Talanta 128 (2014) 466–472

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Determination of arsenic speciation in sulfidic waters by Ion Chromatography Hydride-Generation Atomic Fluorescence Spectrometry (IC-HG-AFS)

Nicole S. Keller [a,*], Andri Stefánsson [a], Bergur Sigfússon [b,1]

[a] Institute of Earth Sciences, University of Iceland, Sturlugata 7, 101 Reykjavik, Iceland
[b] Reykjavik Energy, Bæjarhals 1, 110 Reykjavik, Iceland

ARTICLE INFO

Article history:
Received 11 February 2014
Received in revised form
7 April 2014
Accepted 15 April 2014
Available online 30 April 2014

Keywords:
Arsenic speciation
Ion chromatography
Hydride Generation Atomic Fluorescence Spectrometry
Geothermal fluids
On-site chemical analysis

ABSTRACT

A method for the analysis of arsenic species in aqueous sulfide samples is presented. The method uses an ion chromatography system connected with a Hydride-Generation Atomic Fluorescence Spectrometer (IC-HG-AFS). With this method inorganic As^{III} and As^{V} species in water samples can be analyzed, including arsenite ($H_nAs^{III}O_3^{n-3}$), thioarsenite ($H_nAs^{III}S_3^{n-3}$), arsenate ($H_nAs^{V}O_4^{n-3}$), monothioarsenate ($H_nAs^{V}SO_3^{n-3}$), dithioarsenate ($H_nAs^{V}S_2O_2^{n-3}$), trithioarsenate ($H_nAs^{V}S_3O^{n-3}$) and tetrathioarsenate ($H_nAs^{V}S_4^{n-3}$). The peak identification and retention times were determined based on standard analysis of the various arsenic compounds. The analytical detection limit was ~1–3 μg L^{-1} (LOD), depending on the quality of the baseline. This low detection limit makes this method also applicable to discriminate between waters meeting the drinking water standard of max. 10 μg L^{-1} As, and waters that do not meet this standard. The new method was successfully applied for on-site determination of arsenic species in natural sulfidic waters, in which seven species were unambiguously identified.

1. Introduction

Arsenic occurs in the natural environment in variable forms including arsenate, arsenite, dimethyl- and trimethylarsine and other organoarsenic compounds, and complexed with inorganic ligands like chloride and sulfide. The chemical behavior of arsenic is largely determined by its aqueous speciation. Therefore, reliable analytical methods for arsenic species determination are required for assessing the behavior of arsenic in the environment.

Many different methods have been successfully used for arsenic speciation including spectrophotometry [1,2], hydride generation atomic spectroscopy [3–5], electrochemical techniques [6,7], capillary zone electrophoresis [8] and chromatographic techniques combined with mass spectrometry [9–11].

Many natural aqueous systems are reduced with dissolved sulfide dominating the sulfur speciation [12–14]. Recent studies have demonstrated that the speciation of arsenic in sulfidic waters may be dominated by thioarsenic compounds [15–18]. In absence or at very low concentrations of dissolved aqueous sulfide, arsenic forms predominantly oxyanions, arsenite and arsenate. However, in sulfidic waters the oxyanions are progressively replaced by thioanions with increasing dissolved sulfide concentration. Both oxidation states of arsenic can form thioanions and the replacement of oxygen by sulfur is progressive [2,15–17,19–22]. However, the quantitative analysis of thioarsenic compounds in water samples remains somewhat precarious, including peak identification when using ion chromatographic techniques and speciation preservation upon sample storage.

In an attempt to minimize post-sampling speciation changes, we developed and tested a mobile analytical method enabling on-site arsenic species determination in sulfidic waters. The analytical setup consisted of an ion chromatography system coupled to Hydride-Generation Atomic Fluorescence Spectroscopy (IC-HG-AFS). The various arsenic species were identified using standard solutions, and the analytical method was tested on natural sulfidic water.

2. Experimental setup

2.1. Reagents

Standard solutions were made from arsenic(III) oxide (Sigma-Aldrich), sulfur (puriss, Sigma-Aldrich), NaOH (puriss, Sigma-Aldrich), absolute ethanol (Sigma-Aldrich), commercial arsenate

* Corresponding author. Tel.: +354 525 4332.
E-mail address: nic@hi.is (N.S. Keller).
[1] Current address: European Commission, Joint Research Centre, Institute for Energy and Transport, PO Box 2, 1755 ZG Petten, The Netherlands.

http://dx.doi.org/10.1016/j.talanta.2014.04.035
0039-9140/

standard solution of 1000 mg L^{-1} (SPEX CertiPrep), sodium metaarsenite (Aldrich) and sodium arsenate dibasic heptahydrate (Aldrich).

The reagents for the hydride formation in the HG-AFS were 37% HCl (proanal. Merck), sodium tetraborate ($NaBH_4$) (Fluka), and 8 M NaOH solution (Fluka). For the sodium tetraborate solution, a solution of 0.1 M NaOH was prepared by dilution of 8 M NaOH solution with deionized water followed by addition of approx. 8 g of sodium tetraborate to make 0.2 M $NaBH_4$ solution. This solution is unstable, therefore fresh solution was prepared every 4 h. 12.5% HCl was made from 37% HCl by dilution with deionized water. The carrier and drier gas used was Ar grade 5.0 and industrial grade, respectively. All reagent concentrations are listed in Table 2.

2.2. Standard preparation

Standard solutions were prepared under oxygen-free N_2 atmosphere using freshly boiled and degassed deionized water (Milli-Q > 18 MΩ) according to previously published procedures with some modification [8,23]. All work standard solutions were made within the range of 1–1000 μg L^{-1} by dilution with deionized water. The solutions were always degassed except in the case of the arsenate standard solutions. A summary of the standard preparation is given in Table 1.

Arsenite ($H_nAs^{III}O_3^{n-3}$) and thioarsenite ($H_nAs^{III}O_3^{n-3}$) solutions were prepared by dissolving $NaAsO_2$(s) in degassed water. For the thioarsenite standard, the H_2S was added to the arsenite solution by dissolving Na_2S(s) into it. The molal ratio of S to As was made > 100. Fresh solutions were extracted into a syringe and analyzed immediately. The procedure for the thioarsenite standard solutions resulted in the formation of various additional sulfur-bearing arsenic species at low concentrations.

Arsenate ($H_nAs^{III}O_4^{n-3}$) standard solutions were prepared by dilution of a commercial As standard solution (SPEX CertiPrep).

Monothioarsenate ($H_nAs^{V}SO_3^{n-3}$) – to a mixture of 5.00 g of As_2O_3 and 6.00 g of NaOH in 20 mL water, 1.44 g of elemental sulphur was added and the solution was heated to 100 °C for 2 h. Subsequently, the excess sulphur was filtered off and the solution cooled. The crystals formed were re-dissolved in water and the solids re-precipitated by addition of ethanol to the solution. The crystals obtained were filtered off and dried to obtain $Na_2AsO_3S \cdot 7H_2O$. To prepare the aqueous monothioarsenate standard solution, the $Na_2AsO_3S \cdot 7H_2O$ solid was dissolved in degassed water under N_2-atmopshere. The solution was then extracted with a syringe and analysed immediately.

Dithioarsenate ($H_nAs^{V}S_2O_2^{n-3}$) – to a mixture of 5.00 g of As_2O_3 and 6.00 g of NaOH in 20 mL water, 5.76 g of elemental sulfur were added and the solution heated to 100 °C for 4 h. Subsequently, the excess sulfur was filtered off and the solution cooled. The crystals obtained were dried under vacuum to obtain $Na_2AsO_2S_2 \cdot 7H_2O$. To analyze the aqueous dithioarsenate standard solution, the $Na_2AsO_2S_2 \cdot 7H_2O$ solid was dissolved in degassed water under N_2-atmosphere, the solution extracted with a syringe and analysed immediately. This standard solution was also found to contain other arsenate species including arsenate, mono-, tri- and tetrathioarsenate. This is not surprising as the molal ratio of S to As was almost 4, i.e. the synthesis was done in large excess of S over As relative to the ratio in dithioarsenate sodium salt.

Tetrathioarsenate ($H_nAs^{V}S_4^{n-3}$) – 8.38 g of $Na_2HAsO_4 \cdot 7H_2O$ were dissolved in 100 mL degassed water under N_2-atmopshere and H_2S gas bubbled through the solution for ~30 min. The H_2S gas was produced in-line by stepwise addition of 1 M HCl to Na_2S solids under N_2-atmopshere, transported with the N_2-gas through scrubbers and finally into the $Na_2HAsO_4 \cdot 7H_2O$ solution. The precipitate formed was As_2S_5, which was filtered off and dried. 3.48 g of As_2S_5 were added to a mixture of 2.68 g Na_2S and 1.35 g NaOH in 100 mL degassed water. The solids were precipitated by addition of ethanol, filtered and dried, redissolved in 0.2 M NaOH, reprecipitated by addition of ethanol, filtered and dried. The material obtained was $Na_2AsS_4 \cdot 8H_2O$. To prepare the aqueous tetrathioarsenate standard solution, the $Na_2AsS_4 \cdot 8H_2O$ solid was dissolved in degassed 0.1 M NaOH under N_2-atmopshere, an aliquot of solution was extracted with a syringe and analysed immediately. The standard solution produced contained both trithioarsenate and tetrathioarsenate compounds, in accordance with previous findings [23].

2.3. Sampling of natural sulfidic water

Samples of natural sulfidic geothermal water including surface hot-springs and two-phase well discharges were collected and analyzed on-site within ~5 min of sampling. All samples were filtered through 0.2 μm filter (cellulose acetate) into pre-cleaned

Table 1
Standard material synthesis and preparation.

Material	Reagents	Procedure	Source
As(III)			
$H_nAsO_3^{n-3}$(aq) (arsenite)	35 mg $NaAsO_2$, 200 mL H_2O	$NaAsO_2$ dissolved in degassed H_2O under N_2 followed by dilution with H_2O to make < 1 mg L^{-1} As	This study
$H_nAsS_3^{n-3}$(aq) (trithioarsenite)	35 mg $NaAsO_2$, 200 mL H_2O 10 mg Na_2S, 200 mL H_2O	Na_2S dissolved in degassed H_2O under N_2 followed by addition to arsenite standard solution to make < 1 mg L^{-1} As	This study
As(IV)			
$H_nAs^{V}O_4^{n-3}$(aq) (arsenate)	1000 mg L^{-1} As^{V} standard	Commercial standard diluted in H_2O to give 1 μg L^{-1} to 1 mg L^{-1}	SPEX CertiPrep
$Na_3AsO_3S \cdot 7H_2O$ (monothioarsenate)	1.44-g S, 5.00 g As_2O_3, 6.00-g NaOH, 20 mL H_2O	Mixed and heated for 2 h at 100 °C, cooled at 4 °C. Filtered and dried under vacuum Redissolved in H_2O, recrystallised in ethanol. Filtered and dried under vacuum Dissolved and diluted in degassed H_2O to make < 1 mg L^{-1}.	[8]
$Na_3AsO_2S_2 \cdot 7H_2O$ (dithioarsenate)	5.76-g S, 5.00-g As_2O_3, 6.00-g NaOH, 20 mL H_2O	Mixed and heated for 4 h at 100 °C, filtered and cooled to 4 °C. Dried under vacuum. Dissolved and diluted in degassed H_2O to make < 1 mg L^{-1}.	[8], This study
$Na_3AsS_4 \cdot 8H_2O$ (tetrathioarsenate)	(1) 8.34-g $Na_2HAsO_4 \cdot 7H_2O$, 100 mL H_2O, H_2S(g)	Reagents mixed together followed by 30-min bubbling of H_2S(g). Settle for 1 h, filter and dry under vacuum.	[24]
	(2) 3.48-g As_2S_5, 2.68-g Na_2S, 1.35-g NaOH, 100 mL H_2O, ethanol (3)0.2 M NaOH, ethanol	Reagents mixed, precipitate filtered off and mixed with ethanol to crystallise. Crystals redissolved in NaOH solution and colloidal material filtered off. Filtrate titrated with ethanol. Dried under vacuum. Dissolved and diluted in degassed 0.1 M NaOH to make < 1 mg L^{-1} As.	

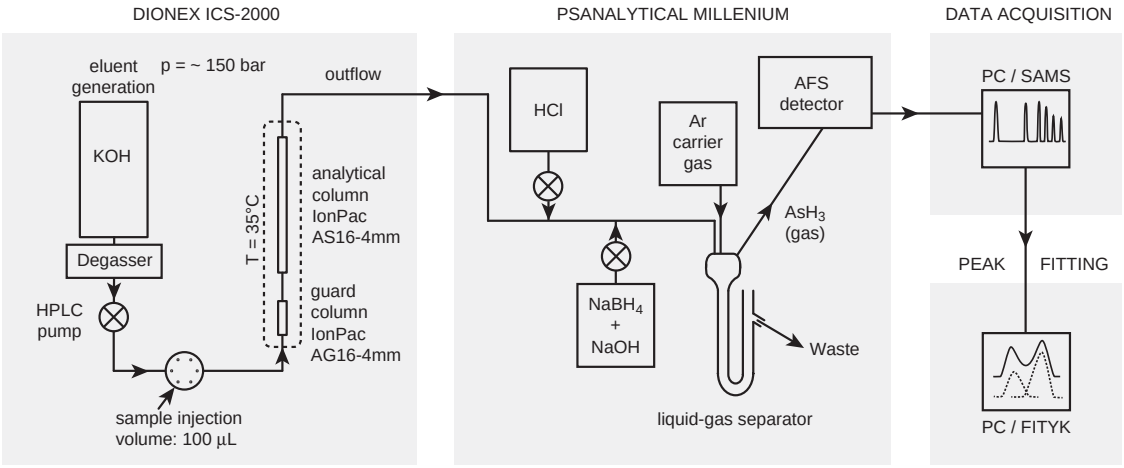

Fig. 1. Schematic drawing of the IC-HG-AFS set up.

Table 2
Instrumental setup and analytical procedure.

IC separation		
Instrument:	Dionex ICS-2000	
Software	Chromeleon v.6.8 (Dionex)	
Guard column	IonPac AG16 4 × 50 mm, Dionex/Thermo Scientific	
Analytical column:	IonPac AS16 4 × 250 mm, Dionex/Thermo Scientific	
Eluent:	1 mL min^{-1} KOH, automated eluent generation	
Eluent concentrations:	0–7 min	20 mM
	7–17 min	20 mM → 100 mM
	17–25 min	100 mM
	25–28 min	100 → 20 mM
Sample loop volume:	100 µL	
Column temperature:	35 °C	
No chemical suppression		
Hydride-generation atomic fluorescence spectroscopy (HG-AFS) detection		
Instrument:	PSAnalytical Millenium Excalibur	
Software	SAMS v.2.0 (PSAnalytical)	
Reductant:	12.5% HCl, red–red tubing, pump 50%	
	0.8% $NaBH_4$ in 0.1 M NaOH, grey–grey tubing, pump 100%	
Carrier gas:	Ar (5.0 grade), flow rate 300 mL min^{-1}	
Dryer gas:	Ar (industrial grade), flow rate 2.5 L min^{-1}	
Lamp:	Boosted discharge hollow cathode lamp (BDHCL)	
Primary current:	27.5 mA	
Boost current:	35.0 mA	

bottles or syringes. Sulfide concentration and pH were further analyzed on site [13,24]. General sampling and major element analysis was done using standard methods described elsewhere [24].

2.4. Instrumental setup

A schematic plan of the analytical setup is shown in Fig. 1, and Table 2 presents a list of all technical information pertaining to the method. It consist of an Ion Chromatograph system (IC) (Dionex-ICS2000) used to separate the various aqueous As species, with the outflow of the IC connected to an Arsenic-specific Hydride Generation Atomic Fluorescence Spectrometer (HG-AFS, PS Analytical Millennium Excalibur) operating in continuous mode. The IC-HG-AFS instruments and data acquisition were conducted using Chromeleon version 6.8 (Dionex) and Sams version 2.0 (PS Analytical).

The IC system used for the separation of the arsenic species was set up with an IonPac® AG16 guard column and an AS16 analytical column, and the mobile phase was a KOH eluent that was degassed by vacuum degasser and produced electrochemically, both in-line. The sample loop had a volume of 100 µL.

In the HG-AFS system, the sample is first acidified in-line with 12.5% HCl (~8.3% HCl after acidification), then mixed with alkaline 0.2 M $NaBH_4$ solution (~0.11 M $NaBH_4$ after mixing)to produce arsine gas (AsH_3). This reaction also produces excess H_2, which is then taken up by the Ar carrier gas together with the AsH_3, The excess H_2 is used to produce a hydrogen flame in which the arsine is atomized. The arsenic concentration in the flame can then be analyzed, using a boosted discharge hollow cathode lamp (BDHCL) E033L001 (Photron), at 193.7 nm, at a 90° angle as an excitation source for the atomic fluorescence,

As a result of the IC separation, the various species have different yet species-specific travel times through the whole setup, and a time-resolved acquisition of the AFS signal results in a chromatogram with discrete peaks coming out at different times corresponding to the various arsenic species present in the sample.

2.5. Data treatment

The analytical chromatograms were treated with the aid of the Fityk program [25]. In most cases, HG-AFS arsenic peaks were found to follow a log-normal distribution. Single peaks with a large signal-to-noise ratio were found to be easily fitted with a log-normal distribution function with consistent peak shape parameters (peak asymmetry and full width at half maximum). The uncertainties in the relative amount of such peaks were $< 5\%$. Split peaks, on the other hand, were more difficult to fit. This leads to a larger uncertainty in the relative amounts of such peaks, with an estimated error on the smaller of the double peak that could amount to up to 20%.

Due to the fact that the IC run and the AFS data acquisition had to be started one after the other manually, small differences in retention times were observed on the AFS chromatograms. All arrival times reported in this study were therefore normalized using the average retention time of arsenite as a reference, as this species was present in most samples analyzed. This allows for direct comparison of peak retention times between various samples.

3. Results and discussion

3.1. Peak identification

The analyses of all standard solutions described above allowed the identification of seven peaks, considered to be arsenite ($H_nAs^{III}O_3^{n-3}$), thioarsenite ($H_nAs^{III}S_3^{n-3}$), arsenate ($H_nAs^{V}O_4^{n-3}$),

monothioarsenate ($H_nAs^VSO_3^{n-3}$), dithioarsenate ($H_nAs^VS_2O_2^{n-3}$), trithioarsenate ($H_nAs^VS_3O^{n-3}$) and tetrathioarsenate ($H_nAs^VS_4^{n-3}$). The retention times are listed in Table 3. The peak identification was made from multiple runs of various standard solutions that had slight variation of timing of the signal collection due to the manual start of the Sams data acquisition program. Therefore, all chromatograms were normalized to the peak position of arsenite that was assigned to time zero. Representative chromatograms for various standard solutions are shown in Fig. 2.

The arsenite standard solution was prepared from $NaAsO_2$(s) in degassed water under N_2-atmosphere. Immediate analysis of this solution resulted in one peak on the IC-HG-AFS system (Fig. 2A, peak #1). This peak was assigned to aqueous arsenite, $H_nAs^{III}O_3^{n-3}$. Upon addition of dissolved H_2S to the arsenite solution, the OH^- groups on the arsenite are replaced by HS^- to form thioarsenite ($H_nAs^{III}S_nO_{3-n}^{n-3}$). The standard solution was prepared by addition of Na_2S(s) to the previous standard solution. This resulted in a shift of the arsenite peak by 0.6 min, considered to be thioarsenite, $H_nAs^{III}S_nO_{3-n}^{n-3}$ (Fig. 2A, peak #2). This conclusion is in line with thermodynamic aqueous speciation of As^{III} in sulfidic water [2]. Previously, similar results have been reported on aqueous As speciation in sulfidic water based on IC-ICP-MS analysis [16–17,21]. Planer-Friedrich et al. [21] noted similar peak splitting in sulfide-rich As^{III} solutions as observed in this study. However, in Planer-Friedrich et al.'s study, the split peak was not associated with sulfur and based on that the authors concluded that thioarsenite could not be analyzed using ion chromatography. Our approach, however, seems to indicate that it is indeed possible to identify thioarsenite, based on standard preparation and consideration of exchange rates. Within the IC column the sulfide on the thioarsenite is exchanged for hydroxide. The exchange rate for OH^- in $H_2As^{III}O_3^-$ occur within milliseconds [26] whereas the OH^- exchange rate on $As^VO_4^{3-}$ are slow with half time of exchange of ~5 days [27]. Assuming the exchange rates for SH^- to be of similar magnitude as for OH^-, the HS^- will be exchanged for OH^- in the case of thioarsenite to form arsenite in the alkaline KOH eluent whereas such exchange is unlikely in the case of thioarsenate. In the IC system, the sample is transported initially as a discrete unit within the eluent without reacting with it until it hits the ion-exchange column. For species with fast ligand to eluent (OH^-) exchange rate like arsenite and thioarsenite, HS-ligands may be quickly replaced by OH-ligands of the eluent when the ions hit the ion exchange column, thus thioarsenite converts to arsenite. Assuming arsenite to be present to start with, such ligand exchange may result in a peak shift that may look like a doublet when both forms are present, one peak representing the true original aqueous arsenite and the other the converted aqueous thioarsenite species. As a result of this conversion, sulfur cannot be detected in association with the thioarsenite peak in studies such as that of Planer-Friedrich et al. [21] since the sulfide ligand has been exchanged and eluted as HS^- or S^{2-} depending on eluent pH. On the other hand, the exchange of the sulfide ligand in thioarsenate species with the OH^- of the eluent occurs much slower than the analytical time (which is typically <20 min),

Table 3
Analytical retention times normalized to the average retention time of arsenite.

Peak #	Species	Formula[a]	Time (min)	Comment
1	Arsenite	$H_nAs^{III}O_3^{n-3}$	0.00	Singlet (split peak if thioarsenite present)
2	Thioarsenite	$H_nAs^{III}S_3^{n-3}$	0.61	Split peak
3	Arsenate	$H_nAs^VO_4^{n-3}$	9.50 ± 0.02	Singlet
4	Monothioarsenate	$H_nAs^VSO_3^{n-3}$	10.87 ± 0.03	Singlet
5	Dithioarsenate	$H_nAs^VS_2O_2^{n-3}$	12.46 ± 0.06	Singlet
6	Trithioarsenate	$H_nAs^VS_3O^{n-3}$	14.01 ± 0.06	Singlet
7	Tetrathioarsenate	$H_nAs^VS_4^{n-3}$	15.38 ± 0.08	Singlet

[a] The listed species have different protonation values, with $n=0$–3 depending on pH.

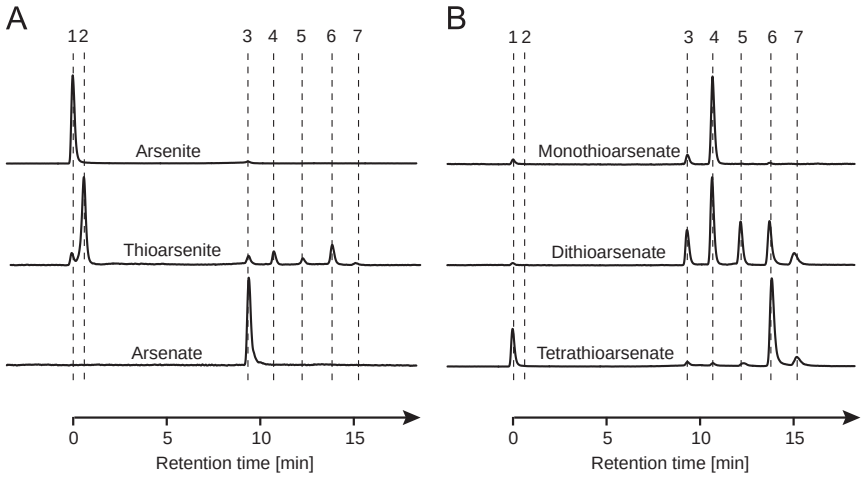

Fig. 2. Representative chromatograms for various standard solutions. (A) arsenite, thioarsenite and arsenate standard solutions; (B) mono-, di- and tetrathioarsenate. The label for each chromatogram represents the compound that was attempted to synthetize according to the described methods. As discussed in the text, di- and tetrathioarsenate represent a mixture of various (thio)arsenic compounds, reflecting the fact that the yield for those reactions is far less than 100%. Dashed lines are visual aids reflecting the peak positions. Peak #1=arsenite, peak #2=trithioarsenite, peak #3=arsenate, peak #4=monothioarsenate, peak #5=dithioarsenate, peak #6=trithioarsenate, peak #7=tetrathioarsenate (see also Table 3). The retention time scale starts at 0 min=appearance of arsenite.

hence the true aqueous thioarsenate species are analysed as the respective moieties.

Arsenate standard solution was prepared from commercial As standard (SPEX CertiPrep) by dilution with DI H_2O. The peak identified had a retention time of 9.5 min and was assigned to aqueous arsenate ($H_nAs^VO_4^{n-3}$, Fig. 2A, peak #3). Mono-, di-, tri- and tetrathioarsenate standard solutions were prepared from the respective salts as possible. With the exception of monothioarsenate, the synthesis always resulted in mixtures of compounds (Fig. 2B). However, based on systematic evaluation, four peaks were observed from the various standard solutions, and were assigned to aqueous monothioarsenate ($H_nAs^VSO_3^{n-3}$, peak #4), dithioarsenate ($H_nAs^VS_2O_2^{n-3}$, peak #5), trithioarsenate ($H_nAs^VS_3O^{n-3}$, peak #6) and tetrathioarsenate ($H_nAs^VS_4^{n-3}$, peak #6).

3.2. Calibration and detection

The calibration of all As peaks was based on aqueous arsenate calibration using a commercial arsenate standard stock solution of 1000 mg L^{-1} (SPEX CertiPrep). The various working standards were made by sequential dilution with deionized H_2O by weight. The calibration curve was produced by plotting peak area as a function of standard concentration, and a linear regression curve was calculated. This equation was then used to quantify all arsenic species based on their peak area. A representative calibration curve is shown in Fig. 3. Based on blank, standard and sample analysis, the lower limit of detection was taken to be ~1–3 μg L^{-1}. The exact detection limit was found to depend on the quality of the baseline, which in turn is dependent on the quality of reagents and the Ar-gas as well as the stability of the flame. The flame stability appears to be affected directly by the ventilation and external constraints such as wind and air temperature when the setup is used in the field. Therefore detection limits are typically lower in laboratory settings (around 1 μg L^{-1}), whereas in the field the detection limits can be somewhat higher (2–3 μg L^{-1}) since the instruments are exposed to some extent to the weather conditions. It is worth noting that even in the field, the detection limit is below the drinking water standard of 10 μg L^{-1}, thus making this method applicable to waters relevant to human health.

The choice of a single species standard solution was based on two factors. Firstly, the preparation of most standard solutions involving As^{III} and As^V in sulfidic waters resulted in formation of more than one compound, making quantitative calibration difficult. Secondly, the calibration curve is the same for the various aqueous As species as the species are first separated by IC followed by hydride generation to form arsine, i.e. all peaks represent the concentration of arsine in the flame of the AFS. The choice of calibration solution was therefore made based on the accuracy, stability and ease of handling of the standard solution, found to be best for arsenate. Previous work by Sigfússon et al. [18] showed that there is a good agreement between total As measurment (where all species are converted to As^{5+} prior to analysis) and the sum of all As species, therefore it is assumed that the conversion of all species to arsine is quantitative.

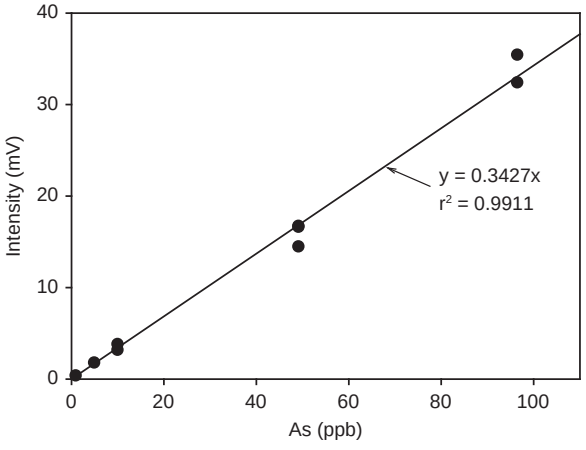

Fig. 3. Calibration curve determined using a commercially available arsenate stock standard.

3.3. Sample stability

The strength of the proposed method resides in its mobility, which is a key for successful analysis of As speciation in natural waters. Previously proposed methods involve instrumentation like IC-ICP-MS or synchrotron that cannot be transported to the field site. However, sulfidic waters containing As are unstable upon storage, i.e. the aqueous speciation cannot be preserved readily from the field to the laboratory for later analysis. To illustrate this problem, Fig. 4 shows the analyzed aqueous speciation of As in natural sulfidic waters as a function of time from sampling. As observed, the distribution of various aqueous species changes

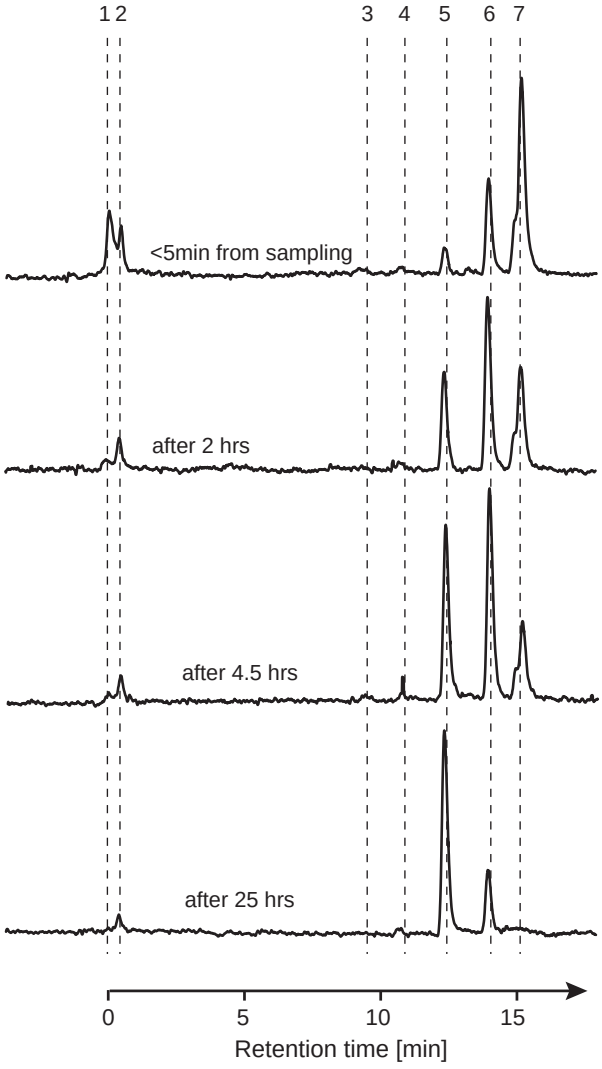

Fig. 4. Example of speciation change with time of sample storage in natural sulfidic waters. This sample was taken from the liquid fraction of a two-phase well in Hellisheidi, with a S^{2-} concentration of 57.3 mg L^{-1}, analysed immediately upon sampling, then stored in a plastic bottle and reanalyzed after 2, 4.5 and 25 h. Peak position lines are as listed in the caption of Fig. 2.

markedly with time, with significant speciation changes in as little as 2 h from sampling. Acidification will not help, nor will making the solution alkaline as this will result in H_2S degassing and possible reactions among the various As species [23], respectively. Tests were also done on the effectiveness of flash-freezing samples into dry ice (Fig. 5). The comparison between on-site analysis and post-flash-freezing showed significant changes in the relative abundances of species present. In the example shown in Fig. 5, the dominant species in the flash-frozen sample was tetrathioarsenate, with dithioarsenate the least abundant species. In the non-flash-frozen sample, dithioarsenate was the most abundant species, whereas tetrathioarsenate accounts for only ca. 30% of the total As. Furthermore, the total As was 10% lower in the flash-frozen sample than in the non-flash-frozen sample. Thus it appears that the only reliable way to determine arsenic speciation in sulfidic waters is to analyse the samples on site.

3.4. As speciation in natural waters

The proposed analytical method was field-tested and used for on-site analysis of aqueous As speciation in natural geothermal waters. Examples of three contrasting sites are shown in Fig. 6.

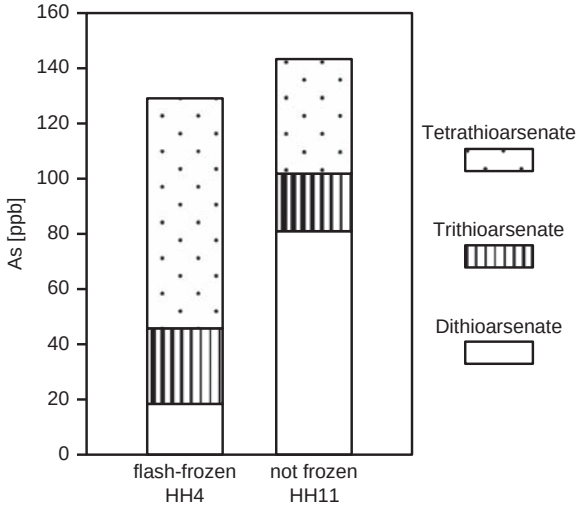

Fig. 5. Species distribution for two samples taken at the same site (at the Hellisheidi power plant). One sample was flash-frozen by immersion of the sample tube into dry ice immediately upon sampling, whereas the other sample was analysed without freezing it beforehand.

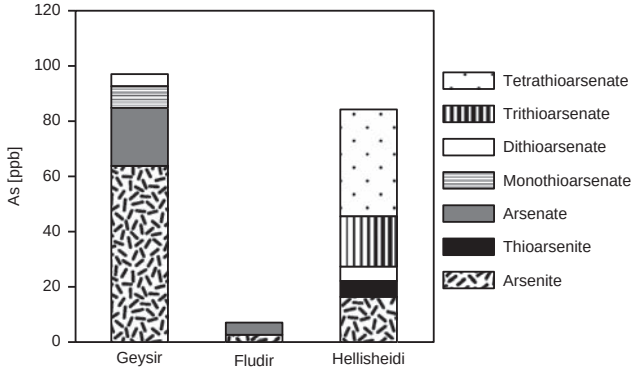

Fig. 6. Species distribution for three examples of geothermal samples with various sulfide contents. The sample collected at Geysir was taken in the Geysir Hot Spring, the sample from Fludir was collected 13 m below the outflow of a single-phase well, and the Hellisheidi sample was taken from the liquid fraction of a two-phase high-temperature well.

At Geysir, where the reduced sulfidic geothermal waters rise from depth and interact with oxygenated shallow ground water, the predominant species are arsenite, arsenate and lesser amounts of mono-and dithioarsenate. In Fludir, where there is very little sulfide present in the aquifer, no thioarsenic species are present, and the arsenate is reflecting rapid oxidation of arsenite upon exposure to atmospheric O_2. At Hellisheidi, where the sample represents the fluid at depth with high sulfide content, the speciation is dominated by tri- and tetrathioarsenate, with arsenite also important.

4. Conclusions

A method for analysis of arsenic species in aqueous sulfide samples was developed using ion chromatography system connected with a Hydride Generation Atomic Fluorescence Spectrometer (IC-HG-AFS). Using this method, seven aqueous species can be analyzed within 30 min including arsenite ($H_nAs^{III}O_3^{n-3}$), thioarsenite ($H_nAs^{III}S_3^{n-3}$), arsenate ($H_nAs^{V}O_4^{n-3}$), monothioarsenate ($H_nAs^{V}SO_3^{n-3}$), dithioarsenate ($H_nAs^{V}S_2O_2^{n-3}$), trithioarsenate ($H_nAs^{V}S_3O^{n-3}$) and tetrathioarsenate ($H_nAs^{V}S_4^{n-3}$). The analytical detection limits was $\sim$1–3 μg L^{-1} (LOD) and largely dependent on the quality of the baseline. The strength of the proposed method is based on instrumental mobility for analysis of natural waters. Previously proposed methods involve instrumentation like IC-ICP-MS that cannot be transported to the location of the water to be studied. However, samples containing reduced sulfur and arsenic are unstable upon storage and aqueous speciation may not be preserved readily from the field to the laboratory for later analysis.

Acknowledgements

The present study was supported by the Icelandic Research Fund (Rannis Grant no. 90229021). We are thankful to J. Gunnarsson Robin, Á. Sigurdardottir and I.M. Galeczka for their help with the field work. We also wish to thank an anonymous reviewer whose comments helped clarifying the text, and Dr. J.-M. Kauffmann for editorial handling.

References

[1] T. Rupasinghe, T.J. Cardwell, R.W. Cattrall, M.D.L. de Castro, S.D. Kolev, Anal. Chim. Acta 445 (2001) 229–238.
[2] V.P. Zakaznova-Herzog, T.M. Seward, Geochim. Cosmochim. Acta 83 (2012) 48–60.
[3] B.A. Manning, D.A Martens, Env. Sci. Technol. 31 (1997) 171–177.
[4] C.I.S. Narcise, L.D. Coo, F.R. del Mundo, Talanta 68 (2005) 298–304.
[5] M.A. Wahed, D. Chowdhury, B. Nermell, S.I. Khan, M. Ilias, M. Rahman, L. A. Persson, M. Vahter, J. Health Popul. Nutr. 24 (2006) 36–41.
[6] S.B. Rasul, A.K.M. Munir, Z.A. Hossain, A.H. Khan, M. Alauddin, A. Hussam, Talanta 58 (2002) 33–43.
[7] T.W.T. Rupasinghe, W.T. Thusitha, T.J. Cardwell, R.W. Cattrall, S.D. Kolev, Anal. Chim. Acta 652 (2009) 266–271.
[8] G. Schwedt, M. Rieckhoff, J. Chromatogr. A 736 (1996) 341–350.
[9] D.T. Heitkemper, N.P. Vela, K.R. Stewart, C.S. Westphal, J. Anal. Spectrom. 16 (2001) 299–306.
[10] E. Vassileva, A. Becker, J.A.C. Broekaert, Anal. Chim. Acta 441 (2001) 135–146.
[11] I. Komorowicz, D. Baralkiewicz, Talanta 84 (2011) 247–261.
[12] A. Stefánsson, S. Arnórsson, Á.E. Sveinbjornsdóttir, Chem. Geol. 221 (2005) 289–311.
[13] H. Kaasalainen, A. Stefánsson, Talanta 85 (2011) 1897–1903.
[14] H. Kaasalainen, A. Stefánsson, Geochim. Cosmochim. Acta 75 (2011) 2777–2791.
[15] S. Stauder, B. Raue, F. Sacher, Environ. Sci. Technol. 39 (2005) 5933–5939.
[16] B. Planer-Friedrich, J. London, R.B. McCleskey, D.K. Nordstrom, D. Wallschlager, Env. Sci. Technol. 41 (2007) 5245–5251.
[17] D. Wallschläger, C.J. Stadey, Anal. Chem. 79 (2007) 3873–3880.
[18] B. Sigfússon, S.R. Gislason, A.A. Meharg, Appl. Geochem. 26 (2011) 553–564.
[19] R.T. Wilkin, D. Wallschlager, R.G. Ford, Geochem. Trans. 4 (2003) 1–7.
[20] B.C. Bostick, S. Fendorf, G.E. Brown, Mineral. Mag. 69 (2005) 781–795.

[21] B. Planer-Friedrich, E. Süss, A.C. Scheinost, D. Wallschläger, Anal. Chem. 82 (2010) 10228–10235.
[22] G.R. Helz, J.A. Tossell, Geochim. Cosmochim. Acta 72 (2008) 4457–4468.
[23] E. Suess, A.C. Svheinost, B.C. Bostick, B.J. Merkel, D. Wallschläger, B. Planer-Friedrich, Anal. Chem. 81 (2009) 8318–8326.
[24] S. Arnórsson, J.O. Bjarnason, N. Giroud, I. Gunnarsson, A. Stefánsson, Geofluids 6 (2006) 203–216.
[25] M. Wojdyr, J. Appl. Cryst. 43 (2010) 1126–1128.
[26] W.C. Copenhafer, P.H. Riege, J. Am. Chem. Soc. 100 (1978) (3776-2780).
[27] A. Okumura, Y. Matsumiya, K. Yamamoto, R. Ueno, M. Suzuki, S. Yamabe, Bull. Chem. Soc. Jpn. 68 (1995) 1839–1849.