



# Simple and fast colorimetric detection of inorganic arsenic selectively adsorbed onto ferrihydrite-coated silica gel using silver nanoplates



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## ABSTRACT

The optical detection for inorganic arsenic (As) semi-quantitative determination is presented by using silver nanoplates (AgNPs). The color of AgNPs is immediately changed in the presence of As(III) and As(V) with the same sensitivity. To improve the selectivity of AgNPs for As detection, ferrihydrite-coated silica gel (SiO<sub>2</sub>-Fh) was specifically exploited as adsorbent for arsenic prior to As detection by AgNPs. The developed method provides the detection limit of 0.5 ppm with the detection range between 0.5 ppm and 30.0 ppm for As determination observed with naked eye, and allows to determine total inorganic arsenic. This is the first report of As detection approach combining As removal technology together with nanotechnology. This combined technique provides a rapid, sensitive and selective method for monitoring As levels in aqueous samples, and can be employed as a testing field kit to screen arsenic contamination outside of a laboratory.

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## 1. Introduction

Arsenic is a serious environmental contaminant because of its toxicity and also carcinogenicity. This toxic element occurs as a major constituent in more than 200 minerals. Arsenic is unevenly distributed in the earth's crust and is found in soil, rocks, and minerals around the world. Furthermore, arsenic contamination of water resources both surface and subsurface has been reported in many parts of the world, as arsenic can be released into water systems once mineral deposits or rocks containing arsenic are dissolved. In addition, some anthropogenic activities also accelerate arsenic exposure to the environment e.g. mining, agricultural and industrial activities, and waste and fossil-fuel burning. Arsenic exists in four oxidation states: As(-III), As(0), As(III) and As(V) with numerous forms, both organic and inorganic, resulting in complexity of its chemistry and mobility in the environment. The major arsenic species found in environmental and biological samples are arsenite As(III), arsenate As(V), arsenious acids, arsenic acids, monomethylarsonate (MMA), dimethylarsinate (DMA), arsenobetaine (AB), arsenocholine (AC), and arsenosugars. Different species of arsenic have different toxic levels of which organic species are considered to be substantially less harmful in comparison to inorganic forms. Among the existing arsenic species in

the environment, arsenite and arsenate, inorganic species, are the most concerned species because of their high toxicity in which arsenite is 10 and 70 times more toxic than arsenate and the methylated species, respectively [1,2].

Due to its toxicity, arsenic contaminations in a wide range of samples such as water, food, soils, and plants etc. were monitored [3–8]. To determine the accurate quantity of arsenic in samples, expensive and sophisticated instruments and facilities together with skilled staff are required. Several analytical techniques have been applied for arsenic determination such as atomic absorption spectroscopy (AAS) [3,9], atomic emission spectroscopy (AES) [10–12], electrochemical methods [13–16], atomic fluorescence spectrometry [17,18], neutron activation analysis (NAA) [19,20], capillary electrophoresis (CE) [21,22], and chromatographic methods (hyphenated techniques) [3,9,23,24]. To date, field test kits for determining arsenic semi-quantitatively have been developed and extensively used for arsenic in water samples. Most of the test kits commercially available are based on the classical Gutzeit method, developed over 100 years ago [25] used for hydride generation to generate a toxic arsine gas, AsH<sub>3</sub>. However, the user must be very careful, as the test kit protocols involve the use of a strong reducing agent and acid, and toxic gas production.

Nowadays, nanoparticle optical detection based on colorimetry have been gaining great attention from researchers especially for biological and environmental sample analysis because of their simplicity, low cost, less time consuming, and ease of data interpretation. Nanotechnology is rapidly growing in the field of optical

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detections, as nanoparticles (NPs) have unique physical, chemical, and biological properties compared to their macro-scaled counterparts. Different types of NPs provide different optical, fluorescent and magnetic properties. Therefore, NPs with distinctive optical property related to the size and shape of the NPs especially gold- and silver-NPs show potential to be exploited in a wide range of applications. Gold nanoparticles (AuNPs) have been intensively studied for numerous applications as optical detections for heavy metals [26–29] including As(III) [30] and As(V) [31], aromatic compounds [32,33], organophosphate [34], and stimulant [35] etc. Colorimetric detections of mercury(II) ion using AgNPs were reported for environmental [36,37] and biological sample [38] analyses. The selective detection of  $\text{Co}^{2+}$  using glutathione-modified AgNPs was also presented [39].

In this study, silver nanoplates (AgNPLs) were elucidated for As(III) and As(V) detections. However, due to the matrix effect which possibly interferes the detection, iron oxide-coated silica gel was exploited to selectively adsorb arsenic prior to the detection with AgNPLs. Since several technologies have been used for arsenic removal from water to improve the water quality such as oxidation [40], co-precipitation [41], ion exchange [42,43], and membrane [44] etc. Adsorption onto sorptive media [45–51] is one of the most common technologies utilized to remove arsenic. Iron(III) oxide is widely used as arsenic adsorbent [45–48]. The synthesis and properties of ferrihydrite-coated silica gel ( $\text{SiO}_2\text{-Fh}$ ) for As removal were studied and explained clearly by Arifin [45].  $\text{SiO}_2\text{-Fh}$  showed good efficiency on both As(III) and As(V) removals with easy synthesis procedure. Therefore, the iron oxide-coated silica gel was applied for arsenic detection herein. Thus, the developed approach of using the As removal technology combined with silver nanotechnology was first demonstrated for the detection of inorganic arsenic in contaminated water for the first time.

## 2. Experimental section

### 2.1. Chemicals and materials

Silver nanoplates (AgNPLs) with dark blue color were obtained from the Sensor Research Unit at the Department of Chemistry, Chulalongkorn University. Synthesis of AgNPLs employed a facial method that used starch as the stabilizer without capping agents. Analytical grade reagents and 18 M $\Omega$  cm resistance deionized water (obtained from a Millipore Milli-Q purification system) were used throughout. Arsenic trioxide, arsenic pentoxide, iron(III) nitrate nonahydrate, mercury chloride, silver nitrate, trisodium phosphate were purchased from Sigma-Aldrich. Sodium chloride, zinc chloride, magnesium chloride, lead nitrate, sodium sulfate, sodium carbonate, calcium chloride, ammonium chloride, and magnesium sulfate were purchased from Analytical univar reagent Ajax Finechem.

### 2.2. Preparation of the ferrihydrite-coated silica gel

Ferrihydrite-coated silica gel ( $\text{SiO}_2\text{-Fh}$ ) was modified from the protocol developed by Eric Arifin et al. [45]. Briefly, 20 g of silica gel 60 (70–230 mesh ASTM) and 2.8 g of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and 50 mL deionized water were loaded into 250 mL flask. The pH of the mixture was adjusted to neutral (pH 7) by using  $\text{NH}_4\text{OH}$  solution. The mixture was stirred for 2 h at room temperature. The modified silica bead was then filtered using vacuum filtration and washed with deionized water to remove free ferrihydrite from the beads. Finally, the  $\text{SiO}_2\text{-Fh}$  was oven dried at 60 °C for 2 h, and then stored in a glass vial for further use.

### 2.3. Arsenic adsorption on the ferrihydrite-coated silica gel

Approximate 0.3 g of  $\text{SiO}_2\text{-Fh}$  was added to the 100 mL of sample solution and then stirred with slow speed for 45 min. The solid was then filtrated using vacuum filtration and washed with large volume of deionized water. The solid was oven dried at 50 °C for 1 h, and then stored in a glass vial until the determination.

### 2.4. Colorimetric measurements of inorganic As and AgNPLs

The absorption spectra of the AgNPLs with and without inorganic arsenic added were obtained by using a UV–vis absorption spectrometer (Shimadzu, 2401 PC). In addition, AgNPLs were characterized and reported in our previous work [36].

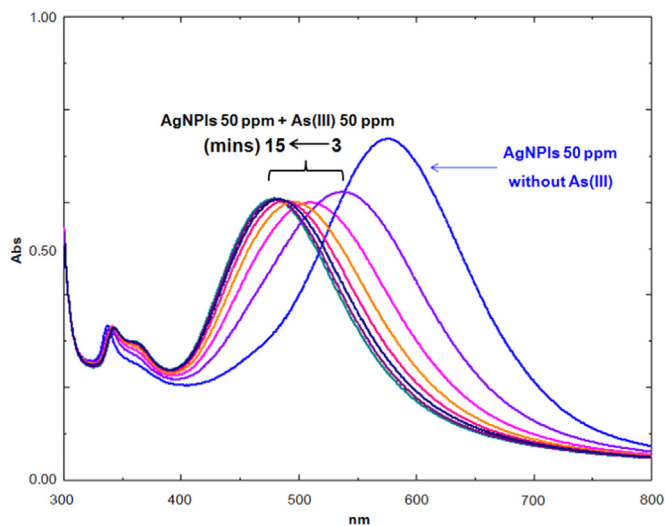
### 2.5. Analysis of real samples

To test the practical application capability of the develop approach, water samples from different sources were collected and filtered through a 0.45  $\mu\text{m}$  membrane. Standard addition method was applied to prepare a series of samples by spiking standard solutions of As(III) to tap water, groundwater, and canal water. Prior to arsenic determination using AgNPLs, the pretreated water samples were applied to  $\text{SiO}_2\text{-Fh}$  following the procedure described in Section 2.3. In addition, inductively coupled plasma-optical emission spectrometry (Thermo Scientific iCAP 7000 Series ICP-OES) was exploited as validation method for the proposed approach.

## 3. Results and discussion

### 3.1. Conditions of AgNPLs for inorganic As determination

The dark blue colored AgNPLs were obtained with an initial concentration of 400 ppm. The AgNPLs showed maximum absorption at 575 nm. The dark blue color of AgNPLs was changed to purple, pink, orange, and yellow, respectively, depending on the concentrations of As added to the solution. Fig. 1 is UV–vis spectra of 50 ppm AgNPLs and also of the 50 ppm AgNPLs with 50 ppm As(III) at the ratio 1:1. The spectra of AgNPLs containing As(III) were



**Fig. 1.** The UV–vis spectra of AgNPLs at 50 ppm without As(III) added (Blue line) and with 50 ppm As(III) addition, which were recorded every 2 min for 15 min started from the third minute after adding As(III) to AgNPLs. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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