Cryogenic trapping with a packed cold finger trap for the determination and speciation of arsenic by flow injection/hydride generation/atomic absorption spectrometry

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An innovative analytical system based on the combination of cryogenic trapping and unambiguous gas chromatographic separation performed within a packed cold finger trap (PCFT) has been developed here. In this hydride generation-packed cold finger trap-atomic absorption spectrometry (HG-PCFT-AAS) system, the carrier gas (He) and heating voltage were optimized from a complete factorial experiment and in accordance with a base-line resolution ($R_S > 1.4$) between monomethylarsonic acid (MMA) and dimethylarsenic acid (DMA); the sheath gas argon (Ar) flow rate, on the other hand, was optimized from a single factorial experiment to obtain the highest signal-to-noise (S/N) ratio. Here, for MMA and DMA analysis, compromised levels of the parameters for hydride generation were determined from an L$_{16}(4)^5$ orthogonal array experimental design following the principle of the larger-is-better S/N ratio. The hydride evolution after the addition of a citrate buffer was employed to selectively measure arsenite ($\text{As}^{III}$). With an atomic absorption spectrometer (AAS) serving as the detector, the limits of detection were 0.9, 0.8, 0.5, and 0.6 ng for $\text{As}^{III}$, $\text{As}^V$ (arsenate), MMA and DMA, respectively. The results of the application of the method in freshwater and seawater showed spike recovery ranges from 82–113% and relative standard deviation of triplicate analysis ranges from 3–10%, depending on the arsenic species. Accuracy of the established method was also validated by analyzing two standard reference materials, NASS-5 and SLEW-3, in which two arsenic species, $\text{As}^{III}$ and $\text{As}^V$, are detected.

Introduction

Based upon the biological activity of the hydrosphere, dissolved arsenic is generally distributed in such various chemical forms as arsenite ($\text{As}^{III}$), arsenate ($\text{As}^V$), monomethylarsonic acid (MMA) and dimethylarsenic acid (DMA). Arsenic speciation has therefore become a topic of great interest in the field of hydrospheric biogeochemistry in that it is closely associated with the food chain through primary producers. It has, in fact, been found that many marine algae take up and transform $\text{As}^V$ into $\text{As}^{III}$ and methylarsenicals through the processes of reduction and methylation; hence, methylarsenicals are often found in the photic zone, and a positive correlation exists with primary productivity. On account of the chemical similarities between arsenate and phosphate, it has also been claimed that $\text{As}^V$ is taken up in plants by the phosphate transport system; however, arsenic is considered a toxic substance because it uncouples phosphorylation and inhibits phosphate uptake.

Principally, arsenic speciation studies fall into two categories. The first is a detector coupled with HPLC, for example, the hyphenated high performance liquid chromatography-hydride generation-inductively coupled plasma-mass spectrometry (HPLC-HG-ICPMS), which is designed with chromatographic separation prior to hydride generation. One advantage of this type of hyphenated technique is that it provides more information vis-à-vis various arsenicals within a single chromatogram. The detection limits of hyphenated HPLC system, however, are somewhat restricted by the volume of sample injection.

The other category is referred to as hydride generation-cryogenic trapping (HG-CT). In this hyphenated system, gaseous arsines which are derived by the reduction of arsenicals in an aqueous sample are cryofocussed with a cold trap prior to fractional vaporization and the detection of arsenicals as sequentially determined by increases in their boiling point (BP). Such a system permits the separation of corresponding hydride species, such as AsH$_3$ (BP $\sim$ 55 °C, derived from $\text{As}^{III}$ and $\text{As}^V$), CH$_3$AsH$_2$ (BP 2 °C, derived from MMA) and (CH$_3$)$_2$AsH (BP 35.6 °C, derived from DMA).

In this work, a continuous flow injection hydride generation system combining a PCFT module which functions as not only a cold trap but also a separation column was devised and examined to assess its capacity to accurately identify the major arsenic species in freshwater and seawater. Independent instrumental parameters were optimized from a single factorial experimental design following a step-by-step procedure. The criteria were chromatographic base-line resolution ($R_S > 1.4$) between MMA and DMA as well as the shortest operation time. An L$_{16}(4)^5$ Taguchi’s orthogonal array experimental design was also designed to obtain the compromised combination of hydride generation parameters for a quantitative analysis of MMA and DMA. Orthogonal array design is a chemometric approach combining the advantage of both the simplex and factorial design. Much more information can be obtained from a limited number of experiments. In addition to this, an operational procedure was carefully constructed for the selective hydride generation of $\text{As}^{III}$ and total inorganic arsenic (TiAs = $\text{As}^{III}$ + $\text{As}^V$). Finally, the applicability of this newly-established method with different matrix water samples was evaluated, and the results are presented in this paper.

Materials and experimental

Reagents

Standard solutions of arsenite ($\text{As}^{III}$), arsenate ($\text{As}^V$), monomethylarsonic acid (MMA) and dimethylarsenic acid (DMA) were prepared from arsenic trioxide (As$_2$O$_3$)(Sigma), sodium arsenate heptahydrate (Na$_2$HAsO$_4$·7H$_2$O) (J.T. Baker), sodium
monomethylarsenonate sesquihydrate (CH$_3$As O(OH)(ONa)·1.5H$_2$O) (Chem Service, purity ca. 98%) and dimethyl arsine acid ((CH$_3$)$_2$AsO(OH))(Sigma, purity ca. 98%), respectively. Arsenic concentrations of those stock standards were calibrated with primary arsenic standard employing inductively-coupled plasma mass spectrometry (ICP-MS) prior to a quantitative analysis (courtesy of Professors M. H. Yang and Y. C. Sun, Department of Nuclear Science, National University Tsing Hua, Taiwan).

An on-line acidified reagent consisted of hydrochloric acid (Riedel-de Haén, 37% Reagent Grade), while sodium borohydride (NaBH$_4$) (Riedel-de Haén) solutions were prepared on a daily basis in 0.4% (w/v) sodium hydroxide (Riedel-de Haén). The pre-reduction reagent 20% KI for TiAs analysis was prepared with potassium iodide (Riedel-de Haén) dissolved in distilled water. The 0.5 M citrate buffer for selective hydride evolution consisted of citric acid monohydrate (C$_6$H$_5$O$_7$·H$_2$O) (Riedel-de Haén), and the pH was adjusted to 6.4 with an ammonia solution (Riedel-de Haén).

**Instrumentation**

The schematic diagram of the HG-PCFT-AAS system is presented in Fig. 1. The continuous flow hydride generator compartment included sample inlet vials, bottles of on-line hydride generation reagents and a U-shaped gas-liquid separator. The unit was immersed in a water bath kept at 25 °C in order to prevent any inconsistencies in the reaction rates for arsine generation that could have been caused by ambient temperature variations. Sample inlet tubing, on-line connecting tubing and 80-cm reaction coils were made of polytetrafluoroethylene (PTFE) with id 0.5 mm. The samples, reagents and the regular drains were controlled by a single peristaltic pump (Lachat Model 1200) with id 2.28 mm tubing (Gibson Alpken®) in a pump cassette.

Arsine was separated from the liquid and delivered to the cold trap by being purged with helium in the gas-liquid separator. It should be kept in mind that the boiling point of argon (−185.7 °C) is higher than that of nitrogen (−195.8 °C), which means there would have been a strong likelihood for the argon to get clogged in the cold trap if argon had been chosen as the purging gas. An opening, labeled ‘safety drain’, was therefore incorporated into the design to allow for free drainage in case the liquid were to have overflowed into the hyphenated units which followed.

The swept mixed gas stream was passed through a Nafion membrane (Perma Pure, module MD-110-12F) to selectively remove water vapor. The flow rate of the drying gas N$_2$ was set at 0.6 L min$^{-1}$ in accordance with the manufacturer’s instructions.

Having passed through the drying tube, the evolved hydrides derived from the corresponding analytes were condensed inside our newly-designed PCFT module. The components of the PCFT, i.e., the inner glass tube (od × id: 3.2 × 1.6 mm) and the outer glass tube (od × id: 9.6 × 8.0 mm) with a round bottom base, are presented in Fig. 2. The whole interior of the PCFT was silanized with dimethyldichlorosilane$^{20}$ and 10% OV-101 on Chromosorb (W-HP 60/80 mesh, Ohio Valley) packed in the space between the inner and outer tubes. The interior of the round bottom base bubble served as the trapping site, thereby preventing liquefied material from promptly condensing at the front end of the packings; in this way, clog times were extended, while larger sample inlet volumes were assured.

The exterior of the PCFT was wrapped with ca. 0.5 m of fiberglass heating cord (ca. 20 Ω) and a K-type thermal couple. Once the trapping had been completed, the liquid N$_2$ Dewar flask was removed, and the PCFT was heated with a DC power supply at optimal voltage. After all relevant chromatographic peaks had evolved, the power supply was set at an elevated voltage of 30 V until the temperature of the PCFT reached 150 °C so as to clean the gas stream path inside the PCFT module.

As shown in Fig. 1, prior to reaching the atomizer, the gas stream was stabilized by a sheath tube in the hyphenated system; both the inner tube (od × id: 3.2 × 1.6 mm) and outer tube (od × id: 9.5 × 6.4 mm) were PTFE. The sheath tube was wrapped with a fiberglass heating cord and kept at 70 °C to prevent adsorption of the arsine inside the pathway.

Those arsines which desorped from the PCFT due to vapor pressure were detected with an Hitachi Z-8200 atomic absorption spectrometer (AAS) with a flame heated quartz-tube atomizer (QTA) set at the selected parameters, as shown in Table 1. No background correction function was set since the magnet had to be removed when the QTA was assembled in this AAS model. Finally, the analyte signals were collected and integrated using a data acquisition system (SISC version 2.01, in Chinese language).

**Experimental design for the MMA and DMA analysis**

Firstly, two three-level factors in the complete factorial experiment involved determining the carrier gas flow rate and an appropriate heating voltage of the PCFT. These were selected to obtain the base-line resolution between MMA

![Fig. 1 Schematic diagram of the hydride generation-packed cold finger trap-atomic absorption spectrometric (HG-PCFT-AAS) system.](Image 343x76 to 513x254)

![Fig. 2 Schematic diagram of the packed cold finger trap (PCFT).](Image 53x85 to 289x321)
and DMA. Thereafter, in an attempt to reach the best S/N ratio of MMA and DMA, another physical parameter, namely the sheath gas flow rate, was selected using a single factorial experiment. The most suitable conditions under which the hydride generation rates were affected by the concentrations of the reagents and the reaction times were determined from an L₃₀⁻¹₆(4)₅ orthogonal array experimental design. With the application of Taguchi’s S/N ratio analysis, this robust design clearly demonstrated the compromised parameter combination of hydride generation for MMA and DMA analysis.

### Determination of TiAs, As³⁺ and As⁵⁺

Although various buffer systems have been postulated for the selective hydride generation of As³⁺, the citrate buffer was chosen in this study after several screen tests had been performed (not in this paper). In the meantime, another parallel sample was acidified with concentrated HCl, and then whole inorganic arsenic was pre-reduced to As³⁺ with a KI solution, which identified the values of As³⁺ (labeled TiAs in this paper). In the final stage, the As⁵⁺ concentration was calculated as the difference between TiAs and As³⁺:

\[
[\text{As}^5] = [\text{TiAs}] - [\text{As}^3].
\]

### Safety precautions

As arsines are highly toxic, inhalation should be avoided; preserving drain wastes in alkaline and having a well ventilated work space are highly recommended.

### Results and discussion

#### Optimization of the instrumental parameters for the MMA and DMA analysis

Fig. 3 presents the results of a complete factorial experiment composed of a specified carrier gas flow rate and heating voltage on the PCFT, with each testing sample containing 20 ng (expressed as As) of As³⁺, MMA and DMA. Exp. No 5 yielded an \( R_S \) value of 1.44 between MMA and DMA; thus the carrier gas flow rate of 18 mL min⁻¹ and a heating voltage of 5 V were considered reasonable settings.

The results of the sheath gas flow rate experiments are presented in Fig. 4. There, the S/N ratios were calculated by dividing the height of the individual peaks by the standard deviation of the first one-minute signal intensity recorded on the chromatogram. Three analytes all showed the best S/N when the sheath gas flow rate was set at 377 mL min⁻¹ and the \( R_S(\text{MMA}, \text{DMA}) \) remained close to 1.4.

### Hydride generation parameter levels for the MMA and DMA analysis

The experimental variables and levels for the optimal hydride generation conditions of MMA and DMA of the robust design are shown in Fig. 5. The variables and their levels of NaBH₄ concentrations, on-line HCl concentrations and peristaltic pump rates were assigned to the columns of an L₃₀⁻¹₆(4)₅ orthogonal array. Triplicates were performed

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**Table 1** Operation parameters and conditions of HG-PCFT-AAS measurement

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>On-line NaBH₄ concentration</td>
<td>0.75%</td>
</tr>
<tr>
<td>On-line HCl concentration</td>
<td>1% for As³⁺ mode</td>
</tr>
<tr>
<td>Peristaltic pump rate</td>
<td>5% for other modes</td>
</tr>
<tr>
<td>Carrier gas He flow rate</td>
<td>7.0 (equal flow rate for all of the sample inlet and on-line reagents)</td>
</tr>
<tr>
<td>Sheath gas Ar flow rate</td>
<td>18</td>
</tr>
<tr>
<td>PCFT</td>
<td></td>
</tr>
<tr>
<td>Nafion drying gas N₂ flow</td>
<td>0.6</td>
</tr>
<tr>
<td>Heating voltage (V)</td>
<td>5</td>
</tr>
<tr>
<td>Drying voltage (V)</td>
<td>30</td>
</tr>
<tr>
<td>AAS</td>
<td></td>
</tr>
<tr>
<td>Wavelength (nm)</td>
<td>193.7</td>
</tr>
<tr>
<td>Lamp current (mA)</td>
<td>10.0</td>
</tr>
<tr>
<td>Band pass (nm)</td>
<td>1.3</td>
</tr>
<tr>
<td>Acetylene flow rate (L min⁻¹)</td>
<td>1.4</td>
</tr>
<tr>
<td>Air flow rate (L min⁻¹)</td>
<td>13.6</td>
</tr>
<tr>
<td>Time constant (s)</td>
<td>2.0</td>
</tr>
</tbody>
</table>

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### Notes

* Peaks in sequence as As³⁺, MMA and DMA; labeled values were \( R_S \) between MMA and DMA.

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**Fig. 3** Optimization for the carrier gas flow rate and PCFT heating voltage.

**Fig. 4** Optimization for the sheath gas flow rate.

**Fig. 5** Effects of the experimental variables on the signal-to-noise ratios.
separately on three different dates so as to calculate the residual errors, making for a total of 48 trials. In each sample, the integrated peak areas of arsenics were measured with the pre-determined physical parameters. Results of the orthogonal experimental raw data are converted to the large-is-better S/N ratios. In the next stage, the Taguchi linear diagram\(^{21,22}\) was employed to identify the best combination of hydride generation parameters.

The diagrams (Fig. 5) revealed only an insignificant variance for the NaBH\(_4\) concentrations among 0.5–1.0% for both analytes; accordingly, 0.75% NaBH\(_4\) was selected for the remainder of the work. The level of on-line HCl concentration is normally a critical parameter because a DMA analysis typically reveals a trend of a decreasing response as the HCl concentration increases. However, here, the HCl concentrations between 5.0–7.5% in the MMA analysis showed negligible variations, but since HCl in 5% level resulted in a better S/N response in the DMA analysis, it was chosen for our remaining work. Although the Taguchi linear diagram illustrated that the pump rate effect did not have a significant impact on both MMA and DMA analysis, it demonstrated however that for the DMA analysis, the best S/N response was observed in 7 mL min\(^{-1}\); therefore, we selected this as the pump rate for our future work.

**Validation of selective hydride generation for As\(^{III}\)**

Since the chromatographic peak labeled TiAs in Fig. 6 was possibly from As\(^{III}\) and/or As\(^{V}\), it is necessarily to selectively determine the relative contributions of As\(^{III}\) and As\(^{V}\) to the TiAs. The procedure for TiAs pre-treatment involved the following steps: the addition of 2 mL concentrated HCl and a 2 mL 20% KI solution into each 20 mL aliquot and digestion in an 80°C water bath for 1 h. The first four chromatograms in Fig. 6a–d demonstrated that once the TiAs pre-treatment procedure was employed, the peak integrated values of TiAs were very close as the relative percent difference less than 5%. These results also implied that neither MMA nor DMA could have affected the quantitative measurements of i-As.

The last four chromatograms in Fig. 6e–h showed that with the addition of 0.5 mL of the 0.5 M citrate buffer per 20 mL of water sample, only As\(^{III}\) generated hydride vapor (on-line 1% HCl).

<table>
<thead>
<tr>
<th>Analytical mode</th>
<th>Species spiked</th>
<th>Chromatograms</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiAs</td>
<td>(a) As(^{III}) + MMA + DMA</td>
<td>0.10 1.65 0.55</td>
</tr>
<tr>
<td></td>
<td>(b) As(^{III})</td>
<td>0.10 0.97 0.40</td>
</tr>
<tr>
<td></td>
<td>(c) As(^{V}) + MMA + DMA</td>
<td>0.03 0.13 0.39</td>
</tr>
<tr>
<td></td>
<td>(d) As(^{V})</td>
<td>0.03 0.37 0.61</td>
</tr>
<tr>
<td>As(^{III}) selective</td>
<td>(a) As(^{III}) + MMA + DMA</td>
<td>0.03 0.90 0.11</td>
</tr>
<tr>
<td></td>
<td>(b) As(^{III})</td>
<td>0.03 0.39 0.40</td>
</tr>
<tr>
<td></td>
<td>(c) As(^{V}) + MMA + DMA</td>
<td>0.02 0.14 0.36</td>
</tr>
<tr>
<td></td>
<td>(d) As(^{V})</td>
<td>0.02 0.35 0.43</td>
</tr>
</tbody>
</table>

- **Notes:**
  - TiAs mode: adding concentrated HCl 2 mL, 20% KI 2 mL, 80°C digestion 1 hour, and on-line hydride generation acid: 5% HCl.
  - Selective As\(^{III}\) mode: adding 0.5 M citrate buffer 0.5 mL, and on-line hydride generation acid: 1% HCl.
  - 10 ng (as As) of listed arsenic species in 20 mL solution.
  - Labelled values were relatively normalized peak integration values.

* Fig. 6 Chromatograms for selective hydride generation of As\(^{III}\).

**Method validation and application**

To prevent the condensation of water vapor and frozen ice in the trap packing was extremely important because this would have limited the inlet sample volume, which obviously would have then affected the detection limits. The cold finger was adopted as the cryogenic trapping unit in this research owing to its availability for samples of large volumes (as much as 100 mL of the sample and still maintain the gas flow). Consequently, we design the various sample volume per measurement as 20, and 100 mL for analyzing inorganic arsenic (TiAs and As\(^{III}\)) and organic arsenic (MMA and DMA), respectively. The final analytical procedures and operation parameters for identifying As\(^{V}\), As\(^{III}\), MMA, DMA, and TAs in the aqueous samples are presented in Fig. 7 and Table 1, in which TAs is the total arsenic analyzed by a conventional HG-AAS hyphenated system.

As stated earlier, As\(^{V}\) was obtained by determining the difference between the results of TiAs and As\(^{III}\). From the analytical performance data listed in Table 2, it is obvious that the analytical sensitivity of TiAs (as represented by the slope indicated with the symbol ‘m’) is approximately twice as that of MMA and about three times that of both As\(^{III}\) and DMA. The limits of detection (LOD) were calculated using 7 replicate

**Fig. 7** Flow chart of the analytical procedures for arsenic speciation.

[Image showing the flowchart of the analytical procedures for arsenic speciation]

HCl); that is, arsenic generation from As\(^{V}\) was definitively inhibited once the citrate buffer was added and on-line HCl was kept at 1%. Also suggested is that neither MMA nor DMA could have significantly interfered with the selective As\(^{III}\) measurements.

**Table 2 Analytical performance data**

<table>
<thead>
<tr>
<th>Species</th>
<th>LOD</th>
<th>r²</th>
<th>µg L(^{-1})</th>
<th>min</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiAs</td>
<td>6.38</td>
<td>0.998</td>
<td>0.12</td>
<td>0.012</td>
</tr>
<tr>
<td>As(^{III})</td>
<td>1.51</td>
<td>0.996</td>
<td>0.94</td>
<td>0.047</td>
</tr>
<tr>
<td>As(^{V})</td>
<td>NA</td>
<td>NA</td>
<td>0.84</td>
<td>0.042</td>
</tr>
<tr>
<td>MMA</td>
<td>4.13</td>
<td>0.998</td>
<td>0.45</td>
<td>0.0045</td>
</tr>
<tr>
<td>DMA</td>
<td>1.73</td>
<td>0.998</td>
<td>0.63</td>
<td>0.0063</td>
</tr>
</tbody>
</table>

*Note: m and r² were the slope and correlation coefficients in the range of 0–20 ng, of the linear equation, respectively; LOD: limit of detection, 3 x SD of 7 replicate analyses of 2 ng standard (expressed as As) fortified samples; As\(^{III}\) standard was employed both in As\(^{III}\) and Ti-As mode; RSD = mean ± 1 SD of retention times extracted from 5 chromatograms; and [As\(^{V}\)] was calculated from [Ti-As] − [As\(^{III}\)] sample volume for converting to concentration detection limit as shown in Fig. 7; NA means not available.*
samples containing 2 ng (expressed as As) of individual arsenic species, and this resulted in 0.94, 0.84, 0.45 and 0.63 ng as the absolute LOD values, and equivalent to 0.047, 0.042, 0.0045, and 0.0063 μg L⁻¹ as the concentration LOD values, for As³⁺, As⁵⁺, MMA and DMA, respectively. Retention time agreement was confirmed by the relative standard deviations of the retention times extracted from 5 chromatograms; values ranged from 2 to 5% for the respective peaks.

A coastal seawater sample, a lake water sample, and a shrimp fishery water sample were collected in northern Taiwan for the validation of this newly-established speciation analytical method. Both samples were immediately filtered through the Nucleopore membrane (0.4 μm); then followed the analytical steps described in Fig. 7. The sample matrix effect was examined by adding particular arsenic speciation standards, and this resulted in a spike recovery ranging from 82 to 113% with the respective arsenic species, as shown in Table 3. As shown in Table 4, MMA was only detected in fishery water, however DMA was detected in seawater and fishery water with > 3 × LOD concentrations.

Inorganic form As⁵⁺ is the predominant species in most samples, nonetheless, the As³⁺ species behaved in the concentration level alike As⁷⁺. The results shown in Table 4 are in general agreement with those reported in the literature. In addition, method precision was evaluated from a triplicate analysis of each sample, and this revealed relative standard deviations below 10% for all speciation analysis. The accuracy of this method was also verified by TAs analysis with two reference materials, NASS-5 (seawater) and SLEW-3 (estuarine water). The resulting values as shown (Table 4) were all within the confidence interval of the reference values, and the detectable arsenic species were As³⁺ and As⁵⁺ in these two reference materials.

Discussion of the use of PCFT for arsenic speciation

A typical HG-CT system has until now been equipped with a U-shaped tube, which collected arsenics in accordance with cooled liquid nitrogen. Aside from this, in general, a U-trap most commonly seen, is partially filled with various types of packings, such as glass beads, glass wool, OV-3 coated Chromosorb W-HP or SP-2100 on Supelcorep. By sharp contrast, in the present work we adopted a cold finger packed with 10% OV-101 on Chromosorb W-HP, and this distinctly resulted in peaks with good resolution. Because the PCFT can extend clog times relative to the conventional U-shaped trap, much more volumes of the inlet sample are available per measurement. Therefore, the PCFT module is very useful for the trace arsenic analysis. In addition, the PCFT cut back on the consumption of liquid N₂ by as much as 200 mL per sample when compared with the ordinary U-shaped cold trap.

Until now, NaBH₄ has been widely used as a reliable reagent to convert a number of aqueous arsenic species to their corresponding arsines. Nevertheless, hydride generation efficiencies are also sensitive to reaction acidity, perhaps related to the pKa values of the respective arsines. Also previously reported is the fact that the best efficiency for hydride generation either for MMA or DMA appears in particular degrees of acidity. Although, as a general rule, the AAS absorption signal of the derived arsines increases as the reaction acidity increases, here it was found that the signal of DMA decreased once reaction acidity surpassed the critical values. Therefore in this work, we employed a Taguchi’s experimental design to obtain the optimal settings for the hydride generation efficiency of MMA and DMA.

With respect to the HG-CT system, both TiAs and As³⁺ must be determined separately since the hydride generation efficiency of each arsenic species is related to the particular conditions of the reaction medium. From this perspective, our results closely resemble those of previous investigations which have demonstrated that the pre-reduction of As⁵⁺ to As³⁺ using potassium iodide under high acidity conditions obtained the value of TiAs and that interferences from MMA and DMA were negligible. Several investigations have claimed that only As³⁺ was reduced in buffered samples such as Tris, acetate, phosphate, KHP and citrate. We screened several buffers (not published) as well as their effectiveness for the selective hydride generation of As³⁺. Subsequently, we demonstrated that the addition of the citrate buffer was indeed a highly reliable method for As³⁺ selective analysis.

It has also been reported elsewhere that hydrogen plus small amounts of oxygen are needed for the efficient atomization of hydride with a quartz-tube atomizer (QTA). In our system, hydrides were transported to a QTA heated with an acetylene–air flame, and H₂ was continuously provided by BH₄⁻ and HCl reactions. The result was that this hyphenated system greatly improved arsenic atomization efficiency.

Conclusions

The developed hyphenated system, HG-PCFT, proved to be a useful tool for the determination of trace arsenic speciation in water samples. One of the attractions of our procedure was the much inlet sample volume allowed per measurement which resulted in the lower concentration detection limit. It is especially useful for the determination of organic arsenic species (MMA and DMA) which, in general, can be found in extremely low concentrations in the hydrosphere. The analytical performance have successfully illustrated that this newly-established method is not only reproducible but also highly accurate. Aside from this, a tentative procedure was designed here for arsenic speciation analysis. On account of the

<table>
<thead>
<tr>
<th>Table 3 Spike recovery values for various matrix samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample type</td>
</tr>
<tr>
<td>Seawater</td>
</tr>
<tr>
<td>Lake water</td>
</tr>
<tr>
<td>Fishery water</td>
</tr>
</tbody>
</table>

* Samples concentration, as shown in Table 4. * Spikes were 5 ng (as As) for As³⁺ and 2 ng (as As) for other species. * Results expressed as mean ± 1 SD of triplicate analysis.

<table>
<thead>
<tr>
<th>Table 4 Concentrations of arsenic in different matrix water samples (unit: μg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
</tr>
<tr>
<td>Seawater</td>
</tr>
<tr>
<td>Lake water</td>
</tr>
<tr>
<td>Fishery water</td>
</tr>
<tr>
<td>NRCC-NASS-5</td>
</tr>
<tr>
<td>NRCC-SLEW-3</td>
</tr>
</tbody>
</table>

* Results expressed as mean ± 1 SD of (n = 3). * Results expressed as mean ± 1 SD of (n = 5). * NRCC-NASS-5, trace metal in seawater, reference value 1.27 ± 10%. * NRCC-SLEW-3, trace metal in estuarine water, reference value 1.36 ± 7%. * Determined by TAs mode as shown in Fig. 7.
simplicity of the PCFT module, the development of an automatic HG-PCFT-AAS is currently in progress.

Acknowledgements

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