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Determination of inorganic arsenic species by hydride generation–inductively coupled plasma optical emission spectrometry

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ABSTRACT: A hydride generation–inductively coupled plasma optical emission spectrometry (ICP-OES) technique was developed to determine inorganic As, including total As, As(III), and As(V), in drinking water samples in optimized conditions as follows: wavelength of 193.7 nm, integration time of 5–10 s, RF power of 1.3 kW, and the flow rates of plasma gas and auxiliary gas of 15 and 0.2 l/min for ICP-OES, the sample flow rates of 1.2 ml/min, reductant, and acid 0.4 ml/min and carrier gas 0.3 l/min, 0.4% (w/v) $NaBH_4$ with 40% (w/v) KI within 10 min as a reductant for total As, 0.4% (w/v) $NaBH_4$ for As(III) and 2 mol/l HCl for hydride generation. As(V) was obtained from the difference between total As and As(III). The linear dynamic range was 1–100 μg/l with a correlation coefficient of 0.9998. The limit of detection of total As, As(III), and As(V) was 0.38, 0.07, and 0.37 μg/l, respectively. The limit of quantification of total As, As(III), and As(V) was 1.28, 0.24, and 1.17 μg/l, respectively. 94.9–99.1% recovery for each As species was achieved. This fast and easy method was applied to determine arsenic in drinking water samples with satisfactory recovery (79–112%).

KEYWORDS: drinking water, HG-ICP-OES

INTRODUCTION

Inorganic arsenic is known as one of the most hazardous elements widely distributed in the earth crust. It has received increased attention in recent years because of its high toxicity, especially its carcinogenic properties[1,2]. Its contamination in drinking water has been found to be the most frequent cause of poisoning cases in Thailand[3]. The determination and speciation of arsenic contamination in environmental systems are essential, mainly because the toxicity and bioavailability of this element is species dependent. In the environment, arsenic is found to combine with other elements such as carbon and hydrogen which is referred to as organic arsenic whereas that with oxygen, chlorine, and sulphur is called inorganic arsenic[4].

Inorganic arsenic is considered to be the most toxic form found in groundwater, surface water, and food[2,5]. Its toxicity[6] and mobility depend on the existing chemical forms; the most toxic species are arsenite As(III) and arsenate As(V) which are main forms in the environment[4]. In addition, inorganic arsenic can increase the risk of lung cancer, skin cancer, bladder cancer, liver cancer, kidney cancer, and prostate cancer. The World Health Organization (WHO), the Department of Health and Human Services (DHHS) and the Environmental Protection Agency have reported that inorganic arsenic is a human carcinogen[1]. The American Conference of Governmental Industrial Hygienists (ACGIH) also classified inorganic arsenic forms as confirmed human carcinogens; cancer category A1. The high potential risk makes arsenic one of the most intensively studied elements in speciation analysis (WHO, 2001)[1].

The most popular technique to determine inorganic arsenic species is hydride generation (HG). In environmental samples, this technique has been combined with inductively coupled plasma optical emission spectrometry (ICP-OES) since 1978[7]. More recently, USEPA has been developing this technique and has combined it with a continuous flow system[8] in which the acidified sample, blank or standard continuously flows and is mixed with a stream of reductant, usually sodium borohydride, to produce the gaseous hydride of arsenic or arsine gas and hydrogen gas as a by-product. A flow of argon is added to this mixture and the hydride is 'stripped' into the gas phase. A gas/liquid separator allows

the gaseous, hydride containing phase, to enter the ICP for analysis, and the remaining liquids to be pumped to waste. Limits of detection can generally be improved by about two orders of magnitude over simple solution nebulization using hydride generation. Besides, continuous flow hydride generator for ICP-OES analysis is simple and inexpensive[9]. With specific sample preparation, the limit of detection (LOD) can be lowered much further[10].

Hydride generation combined with inductively coupled plasma optical emission spectrometry (HG-ICP-OES) is developed and optimized here to determine inorganic As species including total As, As(III), and As(V) and then applied to quantitative analysis of the species in drinking water samples.

MATERIALS AND METHODS

Apparatus

A Perkin-Elmer Model 4300 DV inductively coupled plasma optical emission spectrometer with axial plasma view equipped with a continuous flow hydride generator (Shimadzu Model HGV-1) was used in this experiment. Standard and reagent preparation, instrumental setup, optimization of HG-ICP-OES conditions, linear dynamic range, detection limit, and accuracy were investigated to determine inorganic As species in drinking water samples.

Instrumental setup

The continuous hydride generation system consisted of a three-channel peristaltic pump (4300DV ICP-OES instrumental) with three pump tubes (Tygon, 6.5 mm i.d. for sample and Tygon, 3.5 mm i.d. for $NaBH_4$ and HCl), a mixing coil and gas-liquid separator. The flow rate of sample was first selected at 3.6 ml/min, HCl and $NaBH_4$ both 1.2 ml/min. Arsenic in the sample was reduced to arsine or hydride gas by using the reductant in an acid medium. The three solutions were pumped by a three channel peristaltic pump into the manifold. After mixing the solutions were transported with argon carrier gas into the mixing coil and passed to the gas/liquid separator to separate arsine gas into the hydride connector of the ICP-OES system for analysis. The data of arsenic emission signals were relayed to a printer and the data acquisition was processed by specific software, Winlab32. Peak integration was achieved by area measurement.

Reagents, solutions, and samples

All chemicals used in the experiment are of analytical-reagent grade (AR grade). The stock working standard 100 μg/l of As(III) and 100 μg/l of As(V) were prepared daily with deionized (DI) water. To study inorganic As species, 4 mol/l HCl and 0.4% (w/v) of $NaBH_4$ in 0.6% (w/v) of NaOH for hydride generation and 10% KI were also prepared. Five drinking water samples were purchased from the supermarket in Hat Yai, Songkhla.

Preparation of working As(III) and As(V) standard solutions

As(III) stock standard solution was prepared by weighing 0.1320 g of As_2O_3 which was dissolved in 1 mM NaOH. Then the pH of the solution was adjusted with concentrated HNO_3 and its volume was made up to 250 ml with DI water. As(V) stock standard solution was prepared by weighing 0.1654 g of As_2O_5 and then its volume was adjusted to 250 ml with DI water. The standard working solutions 100 μg/l of As(III) and As(V) were prepared by diluting the stock standard solutions above.

Preparation of $NaBH_4$ solution

The reductant solution of $NaBH_4$ 0.4% (w/v) used was prepared fresh daily by weighing 1 g of $NaBH_4$ and 1.25 g of NaOH then dissolved with DI water to a final volume of 250 ml.

RESULTS AND DISCUSSION

Optimization of the HG-ICP-OES conditions

The instrumental conditions of hydride generation combined with an inductively coupled plasma optical emission spectrometry (HG-ICP-OES) were investigated in order to yield an optimal signal/noise ratio, including wavelength, integration time, RF power, flow rates of plasma, auxiliary and carrier argon gas, concentration, and flow rate of sodium borohydride ($NaBH_4$), HCl concentration and flow rate of sample solution.

Wavelength

The emission signals of the As(III) at four wavelengths, i.e., 189.0, 193.7, 197.2, and 288.8 nm revealed the greatest intensity at 193.7 nm. The result was in good agreement with previous studies[11,12] and selected for the next experiment.

Integration time

The integration time was varied in the range of 1–5, 5–10, 10–20, and 20–50 s. The highest signal was obtained at 5 s and not significantly varied during 5–10 s (Fig. 1a). This behaviour was similar to that previously reported[13]. Thus the integration time selected for further studies was 5–10 s.

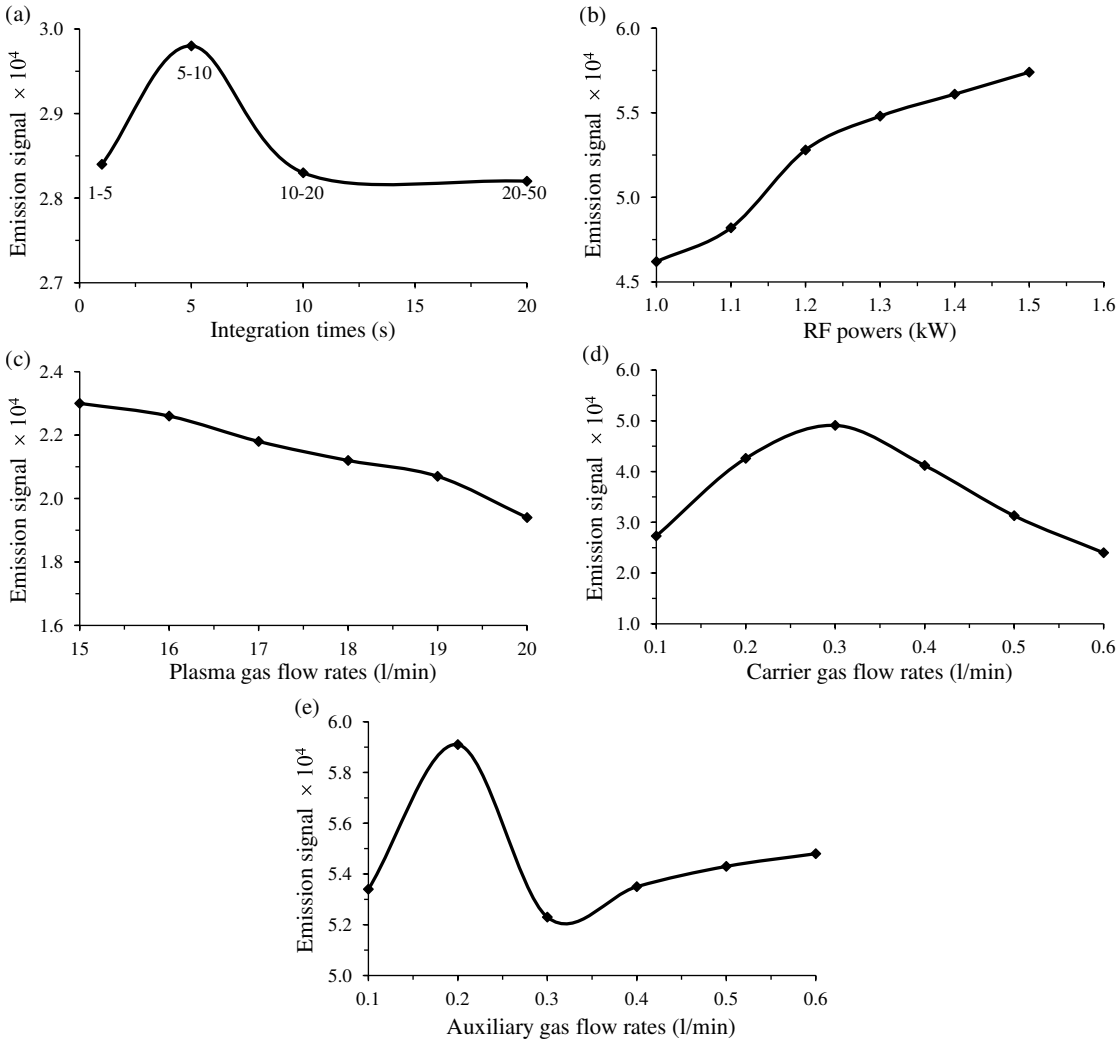

Fig. 1 The relative emission signal of As(III) at various (a) integration times, (b) RF powers, (c) plasma gas flow rates, (d) carrier gas flow rates, and (e) auxiliary gas flow rates.

RF power

The radio frequency generator (RF) powers were investigated at 1.0, 1.1, 1.2, 1.3, 1.4, and 1.5 kW in order to provide the best generation of the plasma discharge. As shown in Fig. 1b, high RF power levels can be used to increase the signal level up to about 1.5 kW, in good agreement with previous reports[14] and 1.3 kW was selected for further experiments due to higher precision.

Plasma gas flow rate

The plasma gas flow rates were studied from 15–20 l/min with fixed carrier and auxiliary gas flow rates. Since the minimum output plasma flow rate of the system was 15 l/min and the emission signal decreased with an increase of the flow rate of plasma gas (Fig. 1c), this flow rate was selected for the next experiment.

Carrier gas flow rate

Carrier gas can affect transference and extraction efficiency of AsH_3 from the gas-liquid separator. When assessed over the range of 0.1–0.6 l/min, a higher flow rate of carrier gas resulted in signal instability and decreased in sensitivity of the emission signal (Fig. 1d), similar to previous report[15]. The highest signal was at the carrier gas flow rate of 0.3 l/min which was chosen for the next experiment.

Auxiliary gas flow rate

Fig. 1e shows that, with the increase of auxiliary gas flow rate from 0.1–0.6 l/min, the signal intensity

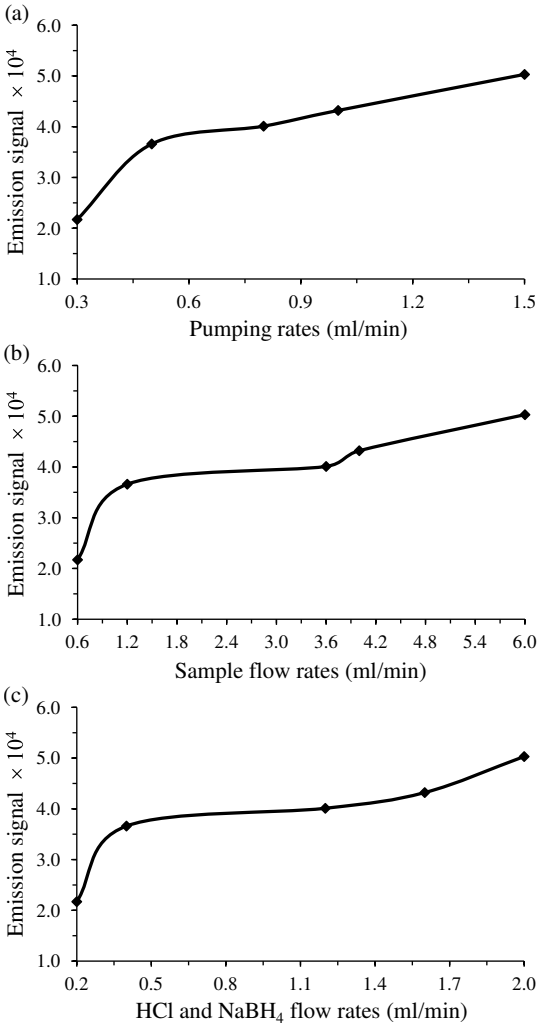

Fig. 2 The relative emission signal of As(III) at various (a) pumping rates, (b) sample flow rates, and (c) HCl and $NaBH_4$ flow rates.

and sensitivity decreased. The highest intensity was obtained at an auxiliary gas flow rate of 0.2 l/min and was chosen for further experiments.

Pumping rates

The pumping rates were studied in order to obtain the optimum flow rate of the sample, HCl and $NaBH_4$ solutions. As shown in Fig. 2, the emission signal increased significantly up to a pumping rate of 0.5 ml/min, with the lowest %RSD. For higher flow rates, the precision decreased and plasma was less stable. It can be concluded that the optimum flow rates of the sample, HCl and $NaBH_4$ were 1.2, 0.4, and 0.4 ml/min, respectively, and were selected for the next experiments.

HCl concentration

The effect of HCl concentration from 0.5–4.0 mol/l on hydride generation was investigated. The concentration of $NaBH_4$ was 0.4% (w/v). As shown in Fig. 3a, the emission signal rapidly increased when the HCl concentration was increased up to 2 mol/l, reaching maximum and constant value at concentrations above 3 and 4 mol/l, similar to previous reports[7,16]. The optimum concentration of HCl chosen was 2 mol/l because of the lowest %RSD.

Reductant concentration

The effect of the concentration of $NaBH_4$ as a reducing reagent of 0.1, 0.2, 0.4, 0.6, 0.8, and 1% (w/v) on changing arsenic to arsine gas was investigated. The signal rapidly increased when the $NaBH_4$ concentration was increased up to 0.4% and reaching constant value at the concentrations above 0.4–1% (Fig. 3b), in good agreement with previous report[17]. Since the signal intensity reached a maximum with 0.4% $NaBH_4$, this concentration was chosen as the working concentration for further experiments.

Pre-reductant concentration

The concentration of KI, a more potent reducing agent than $NaBH_4$[18,19] used as a pre-reductant, is one of most important parameters for reducing As(V) to As(III). Fig. 3c shows the effect of 5–60% (w/v) KI concentrations. The optimum pre-reductant concentration was found to be 40% due to the highest emission signal.

Pre-reductant time

The reaction time for complete reduction of As(V) to As(III) was examined from 5–30 min. The optimum reduction time with the greatest signal was found to be 10 min (Fig. 3d). The optimum conditions for HG-ICP-OES determination of inorganic As species include, for ICP, the wavelength of 193.7 nm, maximum and minimum integration time of 10 and 5 s, respectively, RF power of 1.3 kW, argon flow rate of 0.3 l/min, 15 l/min, 0.2 l/min as carrier, plasma and auxiliary, respectively, generator frequency of 40 MHz and delay time of 30 s with five replicates and axial plasma viewing and for HG, pumping rate of 0.5 ml/min, sample flow rate of 1.2 ml/min, $NaBH_4$ and HCl flow rate of 0.4 ml/min, concentrations of $NaBH_4$, HCl, and KI of 0.4% (w/v), 2 mol/l and 40% (w/v), respectively, and the reduction time of 10 min.

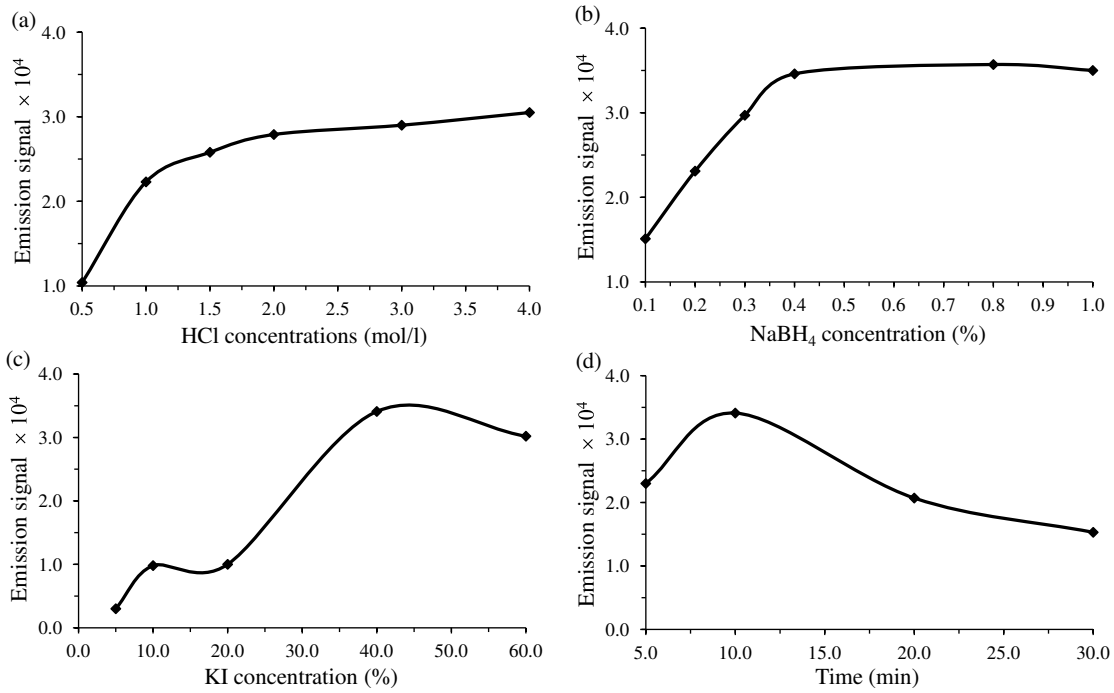

Fig. 3 The relative emission signal of As(III) at various (a) HCl concentrations, (b) $NaBH_4$ concentrations, (c) KI concentrations, and (d) periods of reaction time.

Linear dynamic range, LOD and LOQ of total As, As(III), and As(V)

The emission signal responses at various total As, As(III), and As(V) concentrations are shown in Fig. 4 with a relative standard deviation (RSD) of less than 3% for five replicates and an optimum linear dynamic range of 1–100 μg/l with good correlation coefficients, $R^2 > 0.9999$, 0.9998, and 0.9998, respectively. This is in agreement with 50–200 μg/l[11] and 50–100 μg/l[20], covering 1 up to 100 μg/l which are common As concentrations in nature and in drinking water.

The LOD and limit of quantification (LOQ) of total As and As(III) based on the calibration curve (seven standard solutions ranging from 1–100 μg/l, correlation coefficient $R^2 = 0.9998$) was determined by plotting peak areas against total As concentrations and then the LOD (3σ) and LOQ (10σ) were calculated from the equation $C_L = kS_B/m$ with 10 replicate peak area measurements; where C_L is LOD concentration value (IUPAC definition)[21], k is 3 (for LOD), and 10 (for LOQ) which allows a confidence level of 99.86%, S_B is the standard deviation of blank, and m is the analytical sensitivity. The obtained LOD and LOQ of 0.38 and 1.28 μg/l for total As, 0.07 and 0.24 μg/l for As(III), and 0.37 and 1.17 μg/l for As(V) are better than previous values of LOD 1 μg/l and LOQ 10 μg/l[13] and 36 μg/l[22], indicating the scope of the method regarding its applications to real samples is excellent for drinking water.

Accuracy

The accuracy of this method was investigated by percentage recovery. The percentage recovery of total As and As(III) was performed experimentally whereas percentage recovery of As(V) concentration was obtained by the difference between total As and As(III). Total As and As(III) concentrations of 4, 8, 16, and 24 μg/l were prepared in deionized water and tested with the HG-ICP-OES system. The calibration curve was then created by plotting peak area against total As and As(III) concentrations as shown in Table 1 and that with added total As and

Table 1 The relative emission signal at various total As or As(III) concentrations.

Concentration (μg/l)	Total As†	As(III)†
4	0.4 ± 3.0	1.8 ± 3.0
8	0.8 ± 2.9	4.2 ± 3.0
16	1.6 ± 2.5	8.6 ± 2.1
24	2.3 ± 2.1	13.4 ± 1.4

† Emission signal × 10^3 ± %RSD, 5 replications.

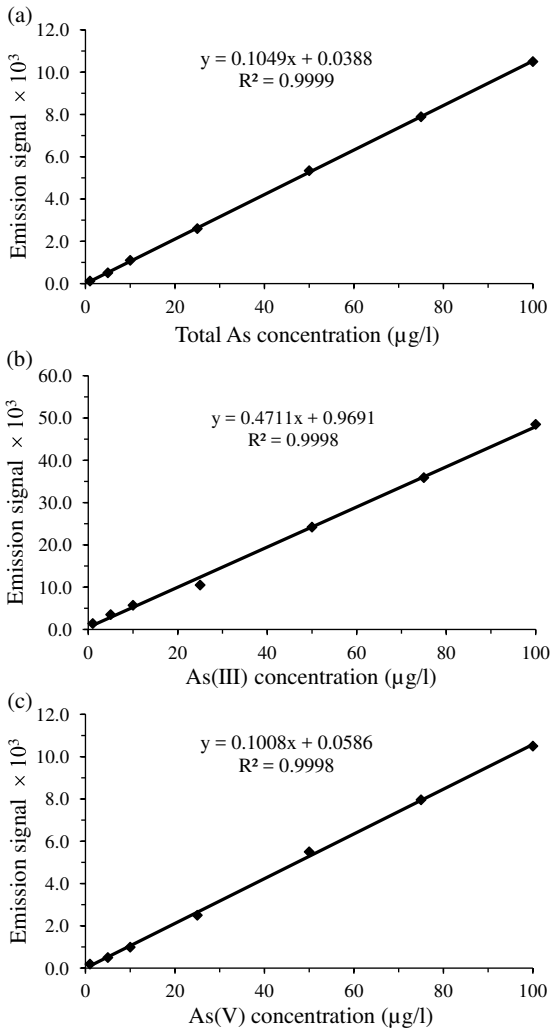

Fig. 4 The calibration graph of (a) total As, (b) As(III), and (c) As(V).

As(III) amounts of 8 and 16 µg/l in Table 2.

Recovery of As(V)

The As(V) concentration was obtained by the difference between total As and As(III) concentration to obtain the percentage recovery of As(V) of 96.9 and 98.3%, respectively (Table 3). Since the accuracy values of three As species are found in the range of 94.9–99.1% recovery, this method can be successfully applied to selective determination of these three As species in natural and drinking water samples.

Sample analysis

Quantitative analysis of total As, As(III), and As(V) was evaluated by using the calibration graph and spiking technique to check the accuracy of this method with drinking water samples.

Table 2 Recovery of total As and As(III) with added total As and As(III).

Added conc.†	Total As		As(III)	
	Found†	Recovery (%)	Found†	Recovery (%)
8	7.59	94.9	7.83	97.8
16	15.69	98.1	15.85	99.1

† µg/l.

Table 3 Recovery of As(V) with added total As.

Added total As†	Found concentration†			Rec. of As(V) (%)
	Total As	As(III)	As(V)	
8	7.59	3.72	3.87	96.9
16	15.69	7.83	7.86	98.3

† µg/l.

Quantitative analysis of total As and As(III) in drinking water

The calibration curve method was used to determine total As and As(III) concentration in drinking water samples with the optimum conditions previously described. This method is not suitable for very low concentration of both total As and As(III) since the concentration of As in drinking water is lower than the detection limit of the method. Further analysis was then carried out with a calibration curve of total As and As(III) at concentrations of 4, 8, and 12 µg/l then spiked with 8 and 16 µg/l of total As or As(III) into the drinking water samples to evaluate percentage recovery (Tables 4 and 5). The recoveries of 8 and 16 µg/l total As were in the range of 86.3–93.8 and 92.7–100.9%, respectively, and for As(III) the recoveries of the 4, 8, and 12 µg/l spikes were in the range of 89.7–98.2, 90.1–94.6, and 91.3–93.1%, respectively.

Quantitative analysis of As(V)

The As(V) concentration was obtained by calculating total As−As(III). The result from Table 6 shows the percentage recovery was in the range of 79.4–94.3% for 4 µg/l As(V) and 90.7–111.6% for 8 µg/l As(V). When applied to drinking water samples, As was not detected because the amounts of these As species in drinking water samples are lower than the LOD of this technique as well as standard value in drinking water (WHO, 2003)[23]. However, after spiking, the percentage of recoveries of these As

Table 4 Recovery of total As with spikes in drinking water samples.

Sample no.	8 μg/l spike		16 μg/l spike	
	Total As†	Rec. (%)	Total As†	Rec. (%)
1	7.50	93.8	16.14	100.9
2	7.13	89.1	15.42	96.3
3	7.36	92.0	15.14	94.6
4	6.97	87.2	15.07	94.2
5	6.90	86.3	14.83	92.7

† Total As found (μg/l).

Table 5 Recovery of As(III) with spikes in drinking water samples.

Sample no.	4 μg/l spike		8 μg/l spike		12 μg/l spike	
	As(III)†	Rec.‡	As(III)†	Rec.‡	As(III)†	Rec.‡
1	3.73	93.2	7.21	90.1	11.00	91.7
2	3.59	89.7	7.38	92.3	11.01	91.8
3	3.93	98.2	7.57	94.6	11.17	93.0
4	3.80	95.0	7.56	94.5	11.06	92.2
5	3.61	90.1	7.58	94.5	10.95	91.3

† As(III) found (μg/l). ‡ Recovery (%).

species in five drinking water samples were 79.3–111.6%, reflecting high accuracy.

The method developed here is therefore suitable to determine inorganic As species for the safety of drinking water because it is easy to manipulate, rapid, and economic. However, for very low concentrations (part per trillion, μg/l), preconcentration is required.

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Table 6 Recovery of As(V) with spikes in drinking water samples.

Sample no.	4 μg/l spike		8 μg/l spike	
	As(V)†	Rec. (%)	As(V)†	Rec. (%)
1	3.77	94.3	8.93	111.6
2	3.54	88.5	8.04	100.5
3	3.44	85.9	7.57	94.6
4	3.17	79.3	7.51	93.9
5	3.29	82.3	7.25	90.6

† As(V) calculated from Tables 4 and 5 (μg/l):
As(V) [at 4 μg/l] = Total As [at 8] − As(III) [at 4]
As(V) [at 8 μg/l] = Total As [at 16] − As(III) [at 8]

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