Automatic determination of arsenate in drinking water by flow analysis with dual membrane-based separation

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Abstract

The sequential application of a polymer inclusion membrane (PIM), composed of poly(vinylidenefluoride-co-hexafluoropropylene) and the anionic extractant Aliquat 336, and a microporous polytetrafluoroethylene (PTFE) gas-permeable membrane was utilized for the first time to develop a flow analysis (FA) system, for the automatic determination of trace levels of arsenate (As(V)) in drinking water as arsine. The system incorporated a flow-through extraction cell for separation and preconcentration of arsenate and a gas-diffusion cell for the separation of arsine prior to its spectrophotometric determination based on the discoloration of a potassium permanganate solution. Under optimal conditions the FA system is characterized by a limit of detection of 3.0 μg L^{-1} As(V) and repeatability of 1.8% (n=5, 25 μg L^{-1} As(V)) and 2.8% (n=5, 50 μg L^{-1} As(V)). The newly developed FA method was successfully applied to the determination of arsenate in drinking water samples in the μg L^{-1} concentration range.

Keywords: drinking water; arsenate; flow analysis; polymer inclusion membrane (PIM); gas-diffusion separation; hydride generation.

1. Introduction

Arsenic is a naturally occurring toxic element, which is present in natural waters around the world (Villaescusa & Bollinger, 2008). Inorganic arsenic species, such as arsenate (As(V)) and arsenite (As(III)), are the most common and toxic forms of arsenic found in aquatic systems (Vera, Fontas, & Antico, 2017). Arsenic is considered a leading pollutant since it is often found at elevated levels in natural waters and long-term exposure to its forms have been associated with skin, lung, urinary tract, kidney, and liver cancer (Bissen & Frimmel, 2003). Therefore, the World Health Organization (WHO) has set the guideline concentration for arsenic in drinking water at 10 μg L^{-1} (WHO, 2011). It should be pointed out that arsenic in drinking water is present very often almost entirely as arsenate (As(V)) (Döker & Yılmaz, 2018; Komorowicz & Barałkiewicz, 2016). The low regulated level of arsenic and its complex chemistry represent a challenge from an analytical point of view. Hence, a great number of highly sensitive analytical techniques have been developed and employed for the determination of arsenic in environmental samples, namely graphite furnace atomic absorption spectrometry (GFAAS) (Alves, Neri, Borges, Carvalho, & Coelho, 2017), hydride generation atomic absorption spectrometry (HG-AAS) (Susko, Bloom, Neamtiu, Appleton, Surdu, Pop, et al., 2017), hydride generation atomic fluorescence spectrometry (HG-AFS) (Chen, Lai, Mao, Chen, & Chen, 2017), inductively coupled plasma atomic emission spectrometry (ICP-AES) (Güell, Anticó, Kolev, Benavente, Salvadó, & Fontàs, 2011), and inductively coupled plasma mass spectrometry (ICP-MS) (Fontàs, Vera, Batalla, Kolev, & Anticó, 2013; Vera, Fontas, & Antico, 2017). These techniques provide the sensitivity required to directly measure arsenic concentrations in water samples at the μg L^{-1} level. However, the techniques mentioned above require expensive equipment and highly trained laboratory technicians.

Flow injection analysis (FIA) is a technique suitable for performing analysis on-line in an automatic fashion and it is highly efficient in minimizing both reagent and sample consumption

as well as the overall analysis time and associated costs (Cerda & Estela, 2008; Valcarcel & Luque de Castro, 1987). Different detection techniques have been successfully applied in FIA systems for the determination and speciation of arsenic (e.g., voltammetry (Fogg & Bsebsu, 1981), amperometry (Farrell, Iles, & Yuan, 1996; Rupasinghe, Cardwell, Cattrall, & Kolev, 2009), chemiluminescence (Lomonte, Currell, Morrison, McKelvie, & Kolev, 2007), or spectrophotometry (Boonjob, Miró, & Kolev, 2013; Rupasinghe, Cardwell, Cattrall, Luque de Castro, & Kolev, 2001; Rupasinghe, Cardwell, Cattrall, Potter, & Kolev, 2004). A great number of spectrophotometric methods for arsenic are based on the method proposed by Johnson and Pilson (Johnson & Pilson, 1972), in which an arsenomolybdenum blue complex is formed. However, this method is affected by severe interferences from silicate or phosphate, often present in arsenic samples, which impose serious limitations on the applicability of this method. To avoid the interference of phosphate and silicate, some authors have used anion-exchange columns to retain the interfering anions (Frenzel, Titzenthaler, & Elbel, 1994; Narusawa, 1988) or optimized the molybdenum blue method to improve its selectivity for arsenate over phosphate, as reported by Dhar et al. (Dhar, Zheng, Rubenstone, & Van Geen, 2004). Rupasinghe et al. (Rupasinghe, Cardwell, Cattrall, Potter, & Kolev, 2004) and Toda et al. (Toda & Ohba, 2005) have reported on the development of FIA systems based on hydride generation where arsenic is converted into arsine followed by bleaching an oxidant acceptor solution containing $KMnO_4$. The concentration of arsenic in many water samples is at trace level and preconcentration is often required.

Membrane-based extraction procedures involving liquid membranes have emerged as promising alternatives to ion-exchange based separation and preconcentration where retention and stripping of the analyte take place sequentially. In liquid membrane-based separation the extraction and back-extraction of the analyte from a donor aqueous stream into an acceptor aqueous stream occur simultaneously. Supported liquid membranes (SLMs), which are

86 considered as the most frequently used type of liquid membranes at present, have been used
87 successfully in the determination of arsenate in drinking water (Kamyabi & Aghaei, 2016).
88 However, in this type of membranes the membrane liquid phase, consisting of an extractant and
89 diluent, is retained in the micrometre size pores of a hydrophobic polymeric membrane and this
90 leads to leaching of the membrane liquid phase into the donor and acceptor aqueous phases,
91 thus causing potential deterioration in the performance of the SLM (Almeida, Cattrall, & Kolev,
92 2017).

93 Recently, polymer inclusion membranes (PIMs) have been shown to have a better stability
94 than SLMs (Almeida, Cattrall, & Kolev, 2012). PIMs are cast from a solution of a base-polymer,
95 extractant and in some cases plasticizer or modifier in a suitable solvent (Almeida, Cattrall, &
96 Kolev, 2012; Nghiem, Mornane, Potter, Perera, Cattrall, & Kolev, 2006)**.** The reason behind
97 their superior stability compared to SLMs stems from the fact that the membrane liquid phase
98 of PIMs (i.e., extractant and plasticizer/modifier) is retained between the entangled polymer
99 chains of the base-polymer, thus minimizing significantly its leaching to the adjacent aqueous
100 solutions. The base-polymer provides mechanical strength to the PIM, while the extractant
101 (carrier) is responsible for the extraction/transport of the chemical species of interest. The
102 plasticizer or modifier are often added to the PIM composition to provide elasticity or increased
103 solubility of the extracted species in the membrane liquid phase, respectively (Nghiem,
104 Mornane, Potter, Perera, Cattrall, & Kolev, 2006). PIMs have been successfully employed in
105 flow analysis (FA) systems for the on-line separation and preconcentration of Zn(II) (L. L.
106 Zhang, Cattrall, Ashokkumar, & Kolev, 2012; L. L. Zhang, Cattrall, & Kolev, 2011),
107 orthophosphate (Nagul, Fontàs, McKelvie, Cattrall, & Kolev, 2013) and vanadium(V) (Yaftian,
108 Almeida, Cattrall, & Kolev, 2018).

109 The present paper reports on the development of a spectrophotometric FA system
110 implementing on-line preconcentration of arsenate using a PIM consisting of poly(vinylidene

fluoride-co-hexafluoropropylene) (PVDF-HFP) and Aliquat 336 followed by on-line generation of arsine which diffuses across a gas-permeable membrane into a $KMnO_4$ solution causing its discoloration. To the best of our knowledge this is the first use of a PIM in an FA system for the determination of arsenate in drinking waters at low μg L^{-1} levels and the first coupling of on-line membrane-based extractive separation with on-line membrane-based gas-diffusion separation.

2. Experimental

2.1. Reagents and solutions

All reagents and solvents used in this study were of analytical reagent grade. The polymers PVDF-HFP (Aldrich, USA) and poly(vinyl chloride) PVC (Fluka, Italy), the extractant Aliquat 336 (Aldrich, USA), and the modifier 1-tetradecanol (Aldrich, USA) were used as constituents of the PIMs studied. Tetrahydrofuran (THF) without a stabilizer, purchased from VWR (Australia), was used as the membrane casting solvent. The acceptor solution used in the PIM-based separation step contained 0.1 mol L^{-1} NaCl (Chem-Supply, Australia) as the stripping reagent for arsenate. The reduction of As(V) to As(III) was conducted using a reductant solution composed of 4 mol L^{-1} HCl (32%, RCI Labscan, Thailand), 1% (w/v) KI (Aldrich, USA), and 0.5% (w/v) ascorbic acid (AA) (Ajax Finechem, Australia). The sodium borohydride reagent stream used for arsine generation contained 0.5% (w/v) $NaBH_4$ and 0.05 mol L^{-1} NaOH (Chem-Supply, Australia). Arsine was absorbed and oxidized in the gas-diffusion acceptor stream containing 0.2 mmol L^{-1} $KMnO_4$ (Chem-Supply, Australia) and 0.05 mol L^{-1} NaOH (Chem-Supply, Australia).

The interference studies were performed with working solutions prepared by dilution of stock solutions containing 500 mg L^{-1} $H_2PO_4^-$, Cl^-, NO_3^-, HCO_3^-, or SO_4^{2-}. These stock solutions were prepared by dissolving Na_2HPO_4 (BDH, Australia), NaCl, $NaNO_3$ (Ajax,

Australia), $NaHCO_3$ (Chem-Supply, Australia), or Na_2SO_4 (Chem-Supply, Australia) in ultrapure water (≥18.2 MΩ cm, Millipore, Synergy 185, France), used in the preparation of all aqueous solutions.

2.2. Instrumentation

On-line spectrophotometric detection was conducted with a Pharmacia Novaspec II UV-Vis spectrophotometer (Pharmacia Biotech, Sweden) fitted with a flow-through cell made of quartz (10 mm optical path length, Starna, UK). The spectrophotometer was interfaced with a PowerChrom 280 (Model ER280) data recording system linked to a PC and run by the Chart software package (eDAQ, Australia).

The PIMs thickness was measured using an optical microscope (Model LH50A, Olympus, Japan) with a calibrated lens (Carton Optical Ind., Japan).

For method validation the samples were also analysed after off-line pre-reduction with a solution containing a mixture of 1% (w/v) KI and 0.5% (w/v) ascorbic acid by inductively coupled plasma optical emission spectrometry (ICP-OES, Model Optima 4300 DV, Perkin-Elmer) incorporating a home-made hydride generation unit.

2.3. Flow Analysis (FA) manifold

The FA manifold developed in the present study for arsenate preconcentration, separation and detection involving hydride generation is depicted in Figure 1.

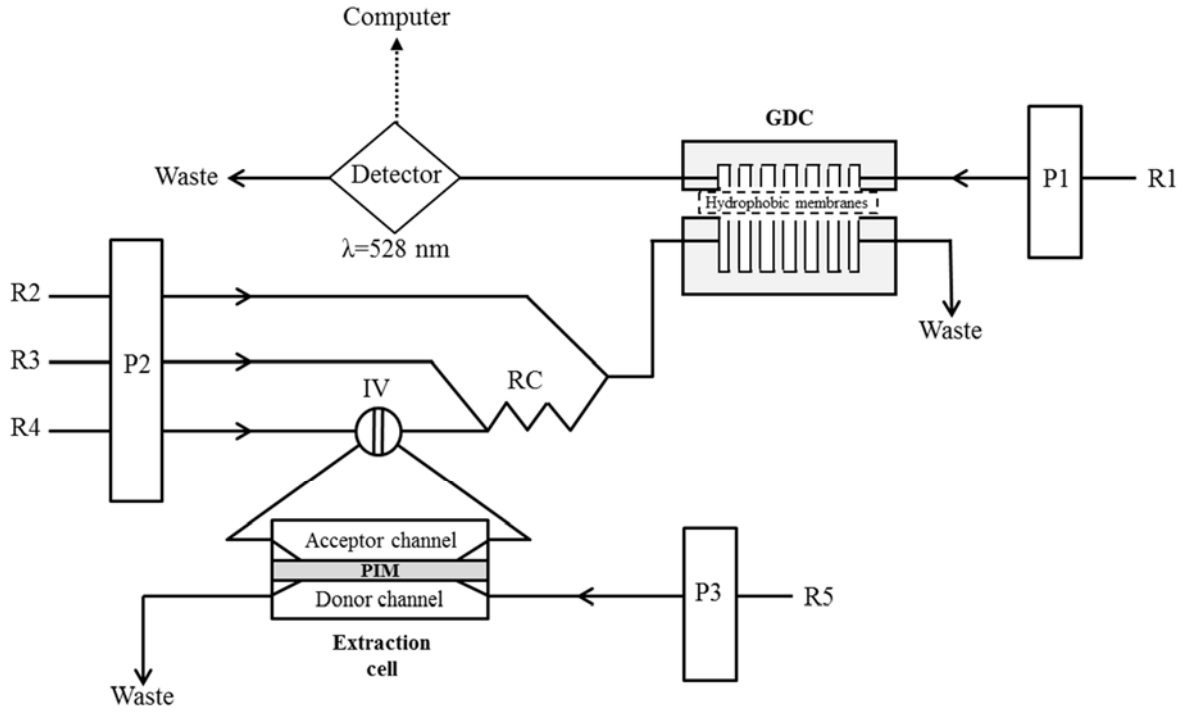


Figure 1. Schematic of the FA manifold. P1-P3: peristaltic pumps; R1: gas-diffusion acceptor stream (0.2 mM M $KMnO_4$, 0.05 M NaOH); R2: $NaBH_4$ stream (0.5% (w/v) $NaBH_4$, 0.05 mol L^{-1} NaOH); R3: reductant stream (4 M HCl, 1% (w/v) KI, 0.5% (w/v) ascorbic acid); R4: PIM acceptor stream (0.1 M NaCl); R5: PIM donor stream; RC: reaction coil; IV: injection valve; GDC: gas-diffusion cell; PIM: polymer inclusion membrane.

The system consisted of 3 four-channel peristaltic pumps, i.e., Pump 1 and Pump 2 (Model VS4, Watson Marlow Alitea, Sweden) and Pump 3 (Gilson Minipuls-3, France). All the pumps were fitted with Tygon tubing of suitable internal diameter (TACS, USA). Polytetrafluoroethylene (PTFE) tubing of 0.5 mm i.d. was used throughout the manifold, except for the gas-diffusion acceptor stream outlet tubing, which was of 3 m length and 0.3 mm i.d. to provide sufficient back-pressure. The latter was required to prevent the diffusion of H_2, generated by the decomposition of $NaBH_4$, across the hydrophobic microporous membranes and the filter paper of the gas-diffusion cell (GDC, Fig. 2a) into Stream R1 where it would have interfered with the analytical measurements. The following hydrophobic microporous

membranes were used in the present study: Durapore® and SureVent® membranes (Merck Millipore, USA), PTFE membranes (Reece, Australia), and polypropylene membranes (Chemplex, Zimbabwe). The flow rates of all streams were measured gravimetrically by weighing the mass of water of known temperature pumped through the corresponding tubing over a 5 min period. On-line preconcentration of arsenate was performed using a home-made extraction cell similar to the one described previously by us (L. L. Zhang, Cattrall, & Kolev, 2011), which consisted of two Perspex blocks (150 mm length, 30 mm width and 15 mm height, each) clamped together by stainless steel screws. The two channels of the extraction cell were serpentine shaped and were 157, 1 and 0.25 mm in length, width and depth, respectively. Arsine was separated in a homemade GDC (Figure 2) made of Perspex and identical to the one used previously by us (Y. Zhang, Miró, & Kolev, 2015) where arsine diffused from the gas-diffusion donor stream (Streams R2+R3+R4, Figure 1) across an assembly of a filter paper disc (No. 54, Whatman, Britain) sandwiched between two hydrophobic microporous membranes (Figure 2a) into the gas-diffusion acceptor stream (Stream R1). The filter paper was used as a physical support for the hydrophobic membranes, which otherwise could have stretched as a result of the pressure difference between the two channels of the GDC (Figure 2a) thus changing the channels' volume and impacting negatively on repeatability. The shape of the two channels of identical width and length (Figure 2b), i.e., 1.8 mm and 100 mm, respectively, ensured efficient mixing of the gas-diffusion donor and acceptor streams which improved the generation, trans-membrane transfer and oxidation of arsine in the gas-diffusion acceptor stream (Stream R1) (Y. Zhang, Miró, & Kolev, 2015). The depths of the acceptor and the donor channels were 0.5 and 6 mm, respectively, and the corresponding volumes were 90 μL and 1080 μL, respectively. This volume difference coupled with appropriately selected flow rates of Streams R1 – R4 allowed a degree of preconcentration of arsenic as arsine in the gas-diffusion acceptor stream (Stream R1).

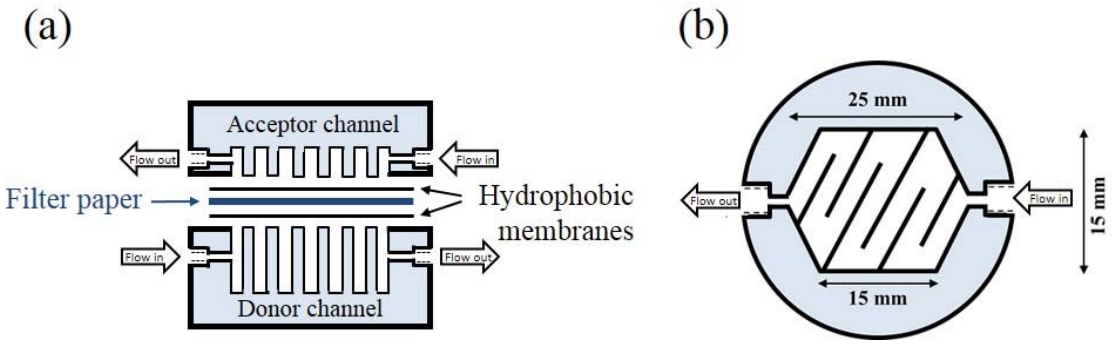


Figure 2. Schematic of the GDC used in the on-line separation of arsine. (a) Cross-section (donor and acceptor channels depths - 6 and 0.5 mm, respectively) and (b) top view of one of the halves of the GDC.

2.4. FA procedure

The standard/sample solution (Stream R5, Figure 1) was propelled for a predetermined period of time through the donor channel of the extraction cell where a PIM separated the sample (donor) stream (Stream R5) from the acceptor stream (Stream R4). The acceptor stream was stopped for a predetermined period of stop-flow time during the sample passage through the donor channel of the extraction cell to allow preconcentration of arsenate in the static acceptor solution located in the acceptor channel of the cell. At the end of the stop-flow time, the acceptor stream (R4) was re-started and arsenate was reduced to arsenite by merging the acceptor stream of the extraction cell (R4) with a reagent stream (R3) containing HCl, KI and ascorbic acid. Subsequently, arsine was generated by merging the combined R4+R3 stream with a sodium borohydride stream (R2). The generated arsine in the combined stream R4+R3+R2 diffused across the hydrophobic membrane of the GDC into the acceptor solution of the gas-diffusion cell (R1) where it was oxidised by $KMnO_4$ resulting in a decrease in the $KMnO_4$ absorbance, monitored continuously at 528 nm in the spectrophotometric measuring cell of the manifold. In all measurements, the analytical signal recorded was the maximum decrease in $KMnO_4$ absorbance relative to the baseline level.

218

219 *2.5. Optimization of the FA method*

220 The optimization of the reaction coil (RC) length (Figure 1) and the flow rate of Stream
221 R1 and the selection of the most appropriate hydrophobic gas-diffusion membrane were carried
222 out in a FA system similar to the one shown in Figure 1 where the extraction cell was replaced
223 with an injection valve with a 500 μL sample loop. The standards injected in these experiments
224 contained 1000 μg L^{-1} As(V).

225 The suitability of different PIM compositions was tested in the FA manifold shown in
226 Figure 1 using a stop-flow procedure in which 5 mL of a 1000 μg L^{-1} As(V) standard solution
227 were propelled at a flow rate of 0.2 mL min^{-1} through the donor channel of the extraction cell.
228 The influence of the stop-flow time and the flow rate of Stream R5 was studied by propelling
229 a standard solution containing 500 μg L^{-1} As(V) through the donor channel of the extraction
230 cell.

231

232 *2.6. PIM preparation*

233 PVC-based PIMs containing 70% (w/w) PVC and 30% (w/w) Aliquat 336 were prepared
234 by dissolving 180 mg of Aliquat 336 in 18 mL of THF, followed by slow addition of 420 mg
235 of PVC into the casting solution, which was constantly stirred to avoid aggregation of the
236 polymer. Finally, the resulting mixture was poured into a 16.5 cm in diameter glass ring sitting
237 on a flat glass plate. The ring was covered with filter paper and a watch glass to slow down the
238 evaporation of THF in the next 15 h after which the resulting PIM was carefully peeled from
239 the glass plate (Fontàs, Vera, Batalla, Kolev, & Anticó, 2013; Nagul, Fontàs, McKelvie, Cattrall,
240 & Kolev, 2013).

241 PIMs containing 1-tetradecanol as a modifier were also prepared by the casting method
242 outlined above. However, in this case 60 mg of this compound and 120 mg of Aliquat 336 were

dissolved in the casting solution together with 420 mg of PVC and the corresponding PIMs contained 70% (w/w) PVC, 20% (w/w) Aliquat 336 and 10% (w/w) 1-tetradecanol.

The PVDF-HFP-based membranes were prepared following the procedure described by O'Bryan et al. (O'Bryan, Cattrall, Truong, Kyratzis, & Kolev, 2016). In this method, 700 mg of PVDF-HFP and 300 mg of Aliquat 336 were dissolved in 8 mL of THF at 50 °C and the mixture was mechanically stirred until the complete dissolution of all PIM components. The casting solution was then spread onto a glass plate using a casting knife with 0.5 mm depth setting (O'Bryan, Cattrall, Truong, Kyratzis, & Kolev, 2016). The glass plate was covered with an aluminium tray to allow the slow evaporation of THF in the next 48 h after which the membrane was peeled from the glass plate.

2.7. Interference studies

The effect of common anions in appropriately selected concentration ranges (i.e., 0.15 mg L^{-1} – 140 mg L^{-1} in the case of $H_2PO_4^-$ and 1.0 mg L^{-1} - 40 mg L^{-1} in the case of NO_3^-, Cl^-, HCO_3^-, and SO_4^{2-}) on the analytical signal for a 0.05 mg L^{-1} (0.67 μmol L^{-1}) As(V) standard was studied.

2.8. Sample analysis

Spiked with arsenate at the μg L^{-1} level tap and mineral water samples were analysed by both the newly developed FA method and ICP-OES. The tap water was obtained from Melbourne's public water supply, and the commercial mineral waters analysed were: Voss Still Water (Norway), Woolworths Mountain Spring Water (Australia) and Icelandic Spring Water (Iceland). All samples were analysed by the standard addition method, involving at least 3 standard additions, and the measurements were performed in triplicate (unless otherwise stated).

3. Results and discussion

3.1. Optimization of the FA system parameters

The optimization range and the initial and optimal values for each of the design and operational parameters of the newly developed FA system investigated in this study are summarized in Table 1 in the order in which the optimization was done. The initial value of a parameter was the value used in the experiments prior to the optimization of this parameter. The compositions of the Streams R1 (0.2 mmol L^{-1} $KMnO_4$ and 0.05 mol L^{-1} NaOH), R2 (0.5% (w/v) $NaBH_4$ and 0.05 mol L^{-1} NaOH) and R3 (4 M HCl + 1% (w/v) KI + 0.5% (w/v) ascorbic acid) were selected on the basis of the results obtained in an earlier study involving the determination of arsenic by a gas-diffusion/hydride generation approach (Y. Zhang, Miró, & Kolev, 2015). To simplify the operation of the FA system, Streams R2, R3 and R4 were kept at the same flow rate of 0.12 mL min^{-1}.

Table 1. Optimization of the FA system for the determination of As(V).

Parameter	Range studied	Initial value	Optimal value
Reaction coil length (m)	0 – 3.00	2.50	0.25
Stream R1 flow rate (mL min^{-1})	0.06 – 0.46	0.24	0.06
Gas-diffusion membrane	Polypropylene		
	Durapore®		SureVent®
	SureVent®		
	PTFE		
PIM composition (% (w/w))	70 PVC, 30 A336		
	70 PVC, 20 A336, 10 1-TD		70 PVDF-HFP, 30 A336

	70 PVDF-HFP, 30 A336		
[NaCl] in R4 (mol L^{-1})	0.05 – 0.2	0.1	0.1
Stream R5 flow rate (mL min^{-1})	0.2 – 3.0	0.2	2.5
Stop-flow time of the acceptor stream of the extraction cell (min)	2 – 30	25	15

A336 – Aliquat 336, 1-TD – 1-tetradecanol

3.1.1. Effect of the reaction coil length, flow rate of Stream R1 and type of the gas-diffusion membrane

As mentioned earlier, the influence of these parameters was studied in an FA system, similar to the one shown in Figure 1, where the extraction cell was replaced with an injection valve with a 500 μL sample loop.

The length of the reaction coil (RC, Figure 1), where Streams R3 and R4 were merged, was varied between 0 m (i.e., no reaction coil) and 3 m. The RC length affected both the efficiency of mixing between the two streams mentioned above and the dispersion of arsenic in the donor stream of the gas-diffusion cell. As expected, a longer RC enhanced arsenic dispersion which offset any increase in the analytical signal due to better mixing between Streams R3 and R4. The highest analytical signal was obtained when the length of the RC was 0.25 m and this length of the RC was used in the subsequent experiments. The percentage of As(V) converted into As(III) under these experimental conditions was calculated as equal to 70%, by comparing the analytical signals for standards containing 1000 μg L^{-1} of either As(III) or As(V).

As expected, higher analytical signals were recorded when lower flow rates of Stream R1 were used due to the fact that arsine generated in the RC was transferred into a smaller volume of the $KMnO_4$ acceptor solution of Stream R1. Experiments involving stopping Stream R1

during arsine generation were also conducted but they resulted in unstable baseline due to the transfer of greater and irreproducible amounts of H_2 into the static $KMnO_4$ solution located in the acceptor channel of the gas-diffusion cell (Figure 1). In addition, no enhancement in the analytical signal was observed. Hence, 0.06 mL min^{-1} was selected as the optimal flow rate of Stream R1 since this was the lowest flow rate that could be reproducibly maintained by Peristaltic pump P1.

Four different hydrophobic microporous membranes (i.e., Durapore®, SureVent®, PTFE, and polypropylene membranes) were compared with respect to their permeability to arsine, which was estimated on the basis of the corresponding analytical signal values. In each case the two channels of the gas-diffusion cell were separated by two membrane layers and a filter paper disc sandwiched between them. When the Durapore® membrane was tested a rapid formation of a brown stain on both membrane surfaces was observed due to manganese dioxide formation, and for this reason this membrane was discarded. The average analytical signals based on 10 replicate measurements of a 1000 μg L^{-1} As(V) standard for the remaining three membranes were 0.081 ± 0.004 for the polyprolylene membrane, 0.101 ± 0.004 for the PTFE membrane, and 0.102 ± 0.004 for the SureVent® membrane. Although no significant difference between the last two membranes was obtained, the baseline was not very stable when using the PTFE membrane, possibly due to its malleability. SureVent® membrane was selected for further use because it was slightly thicker and more robust than the PTFE membrane and no issues with baseline stability were observed.

3.1.2. Effect of the PIM and the compositions of Stream R4

Fontàs et al. (Fontàs, Vera, Batalla, Kolev, & Anticó, 2013), reported on the successful use of a PIM composed of the base-polymer PVC and the carrier Aliquat 336 for the preconcentration of arsenate in groundwater samples. The optimal composition of this PIM, i.e.,

327 70% (w/w) PVC and 30% (w/w) Aliquat 336, was determined in a previous study by the same
328 research team (Güell, Anticó, Kolev, Benavente, Salvadó, & Fontàs, 2011). In this and other
329 studies (Güell, Anticó, Kolev, Benavente, Salvadó, & Fontàs, 2011; Güell, Fontàs, Anticó,
330 Salvadó, Crespo, & Velizarov, 2011) 0.1 M NaCl was found to be the most suitable receiving
331 solution for arsenate. The separation of arsenate using an Aliquat 336-based PIM involves the
332 extraction of the $HAsO_4^{2-}$ anion from the sample solution into the PIM, followed by the
333 diffusion of the corresponding adduct of this anion with the quaternary alkylammonium cation
334 of Aliquat 336 (A^+) across the membrane and the back-extraction of $HAsO_4^{2-}$ into the acceptor
335 solution containing NaCl as the stripping reagent (Güell, Anticó, Kolev, Benavente, Salvadó,
336 & Fontàs, 2011). The equilibrium, described by Eq. (1), is shifted to the right (extraction into
337 the PIM) at the sample solution/PIM interface and to the left (back-extraction into the acceptor
338 solution) at the PIM/acceptor solution interface.

339 $$HAsO_4^{2-} + 2\,(A^+Cl^-)_{PIM} \leftrightarrows [(A^+)_2\,HAsO_4^{2-}]_{PIM} + 2\,Cl^- \quad (1)$$

340 The PIM and the receiving solution, mentioned above, were initially used in the newly
341 developed FA system for the on-line preconcentration of As(V). However, the analytical signals
342 obtained in 3 consecutive measurements of a 1000 μg L^{-1} As(V) standard (0.09, 0.08, 0.03)
343 were relatively low. The poor repeatability was most likely due to the leaching of the PIM liquid
344 phase consisting of Aliquat 336 into the adjacent aqueous phases. Therefore, other PIM
345 compositions were explored.

346 One of them was the composition reported by Cho et al. (Cho, Xu, Cattrall, & Kolev, 2011)
347 for the extraction of thiocyanate from weakly alkaline aqueous solutions which consisted of
348 20% (w/w) Aliquat 336, 10% (w/w) 1-tetradecanol and 70% (w/w) PVC. This study
349 demonstrated that the addition of a modifier (e.g., 1-tetradecanol) of a very low water solubility
350 reduced significantly the leaching of the PIM liquid phase. However, the analytical signal
351 achieved with this PIM composition (i.e., 0.041, 0.017, 0.023), though higher than the one for

352 the PIM composed of only 70% (w/w) PVC and 30% (w/w) Aliquat, also showed poor
353 repeatability.
354 O'Bryan et al. (O'Bryan, Cattrall, Truong, Kyratzis, & Kolev, 2016) demonstrated that
355 PVDF-HFP-based PIMs containing 30% (w/w) Aliquat 336 and 70% (w/w) PVDF-HFP
356 exhibited a significantly higher extraction and back-extraction rates for thiocyanate and higher
357 stability compared to PVC-based PIMs containing the same concentration of liquid phase. This
358 PIM provided much higher analytical signal (i.e., 0.173, 0.173, 0.172) and excellent
359 repeatability and therefore was used in the subsequent experiments.
360 The concentration of NaCl in Stream R4 was varied between 0.05 and 0.20 mol L^{-1}. As
361 expected, the analytical signal increased with increasing the NaCl concentration up to
362 0.1 mol L^{-1} after which no further signal enhancement was observed. Therefore, 0.1 mol L^{-1}
363 was selected as the optimal NaCl concentration in Stream R4.
364
365 *3.1.3. Effect of the flow rate of Stream R5 and the stop-flow time for Stream R4*
366 It can be expected that the analytical signal will depend heavily on both the flow rate of
367 Stream R5 and the stop-flow time (i.e., duration of the sample flow through the extraction cell)
368 because these two parameters determine the sample volume and its contact time with the PIM.
369 The individual effects of these two parameters on the analytical signal are not independent of
370 each other and for this reason their combined effect was studied and the results are presented
371 in Figure 3. It was observed that, independently of the flow rate of Stream R5, the analytical
372 signal increased rapidly with increasing the stop-flow time up to 15 min and then it started
373 gradually to level off. Also, it was observed that independently of the stop-flow time, the
374 analytical signal increased with increasing the flow rate of Stream R5 up to 2.5 mL min^{-1} after
375 which it started decreasing. Therefore, 2.5 mL min^{-1} was selected as the optimal flow rate. The
376 analytical signal did not increase significantly for stop-flow times greater than 15 min (e.g., an

increase in the stop-flow time from 15 to 25 min resulted in only 10% increase in the analytical signal) and this value was selected as the optimal stop-flow time.

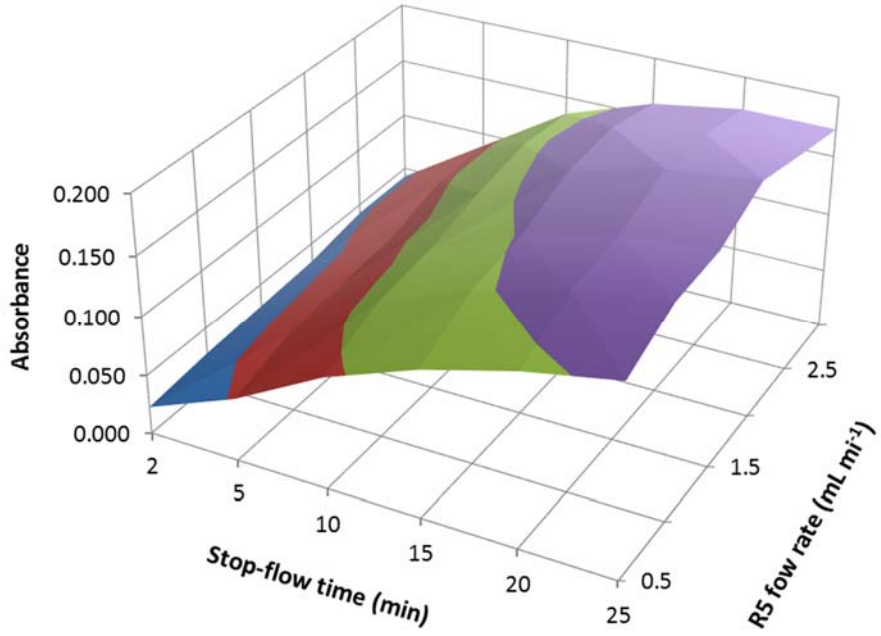
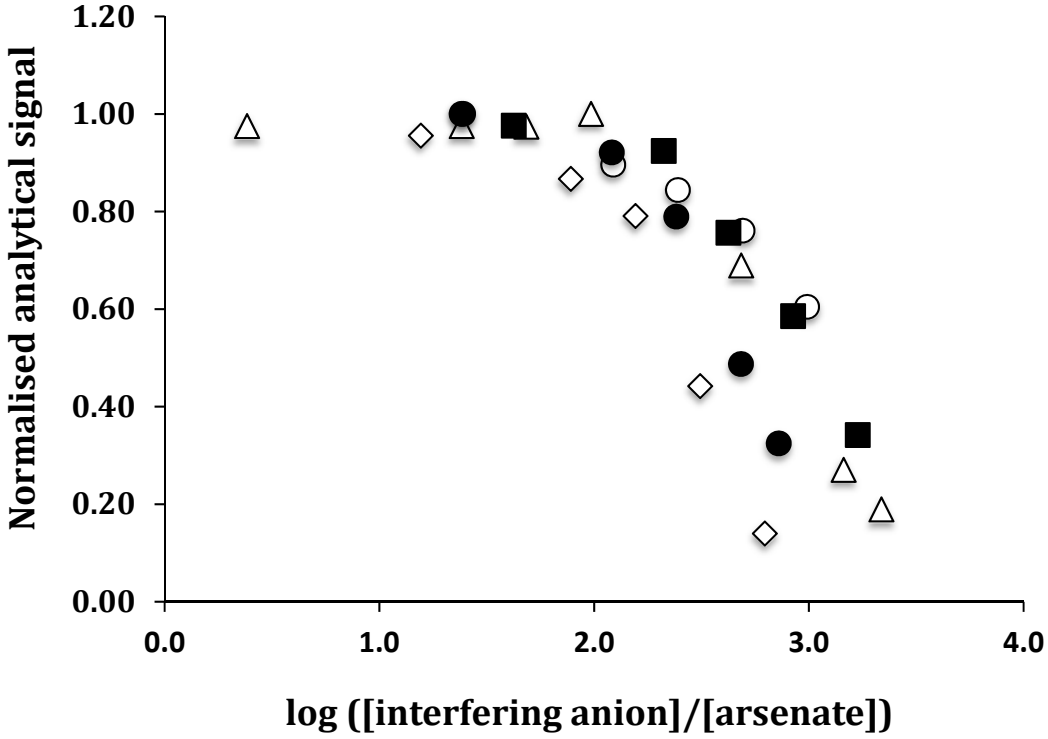


Figure 3. Influence of the stop-flow flow time and the flow rate of Stream R5 on the analytical signal for a 500 μg L^{-1} As(V) standard.

3.2. Interference studies

The presence of common anions in natural water (e.g., $H_2PO_4^-$, Cl^-, NO_3^-, HCO_3^-, and SO_4^{2-}) which can compete with the extraction of arsenate (Fontàs, Vera, Batalla, Kolev, & Anticó, 2013), makes it necessary to investigate their potential interference. No interference effects associated with these anions were expected in the arsine generation, trans-membrane transport and detection steps. Figure 4 shows the normalized analytical signal as a function of the logarithm of the concentration ratio between each one of the anions mentioned above and arsenate. The normalized analytical signal was calculated as a fraction of the analytical signal in the absence of interfering ions. Interference effects were observed only when the concentration of the interfering ions exceeded by 2 orders of magnitude the arsenate

393 concentration (i.e., 50 μg L^{-1}). In the presence of significant interference effects, the standard
394 addition method should be used.



395

396 **Figure 4.** Effect of the concentration of $H_2PO_4^-$ (△), NO_3^- (●), SO_4^{2-} (◇), HCO_3^- (○), Cl^-
397 (■) on the normalised analytical signal for a 0.67 μmol L^{-1} (50 μg L^{-1}) As(V) standard.

398

399 *3.3. Analytical figures of merit*

400 Under optimal conditions (Table 1) the newly developed FA method is characterised by a
401 linear range of 5.0-65 μg L^{-1} As(V) described by the following calibration equation based on 5
402 different concentrations:

403 $$A = (8.94\times10^{-4} \pm 1.77\times10^{-5}) \times C \qquad (R^2=0.998) \qquad (2)$$

404 where A is the absorbance and *C* is the As(V) concentration in μg L^{-1}.

405 The method repeatability, expressed as the relative standard deviation (RSD) of 5 replicate
406 measurements, was calculated as equal to 1.8% for 25 μg L^{-1} and 2.8% for 50 μg L^{-1} As(V),
407 respectively. The limit of detection (LOD) of 3.0 μg L^{-1} was calculated as the analyte

concentration corresponding to an analytical signal equal to the blank signal plus three standard deviations of the blank (Miller & Miller, 2010). The sample solution was propelled for 15 min through the PIM extraction cell while the acceptor solution was stagnant, resulting in a sampling rate of 2.8 h^{-1}.

The newly developed FA method provides better sensitivity for the determination of As(V) than other spectrophotometric FA methods (e.g., 51 μg L^{-1} (Boonjob, Miró, & Kolev, 2013) and 21 μg L^{-1} (Y. Zhang, Miró, & Kolev, 2015)) and sensitivity comparable to that provided by FA methods utilizing bulky and expensive atomic optical detectors (e.g., atomic fluorescence detector - 0.61 μg L^{-1} (Caballo-Lopez & Luque de Castro, 2002) and atomic absorption detector – 0.5 μg L^{-1} (Y. Zhang & Adeloju, 2008).

3.4. Analysis of drinking water samples

As mentioned earlier, in most cases arsenic in drinking water consist almost entirely of As(V) (Döker & Yılmaz, 2018; Komorowicz & Barałkiewicz, 2016) and therefore the newly developed method was validated by determining the As(V) concentration in 4 drinking water samples using the standard addition method (Table 2). The standard addition method was used instead of the calibration curve method because of the high concentrations of common anions relative to the As(V) concentration. All standard additions curves were characterised by excellent linearity ($R^2 \geq 0.997$) and the repeatability of the slopes of replicate samples (n=4) expressed as RSD was 5.6%. The As concentration in the spiked samples was also determined by HG-ICP-OES using the calibration curve method. There was no statistically significant difference at the 95% confidence level between the results obtained by both methods (Table 2).

433 **Table 2.** As(V) concentration in spiked drinking water samples determined by the newly
434 developed FA method and HG-ICP-OES.

Sample	Spiked As(V) concentration ($\mu g\ L^{-1}$)	Measured As(V) concentration ± SD ($\mu g\ L^{-1}$)	
		FA (n=3)	HG-ICP-OES (n=3)
Tap water	6.0	6.5 ± 0.5	6.6 ± 0.4
	10.0	9.1 ± 0.7	10.5 ± 0.8
	15.0	14.0*	15.8 ± 0.9
Voss mineral water	6.00	5.5 ± 0.5	6.4 ± 0.5
	10.0	10.0*	10.5 ± 0.4
Spring mineral water	9.00	8.3 ± 0.8	9.4 ± 0.6
	20.0	21.0*	21.6 ± 0.6
Icelandic mineral water	15.0	13.9 ± 0.9	13.7 ± 0.5
	25.0	22.0*	25.0 ± 2.0

435 * experiments performed in duplicate

436 HG-ICP-OES, hydride generation inductively coupled plasma optical emission spectrometry

437

438 **4. Conclusions**

439 The hydride generation FA system for the determination of arsenate in drinking waters at
440 low $\mu g\ L^{-1}$ levels, developed as part of the current study, utilizes for the first time PIM-based
441 on-line extractive separation of arsenate from the sample matrix which is subsequently reduced
442 to arsine, detected spectrophotometrically after its on-line gas-diffusion separation. Under
443 optimal conditions the FA system is characterized by an LOD of 3.0 $\mu g\ L^{-1}$ and a repeatability,
444 expressed as RSD, of 1.8% (n=5, 25 $\mu g\ L^{-1}$) and 2.8% (n=5, 50 $\mu g\ L^{-1}$). Lower limits of

detection could be potentially achieved by using longer stop-flow times for the extraction step, i.e., larger sample volumes. Common anions, such as phosphate, nitrate, sulphate, carbonate, and chloride, were found to interfere in the PIM-based separation process only at a concentrations 100 times higher than that of arsenate. The newly developed FA system allowed the accurate determination of arsenate in drinking water spiked with As(V) at the low μg L^{-1} level using the multi-point standard addition method. Since arsenic in most drinking waters is almost entirely composed of arsenate, it can be expected that the FA system, mentioned above, would be applicable for total arsenic determination of drinking water.

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