Determination of As and Sb in mineral waters by fast sequential continuous flow hydride generation atomic absorption spectrometry

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In this study, a novel analytical method which consists of a combination of Fast Sequential Flame Atomic Absorption Spectrometry (FS-FAAAS) and Continuous Flow Hydride Generation Atomic Absorption Spectrometry (CF-HGAAS) is proposed. The method developed was employed for the sequential determination of As and Sb at sub-µg L⁻¹ levels in bottled mineral waters. A strong enhancement in the analytical throughput was obtained when compared with the traditional monoelement CF-HGAAS with a quartz tube atomizer (QTA). Variables which would affect the method performance such as Ar flow rate, HCl and NaBH₄ concentrations as well as delay and integration time were optimized. A flame atomic absorption spectrometer working in fast sequential mode was used in all experiments. After just 20 s of read delay, As and Sb were sequentially determined in 6 s (3 s each element). A 2³×2 fractional factorial design was employed for studies of potential interferents with transition metals that could be present in mineral water samples. Limits of detection obtained for As and Sb were 0.15 and 0.14 µg L⁻¹, respectively. The accuracy of the proposed method was checked by the use of 2 certified reference materials: Trace elements in water (NIST 1643e) and Trace metals in drinking water (HPS TMDW). Good agreement between certified and found concentrations was observed. Finally, As and Sb were determined in commercial bottled mineral water samples. Adequate sensitivity, high throughput and minimization of reagents and sample consumption are the attractive features of this new method.

Introduction

Arsenic, especially in its inorganic species, has long been recognized as being carcinogenic to humans in addition to causing other adverse effects such as skin damage, and also circulatory and peripheral nervous disorders.¹ In Bangladesh and West Bengal, high natural levels of arsenic are commonly found in drinking waters directly affecting the health of millions of people. In these places, the levels of arsenic can reach more than 1000 µg L⁻¹, which is 100-fold higher than the maximum recommended value set by the World Health Organization (WHO) for drinking water.²

Antimony is considered as an emerging contaminant in bottled mineral waters, mainly due to its use as a catalyst in the manufacture of polyethylene terephthalate (PET).³ Several studies have demonstrated the leaching of Sb from PET bottles into mineral water,⁴⁻⁶ especially when these recipients are exposed to temperatures above 40 °C, and these findings are of special concern due to the intrinsic toxic effects of this element to the human body. In chronic exposure to low Sb concentrations, myocardial atrophy could be observed, meanwhile higher doses may cause lung, liver and bile cancers.⁷⁻⁹ WHO, the US Environmental Protection Agency (USEPA), the European Union, Japan and Brazil regulate Sb in drinking water at a maximum concentration of 20, 6, 5, 2 and 5 µg L⁻¹, respectively.¹⁰⁻¹¹

The concentrations of As and Sb in drinking water samples are usually much lower, therefore, sensitive analytical techniques like ICP-MS (Inductively Coupled Plasma Mass Spectrometry), GFAAS (Graphite Furnace Atomic Absorption Spectrometry) or HGAAS have to be used in order to perform reliable quantitative determinations.

HGAAS is a well established technique which has relevant application in the determination of several hydride-forming elements such as: As, Bi, Ge, Pb, Sb, Se, Sn and Te at sub-µg L⁻¹ levels. The main advantages of this technique are higher sensitivity, selectivity derived from elimination of matrix interferences and low cost of implementation especially when used with a Quartz Tube Atomizer (QTA).¹² Despite these advantages, HGAAS is applied mainly for single element measurements.

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which greatly increases time and reagent consumption of analysis. Nevertheless, a graphite electrothermal atomizer has been used as both the hydride trapping cell and atomization cell for simultaneous multi-element determinations by SIMAA (simultaneous AAS).\textsuperscript{13–15} The analytical throughput can also be improved with sequential or simultaneous determinations by introducing the gaseous species generated into an excitation source such as an ICP for measurement by Optical Emission Spectrometry (OES)\textsuperscript{16–18} or by MS.\textsuperscript{19–21} Unfortunately, those techniques (“in-atmosphere trapping” with SIMAA, HG-ICP-OES and HG-ICP-MS) require strong analytical skills and expensive equipment, and the operation costs are high. However, the analytical throughput of HGAAS with QTA can also be improved if it is used in combination with FS-FAAS. In 2005, Niedzielski\textsuperscript{22} proposed the sequential determination of inorganic species of arsenic (As\textsuperscript{3+} and As\textsuperscript{5+}) and selenium (Se\textsuperscript{4+} and Se\textsuperscript{6+}) using a hyphenation between high performance liquid chromatography and hydride generation with an electrothermal heated QTA and this is the only study published that combines HGAAS with FS-FAAS.

FS-FAAS permits the sequential determination of analytes in decreasing order of wavelengths in one monochromator scan, decreasing the analysis time, and the consumption of reagents and sample. Ease of use is one example of this multi-element technique which maintains the advantages of conventional FAAS.\textsuperscript{23} The combination of TS-FF-AAS (Thermospray Flame Furnace AAS) and FS-FAAS for the sequential determination of Cd, Cu, Pb and Zn was a successful attempt in improving the analytical throughput of TS-FF-AAS.\textsuperscript{24}

The aim of this study was to determine As and Sb using the fast sequential mode of a Fast Sequential Flame Atomic Absorption Spectrometer in order to enhance the analytical throughput of the traditional mono-element HGAAS with a QTA. To attain better conditions for these determinations, parameters such as Ar flow rate, HCl and NaBH\textsubscript{4} concentrations as well as delay and integration time were optimized. Then, figures of merit of HGAAS in multi-element mode were obtained. Finally, As and Sb were determined in bottled mineral water samples using the developed method.

**Experimental**

**Instrumentation**

The HGAAS experiments were performed using a fast sequential flame atomic absorption spectrometer (AA240FS; Varian, Mulgrave, Australia) fitted with a deuterium lamp for background radiation correction. As and Sb hollow cathode lamps were used as primary radiation sources and the parameters set on the spectrometer (wavelength, slit, current for the hollow cathode lamp) were the manufacturer recommended values. In all experiments an air/acetylene (13.5 L min\textsuperscript{-1}/2.0 L min\textsuperscript{-1}) flame was used.

**Arrangement of CF-HGAAS system for multi-element determination**

According to the Vapour Generation Accessory user manual (VGA-77, Varian, Australia), flow rates must be within the range of 6–8 mL min\textsuperscript{-1} for the sample and 0.8–1.2 mL min\textsuperscript{-1} for both HCl and NaBH\textsubscript{4}. A 75 cm length reaction coil is used in the VGA-77. During our study we noticed that both signal noise and dead volume can be minimized by using Tygon\textsuperscript{®} tubes with smaller internal diameters, a higher peristaltic pump speed and a 60 cm length reaction coil. We started our study using a VGA-77 but unfortunately this commercially available system does not provide pump speed and argon flow rate controls. The advantages of the own construction pump/reaction coil over the commercial system is that by controlling these parameters, it is possible to improve limits of detection and analytical throughput. The schematic set-up of the proposed CF-HGAAS system for multi-element sequential determination is shown in Fig. 1. The system was composed by the following devices: a peristaltic pump with 8 channels (MCP model, Ismatec, Switzerland) furnished with 3 Tygon\textsuperscript{®} propulsion tubes with internal diameters (i.d.) of 0.48 mm (HCl, 1.2 mL min\textsuperscript{-1}), 0.48 mm (NaBH\textsubscript{4}, 1.2 mL min\textsuperscript{-1}) and 1.25 mm (sample, 6.8 mL min\textsuperscript{-1}) and a 60 cm Teflon\textsuperscript{®} reaction coil (i.d. = 0.8 mm). A gas/liquid separator and a U-shaped quartz cell atomizer (accessories of the VGA-77 system) were also used. The carrier flow rate (Ar, 140 mL min\textsuperscript{-1}), accurately and precisely regulated by using a mass flow controller (ASA, Sesto San Giovanni, Italy), was chosen as a compromise condition between minimum noise and maximum sensitivity. Multielement CF-HGAAS experiments were performed with the spectrometer working in fast sequential mode. The data acquisition was carried out in integration mode.

**Reagents, analytical solutions and samples**

All reagents were of analytical grade and were purchased from Merck (Germany). Deionized water (18 Ωm cm resistivity) was used to prepare all solutions. All glassware and polypropylene flasks were washed with soap, soaked in 10% v/v HNO\textsubscript{3} for 24 h and rinsed with deionized water prior to use. Standard solutions of arsenic and Sb (from 0.375 to 15 μg L\textsuperscript{-1}) in 1 mol L\textsuperscript{-1} HCl were prepared after successive dilutions of the metals standard stock solutions (1000 mg L\textsuperscript{-1}). A solution mixture containing 12% m/v KI was prepared each time before use. Sodium tetrahydroborate in 0.5% m/v NaOH was prepared prior to use by dissolving an...
appropriate amount of NaBH₄ and NaOH in deionized water. Hydrochloric acid was previously purified using a sub-boiling system (Marconi, Piracicaba, Brazil). For studies of potential interferents, Cu, Co, Ni, Fe, Mn and Zn 1000 mg L⁻¹ stock solutions were used to prepare the working solutions. Bottled mineral water samples were purchased at the local market in three different states from Brazil (Minas Gerais, Rio de Janeiro and São Paulo).

Preparation of certified reference materials and samples

Two certified reference materials (CRMs) were used to estimate the proposed method accuracy: Trace elements in water (NIST 1643e) and Trace metals in drinking water (HPS TMDW). In the proposed method, 10 mL of sample, 1 mL of 12 mol L⁻¹ HCl and 1 mL 12% m/v KI were pipetted into a 15 mL polypropylene flask. The final concentration was 1 mol L⁻¹ for HCl and 1% m/v for KI as recommended by the user manual (Varian, VGA-77). Then, the pre-reduction step was accomplished by heating in a water bath for 10 min at 80 °C. Certified reference materials and calibration solutions were prepared in the same way. Arsenic and Sb determinations in the CRMs were performed after adequate dilution according to the linear calibration range.

Results and discussion

Evaluation of read delay

In the continuous flow introduction mode, once the QTA volume is filled with hydride species and reaches the stationary stage, the absorbance signal becomes constant. At this moment, As and Sb can be determined by the spectrometer in fast sequential mode. It is crucial that the baseline for each analyte returns to zero before measuring another sample in order to avoid memory effects. Then, the read delay must be optimized considering signal stabilization and memory effects. Therefore, a multi-element solution containing As and Sb 15 μg L⁻¹ (highest point of the multi-element calibration curve) was prepared and the signal profile of each analyte was obtained separately. The solution was continuously introduced using the arrangement showed in Fig. 1 and the absorbance was measured at 193.7 nm (As) over a period of 30 s. Then, deionized water was immediately introduced and the signal profile was recorded for a further 30 s, in order to check the time required for the baseline to return to zero. The whole procedure was repeated for Sb (217.6 nm). Fig. 2 shows the signal profiles obtained for As and Sb using the optimized conditions (HCl 5 mol L⁻¹ and 0.8% m/v NaBH₄). As can be deduced from Fig. 2, the necessary time for signal stabilization for both elements is around 20 s and the minimum time to avoid memory effects is around 15 s. Therefore, 20 s was chosen as the read delay.

Evaluation of measurement time

After selecting the read delay, a multi-element solution containing As and Sb 5 μg L⁻¹ was analyzed by CF-HGAAS in multi-element mode using different integration times (0.5 to 4.0 s). The best condition was chosen by considering the relative standard deviation (R.S.D.) obtained for 10 measurements. As can be seen from Fig. 3, precision is improved by extending the integration time. The R.S.D. obtained when using a 3 s measurement time for each element would normally be accepted in routine analysis: As 1.4% and Sb 1.3%. Therefore, after 20 s read delay, As and Sb could be determined in 6 s (3 s each element). It is important to observe that the absorbance measured by the equipment software is actually an average of 60 data points per second. In addition, these R.S.D. values are compatible with those obtained by Freschi et al.¹⁴ (from 1.0 to 3.5% for As and Sb) when "in-atomizer trapping" with SIMAAS was used.

Optimization of HCl and NaBH₄ concentrations using 2² + star central composite design

Two variables that could considerably affect the absorbance signal were identified as reducing agent and acid concentrations. Those variables were evaluated using a 2² + star central composite design. This type of design²⁵,²⁶ permits the study of those variables at five different normalized levels (from −√2 to

![Fig. 2](https://example.com/fig2.png)

**Fig. 2** Signal profiles of As and Sb obtained separately using optimized conditions.

![Fig. 3](https://example.com/fig3.png)

**Fig. 3** R.S.D. obtained for 10 measurements of a solution containing As and Sb 5 μg L⁻¹ using integration times of 0.5 to 4 s.
using only 11 experiments and 3 replicates at the central point (both variables normalized to zero). The full design can be seen in Table 1. Randomization was used in order to avoid systematic errors. The concentrations varied from 2 to 8 mol L$^{-1}$ for HCl and from 0.4 to 0.8% (m/v) for NaBH$_4$. A multi-element solution containing As and Sb 10 µg L$^{-1}$ was used in all the experiments. To verify the maximum absorbance attainable by As and Sb, standard solution, HCl and NaBH$_4$ were introduced according to the arrangement in Fig. 1 with the spectrometer working in fast sequential mode using a delay time of 20 s and measurement time of 3 s for each element.

The maximum absorbance for As and Sb in relation to each experiment can be also seen in Table 1. Two empirical models (As and Sb) were proposed and the analysis of variance (ANOVA) was calculated. All models did not present lack of fit since the ratios between MSLoF (Mean Square for Lack of Fit) and MSPE (Mean Square for Pure Error) was calculated. All models did not present lack of fit (As and Sb) were proposed and the analysis of variance was performed in the central point. Both parameters can be calculated as 275 determinations per hour ignoring any time systematic errors. The concentrations varied from 2 to 8 mol L$^{-1}$ for HCl and from 0.4 to 0.8% (m/v) for NaBH$_4$. A multi-element solution containing As and Sb 10 µg L$^{-1}$ was used in all the experiments. To verify the maximum absorbance attainable by As and Sb, standard solution, HCl and NaBH$_4$ were introduced according to the arrangement in Fig. 1 with the spectrometer working in fast sequential mode using a delay time of 20 s and measurement time of 3 s for each element.

The maximum absorbance for As and Sb in relation to each experiment can be also seen in Table 1. Two empirical models (As and Sb) were proposed and the analysis of variance (ANOVA) was calculated. All models did not present lack of fit since the ratios between MSLoF (Mean Square for Lack of Fit) and MSPE (Mean Square for Pure Error) are lower than the tabulated $F$ value (19.16 with 95% of confidence level). These two parameters have information about the quality of the proposed models. The first one (MSLoF) shows whether the proposed model is well adjusted to the experimental values. The second parameter (MSPE) gives the error information from the replicates performed in the central point. Both parameters can be pooled and MS for Residue (MSr) can be used to calculate the models coefficients of error. In addition, the correlation coefficients performed in the central point. Both parameters can be calculated as

$$\text{As Absorbance} = 0.142 + 0.005\text{HCl} + 0.007\text{NaBH}_4$$

$$\text{Sb Absorbance} = 0.204 - 0.0034(\text{HCl})^3 + 0.0023(\text{NaBH}_4)^2$$

Fig. 4 shows the contour plots and equations for As (Fig. 4a) and Sb (Fig. 4b). The highest analytical signals for As were obtained when both HCl and NaBH$_4$ were at the higher concentration levels. In the case of Sb, the highest analytical signals were obtained when HCl concentration was 5 mol L$^{-1}$ and NaBH$_4$ concentration was 0.4 or 0.8% m/v. Fig. 4c shows the As and Sb contour plots overlaid and the gray region shows the suitable analytical conditions for both elements. In this particular region, HCl and NaBH$_4$ concentrations are 5 mol L$^{-1}$ and 0.8% m/v, respectively. These conditions were used in the experiments that follow.

### Studies with potential interferences

A 2$^{n-2}$ fractional factorial design was performed in order to investigate the influence, on the sequential determination of As and Sb, of transition metal ions commonly found in mineral waters including Co(II), Cu(II), Fe(III), Mn(II), Ni(II) and Zn(II). The concentration levels chosen for the metals were based on several papers which report the concentrations of those metals in mineral waters from 16 countries. In all the experiments the concentrations of the analytes (As and Sb) were fixed at 10 µg L$^{-1}$. The highest concentration levels (+1) for Co, Cu, Fe, Mn, Ni and Zn (potential interferents) were 15, 400, 150, 500, 450 and 300 µg L$^{-1}$, respectively, and the lowest concentration levels (normalized in $-1$) was 0 for all them. No remarkable problems were observed for As and Sb determination and the percentage of interference was lower than 10% (−2.3 to 6.8% for As and −2.2 to 2.0% for Sb).

### Figures of merit of CF-HGAAS in multi-element mode

Multi-element solutions containing As and Sb (0.375–15 µg L$^{-1}$) were prepared and analyzed by sequential multi-element CF-HGAAS using optimized conditions: HCl 5 mol L$^{-1}$, NaBH$_4$ 0.8% m/v, 20 s read delay and measurement time of 3 s for each element. Limits of detection, repeatability, linear ranges, regression equations, correlation coefficients and analytical throughput were determined. The limit of detection (LOD) was defined as the concentration corresponding to 3-fold the standard deviation of 10 measurements of the blank divided by the slope of the analytical curve. Repeatability was expressed as the relative standard deviation (R.S.D. %) obtained by 10 measurements of an intermediate point of the calibration curve: As and Sb 5 µg L$^{-1}$. Figures of merit for As and Sb can be seen in Table 2. The limits of detection obtained for As and Sb were 0.15 and 0.14 µg L$^{-1}$, respectively. These values are better than those obtained by Murphy et al. using a simultaneous multi-element approach with “in-atomizer trapping” electrothermal atomic absorption spectrometry (0.82 and 0.26 µg L$^{-1}$ for As and Sb, respectively). The “maximum theoretical sample throughput” was calculated as 275 determinations per hour ignoring any time

### Table 1 2$^2$ + star central composite design

<table>
<thead>
<tr>
<th>Experiment</th>
<th>HCl Real (mol L$^{-1}$)</th>
<th>Normalized</th>
<th>NaBH$_4$ Real (% w/v)</th>
<th>Normalized</th>
<th>As Absorbance</th>
<th>Sb Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>$-1$</td>
<td>0.5</td>
<td>$-1$</td>
<td>0.128</td>
<td>0.203</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>1</td>
<td>0.5</td>
<td>$-1$</td>
<td>0.144</td>
<td>0.199</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>$-1$</td>
<td>0.7</td>
<td>1</td>
<td>0.143</td>
<td>0.205</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>1</td>
<td>0.7</td>
<td>1</td>
<td>0.151</td>
<td>0.208</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
<td>$\sqrt{2}$</td>
<td>0.6</td>
<td>0</td>
<td>0.132</td>
<td>0.197</td>
</tr>
<tr>
<td>6</td>
<td>8</td>
<td>$\sqrt{2}$</td>
<td>0.6</td>
<td>$\sqrt{2}$</td>
<td>0.146</td>
<td>0.197</td>
</tr>
<tr>
<td>7</td>
<td>5</td>
<td>0</td>
<td>0.4</td>
<td>$-\sqrt{2}$</td>
<td>0.128</td>
<td>0.208</td>
</tr>
<tr>
<td>8</td>
<td>5</td>
<td>0</td>
<td>0.8</td>
<td>$\sqrt{2}$</td>
<td>0.153</td>
<td>0.209</td>
</tr>
<tr>
<td>9</td>
<td>5</td>
<td>0</td>
<td>0.6</td>
<td>0</td>
<td>0.145</td>
<td>0.205</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>0</td>
<td>0.6</td>
<td>0</td>
<td>0.141</td>
<td>0.204</td>
</tr>
<tr>
<td>11</td>
<td>5</td>
<td>0</td>
<td>0.6</td>
<td>0</td>
<td>0.141</td>
<td>0.205</td>
</tr>
</tbody>
</table>

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required for changing and presenting a new sample. For practical work using an auto sampler would then result in a “maximum achievable sample throughput” of approximately 100 determinations per hour, which still is an excellent number for HGAAS. Use of the PROMT mode of the instrument software (with a maximum measurement time of 3 s and a RSD limit of 1.5 to 2.0%) can also shorten analysis time even further.

**Determination of As and Sb in two CRM’s by sequential CF-HGAAS**

The accuracy of sequential multi-element CF-HGAAS was evaluated by determining As and Sb concentrations in two certified reference materials after adequate dilution, as mentioned in the experimental section. The results obtained with the proposed method are in agreement with the certified concentrations for both CRM’s. The recoveries fall in the range of 106–108% and 91–96% for As and Sb, respectively (Table 3).

**Determination of As and Sb in bottled mineral waters**

Arsenic and Sb were determined in 5 different brands of bottled mineral waters purchased in three different regions of Brazil according to “Preparation of certified reference materials and samples” in the Experimental section. Reference solutions containing 0.375–15.0 \( \mu \text{g} \text{L}^{-1} \) were used for calibration. The concentrations in the 5 bottled mineral water samples varied from less than 0.15 (LOD) to 3.96 \( \mu \text{g} \text{L}^{-1} \) for As and from less than 0.14 (LOD) to 0.61 \( \mu \text{g} \text{L}^{-1} \) for Sb. These results, which can be seen in Table 4, are below the WHO maximum recommended concentrations for As (10 \( \mu \text{g} \text{L}^{-1} \)) and Sb (20 \( \mu \text{g} \text{L}^{-1} \)) in drinking water. Güler and Alpaslan\(^27\) analyzed 70 brands of Turkish bottled water and found concentrations of As and Sb of 0.12 to 30.63 \( \mu \text{g} \text{L}^{-1} \) and 0.29 to 1.23 \( \mu \text{g} \text{L}^{-1} \), respectively. In another study, Frengstad et al.\(^28\) determined As and Sb in 32 samples of bottled mineral and spring waters from Norway, Sweden, Finland and Iceland. The levels found for As and Sb varied from 0.02 to 1.72 \( \mu \text{g} \text{L}^{-1} \) and from 0.008 to 0.739 \( \mu \text{g} \text{L}^{-1} \), respectively.

**Relevant benefits of multi-element sequential CF-HGAAS**

The analytical method proposed in this study has some relevant benefits in relation to the mono-element mode such as fast multi-element capability, high sensitivity and low sample consumption. The continuous flow approach, simple to handle in routine work, must be used to attain signal stabilization, allowing multi-element determinations. Unfortunately, there are some limitations related to the simultaneous generation of hydrides of possible analytes of interest (such as As, Bi, Ge, Pb, Sb, Se, Sn and Te) for quantitative multi-element determinations: the elements to be sequentially measured must be in the appropriate oxidation state after the pre-reduction step. However, this is hard to be achieved for all hydride-forming elements at the same time by using the same pre-reduction medium due to the intrinsic differences in the behavior of these elements. The influence of possible interferents must be carefully appraised for the simultaneous quantification of hydride-forming elements, particularly when dealing with more complex matrices. Therefore, once samples and standards are prepared using the same pre-reduction reagent and appropriate masking agents, only few elements with similar behaviors can be sequentially determined. Using the instrument set-up proposed in this work with a read delay of 20 s and a 3 s measurement time per element, an analysis of both

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**Fig. 4** Contour plots and equations for As (a) and Sb (b) experimental design and overlaid contours (c).
Table 2  Analytical figures of merit for As and Sb determinations by CF-HGAAS in multi-element mode

<table>
<thead>
<tr>
<th>Parameter</th>
<th>As</th>
<th>Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear fit</td>
<td>$y = 0.0164x + 0.0056$</td>
<td>$y = 0.0227x + 0.0058$</td>
</tr>
<tr>
<td>Linear correlation factor</td>
<td>0.993</td>
<td>0.96</td>
</tr>
<tr>
<td>Linear range/µg L$^{-1}$</td>
<td>0.375–15</td>
<td>0.375–15</td>
</tr>
<tr>
<td>*Limit of detection/µg L$^{-1}$</td>
<td>0.15</td>
<td>0.14</td>
</tr>
<tr>
<td>*Repeatability ([As and Sb] = 5 µg L$^{-1}$)</td>
<td>1.4%</td>
<td>1.3%</td>
</tr>
<tr>
<td>Maximum theoretical sample throughput (determinations per hour)</td>
<td>275</td>
<td></td>
</tr>
</tbody>
</table>

*a* LOD: limit of detection (3σblank/slope, n = 10). *b* R.S.D.(%): relative standard deviation, n = 10.

Table 3  Recoveries of As and Sb in the certified reference materials and its certified and found concentrations

<table>
<thead>
<tr>
<th>Certified reference material</th>
<th>Element</th>
<th>Certified (µg L$^{-1}$)</th>
<th><em>Found</em> (µg L$^{-1}$)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nist 1643e</td>
<td>As</td>
<td>60.45 ± 0.72</td>
<td>64 ± 2</td>
<td>106</td>
</tr>
<tr>
<td>TMDW-HPS</td>
<td>As</td>
<td>80</td>
<td>86 ± 4</td>
<td>108</td>
</tr>
<tr>
<td>Nist 1643e</td>
<td>Sb</td>
<td>58.30 ± 0.61</td>
<td>53.2 ± 0.8</td>
<td>91</td>
</tr>
<tr>
<td>TMDW-HPS</td>
<td>Sb</td>
<td>10</td>
<td>9.6 ± 0.2</td>
<td>96</td>
</tr>
</tbody>
</table>

$d$ mean ± standard deviation, n = 3.

Table 4  Concentrations of As and Sb found in 5 bottled mineral water samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>As (µg L$^{-1}$)</th>
<th>Sb (µg L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brand A</td>
<td>3.96 ± 0.02</td>
<td>0.61 ± 0.06</td>
</tr>
<tr>
<td>Brand B</td>
<td>&lt;0.15 (LOD)</td>
<td>0.48 ± 0.06</td>
</tr>
<tr>
<td>Brand C</td>
<td>&lt;0.15 (LOD)</td>
<td>&lt;0.14 (LOD)</td>
</tr>
<tr>
<td>Brand D</td>
<td>&lt;0.15 (LOD)</td>
<td>&lt;0.14 (LOD)</td>
</tr>
<tr>
<td>Brand E</td>
<td>&lt;0.15 (LOD)</td>
<td>0.39 ± 0.04</td>
</tr>
</tbody>
</table>

The analytes can be performed in less than half a minute and only 3 mL of sample are required.

Conclusion and perspectives

Fast sequential CF-HGAAS presents attractive features in relation to the traditional mono-element CF-HGAAS such as high analytical throughput and ease of handling. Variables which would affect the method performance were studied for the sequential determination of As and Sb. A read delay of only 20 s provides no memory effects and adequate sensitivity. This proposed method permits a substantial reduction in the analysis time in comparison to the mono-element mode. Another advantage is a reduction in the consumption of reagents and sample, and minimization of waste generation. Lastly, it is worth mentioning that this is the first work which proposes multi-element determinations using CF-HGAAS with a flame heated QTA.

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References

1 Agency for Toxic Substances and Disease Registry, Division of ToxicologyToxicology Information Branch, Public Health Service, U.S. Department of Health and Human Services, Toxicological profile for Arsenic, Atlanta, 2000.