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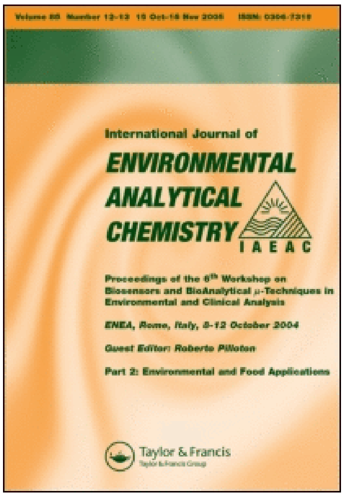

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# Determination of arsenic(III) and total inorganic arsenic in water samples using variable tetrahydroborate(III) and acid concentrations by continuous-flow hydride-generation atomic absorption spectrometry

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A simple procedure was developed for the direct determination of As(III) and total inorganic arsenic in water samples using continuous-flow hydride generation atomic absorption spectrometry without prereduction of As(V). Under optimized conditions, As(III) was determined using 1% w/v of $NaBH_4$ and $0.2\,mol\,L^{-1}$ of HCl, and total arsenic using 5% w/v of $NaBH_4$ and $6\,mol\,L^{-1}$ of HCl. The concentration of As(V) was determined by the difference between total inorganic arsenic and concentration of As(III). Interferences from methylated arsenic species, mutual hydride-forming, and transition elements in the determination of As(III) and total arsenic were evaluated. With the proposed procedure, detection limits of $0.1\,\mu g\,L^{-1}$ for As(III) and $0.25\,\mu g\,L^{-1}$ for total arsenic were achieved. The relative standard deviations were 2.0% for $2\,\mu g\,L^{-1}$ of As(III) and 3.5% for $2\,\mu g\,L^{-1}$ of As(V) determined as total arsenic. Spike recoveries were in the range of 91–111% for As(III) and 91–114% for As(V). The method was validated by analysing certified reference materials SRM-1640 and NASS-5. The developed methodology constitutes an economic, simple, and reliable way to determine inorganic arsenic species in natural waters and other similar samples with negligible or no content of methylated arsenic species. Speciation analysis was satisfactorily applied to different types of natural water samples.

*Keywords:* Arsenic speciation analysis; Hydride generation atomic absorption spectrometry; Inter-element interferences; Natural waters

## 1. Introduction

The occurrence of arsenic in natural waters has received much attention during recent years, because of its potential toxicity on human health. In natural waters, arsenic may occur as arsenite As(III), arsenate As(V), monomethylarsonic acid (MMAA), and dimethylarsenic acid (DMAA) [1]. In groundwater, it exists predominantly in the form of As(III) and As(V) [2]. Methylated arsenic species have rarely been reported to be

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present in groundwaters at levels above 1 $\mu g L^{-1}$ [3]. Among these forms, inorganic arsenic is far more toxic than the organic forms. The levels of toxicity for As(III) and As(V) are so different (i.e. As(III) > As(V)) [4] that it is not sufficient to determine the total content of arsenic in a given sample in order to estimate its physiological or environmental risk.

Hydride generation (HG) coupled with atomic spectrometric techniques such as AAS, AFS, and ICP-AES is currently the most popular technique for the routine determination of arsenic in various matrices at $\mu g L^{-1}$ levels [5]. The efficiency of arsine generation from As(V) is $\approx$30% lower than that of As(III). Hence, total arsenic is determined after reducing As(V) to As(III), and the preferred reductants are KI and L-cysteine. The arsenic species present as oxyions must be fully protonated to generate arsine. Arsenous acid with $pK_1 \approx 9.2$ is fully protonated under normal natural water pH, whereas arsenic acid with $pK_1 \approx 2.3$ requires highly acidic conditions i.e. pH < 1. Thus, utilizing the pH dependency of hydride generation and reduction kinetics, various methods have been reported for the selective determination of As(III) and As(V). Generally, acetic acid/acetate [6, 7] or citric acid/citrate [8, 9] buffers (pH 4–6) are employed for the selective determination of As(III), and total arsenic is determined under highly acidic conditions after prereduction.

Another approach for the selective determination of As(III) is the use of low-sodium tetrahydroborate (THB) and acid concentrations. Narsito and Agterdenbos [10] observed a significant difference in the reduction efficiency between As(III) and As(V) at THB concentrations lower than 1% w/v and 3 $mol L^{-1}$ HCl, suggesting that the trivalent form is converted to the hydride more efficiently than the pentavalent form under these conditions. Borho and Wilderer [11] reported low THB concentrations under highly acidic conditions, i.e. 2 $mol L^{-1}$ HCl to generate $AsH_3$ selectively from As(III). Similar procedures were reported for As(III) determination using HG–ICP–AES [12] and flow-injection (FI) HGAAS systems [13, 14]. However, total arsenic was determined after prereduction.

Determination of total inorganic arsenic without a prereduction step is advantageous, as it minimizes contamination and reduces analysis time and other drawbacks associated with the prereduction step. Hinners [15] observed equal responses from As(III) and As(V), when arsine was generated using 4 $mol L^{-1}$ HCl with sufficient THB (exact concentration not given). Ebdon and Wilkinson [16] and Torralba *et al.* [17, 18] reported that complete volatilization of arsenate in the absence of reducing agent could be achieved using higher THB and HCl concentrations. Lopez *et al.* [19] determined As(III) selectively using citrate buffer (pH 4.5) and total arsenic using 6 $mol L^{-1}$ HCl without prereduction. Bermejo-Barrera *et al.* [20] determined As(III) using citric acid (pH 5) and total inorganic arsenic using 4 $mol L^{-1}$ HCl in an FI–HG–GFAAS system. Coelho *et al.* [21] determined As(III) and total arsenic using 0.1 and 3% w/v THB with 1 $mol L^{-1}$ HCl in a merging zone FI–HGAAS system. Recently, Anthemidis *et al.* [22] reported the determination of As(III) using 0.5% w/v THB and 1.5 $mol L^{-1}$ HCl and total arsenic using 3% w/v THB and 9 $mol L^{-1}$ HCl using a manifold with integrated reaction chamber and gas–liquid separator (RC–GLS). However, these methods utilize complicated manifolds, thus making these procedures less attractive, when a large number of samples are to be analysed. The aim of this study was to develop a sensitive, simple, and reliable method to distinguish between inorganic As(III) and As(V) species without prereduction of As(V) using a commercial continuous flow HGAAS system. Interferences from MMA and DMA on As(III) and total arsenic determinations were studied. Interferences due to other hydride forming and transition elements were systematically studied and reported.

## 2. Experimental

### 2.1 *Instrumentation*

A GBC Avanta AAS with a continuous-flow hydride generator accessory (HG 3000, GBC Scientific Company) was used. The operating conditions of the instrument are given in table 1. The HG 3000 manifold consists of a three-channel peristaltic pump head of fixed speed, mixing chamber, reaction coil (0.76 mm id, 1 m length), gas–liquid separator (GLS, part no. 58-0077-01) and a flame-heated quartz cell. Tygon peristaltic pump tubes (sample 1.85 mm id; acid and THB 0.76 mm id) were used to propel the sample (9 $\mathrm{mL\,min^{-1}}$) and the reagents (2 $\mathrm{mL\,min^{-1}}$). PTFE tubings were used for all connections. The carrier gas (argon) flow was 30 $\mathrm{mL\,min^{-1}}$, which was fixed by the manufacturer.

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### 2.2 *Reagents*

All reagents used were of analytical grade and prepared in deionized water of resistivity 18 MΩ.cm obtained from a Milli-Q (Millipore) water purification system. As(III) standard was prepared from $As_2O_3$ (Sigma) by first dissolving in 20% w/v NaOH (Merck) solution, followed by neutralization with 20% v/v HCl (Aristar, BDH). As(V) was from Merck AAS-grade stock solution (1000 $\mathrm{mg\,L^{-1}}$) preserved in 0.5 $\mathrm{mol\,L^{-1}}$ $HNO_3$. MMA and DMA were prepared from disodium salt of monomethyl arsenic acid

Table 1. GBC Avanta AAS operating parameters.

| System parameter | Setting |
|---|---|
| System type | Flame-heated quartz cell |
| Element | As |
| Light source | Photron super lamp |
| Lamp stabilization time (min) | 20 |
| Lamp current (mA) | 20 |
| Wavelength (nm) | 193.7 |
| Slit width (nm) | 1 |
| Slit height | Normal |
| Instrumental mode | Absorbance BC on |
| Measurement mode | Integration |
| Sampling mode | Manual sampling |
| Flame type | Air–acetylene |
| Acetylene flow ($\mathrm{L\,min^{-1}}$) | 1.0 |
| Air flow ($\mathrm{L\,min^{-1}}$) | 10 |
| Read time (s) | 15 |
| Time constant | 0 |
| Replicates | 5 |
| Calibration mode | Linear least square |

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(Carlo Erba) and sodium salt of dimethylarsenic acid (Sigma). $NaBH_4$ (Merck) solutions were prepared freshly by dissolving appropriate quantities in either 0.1 or $0.01\,mol\,L^{-1}$ of NaOH and filtered through a 0.45 µm membrane filter. In a preliminary study, it was found that the concentration of NaOH was not critical, and $0.01\,mol\,L^{-1}$ was sufficient to stabilize 0.25–9.0% of THB solutions for a week time if stored at 4°C. Acetic acid was prepared from glacial acetic acid ($d = 1.050\,g\,mL^{-1}$, Merck).

Merck AAS-grade stock solutions ($1000\,mg\,L^{-1}$) of Ag(I), Bi(III), Cd(II), Cu(II), Ge(IV), Hg(II), Ni(II), Pb(II), Mn(II), Fe(III), Sb(III), Se(IV), Sn(IV), Te(IV), and Zn(II) were used for interference studies. Cr(VI) was prepared from AR-grade $K_2Cr_2O_7$ (Qualigens, India) and preserved with $0.5\,mol\,L^{-1}$ of $HNO_3$.

### 2.3 *Samples*

Groundwater samples were collected from a suburban area of Chennai city. Seawater samples were collected from the Bay of Bengal along Chennai coast (collected from seashore). River-water samples were collected from Adyar, a river polluted by urban sewage. Rainwater samples were collected from a residential area of Chennai city. All the samples were filtered through a 0.45 µm membrane filter (Millipore) on site, collected in 1-L precleaned polypropylene bottles, acidified with conc. HCl to $pH < 2$, and stored in dark at 4°C [23]. In a preliminary study, we found that this preservation procedure stabilized the arsenic species for 40 days.

### 2.4 *Analytical procedure*

An aliquot of the acidified sample was passed through the sample channel. As(III) was determined using 1% of THB and $0.2\,mol\,L^{-1}$ HCl, and total arsenic using 5% THB and $6\,mol\,L^{-1}$ of HCl. Concentration of As(V) was calculated by the difference between total arsenic and concentration of As(III).

## 3. Results and discussion

### 3.1 *Evaluation of arsine generation conditions*

In an initial optimization study, it was found that the concentration of NaOH used to stabilize THB was critical for arsine generation, when low acid concentrations ($0.1–1.0\,mol\,L^{-1}$) were used. This is because of the neutralization of NaOH by HCl. No signals were observed with THB stabilized with $0.1\,mol\,L^{-1}$ NaOH and acid concentrations of $0.1–0.2\,mol\,L^{-1}$. Hence, THB was stabilized with $0.01\,mol\,L^{-1}$ NaOH for the studies involving acid concentrations $0.1–1.0\,mol\,L^{-1}$.

The effects of varying THB and HCl concentrations on the analyte signal from As(III) and As(V) were investigated. The effect of HCl concentration ($0.1–1.0\,mol\,L^{-1}$) on arsine generation from $10\,\mu g\,L^{-1}$ of As(III) is shown in figure 1. A gradual increase of As(III) signal with HCl concentration was observed when 0.25 and 0.5% THB was used. On the other hand, concentrations as high as $100\,\mu g\,L^{-1}$ of As(V) could not produce any signal with 0.25% THB and $0.1–1.0\,mol\,L^{-1}$ HCl. At concentrations of

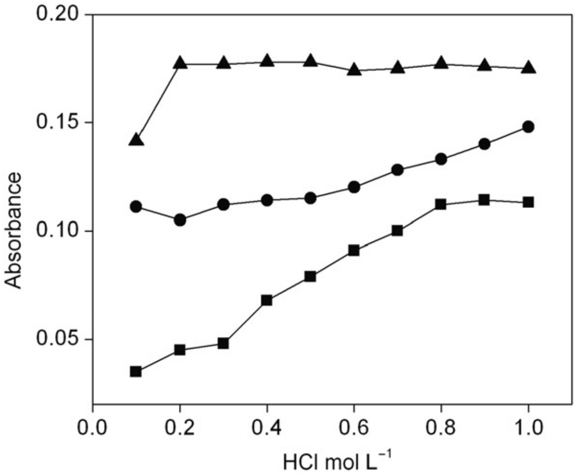

Figure 1. Effect of HCl and THB concentrations on the efficiency of arsine generation from 10 $\mu$g L$^{-1}$ of As(III). (■) 0.25; (●) 0.5; (▲) 1.0% w/v THB.

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1.0% w/v THB and 0.2 mol L$^{-1}$ of HCl, the efficiency of arsine generation from As(III) attained a maximum, with an insignificant (1.5%) As(V) response. Hence, under these conditions, selective determination of As(III) is possible. The signals due to As(V) generated from 0.5 and 1.0 mol L$^{-1}$ of HCl, and 1% THB were 5 and 15% of the signal due to As(III) generated from 0.2 mol L$^{-1}$ HCl and 1% THB. Hence, 1.0% w/v THB and 0.2 mol L$^{-1}$ HCl are the best conditions for the selective determination of As(III). The pH of the drain solution was 7.54.

For comparison, selective determination of As(III) using acetic acid reaction medium (0.5 mol L$^{-1}$) was adopted [6]. The efficiency of arsine generation from As(III) was optimized with respect to acetic acid and THB concentrations. It was observed that increasing THB concentrations more than 0.5% w/v, and acetic acid concentrations more than 0.5 mol L$^{-1}$ induced significant interferences from As(V). Hence, an optimal concentration of 0.5% w/v THB and 0.5 mol L$^{-1}$ of acetic acid was used. The interference of As(V) at this concentration was about 3%. The efficiency of this medium for As(III) determination was 90% compared with that of 1.0% w/v THB and 0.2 mol L$^{-1}$ HCl medium.

### 3.2 *Effects of As(V), MMA, and DMA on $AsH_3$ generation from As(III)*

The interfering effect of 10, 50, and 100 µg L$^{-1}$ of As(V), MMA and DMA on arsine generation from 10 µg L$^{-1}$ of As(III) was studied, and the results are shown in table 2. The interference effect was taken as recovery of the interfering species, relative to the response of 10 µg L$^{-1}$ of As(III) in 0.2 mol L$^{-1}$ HCl and 1.0% w/v THB. As can be seen, both HCl and the acetic acid medium are subjected to potential interferences from As(V), MMA, and DMA. However, As(III) determination using 0.5 mol L$^{-1}$ acetic acid suffers more interference from As(V) compared with that in 0.2 mol L$^{-1}$ HCl. On the other hand, MMA and DMA interfered more in 0.2 mol L$^{-1}$ HCl medium. As inorganic arsenic species are dominant in natural waters, in this work, 0.2 mol L$^{-1}$ HCl was used

Table 2. Relative responses of arsenic hydrides from various arsenic species under different reaction media.[a]

| | | Relative response | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | As(III) | As(V) ($\mu g\,L^{-1}$) | | | MMA ($\mu g\,L^{-1}$) | | | DMA ($\mu g\,L^{-1}$) | | |
| Generating medium | $10\,\mu g\,L^{-1}$ | 10 | 50 | 100 | 10 | 50 | 100 | 10 | 50 | 100 |
| $0.5\,mol\,L^{-1}$[b] | 90 | 2.8 | 7 | 20 | <1 | 2 | 5 | 5 | 10 | 20 |
| $1.0\,mol\,L^{-1}$[b] | 95 | 6 | 21 | 33 | 2 | 5 | 12 | 20 | 35 | 60 |
| $0.1\,mol\,L^{-1}$[c] | 80 | <1 | <1 | 3 | 10 | 15 | 25 | 31 | 53 | 70 |
| $0.2\,mol\,L^{-1}$[c] | 100 | 1.5 | 5 | 8 | 22 | 37 | 50 | 58 | 75 | 86 |
| $0.5\,mol\,L^{-1}$[c] | 98 | 5 | 15 | 28 | 30 | 42 | 63 | 18 | 27 | 61 |
| $1.0\,mol\,L^{-1}$[c] | 95 | 15 | 37 | 62 | 28 | 47 | 68 | 12 | 23 | 48 |

[a] Signals obtained from $10\,\mu g\,L^{-1}$ As(III) in $0.2\,mol\,L^{-1}$ and 1.0% w/v THB are taken as 100%.
[b] Acetic acid medium using 0.5% w/v THB.
[c] HCl medium using 1.0% w/v THB.

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for selective As(III) determinations in real samples. However, it would be better to use acetic acid if the sample is known to contain methylated arsenicals.

### 3.3 *Determination of total inorganic arsenic*

Generally, total inorganic arsenic is determined after prereducing As(V) to As(III) using KI-ascorbic acid or L-cysteine in HCl medium. As THB is a strong reducing agent, it could also be used as a prereductant for reducing As(V) to As(III), and to generate arsine.

**3.3.1 Evaluation of arsine generation conditions using high THB and HCl concentrations.** The efficiency of arsine generation from $10\,\mu g\,L^{-1}$ of As(V) using THB concentrations of 1–9% w/v and HCl concentrations of $1–10\,mol\,L^{-1}$ was studied, and the results are shown in figure 2. The results indicate an increase in absorbance with increase in THB and HCl concentrations. At 5% w/v THB and $6\,mol\,L^{-1}$ HCl concentrations, the signals became maximal, and further increases resulted in a slight decrease in signal, probably due to the dilution caused by the higher amount of hydrogen generated. In addition, THB concentrations more than 5% w/v resulted in a carryover of water droplets into the atomizer, resulting in a shift in the baseline and analyte signals. Hence, 5% w/v THB and $6\,mol\,L^{-1}$ HCl were found to be suitable for total arsenic determinations without any prereduction. The pH of the drain solution was 0.64.

The efficiency of arsine generation using 5% w/v THB and $6\,mol\,L^{-1}$ HCl was the same for As(III) and As(V) species. However, the signals due to As(III) are about 10% lower than that in 1% w/v THB and $0.2\,mol\,L^{-1}$ HCl medium. The interference level of MMA in total arsenic determination was significantly higher. An MMA concentration of $10\,\mu g\,L^{-1}$ enhances the signal by about 20%. In contrast, the interfering effect of DMA is significantly less than that in the As(III) determination. The DMA concentration of $50\,\mu g\,L^{-1}$ enhanced the total arsenic signal by about 11%.

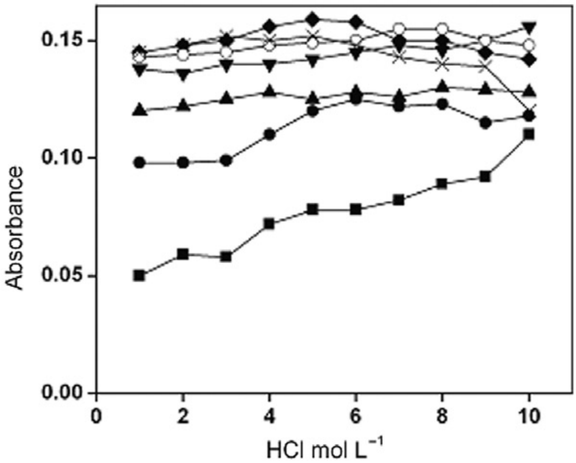

Figure 2. Effect of HCl and THB concentrations on the efficiency of arsine generation from 10 $\mu$g L$^{-1}$ of As(V). (■) 1; (●) 2; (▲) 3; (▼) 4; (◆) 5; (×) 6, and (○) 7% w/v THB.

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### 3.4 *Interference studies*

Interferences in the determination of arsenic due to mutual hydride forming and transition elements have been reported by several authors [24–32], and different mechanisms have been proposed [24, 27, 33–35]. Interferences due to transition metals could be reduced by using a high concentration of HCl and low concentration of THB [36, 37]. Several procedures have been suggested to reduce/mask the interference [38, 39].

**3.4.1 Procedure.** Cross-interferences from mutual hydride-forming elements were investigated by analysing a constant amount of the analyte (10 µg L$^{-1}$) in the presence of successively increasing concentrations of the interfering element. Before changing the interferent element, the quartz cell was cleaned with a mixture of 10 mol L$^{-1}$ of $HNO_3$ and 6 mol L$^{-1}$ of HF for 10 min. After this, the sensitivity of the analyte was checked and compared with the sensitivity obtained without the interferent. When a lower sensitivity was obtained, the HG 3000 system was dismantled and each part thoroughly cleaned with 10 mol L$^{-1}$ $HNO_3$ and deionized water. Utmost care was taken during the entire work to keep a constant flow rate of sample, acid, and THB.

A series of studies were carried out on the influence of common elements that were reported to interfere in the determination of arsenic. Arsenate was used in the total arsenic determination, because it suffers more signal depression than arsenite [40]. The interferent species were added in successively increasing concentrations, to see whether the magnitude of the interference depends on the interferent concentration. The results obtained are summarized in table 3 as the concentration of interferent causing $>10\%$ signal suppression. At a lower concentration range for the hydride-forming elements (up to 50 µg L$^{-1}$), the magnitude of signal suppression depended on the concentration of the interferent, but at a higher concentration range ($>50$ µg L$^{-1}$) the interference due to Bi, Sb, Se, and Sn was not strictly dependent on the interferent concentration. This may be due to the poor precision of the observed signals, i.e. 10–20% RSD.

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Table 3. Tolerance limit[a] ($\mu g\,L^{-1}$) for various interferents with the arsenic species.

| Analyte/ | Se(IV) | Te(IV) | Ge(IV) | Bi(III) | Sb(III) | Sn(IV) | Hg(II) | Ni(II) | Cu(II) | Fe(III) | Mn(II) | Cd(II) | Pb(II) | Cr(VI) | Ag(I) | Zn(II) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| As(III) | 20 | >500 | >500 | 500 | 100 | 20 | 500 | 100 | 500 | 500 | 500 | 500 | 1000 | 500 | 1000 | 500 |
| $As_T$ | 50 | 500 | 500 | 50 | 100 | 50 | 100 | 100 | 500 | 10 000 | 500 | 500 | 1000 | 1000 | 100 | 1000 |

[a] Concentration causing >10% signal suppression.

Although the interference pattern of hydride-forming elements agrees qualitatively with the findings of other workers [28, 41], the tolerance limit (i.e. interferent concentration causing $>10\%$ signal suppression) for Se, Sb, and Sn is higher than that reported by other workers [28]. Similarly, the tolerance limit of transition elements is lower than that reported by others [6, 40, 41]. This could partly be due to the mechanism of interference, as the interference may occur either in the hydride generation/atomization stage(s) or both [31]. Further, the magnitude of interference strongly depends on the concentrations of THB and HCl used, and on the design of the HG manifold [36].

### 3.5 *Statistical estimation of total arsenic determination*

In order to estimate the possibility of using the above strong hydride generation conditions (5.0% w/v THB and $6\,\mathrm{mol\,L^{-1}}$ HCl) for total arsenic determination, the calibration curves of As(III) and As(V) obtained using the strong hydride generation conditions were statistically compared. The statistical test, which uses the regression lines, was applied in order to estimate possible systematic differences between the two calibration standards. According to this approach, the absorbance values obtained form a series of As(III) standard solutions were plotted against the absorbance values obtained from an identical series of As(V) standards. If the calculated slope and intercept from the regression line do not differ significantly from the ideal values of '1' and '0', respectively, then there is no evidence of any systematic differences between the two calibration methods [42]. The calculated values of slope and intercept with their confidence interval (at 95% confidence level) are: $\mathrm{slope} = (1.0074 \pm 0.0020)$, $\mathrm{intercept} = (0.0019 \pm 0.0009)$, showing that the calibration curves for the two inorganic species determination did not differ significantly. Consequently, the strong hydride generation conditions (5.0% w/v THB and $6\,\mathrm{mol\,L^{-1}}$ HCl) can be used for total arsenic determination.

### 3.6 *Analytical performance of the proposed method*

The analytical performance data of the proposed method for the selective determination of As(III) and total arsenic using the optimized conditions are presented in table 4. The accuracy of the method was evaluated by determining the arsenic content in certified reference materials NIST SRM 1640 trace elements in water (diluted CRM was used) and NAAS-5 seawater reference material for trace metals, and the results were in good agreement with the total element certified values. In the two CRMs, As(V) is the predominant form of total arsenic, probably because of the oxidizing property of $HNO_3$ used for preservation. The recovery values of added As(III) and As(V) range from 91 to 111% and from 91 to 114%, respectively. A comparison of limit of detection (LOD) of different reported HGAAS procedures (table 5) for arsenic speciation analysis shows that the method gives a lower or comparable LOD.

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Table 4. Analytical figures of merrit.

| Characteristics | As(III)$^{a}$ | Total As$^{b}$ |
|---|---|---|
| Slope | 0.0157 ± 0.0014 | 0.0154 ± 0.0042 |
| Intercept | 0.011 ± 0.023 | 0.0001 ± 0.0692 |
| Correlation coefficient, $r$ | 0.9988 | 0.9976 |
| Detection limit, ($3\sigma$) $\mu g\,L^{-1}$ | 0.1 | 0.25 |
| Precision (% RSD), $n = 10$; 2.0 $\mu g\,L^{-1}$ | 2.0 | 3.5 |
| Linear range ($\mu g\,L^{-1}$) | 0.2–25.0 | 0.2–25.0 |

$^{a}$HCl = 0.2 mol $L^{-1}$ and THB = 1.0% w/v.
$^{b}$HCl = 6.0 mol $L^{-1}$ and THB = 5.0% w/v.

Table 5. Comparison of LODs of some reported HGAAS procedures.$^{a}$

| | | LOD ($\mu g\,L^{-1}$) | | | |
|---|---|---|---|---|---|
| Sl. no | Technique | As(III) | As(V) | Reaction conditions | Ref. no. |
| 1 | CF–HGAAS | 0.6 | 0.6 | As(III): Acetate buffer<br>$As_T$: Online KI reduction | [6] |
| 2 | HG–ICP–AES | 1 | 1 | As(III): THB 0.05%<br>$As_T$: THB 0.6%, L-cysteine reduction | [12] |
| 3 | FI–HGAAS | 1.4 | 0.6 | As(III): THB 0.035%<br>$As_T$: L-cysteine + ascorbic acid reduction | [13] |
| 4 | CF–HGAAS | 0.5 | 0.5 | As(III): citrate buffer<br>$As_T$: HCl 6 mol $L^{-1}$ | [19] |
| 5 | FI–HGAAS | 0.3 | 0.5 | As(III): THB 0.1%, HCl 1 mol $L^{-1}$<br>$As_T$: THB 3%, HCl 1 mol $L^{-1}$ | [21] |
| 6 | FI–HGAAS | 0.1 | 0.06 | As(III): THB 0.5%, HCl 1.5 mol $L^{-1}$<br>$As_T$: THB 3%, HCl 9 mol $L^{-1}$ | [22] |
| 8 | This work | 0.1 | 0.25 | As(III): THB 1%, HCl 0.2 mol $L^{-1}$<br>$As_T$: THB 5%, HCl 6 mol $L^{-1}$ | |

$^{a}As_T$: total arsenic.

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### 3.7 *Application to environmental water samples*

The method was applied to the analysis of As(III) and total arsenic in environmental water samples including rainwater, polluted river water, tap water, groundwater, and seawater, and the results are given in table 6. In the two rainwater samples analysed, arsenic species are below the detection limit. This is expected because in rainwater, arsenic would be at ng $L^{-1}$ levels. The groundwater samples were collected from shallow dug wells with a depth ranging from 3.32 to 14.15 m below ground level. In all the groundwater samples, As(V) was found to be the dominating species and to account for more than 90% of total inorganic arsenic. This is in accordance with the previously reported values [8]. Furthermore, the values may be considered as background level of groundwater arsenic content of the area. In the river water samples 1 and 2, about 57 and 48% of the total inorganic arsenic was in the form of As(V). As the river is polluted by urban sewage, the arsenic content is higher than the groundwater of the area. Also, the presence of As(III) and As(V) in almost equal proportions in the river water indicates the prevailing redox conditions. In the seawater samples 1 and 2, 75 and 71% of the total inorganic arsenic were in the form of As(V). The results are in general agreement with the previously reported results of similar samples [29].

Table 6. Analytical results (mean ± SD, $n = 5$) of As(III), total arsenic and calculated As(V) in natural waters and certified reference material.

| | | As(III) | | | As(V) | |
|---|---|---|---|---|---|---|
| Sample | As(III): As(V); added ($\mu g\,L^{-1}$) | Found ($\mu g\,L^{-1}$) | R (%) | Total As found ($\mu g\,L^{-1}$) | Calculated ($\mu g\,L^{-1}$) | R (%) |
| Rainwater | – | nd | – | nd | – | – |
| | 2 : 2 | 1.99 ± 0.18 | 99 | 4.28 ± 0.15 | 2.36 ± 0.17 | 114 |
| | 2 : 4 | 2.21 ± 0.08 | 111 | 6.46 ± 0.13 | 4.24 ± 0.20 | 106 |
| River Water 1 | – | 5.48 ± 0.17 | – | 12.66 ±.17 | 7.20 ± 0.06 | – |
| | 4 : 2 | 9.30 ± 0.25 | 98 | 19.63 ± 0.26 | 10.12 ± 0.08 | 107 |
| River Water 2 | – | 3.83 ± 0.08 | – | 7.42 ± 0.14 | 3.59 ± 0.187 | – |
| | 4 : 4 | 8.55 ± 0.17 | 109 | 15.46 ± 0.18 | 6.91 ± 0.19 | 91 |
| Tap water | – | nd | – | 0.52 ± 0.13 | 0.52 ± 0.13 | – |
| | 5 : 5 | 5.17 ± 0.09 | 103 | 10.58 ± 0.06 | 5.29 ± 0.24 | 96 |
| | 5 : 10 | 5.39 ± 0.20 | 106 | 15.72 ± 0.31 | 10.33 ± 0.37 | 98 |
| Groundwater 1 | – | 0.74 ± 0.04 | – | 10.25 ± 0.17 | 9.51 ± 0.15 | – |
| | 2 : 2 | 2.73 ± 0.14 | 100 | 13.99 ± 0.12 | 11.31 ± 0.10 | 98 |
| Groundwater 2 | – | 0.29 ± 0.02 | – | 6.56 ± 0.28 | 6.27 ± 0.27 | – |
| | 4 : 4 | 4.00 ± 0.16 | 93 | 13.82 ± 0.29 | 9.84 ± 0.05 | 99 |
| Groundwater 3 | – | 0.19 ± 0.02 | – | 2.42 ± 0.06 | 2.23 ± 0.07 | – |
| | 6 : 6 | 6.22 ± 0.11 | 100 | 14.49 ± 0.24 | 8.27 ± 0.13 | 100 |
| Groundwater 4 | – | nd | – | 0.56 ± 0.03 | 0.56 ± 0.03 | – |
| | 8 : 4 | 7.76 ± 0.21 | 97 | 12.81 ± 0.10 | 5.05 ± 0.27 | 111 |
| Groundwater 5 | – | 0.28 ± 0.02 | – | 5.18 ± 0.11 | 4.90 ± 0.10 | – |
| | 2 : 2 | 2.18 ± 0.08 | 96 | 9.39 ± 0.14 | 7.21 ± 0.19 | 104 |
| Seawater 1 | – | 0.28 ± 0.03 | – | 1.19 ± 0.13 | 0.91 ± 0.10 | – |
| | 5 : 5 | 5.27 ± 0.0.21 | 100 | 11.89 ± 0.26 | 6.61 ± 0.20 | 112 |
| Seawater 2 | – | 0.31 ± 0.03 | – | 1.05 ± 0.09 | 0.75 ± 0.07 | – |
| | 10 : 5 | 9.63 ± 0.19 | 91 | 16.01 ± 0.11 | 6.39 ± 0.25 | 111 |
| SRM 1640 | 26.7 ± 0.4[a] | 3.12 ± 0.12 | – | 27.52 ± 1.16 | 24.4 ± 0.20 | 103 |
| NASS 5 | 1.27 ± 0.12[a] | nd | | 1.22 ± 0.04 | 1.22 ± 0.04 | 96 |

[a]Certified value of total arsenic; nd: not detected; R: percentage recovery.

## 4. Conclusions

The results of this work have demonstrated the feasibility of the continuous flow hydride generation coupled with AAS for the direct determination of As(III) and total arsenic in water samples without any prereduction of As(V). About 30 mL of sample is required, and 25 samples can be analysed for As(III) and total arsenic per hour. The low cost, easy operation, and high sensitivity of the present system make it very attractive for routine determination of As(III) and As(V) species in natural waters that are not known to contain appreciable amounts of MMA and DMA. Furthermore, most of the transition and hydride-forming elements do not interfere at concentration levels which are higher than those commonly found in natural waters. The disadvantage of the method is the high consumption of THB reagent and the interference of MMA and DMA.

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