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Quantification of Total Arsenic in Groundwater by HG-AAS Using Low Acid Concentration and L-Cysteine

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Abstract: A simple and inexpensive analytical method has been developed and applied for the quantification of total arsenic (arsenite + arsenate + monomethylarsonic acid + dimethylarsinic acid) in groundwater samples collected from various locations in United Arab Emirates. The method utilized HG-AAS and L-cysteine (as a pre-reducing agent) in low concentrations of nitric acid. The optimised experimental conditions were: 0.04 – 0.06 M HNO_3, 2% L-cysteine, and 15 minutes delay time after adding L-cysteine. The method's detection limit is 0.2 µg/L. The accuracy of the method has been checked using a CRM and spike recovery and found to be better than 83% with low standard deviations. The determined total arsenic concentration in the collected water samples was less than 5 µg/L. One advantage of this method over other comparable methods is that, it avoids the use of high acid concentrations. It is also suitable for routine batch analysis.

Keywords: *Arsenite, arsenate, monomethylarsonic acid, dimethylarsinic acid, ground water.*

Introduction

Arsenic is a prevalent element in the environment. Its sources in the environment can be natural or anthropogenic (Ahmad, 2001; Ng *et al.*, 2003). Arsenic occurs in natural waters mainly as arsenite [As(III)], arsenate [As(V)], monomethylarsonic acid (MMA, oxidation state V), or dimethylarsinic acid (DMA, oxidation state V). The former two species are dominant in natural waters (Shraim *et al*., 2002; Hung *et al*., 2004). Toxicity and mobility in the environment of arsenic species is mainly controlled by its oxidation states (Shraim *et al*., 2003; Leermakers *et al*., 2006). Among the arsenic species that are present in natural waters, inorganic arsenicals [As(III) and As(V)] are considered as the most toxic species followed by MMA and DMA (Hughes, 2002; Shraim *et al*., 2003). Inorganic arsenicals have been classified as group-I carcinogens and were included in the US-EPA "list of priority pollutants" (International Agency for Research on Cancer (IARC), 1987). Long-term exposure to arsenic results in chronic poisoning appears as skin lesions (*e.g*. melanosis and keratosis), cancers of the skin, lung, and bladder plus many other non-cancer end points (Hopenhayn-Rich *et al*., 2000; Pi *et al.*, 2000; Berg *et al*., 2001). Due to the toxicity of inorganic arsenicals, many countries have lowered their arsenic drinking water guidelines to less than or equal to 10 µg/L [*e.g.* Australia, WHO, and USEPA] (National Health and Medical Research Council (NHMRC), 1996; World Health Organization (WHO), 2001). But , some countries such as Bangladesh and India still have their guidelines set at 50 µg/L (World Health Organization (WHO), 2001). However, Morales *et.al.* (2000) reported that the cancer risk for individuals who are exposed to arsenic concentrations >50 µg/L via drinking water could be as high as 1 in every 100.

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Contamination of groundwater with arsenic has been reported in many countries including Bangladesh (Nickson *et a*l., 1998; Ahmad, 2001), India (Das *et al*., 1995; Shraim *et al*., 2002), China (Wang *et al.*, 2000; Guo *et al.*, 2001), Taiwan (Chen *et al.*, 1999), Vietnam (Berg *et al*., 2001), Nepal (Maharjan *et al*., 2006), Mexico (Wyatt *et al.*, 1998), USA (Calderon *et al.*, 1999), and Canada (Viraraghavan *et al.*, 1999). The estimated number of people that are at risk of arsenic poisoning as a result of drinking arsenic-contaminated water only in Bangladesh and India is more than 60 million (Ahmad, 2001; Chakraborti *et al.*, 2001).

Several analytical techniques have been reported in the literature for the quantification of total arsenic in water (Aggett & Aspell, 1976; Sakamoto *et al.*, 2001; Hung *et al.*, 2004; Maity *et al.*, 2004; Akter *et al.*, 2005; Anthemidis *et al.*, 2005; Bortoleto & Cadore, 2005; Frank *et al.*, 2005; Behari & Prakash, 2006). Some of these techniques are costly (*e.g.* ICP-MS and neutron activation). Others require long analysis time, use of strong acid media (3-12 M), have high detection limits, or/and may be unsuitable for routine monitoring of large number of samples. Some other techniques that utilise HG-AAS at low acid concentrations with or without L-cysteine for the quantification of arsenic in natural waters can either account for As(III) and As(V) only leaving behind any DMA or MMA that may be present or have not been applied for the analysis of total arsenic in water samples (Chen *et al.*, 1992; Le *et al.*, 1994; Coelho *et al.*, 2002; Wieteska *et al*., 2003).

This article presents a method developed to quantify total arsenic concentration (arsenite + arsenate + monomethylarsonic acid + dimethylarsinic acid) in groundwater using Hg-AAS. The developed method is considered to be simple, reliable, sensitive, inexpensive, and suitable for batch routine analysis. Moreover, any of the four arsenic species can be used for calibration.

Material and Method

Material

An atomic absorption spectrometer (SpectraAA 220 FS, Varian) equipped with a vapour generation accessory (VGA-77, Varian), a flame-heated T-shaped absorption cell, and graphite furnace (GTA 110, Varian) was used for arsenic measurements. The instrumental parameters used are listed in Table 1. A pH meter (Thermo Electron Corporation, Orion 550A) was used for the measurement of pH values.

Table 1. Operating conditions of the HG–AAS system

Instrument mode	Absorbance
Calibration mode	Concentration
Measurement mode	Integration
Slit width (nm)	0.5
Slit height	Normal
Wavelength (nm)	193.7
Flame	Air-acetylene
Sample introduction	Normal
Delay time (s)	40
Time constant	0.05
Measurement time (s)	2.0
Replicates	3
Background correction	On
Sample flow rate (ml min^{-1})	7
$NaBH_4$ flow rate (ml min^{-1})	1
$NaBH_4$ concentration (%)	2% (w/v) in 0.5% (w/v) NaOH

Reagents and Solutions

All chemicals were of analytical-reagent grade unless stated otherwise. All glassware was soaked in 4 M nitric acid for a minimum of 12 h, washed with distilled water and finally rinsed with Milli-Q reagent water (Millipore, Bedford, MA, USA) before use. All water used was obtained from a Milli-Q reagent system (resistivity 18.2 MΩ cm).

Nitric acid (68.0-70.0%) was purchased from Panreac Quimica (Barcelona-Spain); L-cysteine (min 99.5%, Ultra) from Fluka (USA); sodium tetraborohydride (GPR) from BDH (VWR Int'l Ltd, England); sodium hydroxide (pellets, 0.0001% max As) from Scharlan Chemie (Spain); arsenic trioxide (99.995%) and arsenic pentoxide (min 99.99%) from Aldrich (USA); cacodylic acid (min 99 %) from Fluka (USA); and disodium methylarsonate hexahydrate (99.5%) from Chem Services(West Chester, PA, USA). A lake water certified reference material (TM-26.3) that is certified for arsenic (7.9±1.5µg/L) was purchased from Environment Canada (National Laboratory for Environmental Testin, Canada).

Fresh solutions of $NaBH_4$ (2% w/v in 0.5% w/v NaOH) and L-cysteine (2 or 5 % w/v) were prepared daily. The arsenic solutions were prepared as follow: arsenic trioxide [As(III)] and arsenic pentoxide [As(V)] were dissolved in a minimum amount of sodium hydroxide solution (2.0 M), neutralized with nitric acid solution (2.0 M) and diluted to the mark of a volumetric flask with water. Cacodylic acid [dimethylarsinic acid (DMA)] and disodium methylarsonate hexahydrate [monomethylarsonic acid (MMA)] were dissolved in water and diluted to the desired volume. Working arsenic solutions were prepared by appropriate dilution of the stock solution with water. Stock and working arsenic solutions were kept in glass flasks wrapped with aluminium foil and stored refrigerated (4°C).

Collection of groundwater samples

Eleven groundwater samples (duplicates) were collected from different wells or locations in Sharjah and Al-Ain cities in UAE (see Table 2). The samples were placed in acid pre-washed plastic containers (0.5 or 1L). All samples were directly collected from wells except 6 and 7 which were samples of spring water piped to a roadside fountain. Water was withdrawn from wells via existing electric motor pumps. The pumps were let to run for a minimum of 5 minutes before filling the bottles. Nitric acid (concentrated, 5 or 10 mL depending on the volume of the bottle) was then added to each sample bottle to obtain a final acid concentration of 1%. Samples were transported to the lab on the same day and kept inside a refrigerator (4°C) until being analysed. The water of the investigated wells is usually used by local farmers for irrigation purposes.

Table 2. Detail of collected groundwater samples and their arsenic content.

Location No:	Samples' IDs and Source	pH range*	As, µg/L**
1	Well water no 1, Al-Falah , Sharjah	1.05 - 1.08	1.43 (0.23)
2	Well water no 2, Al-Falah , Sharjah	1.11 - 1.14	1.27 (0.00)
3	Well water no 1, Ain Al-Helew, Sharjah	1.12 - 1.15	5.00 (0.07)
4	Well water no 2, Ain Al-Helew, Sharjah	1.09 - 1.11	0.54 (0.02)
5	Well water no 3, Ain Al-Helew, Sharjah	1.12 - 1.14	0.55 (0.12)
6	Spring water, Ain Alfaydah, Al-Ain	1.09 - 1.24	0.53 (0.09)
7	Spring water, Mubazzarat Al-Khadra, Al-Ain	0.96 - 1.11	0.98 (0.01)
8	Well water, Al-Tawiyah, Al-Ain	1.21 - 1.30	< MDL
9	Well water no 1, Al-Jemi, Al-Ain	1.18 - 1.23	0.26 (0.06)
10	Well water no 2, Al-Jemi, Al-Ain	1.21 - 1.25	< MDL
11	Well water no 3, Al-Jemi, Al-Ain	1.23 - 1.27	< MDL

** pH values after the addition of nitric acid on site as a preservative.*

** Average of the duplicate samples. Numbers between brackets are the standard deviation.

Results and Discussion:

The aim of this work was to develop a suitable method that can be applied for the determination of total arsenic in environmental water samples. As noted in the introduction section, arsenic can exist as many species with four oxidation states (–3, 0, +3 and +5). Arsenite [As(III)] is the dominant form under reducing conditions, whereas arsenate [As(V)] is the stable form in oxygenated waters. MMA and DMA can also exist in surface waters. In this method, total arsenic concentration [As(III)+As(V)+DMA+MMA; species that are commonly detected in natural waters] was determined in several water samples using HG-AAS. L-cysteine was used as a pre-reducing agent for the reduction of pentavalent arsenic species to the trivalent state before mixing with $NaBH_4$; the main reducing and hydride generating agent. Several studies have indicated that the use of L-cysteine as a pre-reducing agent provides faster and more effective reduction of arsenic species when using sodium tetraborohydride in low acidic concentrations (Chen *et al.*, 1992; Le *et al.*, 1994; Shraim *et al.*, 1999; Shraim *et al.*, 2000; Wieteska *et al.*, 2003; Anthemidis *et al.*, 2005; Bortoleto & Cadore, 2005). However, complete reduction of pentavalent arsenic species using sodium tetraborohydride alone has been shown to require high concentrations of NaBH4 and strong acidic conditions such as 9 M hydrochloric or perchloric acids (Anthemidis *et al.*, 2005). In this current work, the use of L-cysteine with very dilute solutions of nitric acid mixed with medium concentrations of sodium tetraborohydride has been investigated. Nitric acid was selected in this study because it is widely utilized as a preservative for water samples (Basu *et al.*, 2002; Hirano *et al.*, 2003). Search of current literature reveals that no work has been reported on the use of low concentrations of nitric acid with L-Cysteine for the determination of total arsenic in water samples. However, nitric acid in the presence of L-cysteine has been used for the determination of total arsenic by HG-AAS in urine but not in water samples (Le *et al.*, 1994).

In order to optimise the nitric acid concentration to produce similar absorption signals from the four arsenic species, solutions mixtures with known concentrations of each constituent were prepared inside volumetric flasks in the following sequence: water + dilute nitric acid + arsenic + L-cysteine. Each mixture was left to stand at room temperature, initially for one hour after the addition of L-cysteine (delay time) before being introduced to the HG-AAS instrument. Each mixture was gently shaken for several times during the delay time. Figure 1 shows the effect of nitric acid concentration (ranges from 0.02 to 0.10 M) in the presence of 2% L-cysteine on the absorption signals of the four arsenic species. Similar results were obtained when 5% L-cysteine was used (results are not shown). As shown in Figure 1, the recorded signals for all the four arsenic species are similar and steady in the acid concentration range of 0.02 to 0.07 M. Beyond that range, lower and unequal signals were obtained for the four arsenic species. This experiment was repeated for several times with the same results were obtained. These results are in agreement with a previously reported findings using hydrochloric acid and L-cysteine (real water samples were not analysed) (Carrero *et al.*, 2001). Our findings indicate that total arsenic concentration can be determined using HNO3 concentration in the range of 0.02 to 0.07 M. However, narrower acid range (0.04 to 0.06 M) has been used to optimize the delay time. The effect of the delay time on the absorption signals of the four arsenic species when using 0.05 M HNO3 in 2 and 5% L-cysteine is shown in Figures 2a and 2b respectively. As shown in Figure 2, the minimum delay time needed to produce similar signals from all the four species was 15 and 5 minutes when using 2 and 5% L-cysteine, respectively. Equal and steady signals were obtained up to 120 min (the highest delay time tested). Same results have been reproduced after repeating the analysis using acid concentrations in the range of 0.04 to 0.06 M. Consequently, the optimised experimental conditions that can be used to produce high and equal signals from all the four arsenic species, and hence enabling the determination of total arsenic concentration, are: 0.04 – 0.06 M HNO3, 2% L-cysteine, and a minimum of 15 min as delay time. These conditions have been applied for the determination of total arsenic concentration in the collected groundwater samples. 5 % L-cysteine can also be used if shorter delay times are desirable (Figure 2b). However, the use of 2 % is more economical.

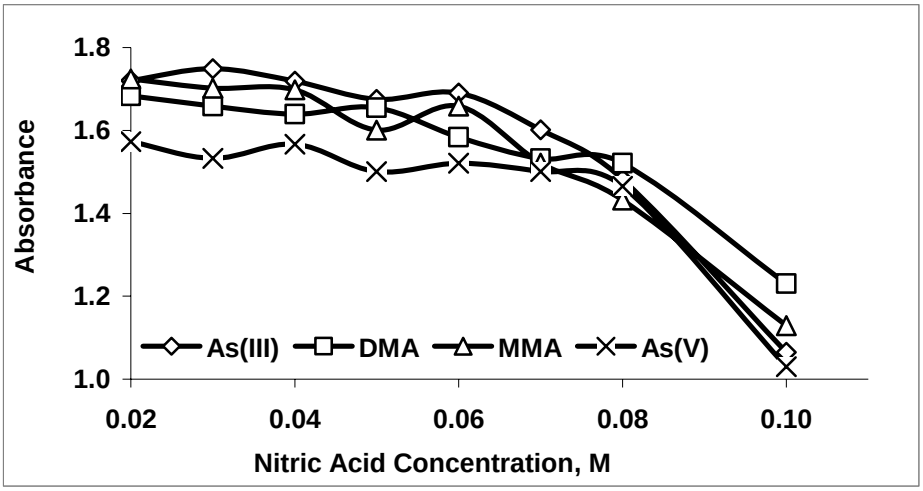

Figure 1. Effect of HNO3 concentration (M) on the absorption signals of As(III), DMA, MMA, and As(V) (10µg/L each) when using 2.0% L-cysteine, delay time 60 min .

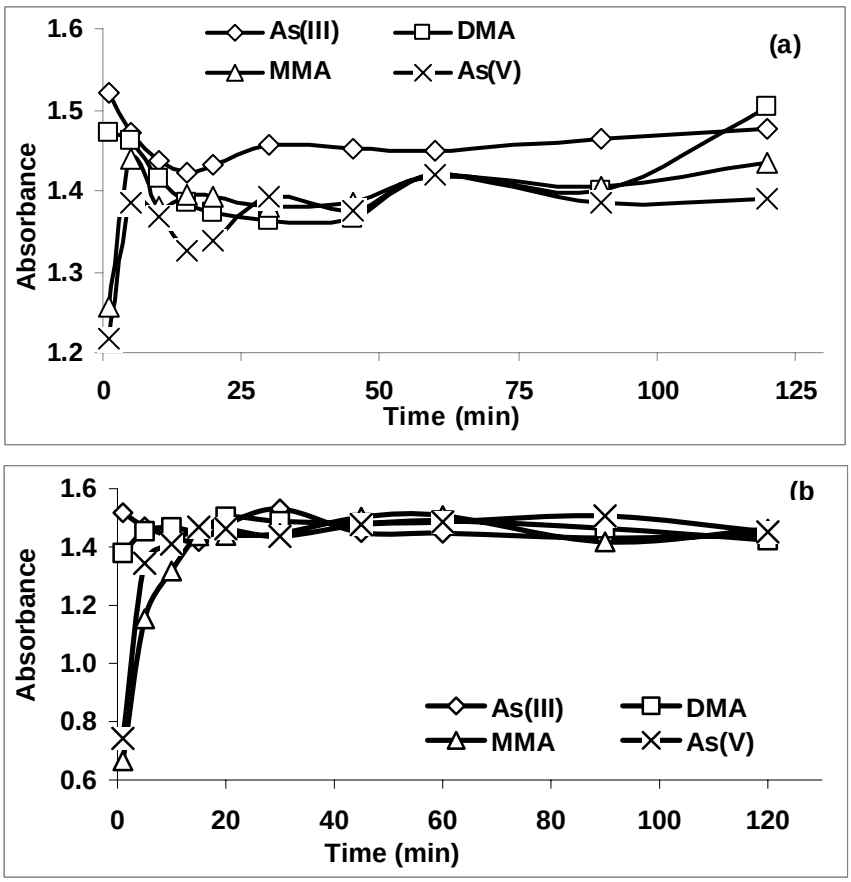

Figure 2. Effect of delay time on the absorption signal of As(III), DMA, MMA, and As(V) (10µg/L each) when using 0.05 M HNO_3 and 2.0 % L-cysteine (**a**) and 5.0 % L-cysteine **(b).**

The above results demonstrate that the pH of the solution is a critical factor for obtaining similar signals from the four arsenic species. Therefore, the acidity of the samples have to be adjusted to fall within the desired acid range (0.04-0.06 M) before accurate results can be

obtained. To ensure this, the pH readings have been used as a measure of acidity. The measured pH values of 0.04-0.06 M HNO_3 solutions were found to be 1.5 - 1.3, which are very close to the calculated pH values from the nitric acid concentrations. As shown in Table 2, the pH values of the collected water samples (preserved onsite with 1 % HNO_3) were in the range of 1.0-1.3. Consequently, the pH values of the samples that does not fall within the desired range (i.e. 1.3-1.5) have been adjusted by a drop wise addition of 1.0 M NaOH before adding L-cysteine.

Using the optimised experimental parameters described above, the following quality control measures have been undertaken. Firstly, instrument calibration using arsenic solutions of two different ranges (0.25 to 5.0 µg/L for low arsenic-containing samples and 1.0 to 50.0 µg/L for the higher range) was run daily or when needed. The best line fit for calibration curves was produced when using second order polynomials with high regression values (R^2 > 0.998). Secondly, a calibration verification check (10.0 µg/L) was run directly after running calibration solutions and after each 20 measurements; the obtained percentage difference was found to be less than 7%. Thirdly, the method's detection limit (MDL; 3 times the standard deviation) was calculated from replicate analysis (n=10) of a sample (from location 5) as well as a blank solution prepared in the same way as the samples. Calculated MDL values were 0.23 and 0.22 µg/L, respectively. Fourthly, the accuracy of the analytical method was assessed using both a certified reference material (TM-26.3) and the spike recovery concept. The obtained value for the TM-26.3 was 7.8-8.3 µg/L (n=3, certified value7.9±1.5µg/L). The spike recoveries of single arsenic species (2, 10, 20, and 50 µg/L of each of the four arsenic species) as well as mixtures of all four species (2.5 and 5 µg/L each, i.e. total arsenic concentration is 10 and 20 µg/L) spiked in water samples were found to be 83-111%. Finally, the precision of the method was assessed by replicate analysis of samples, TM-26.3, and standards. The calculated standard deviation values for samples were 0.1- 0.6 µg/L [samples with different arsenic concentrations of 1, 3, and 13 µg/L have been used (n=6 each, the last one is for a spiked samples)]. Whereas the standard deviation values for TM-26.3 and the 20 µg/L standard were 0.2 µg/L (n=3) and 1.6 µg/L, respectively.

Finally, using this developed method, we have demonstrated that most of the collected groundwater samples contain total arsenic concentration around or below 1.0 µg/L except one sample which found to contain 5.0 µg/L. These results may suggest that the groundwater of Sharjah and Alain cities is not contaminated with arsenic. The values shown in Table 2 indicate that the highest arsenic contamination found is 50 % below the WHO guideline value (10 µg/L).

Conclusions

The detection and quantification of the total arsenic (As(III)+As(V)+MMA+DMA) in groundwater samples can be easily performed using HG-AAS. The developed method is suitable for routine batch analysis of arsenic and does not need high acid concentration to obtain accurate results. The optimised experimental conditions are 0.04-0.06 M HNO_3, 2 % L-cysteine, and a minimum of 15 min as delay time. The detection limit of the method is 0.2 µg/L and its accuracy is better than 83 % with low standard deviation values. The determined total arsenic concentrations in the collected groundwater samples were found to be less than 5 µg/L.

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