Determination of arsenic(III) by flow injection solid phase extraction coupled with on-line hydride generation atomic absorption spectrometry using a PTFE turnings-packed micro-column

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Abstract

A novel flow injection (FI) solid phase extraction method for the determination of arsenic(III) at trace levels was developed, using on-line hydride generation atomic absorption spectrometry (HG-AAS). Selective determination of As(III) was achieved by on-line formation and retention of the pyrrolidine dithiocarbamate arsenic complex As(III)–PDC on the PTFE turnings which are packed in the preconcentration micro-column. The retained complex was eluted by 2 ml 2 mol l\(^{-1}\) HCl and subsequently introduced on-line into the integrated reaction chamber/gas–liquid separator (RC–GLS). A 1.5% (m/v) NaBH\(_4\) solution was used for arsine generation, while a gas stream of N\(_2\) was employed for flash release and transportation towards the atomic absorption flow through cell (AAC) for atomization and measurement. The excellent performance of PTFE turnings as sorbent material and the compact design of the RC–GLS result to high sensitivity, selectivity and sampling frequency. For 60 s preconcentration time and sample consumption 10.4 ml a sampling frequency of 25 h\(^{-1}\) and a detection limit of \(c_L = 0.02\) \(\mu\)g\(\text{ml}^{-1}\) were obtained. The repeatability, expressed as relative standard deviation (R.S.D.), at 1.0 \(\mu\)g\(\text{ml}^{-1}\) As(III), was \(s_r = 2.8\%\). The proposed method was successfully applied to the selective determination of As(III) in natural waters and total arsenic determination in certified reference material.

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Keywords: Arsenic; Solid phase extraction; Flow injection; Hydride generation atomic absorption spectrometry; Polytetrafluoroethylene; Pyrrolidine dithiocarbamate

1. Introduction

Arsenic show different toxicity in human depending strongly on its chemical form. The determination of arsenite in aquatic environmental samples is of particular interest due to the fact that it is ten times more toxic than arsenate and almost 70 times more toxic than the methylated species [1]. The concentration ratio of As(III) to As(V) can be used as a chemical indicator of the red–ox status of underground-water systems [2].

For the determination of arsenic species in natural waters, where the concentrations of arsenic are usually found at trace levels, highly sensitive and selective preconcentration techniques are required. Several analytical techniques have been used for arsenic determination at trace levels including hydride generation (HG) [3–10], electrothermal atomic absorption spectrometry (ETAAS) [11–13] and inductively coupled plasma atomic emission spectrometry (ICP–AES) [14–17] or mass spectrometry (ICP–MS) [18–20]. Using on-line techniques, the drawbacks of batch operation, such as time-consuming, labour-intensive, large sample consumption, great risk of contamination and analyte loss, can be overcome to a great extent, while preconcentration can be further enhanced [21].

The majority of on-line preconcentration methods are based on solid phase extraction (SPE) principals, using as sorbent material ion exchange resins [5,14,15,17,18,22], silica gel bonded with octadecyl functional groups (C\(_{18}\)) [8,13,20], yeast immobilized on controlled pore glass (CPG) [4], activated alumina [9], coated polyurethane foam [16], and open tubes knotted reactors (KRs) [6,10,11,19]. Alternatively, polytetrafluoroethylene (PTFE) turnings-packed micro-columns have been successfully employed for on-line preconcentration of trace elements. The beneficial use of this novel form of PTFE as sorbent material for Cu, Cr, Pb, Co and Hg on-line preconcentration and determination by atomic absorption spectrometry...
(AAS) was actually demonstrated [23–28]. In comparison to the KR systems and other packing materials, PTFE turnings packed column, allows the use of even higher sampling loading flow rates, up to 15 ml min\(^{-1}\), with gain in the preconcentration efficiency. Moreover, KRs suffers from low retention efficiency for most of the common analyte complexes, e.g. 40–53% for M-APDC, 13–40% for M-8HQ and 64–81% for M-DDPA [29,30].

The aim of this work was to develop a sensitive and selective flow injection preconcentration method for the determination of As(III) in natural waters by on-line HG-AAS via its complexation with APDC, using a PTFE turnings-packed micro-column. Because of the very good chemical resistance and the unlimited lifetime of the PTFE material, the column does not need any regeneration or repacking and remains unaltered after preconcentration or elution step. Being to the best of our knowledge, it is the first time that PTFE turnings are used as sorbent material for arsenic preconcentration. The proposed method was optimized and applied to selective determination of As(III) in natural water samples and certified reference material.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer model 5100 PC atomic absorption spectrometer equipped with a deuterium arc background corrector was used as detector. Arsenic electrodeless discharge lamp (EDL) was used as light source operated at 8 mA. The wavelength was set at 193.7 nm resonance line and the monochromator spectral bandpass at 0.7 nm. A time-constant of 0.2 s was used for peak height evaluation. A Perkin-Elmer Hydride System MHS-1 with an electrothermal quartz flow throw cell atomizer was used for the hydride atomization fixed at 950 \(^\circ\) C. The atomic absorption flow throw cell (AAC) was sealed with removable quartz windows at either ends. Two nipples were at the extreme ends to permit exit of the gas flow. The conduit, which connects the outlet of the reaction chamber/gas-liquid separator (RC–GLS) with the inlet of the AAC, was as short as possible (15 cm length, 0.5 mm i.d.) in order to keep the dead volume at low levels for achieving small values of the hydride vapour dispersion.

The integrated reaction chamber/gas–liquid separator RC–GLS was made in our laboratory of a cylindrical glass tube (60 mm length, 15 mm i.d.) and two polytetrafluoroethylene (PTFE) push-fit connections at the ends. The above connections have conical cavities, as they are presented in Fig. 1. This construction facilitates the effective separation and transportation of the released arsine. The upper connection is a “Tee” type confluence connector with a 0.5 mm i.d. horizontal channel and a 1.0 mm i.d. vertical one. The lower push-fit connection has a 0.8 mm i.d. vertical channel. Nitrogen (N\(_2\)) at fixed 0.4 l min\(^{-1}\) flow rate was used, as purge gas during all experiments.

The FI on-line preconcentration hydride generation manifold and its operation are shown schematically in Fig. 1. It consists of three peristaltic pumps P1, P2, P3 (a Watson–Marlow model 205 U/BA and two Gilson model Minipuls-3), two six-port two-position injection valves IV1, IV2 (Reodyne, USA), a preconcentration column C (70 mm length, 4 mm i.d.). The column was firmly packed with PTFE turnings (900 mg, 0.1 mm width), as described previously [23,25]. The geometry of turnings allows high sample flow rates with significantly lower back-pressure than other sorbent materials, thus the sample loading flow rate which can be applied is much higher. The huge effective surface of PTFE turnings and the chaotic construction increases significant the capacity of the column and eliminates the problem of weak retention of the sorbed complexes into the knotted reactors.

![Fig. 1. On-line preconcentration manifold for As(III) determination. (a) Preconcentration step. APDC, 0.05 (m/v) APDC solution; HCl, 2.0 mol l\(^{-1}\) HCl; WS, washing solution 0.01 mol l\(^{-1}\) HCl, NaBH\(_4\), 1.5% (m/v) NaBH\(_4\) in 0.1 mol l\(^{-1}\) NaOH; W, waste; Purge gas, N\(_2\) 0.4 l min\(^{-1}\); P1, P2, P3, peristaltic pumps; IV1, IV2, injection valves in “A” and “B” position, respectively, SV, selection valve; C, PTFE turnings-packed micro-column; RC–GLS, integrated reaction chamber/gas–liquid separator; AAC, electrically heated atomic absorption flow through cell; T, connection tube. (b) IV1, IV2, injection valves in “B” and “A” position, respectively.](image-url)
A Metrohm 654 pH-meter, which was calibrated by NIST standards, was used for the pH measurements.

3. Reagents and samples

All chemicals were of analytical reagent grade and were provided by Merck (Darmstadt, Germany). Ultra-pure quality water was used throughout which was produced by a Milli-Q system (Millipore, Bedford, USA). Working standard solutions of As(III) were prepared by appropriate stepwise dilution of a 1000 mg l\(^{-1}\) As(III) to the required mg l\(^{-1}\) levels just before use. The solution of 1000 mg l\(^{-1}\) As(III) was prepared dissolving 1.2030 g of As\(_2\)O\(_3\) in 25 ml of 20% (m/v) potassium hydroxide solution, followed by neutralization with 20% (m/v) sulphuric acid and diluting to 1000 ml with 1% (m/v) sulphuric acid. Standard solutions of As(V) were prepared by appropriate stepwise dilution of a 1000 mg l\(^{-1}\) As(V) stock standard solution (Thirnol, Merck). Sodium tetrahydroborate solutions in 0.1% (m/v) NaOH were freshly prepared from NaBH\(_4\) (Fluka, As <0.000005%, m/m). Solutions of HCl were prepared by adequate dilution of concentrated HCl (Fluka, As <0.000005%, m/m; 1.16 g ml\(^{-1}\), Cysteine (Fluka, Riedel-de-Haen) solution 1.0% (m/v) NaOH was employed for prereduction of As(V) to As(III). The chelating reagent solution of ammonium pyrrolidine dithiocarbamate (APDC) was prepared fresh daily by dissolving the appropriate amount of APDC in Milli-Q water. Water samples were collected from Axios River, Prespa Lake, Thessaloniki tap water and sea water collected from Northern Greece. All samples were filtered through 0.45 \(\mu\)m membrane filters, acidified to ca. pH 2.5 with dilute HCl and stored at 4\(^\circ\)C in acid-cleaned polyethylene bottles. Certified reference material NIST CRM 1643d (National Institute of Standard and Technology) containing trace elements in water and total arsenic at a certified concentration 56.02 ± 0.73 \(\mu\)g l\(^{-1}\), was analyzed after prereduction of As(V) to As(III) in order to validate the accuracy of the proposed method.

3.1. Procedure

The operating sequence of the FI on-line column preconcentration system for As(III) determination by the proposed HG-AAS method is presented in Table 1.

### Table 1

<table>
<thead>
<tr>
<th>Step</th>
<th>Valves</th>
<th>Pumps</th>
<th>Delivered medium</th>
<th>Flow rate (ml min(^{-1}))</th>
<th>Time (s)</th>
<th>Operation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A B</td>
<td>ON OFF OFF Sample/APDC</td>
<td>10.4/1.0</td>
<td>60</td>
<td>Preconcentration</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>B A</td>
<td>OFF ON OFF 2 mol l(^{-1}) HCl</td>
<td>2.8</td>
<td>40</td>
<td>Elution</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>A A</td>
<td>OFF ON OFF 1.5% m/v NaBH(_4)</td>
<td>4.0</td>
<td>9</td>
<td>As(III) generation</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>A A</td>
<td>OFF ON OFF Purge gas, N(_2)</td>
<td>400</td>
<td>5</td>
<td>As(III) transportation/measurements</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>A A</td>
<td>OFF ON OFF 2.0 mol l(^{-1}) HCl</td>
<td>2.8</td>
<td>5</td>
<td>Filling tube (T) with HCl 2.0 mol l(^{-1})</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>A A</td>
<td>OFF ON OFF Waste</td>
<td>20</td>
<td>10</td>
<td>RC-GLS evacuation</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>B B</td>
<td>OFF ON OFF 0.01 mol l(^{-1}) HCl</td>
<td>15</td>
<td>8</td>
<td>Column conditioning</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>B A</td>
<td>OFF ON OFF Waste</td>
<td>20</td>
<td>8</td>
<td>RC-GLS evacuation</td>
<td></td>
</tr>
</tbody>
</table>

In all steps, except 4, the atomic absorption flow through cell (AAC) is purged by N\(_2\).

In step 1 (preconcentration, Fig. 1a), pump P2 is activated and the injection valve IV1 is in “A” position. During this step the As(III)-APDC complex is formed on-line and is retained onto the surface of PTFE turnings for 60 s. During step 2, 2.0 mol l\(^{-1}\) HCl solution is propelled through the column C, in order to elute and transport the retained As–PDC complex into the reaction chamber/gas–liquid separator RC–GLS. In step 3 (arsine generation), reductant solution 1.5% (m/v) NaBH\(_4\) is pumped into RC–GLS at 4.0 ml min\(^{-1}\) flow rate for 9 s. The produced nascent hydrogen generates the arsine vapor. A significant advantage, which arises from proposed manifold, is that during all steps (except step 4) the purge gas bypasses the RC–GLS flowing only through the AAC. This configuration facilitates the trapping of the generated arsine for few seconds into the RC–GLS, eliminating thus the dispersion and increasing the peak height of the signal. In step 4, SV is actuated to position 2 and N\(_2\) flows through the RC–GLS resulting thus to a flashed release and transport of the AsH\(_3\) into the atomic absorption cell AAC for absorbance measuring. During step 6 and 8, the liquid mixture from the RC–GLS, is propelled towards the waste by the purge gas with practically constant pressure, evacuating the RC–GLS. In steps 5–8, the manifold is prepared for the next cycle. Five replicate measurements per sample were made in all instances. The peak height of the reported signal was proportional to the As(III) concentration and was used for all measurements.

Total inorganic arsenic was determined after off-line pre-reduction of As(V) to As(III), in 1% (m/v) L-cysteine, 0.03 mol l\(^{-1}\) HCl media for 1 h at room temperature [31].

4. Results and discussion

4.1. Optimization of chemical and FI variables

Although, organic solvents such as isobutyl methyl ketone (IBMK), ethanol and methanol have been used as very good eluents in flow injection preconcentration systems, they are not favourable for the subsequent hydride generation. Also, the complex formation and retention of As(III)-APDC on PTFE turnings is not accomplishable in strong acidic medium. Taking into account these points a 2.0 mol l\(^{-1}\) HCl solution was employed as eluent because this solution facilitates both the hydride generation and the elution procedure. The effect of the eluent flow rate was examined in the range 1.5–3.5 ml min\(^{-1}\) for a fixed 1.9 ml
eluent volume. The recorded absorbance was almost constant for flow rates up to 2.8 ml min$^{-1}$, while for higher values the absorbance was decreasing. For all experiments 2.8 ml min$^{-1}$ and 40 s were used, as compromise between the sensitivity and the time which is needed for each determination.

The reductant solution should be added as fast as possible, in order to achieve a flash generation of arsine. Following preliminary experiments 4.5 ml min$^{-1}$ loading flow rate and 8 s loading time were used throughout. The effect of NaBH$_4$ concentration on the absorbance was studied in the range 0.5–2.5% (m/v) NaBH$_4$. The absorbance became higher by increasing NaBH$_4$ concentration up to 1.5% and was stabilized at higher NaBH$_4$ concentrations. For NaBH$_4$ concentration higher than 1.5% (m/v) the loading time must be reduced (6 s) because the huge amount of nascent hydrogen produces an uncontrolled liberation of arsine and double peak signals. Thus, of 1.5% (m/v) NaBH$_4$ was adopted as optimal.

The chemical and FI variables of the proposed manifold, which affect the preconcentration were optimised using 2.0 µg l$^{-1}$ As(III) standard solution. The sample acidity is one of the critical variables for the of As(III)-PDC complex formation, and its retention on the surface of PTFE turnings. Thus, HCl concentration was studied in the range 0.001–1.5 mol l$^{-1}$ at fixed 0.05 (m/v) APDC concentration. As it is presented in Fig. 2, the optimum HCl concentration ranged from 0.03 to 0.2 mol l$^{-1}$ HCl. At HCl concentration higher than 1.0 mol l$^{-1}$ the sensitivity was very low due to the unfavorable complex formation between As(III) and APDC. At 2.0 mol l$^{-1}$ HCl no complex formation was observed. Thus, for further studies HCl concentration of 0.05 mol l$^{-1}$ was used. In addition, it was examined the chelate As(V)-PDC retention on PTFE turnings using 2.0 µg l$^{-1}$ As(V) in 0.05 mol l$^{-1}$ HCl standard solution under the same conditions described above. The recorded absorbance was lower than 10% of the signal obtained from As(III), due to the very slow As(V)-PDC complex formation. This fact facilitates the selective determination of As(III) in the presence of As(V).

The influence of the APDC concentration was tested within the range of 0.01–0.5% (m/v), at fixed 1.0 ml min$^{-1}$ APDC flow rate. The absorbance was almost constant in the studied range, while no preconcentration was observed in the absent of APDC.

Although very small concentration is capable for analyte preconcentration, 0.05% (m/v) APDC solution was used throughout, in order to ensure sufficient excess of the ligand in case of presence of other metals.

The effect of sample loading flow rate on the absorbance was studied within the range 3.3–14.5 ml min$^{-1}$ at fixed 60 s preconcentration time. As it is shown in Fig. 3, the absorbance was increasing almost linearly, by increasing the sample loading flow rate. This fact indicates that the complexation was completed, the contact time was sufficient to allow quantitative retention of the analyte. Consequently, more sample volume can be loaded during a given preconcentration time, resulting thus in higher enrichment factors. For all subsequent experiments, 10.4 ml min$^{-1}$ sample flow rate was selected, as a compromise between high sensitivity and medium sample consumption.

In time-based on-line preconcentration systems the sample loading time value indicates the preconcentration time of the method and reflects the enrichment factor. The loading time was examined in the range between 30 and 180 s at fixed 10.4 ml min$^{-1}$ sample flow rate. The recorded absorbance was practically linear up to a 180 s preconcentration time as it is presented in Fig. 4. This fact proves that even at long loading times and prolonged sample flow, no negative effect is produced.

![Fig. 2. Effect of the sample acidity on the absorbance of 2.0 µg l$^{-1}$ As(III). All other parameters as in Table 1.](image)

![Fig. 3. Effect of the sample flow rate on the absorbance of 2.0 µg l$^{-1}$ As(III). All other parameters as in Table 1.](image)

![Fig. 4. Effect of the loading time on the absorbance of 2.0 µg l$^{-1}$ As(III). All other parameters as in Table 1.](image)
from partial leaching of the complex [32]. Finally, a 60’s loading time was adopted for the proposed method as a compromise between medium sample consumption, high sensitivity and sufficient sampling frequency.

4.2. Interference studies

Although, ammonium pyrrolidine dithiocarbamate does not form complexes with alkali and alkaline earth metals, high concentrations of them were tested, due to their presence in natural water. Cations Na and K were tolerable up to 5 g l⁻¹ while Ca and Mg up to 300 mg l⁻¹. Anions Cl⁻ do not cause any significant interference even in presence of very high concentrations (10 g l⁻¹). On the other hand it is well known that transition metals form strong complexes with APDC, so the recovery of 2.0 μg L⁻¹ As(III) solution was tested in presence of these metals under the optimum conditions described above. The elements Cu(II), Co(II), Cd(II), Cr(III), Fe(III), Ni(II), Pb(II) and Se(IV) were found not to interfere at concentrations up to 100 μg l⁻¹, while Hg(II) was tolerable up to 30 μg l⁻¹.

4.3. Analytical performance of the proposed method

The analytical performance data of the proposed on-line column preconcentration HG-AAS method for As(III) determination, are summarized in Table 2. For 60 s preconcentration time the sampling frequency was 25 h⁻¹ and the enhancement factor was 10 (comparing the proposed method and the direct insertion of aqueous standard solution into RC–GLS). The linear range was found to be 0.04–5.0 μg l⁻¹ As(III). The detection limit calculated by 3 s criterion and found to be \( \chi_L = 0.02 \mu g l^{-1} \). The precision of the method was also studied. The repeatability, as relative standard deviation (R.S.D.), was \( \chi_r = 2.8 % \). calculated from 10 replicate measurements at the 1.0 μg l⁻¹ level of As(III). In Table 3, the performance characteristics of the proposed method are given together with other selected on-line methods.

<table>
<thead>
<tr>
<th>Detection technique</th>
<th>Sorbent material/complexing reagent</th>
<th>Linear range (μg l⁻¹)</th>
<th>SF (hr⁻¹)</th>
<th>( r^2 ) (μg l⁻¹)</th>
<th>( \chi_r ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HG–AAS</td>
<td>Amberlite IRA-410</td>
<td>0.05–2.0</td>
<td>10</td>
<td>0.03</td>
<td>4.8</td>
</tr>
<tr>
<td>HG–AAS</td>
<td>KR/APDC</td>
<td>0.10–10.0</td>
<td>32</td>
<td>0.023</td>
<td>1.3</td>
</tr>
<tr>
<td>HG–UV–vis</td>
<td>C₅₀/DPPA</td>
<td>5.0–50.0</td>
<td>20</td>
<td>0.06</td>
<td>6</td>
</tr>
<tr>
<td>HG–AAS</td>
<td>Activated alumina/Quinolin-8-ol</td>
<td>0–2.0</td>
<td>60</td>
<td>0.05</td>
<td>3.6</td>
</tr>
<tr>
<td>HG–AAS</td>
<td>KR/Co-precipitation with La(OH)₃</td>
<td>0.005–0.30</td>
<td>33</td>
<td>0.003</td>
<td>1.0</td>
</tr>
<tr>
<td>HG–AAS</td>
<td>PTFE-turnings/APDC</td>
<td>0.04–5.0</td>
<td>25</td>
<td>0.02</td>
<td>2.8</td>
</tr>
</tbody>
</table>

* Sampling frequency.
* Detection limit.
* Relative standard deviation.

Table 2: Analytical performance data of the proposed on-line column preconcentration HG-AAS method for As(III) determination.

<table>
<thead>
<tr>
<th>Preconcentration time (s)</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample consumption (ml)</td>
<td>10.4</td>
</tr>
<tr>
<td>Sampling frequency (h⁻¹)</td>
<td>25</td>
</tr>
<tr>
<td>Enhancement factor</td>
<td>10</td>
</tr>
<tr>
<td>0.05% (m/v) APDC consumption (ml)</td>
<td>1</td>
</tr>
<tr>
<td>1.5% (m/v) NaBH₄ consumption (ml)</td>
<td>0.6</td>
</tr>
<tr>
<td>2 mol l⁻¹ HCl consumption (ml)</td>
<td>1.5</td>
</tr>
<tr>
<td>Regression equation (As) in μg l⁻¹, (As) = 0.0074 ± 0.0033</td>
<td></td>
</tr>
<tr>
<td>Correlation coefficient</td>
<td>( r = 0.999 )</td>
</tr>
<tr>
<td>Detection limit (3 s) (μg l⁻¹)</td>
<td>( \chi_L = 0.02 )</td>
</tr>
<tr>
<td>Repeatability (R.S.D., ( n = 10 ), 1.0 μg l⁻¹) (%)</td>
<td>( \chi_r = 2.8 )</td>
</tr>
<tr>
<td>Linear range (μg l⁻¹)</td>
<td>0.04–5.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>As(III) (μg l⁻¹)</th>
<th>As(III) (μg l⁻¹)</th>
<th>As(III) (μg l⁻¹)</th>
<th>As(III) (μg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>River-water</td>
<td>1.15 ± 0.09</td>
<td>3.12 ± 0.21</td>
<td>1.97 ± 0.20</td>
<td>95</td>
</tr>
<tr>
<td>Lake-water</td>
<td>0.59 ± 0.04</td>
<td>1.63 ± 0.12</td>
<td>1.04 ± 0.10</td>
<td>96</td>
</tr>
<tr>
<td>Tap-water</td>
<td>0.56 ± 0.06</td>
<td>0.56 ± 0.06</td>
<td>0.56 ± 0.06</td>
<td>98</td>
</tr>
<tr>
<td>Sea-water</td>
<td>1.90 ± 0.15</td>
<td>3.47 ± 0.22</td>
<td>1.51 ± 0.15</td>
<td>103</td>
</tr>
</tbody>
</table>

Table 3: Comparative performance data and characteristics from selected references on As(III) determination by on-line solid-phase extraction hydride generation methods.

<table>
<thead>
<tr>
<th>Detection technique</th>
<th>Sorbent material/complexing reagent</th>
<th>Linear range (μg l⁻¹)</th>
<th>SF (hr⁻¹)</th>
<th>( r^2 ) (μg l⁻¹)</th>
<th>( \chi_r ) (%)</th>
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<td>2.8</td>
</tr>
</tbody>
</table>

* Sampling frequency.
* Detection limit.
* Relative standard deviation.

Table 4: Analytical results (mean value ± standard deviation, \( n = 5 \)) of As(III), total arsenic and calculated As(V) determination in natural waters samples and certified reference material.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added (μg l⁻¹)</th>
<th>Found (μg l⁻¹)</th>
<th>Calcd (μg l⁻¹)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(III)/As(V)</td>
<td>1.00 ± 0.00</td>
<td>1.00 ± 0.00</td>
<td>1.00 ± 0.00</td>
<td>95 ± 96</td>
</tr>
<tr>
<td>River-water</td>
<td>1.15 ± 0.09</td>
<td>3.12 ± 0.21</td>
<td>1.97 ± 0.20</td>
<td>95 ± 96</td>
</tr>
<tr>
<td>Lake-water</td>
<td>0.59 ± 0.04</td>
<td>1.63 ± 0.12</td>
<td>1.04 ± 0.10</td>
<td>96 ± 94</td>
</tr>
<tr>
<td>Tap-water</td>
<td>0.56 ± 0.06</td>
<td>0.56 ± 0.06</td>
<td>0.56 ± 0.06</td>
<td>98 ± 95</td>
</tr>
<tr>
<td>Sea-water</td>
<td>1.90 ± 0.15</td>
<td>3.47 ± 0.22</td>
<td>1.51 ± 0.15</td>
<td>103 ± 98</td>
</tr>
</tbody>
</table>

* not added; n.d.: not detected.
* Certified value of total arsenic.
solid phase extraction hydride generation methods reported in literature. The accuracy of the proposed method was evaluated, by total arsenic determination in the certified reference material NIST CRM 1643d (56.02 ± 0.73). The obtained recovery was 97% (54.34 ± 3.92 μg L⁻¹, n = 5). The result was in good agreement with the certified value and the calculated recovery was satisfactory. The proposed method was applied to the analysis of local natural water samples (river, lake and sea water) and was validated by spiking the samples with known amounts of As(III) and As(V). The obtained results are presented in Table 4. The recoveries from spiked solutions were varied in the range 95–103%.

5. Conclusions

The application of a new preconcentration column packed with PTFE turnings was demonstrated and evaluated to be promising for on-line As(III) preconcentration and determination by an automated hydride generation manifold combined with AAS. The developed on-line system offers reliable pre-concentration of As(III)–PDC complex on the PTFE turnings in relative high sample flow rates improving thus the sensitivity achieved.

In addition, the direct separation of arsine from the liquid reaction mixture in the integrated reaction chamber gas–liquid separator eliminates the dispersion of the analyte. To our knowledge this is the first work dealing with PTFE turnings as sorbent material in on-line column preconcentration for arsenic determination. The unlimited life time sorbent material and column preconcentration, easy operation and high sensitivity of the proposed system make it attractive for routine determination of the arsenic in natural waters.

References