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Colorimetric aggregation assay for arsenic(III) using gold nanoparticles

Lingling Gong[1] · Bibai Du[1] · Long Pan[1] · Qingju Liu[1] · Kunhao Yang[1] ·
Wei Wang[1] · Hong Zhao[1] · Li Wu[1] · Yujian He[1]

Abstract The authors describe a colorimetric assay for the determination of As(III) in aqueous solution using citrate capped gold nanoparticles (AuNPs) which, in the presence of As(III), undergo aggregation due to the interaction of citrate ion with As(III). This results in an easily detectable color change from wine-red to blue. The ratio of the absorbances at 661 and 519 nm is linearly related to the As(III) concentration in the 4 to 100 ppb range, with a detection limit as low as 1.8 ppb (at 3σ) which is below the guideline value of 10 ppb. The method is rather simple in that it does not require the surface of the AuNPs to be modified. It was successfully applied to the determination of As(III) in spiked drinking water where it gave adequate recoveries.

Keywords Determination of As(III) · Transmission electron microscopy · ICP-OES · Visual test · Spiking · Dialysis · Environmental analysis

✉ Hong Zhao
hongzhao@ucas.ac.cn

✉ Li Wu
wuli@ucas.ac.cn

✉ Yujian He
heyujian@ucas.ac.cn

[1] School of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, NO. 380, JingJia Road, Beijing 100049, China

Introduction

Arsenic is a highly poisonous carcinogen with wide distribution that more than twenty countries have been reported to suffer from arsenic contamination, provoking acute and chronic health issues such as skin lesions, problems with the circulatory system and high risk of cancer in the skin, lungs, bladder and kidneys [1–3]. More serious is that arsenic cannot be removed from the body and accumulates in human tissues [4, 5]. Arsenic predominantly presents as inorganic arsenic (As(III)) and arsenate(As(V)) salts, of which As(III) was considered as the most toxic substance [6, 7]. Drinking water is the main route of arsenic exposure which often exceed World Health Organization's guideline value of 10 ppb, putting about 140 million people's lives at risk [8].

Attributed to its high toxicity, the detection of arsenic has been carried out by a variety of techniques including atomic absorption spectrometry (AAS) [9, 10], inductively coupled plasma spectrometry (ICP) [11–13] and high-performance liquid chromatography (HPLC) [14] which always provide satisfying results for their good accuracy. However, there is still necessary to develop sensitive, time-saving, capable of on-site and cost-effective methods [15–21]. Among reliable methods for As(III) detection, several colorimetric sensors based on gold nanoparticles (AuNPs) have been blossoming for their high sensitivity and simplistic analyte recognition via bare eyes or cost-effective instrument requirement [22–27].

Ray and co-workers reported a glutathione, dithiothreitol, and cysteine modified gold-nanoparticle based on photometric detection and dynamic light scattering assay with a detection limit of 1 ppb and 10 ppt separately [28]. A sensor was also fabricated to detect arsenic down to 0.76 ppb by modifying silver nanoparticles with glutathione using surface-enhanced

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Raman scattering platform [29]. Pei Zhou et al. used arsenic-binding DNA aptamer first discovered by Y. H. Kim and J. Min for the colorimetric detection of As(III) [8, 30–33]. Most of the methods can meet arsenic test standard, but the complicated thiolated or other costly labeled probe preparation processes may lead to a poor repeatability and limit their applications to some extent for the increased steps of modification [34]. In this work, we find out that just after dialyzed by pure water to remove remnant sodium citrate in solution, citrate-capped AuNPs can be used to directly detect As(III) by a UV-vis spectrophotometer or even bare eyes. And for all we know, the single-shot assay based on citrate capped AuNPs reduced by sodium citrate for As(III) detection has not been reported yet.

A citrate-mediated reduction of HAuCl₄ is considered one of the most classic methods for the preparation of AuNPs which can be used to give sensitive and selective analysis for colorimetric detection. It is crucial to know the surface species of the citrate-reduced AuNPs and solution species present during reduction by citrate. In 1995, Smith and co-workers proved the presence of citrate and its decomposition products, acetoacetic acid and formate in solution throughout colloid formation and the relevant experimental results show that citrate but neither acetoacetic acid nor formate was detected as being adsorbed on the surface. A model of interaction and orientation of citrate at the colloid surface was further presented that is one terminal carboxylate and the tertiary carboxylate to the colloid while the second terminal carboxylate remained unbound to form negatively charged colloid surface [35]. Afterwards, glutathione and cysteine and other small molecules containing carboxyl group have been fabricated as colorimetric probes for arsenic detection [28, 29, 36]. Therefore, it implies that the citrate-capped AuNPs that contains abundant carboxyl groups is sensitive to As(III). Based on the above consideration, we use citrate capped AuNPs prepared by the citrate reduction method as sensitive colorimetric probe for the detection of As(III) (Fig. 1). As(III) can bind with citrate-capped AuNPs and directly induce the aggregation of AuNPs, causing a remarkable change in color. As we all know, the peak position of SPR band is closely related to the distance between AuNPs. When exposed to As(III), the state of AuNPs changes from dispersive to aggregated and an obvious red-shift of the SPR peak can be observed. Compared to existing colorimetric sensors for As(III), the method shows
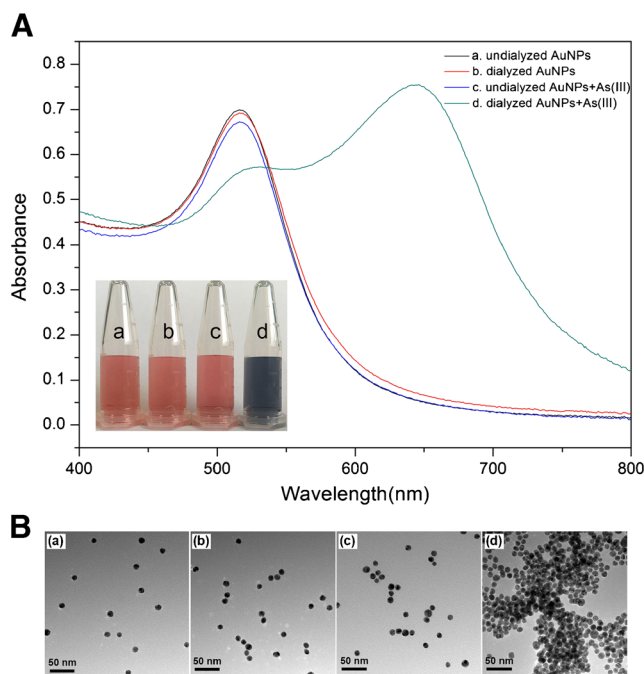

Fig. 2 **A** absorbance spectra of (*a*) undialyzed AuNPs, (*b*) dialyzed AuNPs, (*c*) undialyzed AuNPs in the presence of 909 ppb As(III), (*d*) dialyzed AuNPs in the presence of 909 ppb As(III). Inset photographic images were the corresponding colorimetric response. **B** TEM images of AuNPs, corresponding to (*A*)

multifaceted advantages. First, the single-shot assay greatly simplify the complicated thiolated or other costly labeled probe preparation processes which may lead to a poor repeatability and limit their applications to some extent for the increased steps of modification. Second, citrate capped AuNPs shows excellent anti-disturbed ability to the common interfering analytes in the detection of As(III). Third, the method is rather sensitive to detect As(III) just by using water dialyzed AuNPs. Particularly, the method can be successfully applied to the detection of As(III) in drinking water.

Experimental

Reagents

HAuCl₄·4H₂O was purchased from Sinopharm Chemical Reagent Co., Ltd. (www.sinoreagent.com). Trisodium citrate,

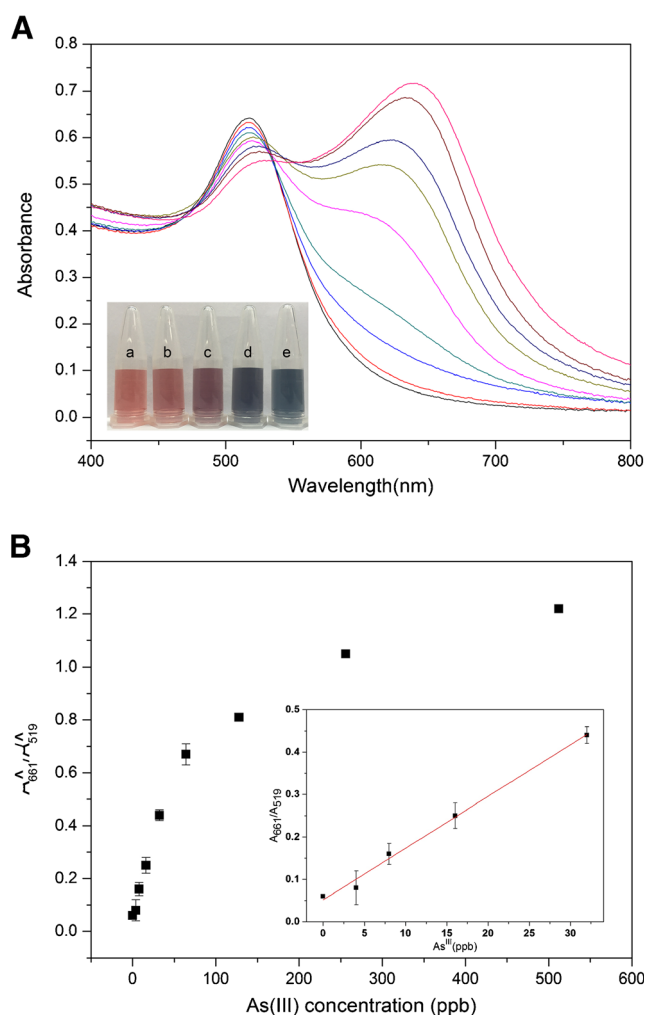**Fig. 1** Schematic illustration of AuNPs-based As(III) detection

A

B
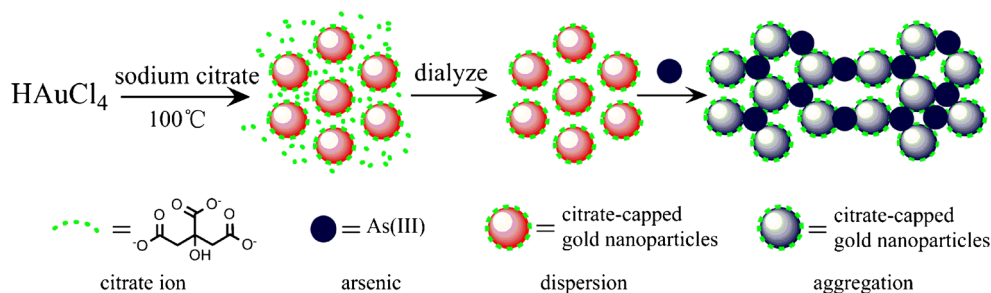
Fig. 3 **A** UV–Vis spectra of citrate capped AuNPs in the presence of different concentrations of As(III). Insert portion was the corresponding photographic images. **B** Absorption ratio A_{661}/A_{519} of citrate capped AuNPs versus the concentration of As(III). Insert portion shows the linear dependence of A_{661}/A_{519} at low As(III) concentration. (error bars represent the standard deviation of three measurements)

sodium hydroxide, hydrochloric acid and all of the metal salts used in this study were obtained from the Beijing Chemical Reagent Company (www.beijingchemworks.com). Sodium arsenite was bought from Xiya Chemical Industry Co Ltd. (www.xiyashiji.com) and sodium arsenate-dibasic heptahydrate was bought from Chem Service, Inc. (www.chemnet.com). Dimethylarsinic acid (DMA) was bought from www.aladdin-e.com. Sodium methylarsonate (MMA) was obtained from www.accustandard.com. All the chemicals were of analytical reagent grade and Milli-Q-purified distilled water was used throughout the experiments.

Apparatus

The UV-vis spectra were recorded with a UV-2550 spectrophotometer (www.shimadzu.com). Transmission electron microscopy (TEM) images were acquired on a FEI Tecnai G^2 F20 (www.fei.com). Inductively coupled plasma optical emission spectrometer (ICP-OES) experiments were carried out by using a PQ 9000 spectrometer (www.analytik-jena.com). All the photographs were taken by a DSC-W150 camera (www.sony.com).

AuNPs synthesis and dialysis

As reported previously, citrate capped AuNPs were synthesized via trisodium citrate reduction method as shown in Fig. 1 [37]. Briefly, the AuNPs were synthesized by adding 15 mL of trisodium citrate solution (38.8 mM) rapidly to a boiling solution of HAuCl$_4$ (1.0 mM, 150 mL) and stirred for 30 min to form a wine-red solution. The resulting solution was cooled to room temperature while being stirred continuously, then stored at 4 °C for further use.

The above AuNPs were diluted with the ratio of 1:3 by Milli-Q-purified distilled water before dialysis. 5 mL of diluted AuNPs was placed in a membrane bag with molecular weight cut off 1000 under continuous stirring for 6 h, then water dialyzed AuNPs was obtained.
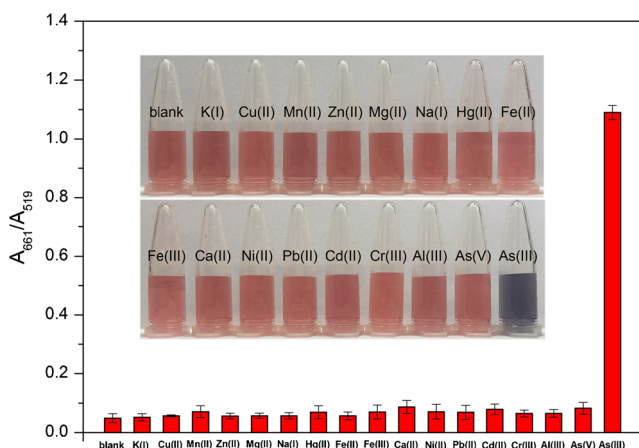
Table 1 Comparison of different methods for the detection of As(III) [39, 40]

Methods	Linear range (ppb)	Limit of detection (ppb)	The need for additional surface modification	Reference
Resonance Rayleigh Scattering	0.1–200	0.2	Yes	[25]
SERS	4–300	0.76	Yes	[22]
SPR	/	Below 10	Yes	[39]
Fluorescence	375–18,750	1.5	Yes	[40]
DLS	/	0.01	Yes	[21]
Colorimetric assay, UV-vis	/	1	Yes	[21]
Colorimetric assay, UV-vis	2–20	2.5	Yes	[28]
Colorimetric assay, UV-vis	/	5.3	Yes	[8]
Colorimetric assay, UV-vis	4–100	1.8	No	This study

Fig. 4 Selectivity of the visual method. Absorption ratio A_{661}/A_{519} of citrate capped AuNPs in the presence of various metal ions (256 ppb). Inset portion shows the corresponding photographic images of the AuNPs colloid

Colorimetric detection of As(III)

In a 1.5 mL centrifuge tube, 20 μL of As(III) solution with varying concentrations were pipetted into water dialyzed AuNPs respectively. After incubating for 6 min at room temperature, the above solutions were measured with UV-Vis spectrophotometry and recorded by photographs. The quantitative analysis of As(III) was achieved by the absorption ratio (A_{661}/A_{519}). Limit of detection (LOD) values were calculated using the following formula:

Limit of detectable response = average response of the blank + (3 × standard deviation of the blank) [38].

Results and discussion

The responses of dialyzed and undialyzed AuNPs for As(III)

Dialyzed and undialyzed AuNPs were performed in the absence and presence of As(III) separately. Figure 2a shows the color change and absorbance spectra. A decrease of maximal absorption at 519 nm and an enhancement of a new peak at 661 nm indicating that the state of the AuNPs changed from dispersion to aggregation. In the presence of As(III), the color

of dialyzed AuNPs changed from red to blue (d of Fig. 2(A)) indicating the aggregation of the AuNPs, which is in accordance with the result of UV-vis spectroscopy. While the presence of 909 ppb As(III) did not induce any change in the undialyzed AuNPs (c of Fig. 2(B)). Therefore, the dialyzed AuNPs show a higher sensitivity to As(III). The As(III) significantly stimulates aggregation of AuNPs which is also evidenced by TEM images (Fig. 2b). In the presence of As(III), the citrate-capped AuNPs undergo aggregation due to the interaction of citrate ion with As(III).

Optimization of method

The following parameters were optimized: (a) The size of the AuNPs (Fig. S1); (b) Concentration of remnant sodium citrate in solution (Fig. S2); (c) Impact of dialytic time (Fig. S3); (d) Impact of pH (Fig. S4); (e) Impact of incubation time (Fig. S5). Respective data and Figures are given in the Electronic Supporting Material. We found the following experimental conditions to give best results: (a) AuNPs size of 13 nm; (b) Without addition of sodium citrate in solution; (c) Dialytic time of 6 h; (d) pH 11; (e) Incubation time of 6 min; (f) Stability for two days.

Colorimetric detection of As(III)

To examine the assay for the direct colorimetric detection of As(III), 20 μL of different concentration of As(III) solution were added into 1 mL of water-dialyzed AuNPs under optimal experimental conditions and tested after mixed for about 6 min. The increase of As(III) concentration can induce a decrease of maximal absorption at 519 nm and an enhancement of a new peak at 661 nm (Fig. 3a). In addition, a gradual color change from wine-red to blue can also be observed that means we can discriminate the concentration of As(III) with bare eyes (the inset of Fig. 3A). The relationship between the ratio of A_{661}/A_{519} and As(III) concentration in the range from 4 to 100 ppb shows excellent linearity with a correlation coefficient of 0.9914 and a detection limit of 1.8 ppb (3σ) which is below guideline value of 10 ppb (Fig. 3B), indicating that the method based on citrate capped AuNPs definitely meets the requirements of routine detection.

Table 2 Determination of As(III) in water samples

Sample	Added (ppb)	Visual method			ICP-OES		
		Mean found (ppb)	Recovery (%)	RSD (%)	Mean found (ppb)	Recovery (%)	RSD (%)
1	16	15.2 ± 0.6	95.0	3.9	15.5 ± 0.3	96.9	1.9
2	32	31.4 ± 0.8	98.1	2.5	32.1 ± 0.9	100.3	2.8
3	64	65.8 ± 1.1	102.8	1.7	66.6 ± 0.7	104.1	1.1

We have listed typical methods for As(III) detection to make intuitive comparison. The method described in reference [28] is highly innovative. It can detect arsenic by photometric detection and dynamic light scattering assay with a detection limit of 1 ppb and 10 ppt separately. The detection limit achieved with this DLS probe represents the lowest among all the reported methods. Although gold nanoparticle sensors for As(III) are described in the literature [28, 29, 36], they usually require some kinds of receptor molecules attached to the particles which result in the specific binding of As(III), like glutathione or aptamer. Here we present a new method for arsenic detection with no need for additional surface modification. We just use the citrate-stabilized gold nanoparticles, utilizing the citrate-induced specific binding of As(III) which greatly simplify the complicated thiolated or other costly labeled probe preparation processes [34]. In order to improve the sensitivity, we utilize dialysis to remove remnant sodium citrate in solution, for that excess sodium citrate can play a counteractive role in the response to As(III) due to the unavoidable binding to As(III) (Fig. S2). The dialysis method can be applied to improve the sensitivity of all the reported colorimetric detection based on gold nanoparticles. We also demonstrate the quantification and the selectivity (by checking with other ions), and finally demonstrate a detection of As(III) down to 1.8 ppb in drinking water (see Table 1). These results indicate that the present sensing system is a promising method for the detection of As(III).

Selectivity of the colorimetric method

The selectivity of the method for As(III) was examined by evaluating the absorbance ratio A_{661}/A_{519} of citrate capped AuNPs in the presence of competing metal ions, including K(I), Cu(II), Mn(II), Zn(II), Mg(II), Na(I), Hg(II), Fe(II), Fe(III), Ca(II), Ni(II), Pb(II), Cd(II), Cr(III), Al(III), As(V), MMA and DMA.

Figure 4 and Fig. S6 show that only As(III) can induce a remarkable aggregation of AuNPs. The results demonstrate that all of the studied ions displayed slight and negligible interferences for As(III) detection. The possible reason is as follows: when pH at 11, only As(III) predominantly presents as H_3AsO_3 and $H_2AsO_3^-$ in the form of stable covalent compound [41, 42], which can form hydrogen bond with citrate ions and induce the obvious aggregation of citrate capped AuNPs [43].

Application in water samples

To validate the applicability of the method, the analysis of As(III) in drinking water was performed. A series of As(III) standard solution was added into the drinking water, and then detected utilizing citrate capped AuNPs based colorimetric method and Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (see Table 2). The results show that the recoveries of 16 ppb, 32 ppb and 64 ppb As(III) are 95.0%, 98.1% and 102.8%, which is in good agreement with the results obtained by ICP-OES (96.9%, 100.3%, 104.1% respectively), demonstrating the potential application of the colorimetric assay for As(III) detection in water samples.

Conclusion

Citrate capped gold nanoparticles were synthesized via citrate reduction method and reported as sensitive, selective, and colorimetric single-shot assay for As(III). As(III) can bind with citrate-capped AuNPs and directly induce the aggregation of citrate capped AuNPs, resulting in an obvious color change from wine-red to blue. It was successfully applied to the determination of As(III) in spiked drinking water where it gave adequate recoveries. However, our method cannot online monitor over time like a pH electrode or an oxygen electrode for that completely aggregated AuNPs no longer show a linearity between the ratio of A_{661}/A_{519} and As(III) concentration.

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