs.

The anti-aggregation mechanism of AuNPs was investigated by UV–vis spectroscopy, transmission electron microscopy (TEM), and dynamic light scattering (DLS). As shown in Fig. 1A, the surface plasmon resonance (SPR) band of AuNPs is observed at 520 nm. Upon addition of D-PC a new absorption band of AuNPs appears at around 650 nm, but in the presence of Cu^{2+}, the D-PC could form a complex with Cu^{2+} and AuNPs remained in dispersed state with a single characteristic SPR band of AuNPs at 520 nm. Furthermore, TEM images (Fig. 1B) and DLS analysis (Fig. 1C) clearly exhibited that Cu^{2+} can prevent the aggregation of AuNPs. Zeta potential measurements were also performed to confirm the proposed mechanism. The zeta potential of the unmodified AuNPs, aggregated AuNPs and anti-aggregated AuNPs were −23, −20.6 and −22 mV, respectively.

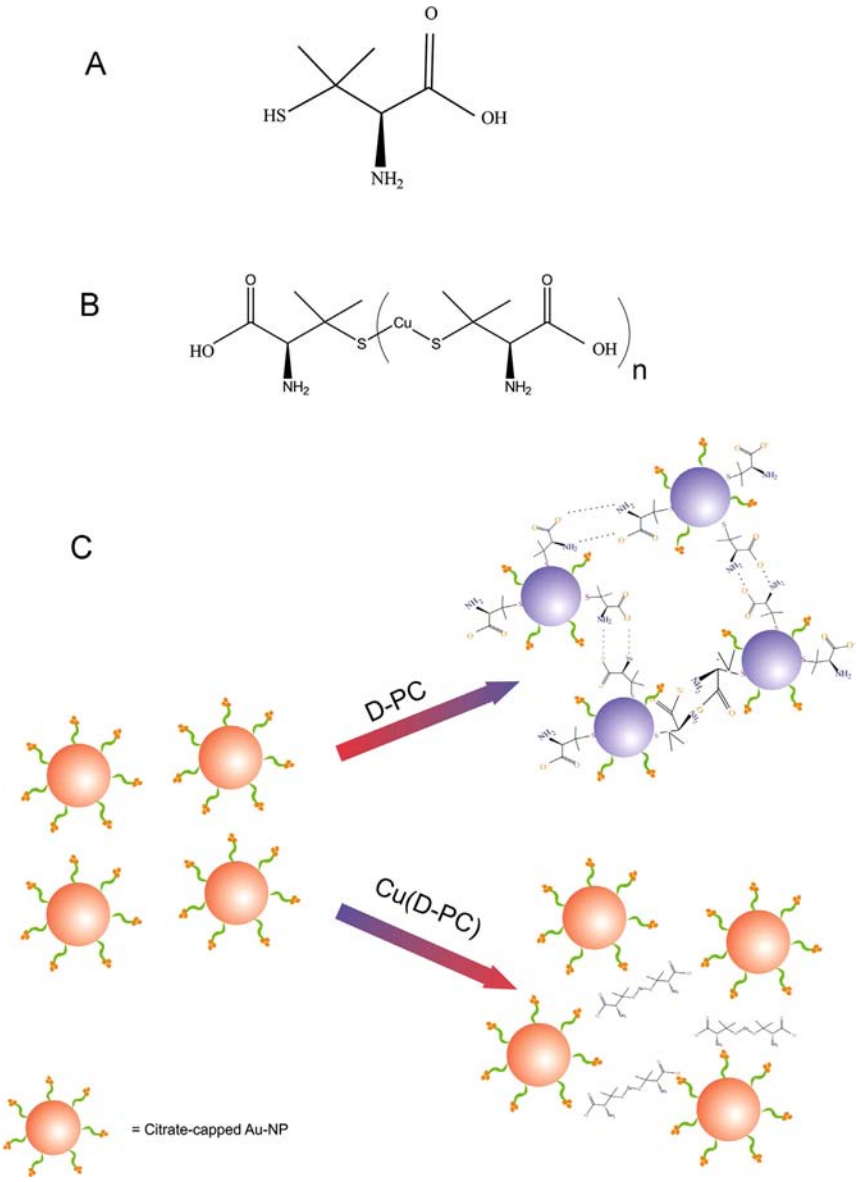
Upon the addition of Cu^{2+}, the amount of uncoordinated –SH groups was decreased yielding to less AuNPs aggregation and a color change from blue to red. The effect of critical parameters on the anti-aggregation process including D-PC concentration, ionic strength, pH, AuNPs concentration, and time have been investigated in order to establish the optimum analytical conditions for the detection of Cu^{2+}.

3.1. Effect of NaCl concentration

It is noteworthy that according to our previous research, aggregation of AuNPs in the presence of D-PC does not take place at low concentrations of NaCl (ionic strength). Also, it has been found that increasing NaCl's concentration above a certain limit induces the aggregation of AuNPs even in the absence of D-PC. Since sodium chloride can constrict the electrical double-layer which aroused from the citrate ions (as capping agents), some control experiments were carried out that revealed the optimum concentration value of 25 mmol L^{-1} for NaCl, in which the aggregation occurs only in the presence of D-PC [41].

3.2. Effect of pH

Due to the presence of carboxyl and amine groups in D-PC, pH strongly influences both the aggregation of AuNPs (in the presence of D-PC), and the anti-aggregation of AuNPs (induced by Cu^{2+}). As shown in Scheme 1C, electrostatic interaction is the dominant



Scheme 1. Chemical structure of A) D-Penicillamine, B) D-penicillamine and Cu complex C) Schematic illustration of the anti-aggregation mechanism for AuNPs in the presence of D-Penicillamine and copper ions .

mechanism responsible for the aggregation of AuNPs. Therefore, the presence of D-PC in its zwitterionic form might enhance the electrostatic interaction. According to the distribution diagram of D-PC shown in Fig. 2, the dominant species (D-PC) is in the zwitterionic form in the pH range of 3– 7 [49]. The effect of pH, varying from 3.0 to 8.0, was investigated on the anti-aggregation process. In acidic pH, the citrate capped AuNPs were not stable and the complex between Cu^{2+} and D-PC was dissociated. In contrast, at high pH values (pH > 8), the copper ions existed in a hydroxide form, $Cu(OH)_2$. Thus, as shown in Fig. SI 1A, pH 7.0 was selected to achieve more anti-aggregation for further experiments.

3.3. Effect of AuNPs concentration

To further optimize the sensitivity of this method, the effect of AuNPs concentration on the anti-aggregation process was also investigated. Thus the concentration of AuNPs was tested in the range of 1.50–3.75 nmol L^{-1}, in the presence of 30 μmol L^{-1} D-PC and 1.00 μmol L^{-1}copper ions. As shown in Fig. SI 1 B, the signal (A_{520}/A_{650}) rises up to 2.7 nmol L^{-1} and reaches a plateau at this value. Thus, a concentration value of 3 nmol L^{-1} was chosen as the optimum concentration of AuNPs.

3.4. Effect of D-PC concentration

The concentration of D-penicillamine as an aggregation agent is an important parameter affecting the sensitivity of Cu^{2+} detection. To evaluate this parameter, the aggregation of AuNPs was monitored at different concentrations of D-PC (0–40 μmol L^{-1}) in the absence of copper ions. As shown in Fig. SI 2, the color of AuNPs solution changed from red to purple and then to blue by increasing the D-PC concentration. It was found that 30 μmol L^{-1} D-PC is the minimum concentration needed to reveal blue AuNPs and provide higher sensitivity and wider linear range.

3.5. Effect of time

Time was found to be important parameter in measurements, both in Cu(DPC) complex formation and in the extent of AuNPs

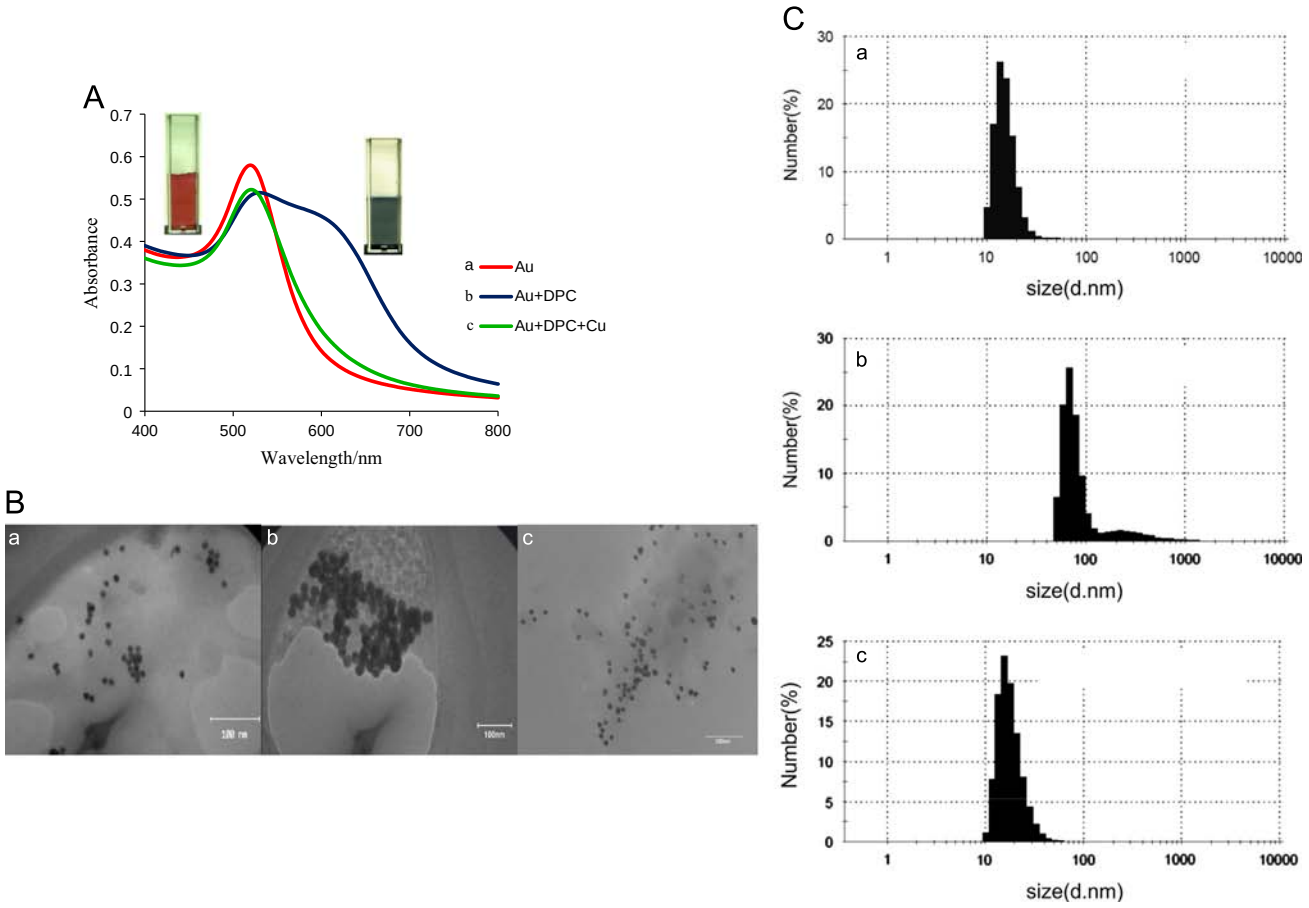


Fig. 1. (A) UV–vis absorption spectra and (B) TEM images (C) size distribution(DLS) of AuNPs with 25 mmol L^{-1} of NaCl a) in the absence of D-PC, b) in the presence of certain quantities of D-Penicillamie, and c) in the presence of D-PC and Cu^{2+} after 15 min.

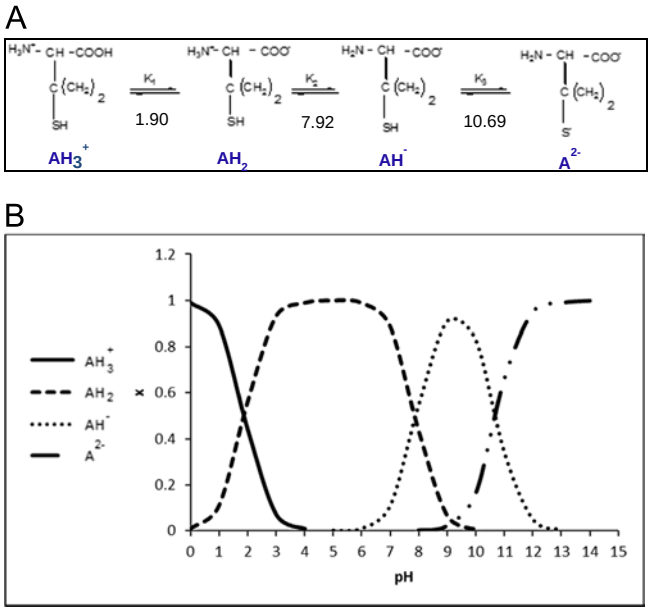


Fig. 2. (A) Different species of D-PC in various pH ranges and (B) distribution diagram of D-PC at different environmental pH.

aggregation. Fig. SI 3 shows the variation of the A_{520}/A_{650} ratio vs. time for different concentrations of Cu^{2+}. It can be deduced that the anti-aggregation upon Cu^{2+} addition is almost 90% completed within 12 min. Therefore, all the A_{520}/A_{650} ratio measurements were performed 12 min after initiation of the reaction.

3.6. Figures of merit

As expected, further experiments under the optimum conditions showed that the increase in absorption ratio (A_{520}/A_{650}) could quantitatively be related to the amount of Cu^{2+} added. Fig. 3A shows that, with increasing the concentration of Cu^{2+}, the absorption at 650 nm (corresponded to aggregated AuNPs) decreased; while the one at 520 nm (corresponded to dispersed AuNPs) increased. Moreover, the color of AuNPs changed from blue to purple and then to red as Cu^{2+} concentration increased. As illustrated in Fig. 3B, the A_{520}/A_{650} ratio increased linearly over the Cu^{2+} concentration range of 0.05–1.85 μmol L^{-1}.Since the linear range in this probe depends on the D-PC concentration, we utilized 120 μmol L^{-1} D-PC instead of 30 μmol L^{-1} D-PC; as a result, the linear range expanded and shifted to 0.75–15 μmol L^{-1} (Fig. SI 4).The limit of detection (LOD) of this probe is estimated (3σ) about 30 nmol L^{-1}. The study of precision, which was made with three independent experiments, revealed relative standard deviations (% RSD) of 1.9% and 6.4% for 0.05μmol L^{-1} and 1.85 μmol L^{-1} of Cu^{2+}, respectively.

3.7. Selectivity

The effect of co-existing metal ions on the determination of Cu^{2+} was also investigated. More than 14 metal ions were examined for their possible interferences in the determination of 1.00 μmol L^{-1} Cu^{2+} under the optimum conditions. The tolerance

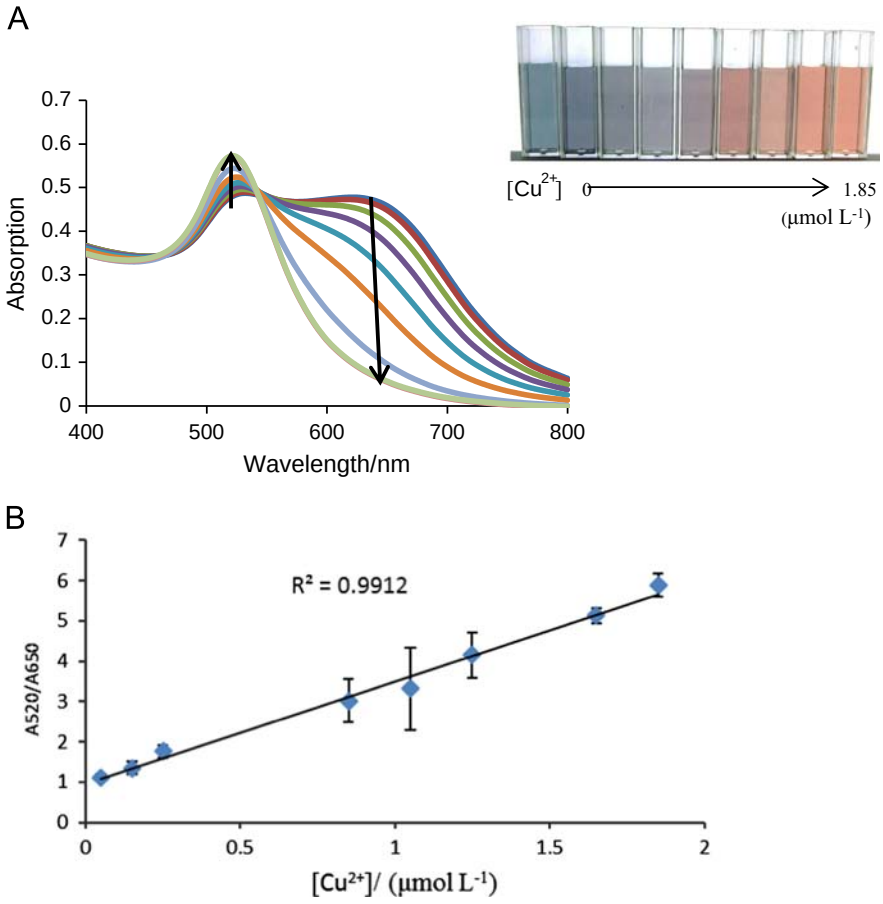


Fig. 3. (A) UV–vis spectra and images of AuNPs in the presence of 30 μmol L^{-1} D-PC and 25 mmol L^{-1} NaCl with different concentrations of Cu^{2+}. (B) Calibration curve of A_{520}/A_{650} versus Cu^{2+} concentrations under optimum conditions in the range of 0.05–1.85 μmol L^{-1}.(For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

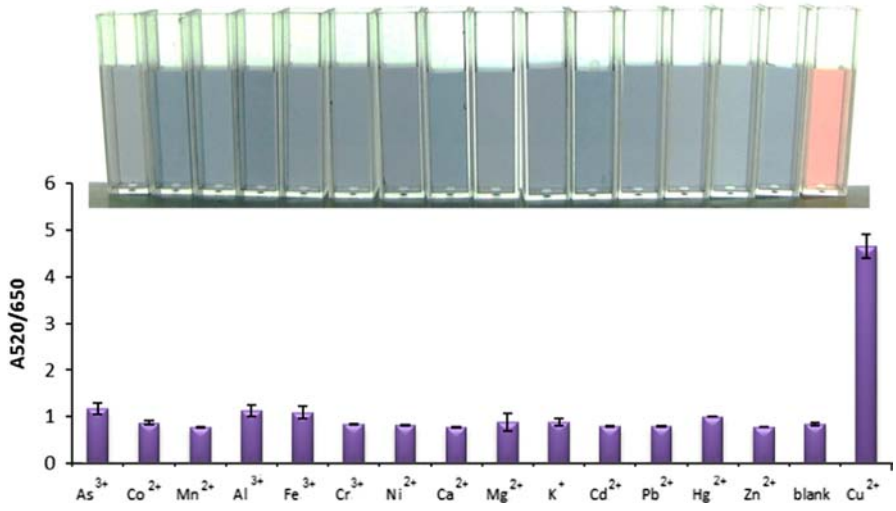


Fig. 4. Colorimetric signals in the presence of 1.00 μmol L^{-1} Cu^{2+} and 50 μmol L^{-1} of different metal ions.

limit was defined as the concentration which gave an error of 3.0% in the determination of 1.00 μmol L^{-1} Cu^{2+}. As shown in Fig. 4, the proposed method is free from interferences of many foreign ions even at high concentrations (50 μmol L^{-1}). This high selectivity arises from selective chelation of Cu^{2+} by D-PC. Significantly, selectivity is one of the advantages of the anti-aggregation probe, due to the high affinity of the analyte to the aggregated reagent.

3.8. Real samples analysis

To investigate the applicability of the proposed technique in real samples, tap water, cascade water and mineral water were tested. The results summarized in Table 1 show the feasibility and usability of this method for determination of copper ions in real samples.

Table 1
Determination of copper ions in different water samples.

Samples	Spiked Cu^{2+} ($\mu mol\ L^{-1}$)	Detected Cu^{2+} by current method ($\mu mol\ L^{-1}$)	Detected Cu^{2+} by AAS ($\mu mol\ L^{-1}$)	Recovery %	RSD %
Tap water	0.25	0.27	0.26	108.00	1.43
	0.95	0.98	0.94	103.16	6.93
	1.65	1.60	1.60	96.97	3.67
Cascade water	0.25	0.21	0.23	85.33	2.70
	0.95	1.04	1.00	109.47	1.42
	1.65	1.52	1.70	92.12	3.15
Mineral water	0.25	0.22	0.24	88.00	3.86
	0.95	0.93	0.95	97.88	3.74
	1.65	1.63	1.65	98.78	3.08

4. Conclusion

This study demonstrates a sensitive and rapid colorimetric method for the determination of Cu^{2+} based on anti-aggregation of the D-penicillamine (D-PC) induced aggregated gold nanoparticles (AuNPs). The system offers a practical potential for trace determination of Cu^{2+} in the presence of a large excess of other metal ions, without the need for any pre-concentration or separation steps. The results show that the system is suitable for measuring trace amounts of copper ions in real samples.

Acknowledgments

The authors wish to express their gratitude to Sharif University of Technology Research Council for the support of this work.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.05.022.

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