Inorganic arsenic speciation analysis of water samples by trapping arsine on tungsten coil for atomic fluorescence spectrometric determination

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A B S T R A C T

Arsine trapping on resistively heated tungsten coil was investigated and an analytical method for ultra-trace arsenic determination in environmental samples was established. Several chemical modifiers, including Re, Pt, Mo, Ta and Rh, were explored as permanent chemical modifiers for tungsten coil on-line trapping and Rh gave the best performance. Arsine was on-line trapped on Rh-coated tungsten coil at 640 °C, then released at 1930 °C and subsequently delivered to an atomic fluorescence spectrometer (AFS) by a mixture of Ar and H2 for measurement. In the medium of 2%/v/v HCl and 3%/m/v KBH4, arsine can be selectively generated from As(III). Total inorganic arsenic was determined after pre-reduction of As(V) to As(III) in 0.5%/m/v thiourea–0.5%/m/v ascorbic acid solution. The concentration of As(V) was calculated by difference between the total inorganic arsenic and As(III), and inorganic arsenic speciation was thus achieved. With 8 min on-line trapping, the limit of detection was 10 ng L−1 for As(III) and 9 ng L−1 for total As; and the precision was found to be ~5% R.S.D. (n = 7) for 0.2 ng mL−1 As. The proposed method was successfully applied in total arsenic determination of several standard reference materials and inorganic arsenic speciation analysis of nature water samples.

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1. Introduction

Gas-phase trapping of volatile hydrides/atoms has advantages of efficient enrichment, simple operation [1,2], and the alleviation/elimination of gas-phase interference in hydride atomization for analytical atomic spectrometry. In the past century, graphite furnace is the predominant trapping device, thanks to the development of chemical modifiers in graphite furnace atomic absorption spectrometry. Recently, several novel trapping materials have also been used: quartz tube [3,4], silica trap [5], molybdenum foil strip [6], tungsten tube [7], tungsten coil [8–14], and gold wire [15]. These novel traps offer substantial advantages over conventional graphite furnace, such as smaller size and lower power requirement. Among these traps, tungsten coil is more attractive due to its broad availability and fast heating rate [16,17].

Arsenic is a ubiquitous element that ranks the 20th in abundance in the earth’s crust, the 14th in the seawater, and the 2nd in the human body [18]. Many epidemiological evidences show that arsenic in drinking water causes diseases such as skin cancer and several internal cancers, especially lung, bladder and kidney cancers [19]. Besides, recent irregular anthropogenic activities have resulted in worldwide arsenic contamination problems, especially in Southeast Asian countries [20]. Inorganic arsenicals are the major species found in water samples, and the trivalent species poses more significant threats to human beings [21]. Being aware of the toxicity of the arsenicals, worldwide authorities have already set 10 μg L−1 as the limit in drinking water [21]. The low concentration of arsenic together with the requirement for arsenic speciation to address the exact toxicity of arsenicals in drinking water has posed significant challenge to scientific community [22–28].

Atomic fluorescence spectrometry (AFS) is a great technique for trace elemental analysis, and especially advantageous for those elements, such as As and Se, that can easily form volatile hydrides for sample introduction. Recently, tungsten coil electrothermal vaporization has also been successfully used for sample introduction into AFS [29,30] in our laboratory. In order to further increase the sensitivity for arsenic determination, we combined the use of tungsten coil for arsine trapping and ETV sample introduction for AFS determination for the purpose of inorganic arsenic speciation.

2. Experimental

2.1. Instrumentation

A model AFS-2202 non-dispersive atomic fluorescence spectrometer (Beijing Haiguang Instrument Co., Beijing, China) was...
used in this work. The instrument is equipped with a programmable intermittent reactor and two gas–liquid separators to facilitate hydride generation and gas–liquid separation. Arsenic high-intensity hollow cathode lamp (HCL, Research Institute of Non-Ferrous Metals, Beijing, China) was used as the radiation source. The working parameters of HG-AFS were optimized and summarized in Table 1.

The tungsten coil electrothermal trapper and its connection to AFS have been described previously [30]. A tungsten coil was extracted from a commercially available slide projector bulb (HLX 64633, OSRAM, Munich, Germany) and assembled to the laboratory-constructed ETV glass cell. The coil temperature in Celsius was based on voltmetermometric measurement. A mixture of Ar and H2 was employed as carrier gas, and Ar was served as shiel gas.

A common microwave oven (Model PJ17C-M, Midea Corporation, Guangdong, China) with a full power of 700 W was used for the closed-vessel (70 mL Teflon containers) microwave sample digestion. An electric hot plate (Model EH20A, LabTech Corporation, Beijing, China) with a controllable temperature range of 40–250 °C was used for the evaporation of the digests.

2.2. Reagents

All reagents used were of analytical-reagent grade, except hydrochloric acid (Beijing Chemical Research Institute, China) was Metal-oxide semiconductor (MOS) grade (with lower blank arsenic levels than analytical grade ones). High purity doubly distilled water (DDW) was used throughout the whole work. All solutions were stored in high-density polyethylene bottles. Plastic bottles and glassware materials were cleaned by soaking in 10% (v/v) HNO3 for 24 h, rinsing five times with DDW and dried in a clean oven.

Standard stock solution of As(III) (1000 mg L−1) was purchased from the National Center for Reference Material (Beijing, China). As(V) (1000 mg L−1) standard stock solution was prepared, by dissolving 0.416 g Na2HAsO4 (Merck) with 100 mL double-distilled water at ambient conditions (2.3 for arsenic acid and 9.2 for arsenicous acid). That is, differentiation of Ar(III) and Ar(V) could be achieved simply by exploiting the concentration dependency of arsenic kinetiks than As(III), that is, differentiation of As(III) and As(V) could be achieved simply by exploiting the concentration dependency of the KBH4 and HCl reaction [31]. Though such an approach is limited for inorganic arsenicals, it is applicable for the arsenic speciation in natural waters where inorganic arsenic species are dominant. In this work, the selective generation of arsine from As(III) was simply accomplished by using KBH4 and HCl reaction [31].

Several certified reference materials were purchased from the National Center for Reference Material (Beijing, China) to validate the accuracy of the proposed method: GBW 07601, human hair; GBW 07605, tea leaf; and GBW(E) 08390 and GBW(E) 08391, simulated water.

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>As hollow cathode lamp</td>
<td>193.7 nm, 80 mA</td>
</tr>
<tr>
<td>Negative voltage of photomultiplier tube</td>
<td>320 V</td>
</tr>
<tr>
<td>Observation height</td>
<td>7 mm</td>
</tr>
<tr>
<td>Read mode</td>
<td>Peak area</td>
</tr>
<tr>
<td>Shield gas flow rate</td>
<td>1200 mL min−1</td>
</tr>
<tr>
<td>Carrier argon flow rate</td>
<td>200 mL min−1</td>
</tr>
<tr>
<td>Carrier hydrogen flow rate</td>
<td>60 mL min−1</td>
</tr>
</tbody>
</table>

Samples of KBH4 was stabilized with 3 g L−1 KOH.

3. Results and discussion

3.1. Separation of arsenic species and optimization of hydride generation parameters

Because of the difference of pK1 between arsenic acid and arsenous acid at ambient conditions (2.3 for arsenic acid and 9.2 for arsenous acid), As(V) can react with KBH4 with lower reaction kinetics than As(III), that is, differentiation of As(III) and As(V) could be achieved simply by exploiting the concentration dependency of the KBH4 and HCl reaction [31]. Though such an approach is limited for inorganic arsenicals, it is applicable for the arsenic speciation in natural waters where inorganic arsenic species are dominant. In this work, the selective generation of arsine from As(III) was simply accomplished by using the appropriate concentration of HCl and KBH4. Then As(V) was reduced upon the pre-reduction with thiourea and ascorbic acid and total amount of As was subsequenly obtained. The concentration of As(V) was obtained via subtraction of As(III) from the total As.

The effect of HCl concentration on the atomic fluorescence intensity of As(III) and As(V) was investigated and the results were shown in Fig. 1a. The signal intensity rises significantly with the concentration of HCl for both As(III) and As(V), and this corresponds to an improvement in the hydride generation efficiency from the two species. The signal intensity of As(III) and As(V) tended to level off when further increasing the HCl concentration after 6% (v/v).

The influence of KBH4 concentration on the generation of arsine from As(V) and As(III) was also studied with the results shown in Fig. 1b. An increase of KBH4 concentration produces an increase of As(III) signal intensity and a decrease of As(V) signal intensity until
Fig. 1. As(III) and As(V) fluorescence signal intensity dependence on HCl concentration and KBH$_4$ concentration: (a) effect of HCl concentration with 2% (m/v) KBH$_4$ and (b) effect of KBH$_4$ concentration with 2% (v/v) HCl. The error bars indicate the S.D. of three replicates. The 100% fluorescence intensity represents the maximum signal intensity during the optimization of the corresponding parameter.

3% (m/v), and then the decrease of both As(III) and As(V) signal intensity was observed after that probably because of the analyte dilution caused by excessive produced hydrogen. Therefore, 2% (v/v) HCl and 3% (m/v) KBH$_4$ were selected for the selective arsine generation from As(III). Although partial overlap of the reduction of As(III) and As(V) to arsine exist (about 6% at the same concentration), this hydride generation condition was only selected for systematic optimization considering both separation efficiency and sensitivity. For higher concentration ratios of As(V) to As(III), the resolution between As(III) and As(V) should be increased by lowering the HCl concentration, as indicated by Kumar and Riyazuddin [31].

It was found that upon pre-reduction for 30 min with 0.5% (m/v) thiourea and 0.5% (m/v) of ascorbic acid at room temperature, As(V) was successfully converted to As(III). Total amount of As was thus determined at the optimal HCl and KBH$_4$ condition, i.e., 6% (v/v) HCl and 2% (m/v) KBH$_4$.

3.2. Optimization of tungsten coil trapping conditions

3.2.1. Evaluation of permanent modifier coating

Permanent chemical modifier was firstly introduced to tungsten coil hydride trapping by Barbosa et al. for selenium hydride trapping [14], later they have investigated the trapping of arsine with rhodium-coated coil [11]. Generally, the use of permanent chemical modifiers in tungsten coil trapping was inherited from the knowledge of hydride trapping in graphite furnace. Bare tungsten coil can trap bismuth hydride [30], as tungsten is also an important chemical modifier in graphite furnace. However, this is not applicable for Se, As and Sb and thus further coating of the tungsten coil with a thin layer of noble metal was indispensable. We also demonstrated that the noble metal coating was more effective than the bare tungsten coil, resulting in 60% increase of trapping efficiency [30]. Preliminary experiments in this work showed that trapping of arsine was not successful with un-coated tungsten coil. Since, several potential chemical modifiers, i.e., Pt, Rh, Re, Ta and Mo (200 µg), were coated on tungsten coil for trapping of arsine. As shown in Fig. 2a, all these metals pose the ability for arsine trapping, but their performances are varied. Ta coating exhibits a best trapping efficiency but the signal intensity was highly unstable. Finally, Rh coating was chosen for the further studies considering both trapping efficiency and stability.

The suitable amount of Rh coated on tungsten coil was investigated in the range of 50–400 µg. As shown in Fig. 2b, for routine trapping, 50 µg amount is enough. Several former studies have shown the coated amount has a close relationship with the lifetime of the coating [11,30,32]. And considering the tedious operation of the metal coating, 400 µg amount was selected. In this work, each coating (400 µg Rh) remained stable for about 300 firings, and up to 10% signal intensity loss could be observed thereafter, thus recoating was needed.

Fig. 2. Effect of W-coil permanent chemical modifiers: (a) comparison of different metal modifiers and (b) comparison of different amounts of Rh modifier. The error bars indicate the S.D. of three replicates. The 100% fluorescence intensity represents the maximum signal intensity during the optimization of the corresponding parameter.
3.2.2. Effect of trapping temperature and vaporization temperature

Coil temperature was a key parameter for W-coil hydride trapping. The optimum trapping temperature of tungsten coil was found to be 640 °C (5.0 A), while Barbosa et al. reported a maximum arsenic trapping efficiency at the temperature of 520 °C on Rh-coated tungsten coil [11] and Dočekal and Marek [7] found 700–900 °C was the best for arsenic trapping on Rh-coated tungsten tube. The difference in trapping temperature between these works probably lies in a comprehensive effect of carrier gas composition and flow rate, mass of Rh modifier as well as the construction of trapping device, which affects the interaction between arsenic hydride and tungsten surface. In order to determine the optimum vaporization temperature, the trapping temperature was set to 640 °C (5.0 A) and the vaporization temperature was varied between 1630 and 2060 °C (7.0–8.5 A). The fluorescence signal intensity increased with temperature up to 1930 °C (8.0 A) and stayed constant between 1930 and 2060 °C (8.0–8.5 A); therefore, 1930 °C (8.0 A) was selected as the vaporization temperature. With vaporization temperature lower than 1930 °C (8.0 A), instability of the signal intensity caused by memory effects was also observed as was reported in our previous work of bismuth trapping [30].

Although the exact mechanism for arsine trapping was absent presently, we can still get some knowledge from the well-known Marsh test used in toxicology for detection of arsenic that arsenic atoms may be the eventual trapped species. After gas–liquid separation, the gaseous phase contains considerable amount of oxygen as an impurity [33]. As indicated by Dočekal [6], very fast reaction of hydrogen with oxygen can be induced upon contact of gaseous species with heated trapping device with catalysts such as noble metals. Accordingly, hydrides may be converted to corresponding atoms and subsequently trapped by the tungsten coil. In our previous work of tungsten coil electrothermal vaporization-AFS [29], the best vaporization temperature for arsenic was 1730 °C, it is expected arsenic atoms were sputtered from the tungsten coil at the vaporization stage. Similar vaporization temperature in these two works may confirm that the analyte species vaporized from tungsten coil in the current work is probably arsenic atoms. However, further study concerning the trapping mechanism is still needed.

3.3. Effect of the gas flow rate

3.3.1. Effect of hydrogen and argon carrier gas flow rates

Carrier gas flow rate was another key parameter for W-coil as was reported in graphite furnace hydride trapping [2]. The effects of the flow rates of Ar and H2 on the trapping of arsenic hydride are shown in Fig. 3. When the W-coil atomizer was used, an addi-
In situ Trapping FAAS 4 4000 ± 10 [38]
W-trap HG-AAS 0.11 160 ± 1.5 [11]
In situ trapping HG-GF-AAS 0.0043 43 ± 10 [36]
In situ trapping tungsten tube atomizer-AAS 0.15 150 ± 1 [7]
HG–cryotrapping–AAS 0.135 80 0.100 60 0.6 [40]
FI on-line sorption HG-AFS 0.023 140 0.023 140 6 [39]
Hydride trapping ETV-ICP-MS 0.014 7 – a –a 0.5 [37]

Comparison of the LODs by similar methods.
Table 3

<table>
<thead>
<tr>
<th>Method</th>
<th>Total As</th>
<th>As(III)</th>
<th>Sample volume (mL)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>W-trap HG-AFS</td>
<td>0.009</td>
<td>430</td>
<td>0.01</td>
<td>48</td>
</tr>
<tr>
<td>HG-AFS</td>
<td>0.07</td>
<td>70</td>
<td>0.09</td>
<td>90</td>
</tr>
<tr>
<td>W-coil ETV-AFS</td>
<td>10</td>
<td>200</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>W-trap HG-AAS</td>
<td>0.11</td>
<td>160</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>In situ trapping tungsten tube atomizer-AAS</td>
<td>0.15</td>
<td>150</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>In situ trapping HG-GF-AAS</td>
<td>0.0043</td>
<td>43</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Hydride trapping ETV-ICP-MS</td>
<td>0.014</td>
<td>7</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>In situ Trapping FAAS</td>
<td>4</td>
<td>40000</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>FI on-line sorption HG-AFS</td>
<td>0.023</td>
<td>140</td>
<td>0.023</td>
<td>140</td>
</tr>
<tr>
<td>HG–cryotrapping–AAS</td>
<td>0.135</td>
<td>80</td>
<td>0.100</td>
<td>60</td>
</tr>
</tbody>
</table>

*a No data available.

Table 4

Analytical results of standard reference materials in comparison with the certified values (n = 3 for each sample).

<table>
<thead>
<tr>
<th>Samples</th>
<th>Certified (µg g–1)</th>
<th>Found (µg g–1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GBW 07601 Human hair</td>
<td>0.28 ± 0.05</td>
<td>0.26 ± 0.01</td>
</tr>
<tr>
<td>GBW 07605 Tea leaf</td>
<td>0.28 ± 0.04</td>
<td>0.27 ± 0.02</td>
</tr>
<tr>
<td>GBW(E) 08390 Simulated water</td>
<td>0.50 ± 0.02</td>
<td>0.48 ± 0.01</td>
</tr>
<tr>
<td>GBW(E) 08391 Simulated water</td>
<td>4.0 ± 0.1</td>
<td>4.0 ± 0.2</td>
</tr>
</tbody>
</table>

Analytical figures of merit

3.4.1. Trapping time

The relation between the analytical signal intensity and the sample volume was investigated with a 0.2 ng mL–1 As(III) solution using the hydride generation parameters for As(III) and total arsenic as shown in Fig. 4. In the current study, the sampling rate was 6 mL min–1. Good linearity of sample volume versus analytical signal intensity was found when the sample volume varied from 6 mL (60 s) to 48 mL (480 s). The reagent blank of As(III) and total arsenic was calculated to be about 0.04 and 0.1 ng mL–1 respectively, which was a limitation for the LOD improvement for the proposed new technique. Reagent blank was thought to be brought by HCl used in the analyte solution.

3.4.2. Signal profile, calibration plots, precision and LOD

After selecting the optimum parameters for W-coil trap system, analytical figures of merit of the W-coil trap AFS for inorganic arsenic speciation are shown in Table 2. The reproducibility of the measurements was <5% R.S.D. (N = 7) for 8 min trapping of 0.2 ng mL–1 As solution. A comparison of AFS signal profile shown in Fig. 5 was obtained for 1 ng mL–1 As standard with and without W-trap, sensitivity improvement can be directly visualized. Without W-coil trap, no obvious signal peak was present; while with 120 s trapping, the signal peak for 1 ng mL–1 is clearly visible. Temporal width of atomic fluorescence peak is as short as 2 s, in comparison, in conventional HG–AAS, signal width is at least 12 s because it accumulates sensitivity from a large sampling volume and thus relatively longer time is needed for delivering the sample to react with KBH4. The calculated LOD (3σ) for the determination is 10 ng L–1 for

Table 5

Determination of inorganic arsenic species in natural water samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Added (µg L–1)</th>
<th>Found (µg L–1)*</th>
<th>Recovery %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As(III)</td>
<td>As(V)</td>
<td>As(III)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lake water</td>
<td>0</td>
<td>0</td>
<td>0.70 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>0.50</td>
<td>1.22 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>1.00</td>
<td>1.76 ± 0.06</td>
</tr>
<tr>
<td>River water</td>
<td>0</td>
<td>0</td>
<td>0.23 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>0.50</td>
<td>0.70 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>1.00</td>
<td>1.00</td>
<td>1.27 ± 0.03</td>
</tr>
</tbody>
</table>

*a Mean of three determinations.

b Calculated value.
As(III) and 9 ng L$^{-1}$ for total As with 480 s trapping time. The limit of detection of the proposed method is compared with the literature values in Table 4. As seen in Table 3, the concentration limit of detection is comparable with the others or better. Compared with the proposed hyphenation system, either ICP-MS or GF-AAS is much more expensive. Furthermore, even better sensitivity can be easily achieved using longer trapping time, due to the good trapping capacity of the Rh-coated tungsten coil.

### 3.4.3. Accuracy test

The accuracy of the proposed method for total arsenic determination was verified by analyzing several certified reference materials. The analytical results are given in Table 4 and a t-test shows that the analytical results by the proposed method have no significant difference from the certified values at the confidence level of 95%. To further verify the accuracy of the proposed method for inorganic arsenic speciation analysis, lake and river water samples were also analyzed. The water samples were filtered through a 0.45 μm membrane filter and analyzed as soon as possible after sampling. In addition, the recovery experiments of different amounts of As(III) and As(V) were carried out, and the results are shown in Table 5. The results indicated that the recoveries were reasonable for trace analysis, ranging from 92 to 110%.

### 4. Conclusions

W-coil hydride trap was successfully applied in inorganic arsenic speciation analysis of water samples. Using proper reaction medium, arsine is selectively generated from As(III), on-line trapped on an rhodium-coated tungsten coil and subsequently vaporized and determined by AFS. Total inorganic arsenic could be determined after conversion of As(V) to As(III) with a reduction treatment by thiourea and ascorbic acid. The W-coil hydride trap greatly improved the sensitivity and the LOD for the determination of arsenic at ultratrace levels. Due to the great improvements of sensitivity as well as simplicity and cost-effectiveness, the proposed method may be used for the speciation of vapor forming organic arsenic species and speciation analysis of other vapor forming elements.

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