A novel low-cost detection method for screening of arsenic in groundwater

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Abstract

In the present work, a novel and simple detection system for As inorganic species contained in groundwater is presented. To reach the required detection limit, the proposed methodology is based on two steps: first the transport and preconcentration of the inorganic arsenic species using a polymer inclusion membrane (PIM) system, and second, the formation of a coloured complex absorbance of which is measured. Different parameters related to the membrane composition and the transport kinetics have been studied and it was found that membranes made of polyvinyl chloride (PVC) as a polymer, and Aliquat 336 as a carrier, ensured efficient arsenic transport when the carrier content was at least 31%(w/w). The implementation of the designed PIM in a special device that contained only 5 mL of the stripping solution (0.1 M NaCl) allowed As preconcentration from a 100 mL water sample, and, thus, facilitating its detection with the colorimetric method. The new method here developed was validated and its analytical figures of merit were determined, i.e. limit of detection of 4.5 µg L⁻¹ at 820 nm and a relative standard deviation within the range 8-10%. Finally, the method was successfully applied to the analysis of different water samples from Catalonia region with naturally occurring As.

Keywords: Arsenic; Polymer Inclusion Membranes; Aliquat 336; Preconcentration; Speciation; groundwater;

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1. Introduction

Arsenic is well-known as a potent human carcinogen, and its presence in water, especially groundwater, is a major problem in different areas of the world (Léonard 1991; Villaescusa and Bollinger 2008). Arsenic in the environment is released as inorganic species which can be transformed to organic compounds due to biological activity. Organic As is considered to be less toxic than inorganic As, and in the case of inorganic compounds, the toxicity decreases in the order arsine>As(III)>As(V).. The rate of transformation from one species to the other depends on many factors, like pH, redox potential, and the presence of microorganisms or other oxidizing agents, among others. Under oxidizing conditions As exists as As(V) compounds, whereas under mildly reducing conditions, it is generally present as As(III) compounds. They both can form different oxyanion species depending on pH.

In the current context of water scarcity, or in developing countries where access to treated water is limited, groundwater that in certain cases may contain high concentrations of arsenic is viewed as a source of drinking water. Globally, over 130 million people are now estimated to be potentially exposed to arsenic in drinking water at concentrations above the World Health Organization (WHO) guideline value of $10 \mu\text{g L}^{-1}$ (Smedley and Kinniburgh 2002).

To avoid arsenic poisoning, it is of paramount importance to do routine analysis. Arsenic can be measured either in laboratories or *in-situ* by commercial kits. Analytical laboratory based techniques usually used for As measurements are Hydride Generation Atomic Absorption Spectroscopy (HGAAS), Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). These techniques provide sensitivity enough to directly detect arsenic in the water sample at $\mu\text{g L}^{-1}$ levels. However, they are expensive to run and require equipped laboratories as well as trained staff. To perform *in-situ* arsenic screening, several kits are commercially available which are economical and simple to use (Arora et al. 2009). Most of the commercial kits are based on Gutzeit method (Kinniburgh and Kosmus 2002). It is based on the transformation of the whole arsenic present in the water sample to arsine by acidifying the sample and adding zinc dust. Then, arsine reacts with mercury bromide impregnated in a paper strip forming a compound with colour varying from yellow to brown depending on the arsine amount generated. It should be noted that the presence of antimony in the sample, as well as the

presence of hydrogen sulphide, may interfere with this method. In addition the method uses toxic mercury bromide and can produce false negative results due to arsine loss.

Other field tests for arsenic detection are based on anode stripping voltammetry (ASV) (Forsberg et al. 1975). These kits include microelectrodes to carry out the measurement. First, arsenic is collected on the working electrode and then it is oxidized and measured.

As an alternative to the methods employing expensive instrumentation and the *in-situ* kits using harmful reagents, we have explored the possibility to perform a simple colorimetric As detection after a preconcentration step. For that, we have adopted the well-established molybdenum-blue colorimetric method adapted by Johnson and Pilson (1972) which was originally developed to detect phosphate in waters. It is based on the reaction between As(V) and ammonium molybdate forming an arsenatomolybdate compound which is colourless. After adding a reducing agent to reduce As(V) to As(III) the intensely blue coloured arsenomolybdenum blue is formed. Since Johnson and Pilson first described in 1972 the experimental conditions for As(V) determination in the presence of phosphate, several improvements have been reported (Dhar et al. 2004; Lenoble et al. 2003; Tsang et al. 2007). Tsang et al. (2007) used this colorimetric method to directly detect As at around $1 \mu\text{g L}^{-1}$ levels using a custom made dual-beam photometer with a 4 cm optical path cell and measuring at $\lambda_{\text{max}} = 880 \text{ nm}$. However, if we consider the use of a simple spectrophotometer or even better, the possibility of a detection of the colour by the naked eye (which would simplify even more the system), arsenic concentrations must be higher than the typical As content in waters. Thus, a preconcentration step is essential to reach the required concentration of As to allow its colorimetric detection.

In this study, we have investigated the use of a device containing a functionalized membrane to transport As from the water sample to a smaller volume of the corresponding stripping solution. Taking advantage of the differences in the volumes, As will be enriched and its colorimetric detection will be possible. Previous results obtained by us have demonstrated that functionalized membranes can be used to extract and transport arsenate species from natural waters. The transport mechanism is based on the fact that inorganic anionic species of As(V) present in waters at neutral pH (mainly H_2AsO_4^- and HAsO_4^{2-}) can be extracted by anion-exchangers carriers, such as Aliquat 336, included in both a supported liquid membrane (SLM) (Güell et al. 2010) and a polymer inclusion membrane (PIM) (Güell

et al. 2011a). Besides, commercial ion exchange membranes (IEM) containing anion-exchange groups were also found to be suitable for the transport of arsenate (Güell et al. 2011b). For all type of membranes mentioned above, a solution of 0.1 M NaCl ensured a quantitative transport of the extracted species due the concentration gradient of NaCl.

Under neutral pH conditions inorganic As(III) transport was negligible since it is mainly present as a neutral species (H_3AsO_3) (Güell et al. 2010; Güell et al. 2011a; Güell et al. 2011b). This different behaviour of As(V) and As(III) inorganic species when contacted with membranes incorporating an anion-exchanger is the basis of As speciation.

On the basis of the above considerations we decided to use a device containing a PIM since this kind of membranes are more stable than SLMs and more versatile than commercial IEMs. Hence, in the present research we present the different parameters related to the method development, as well as method validation and application to several water samples containing naturally occurring elevated levels of As (higher than $10 \mu\text{g L}^{-1}$) from the region of Girona (Spain).

2. Experimental

2.1. Reagents and solutions

Stock solutions (100 mg L^{-1}) of As(V) and As(III) were prepared from the solids $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Merck) and NaAsO_2 (Fluka) respectively. Solutions of As(V) in Milli-Q water were prepared by dilution of the corresponding stock solutions and the resulting pH was 7. However, to establish this pH in the case of As(III), it was necessary to add HCl. Sodium chloride (Fluka) was used to prepare the stripping solution. Hydrogen peroxide (Fluka) was employed to oxidize As(III) to As(V) according to the procedure adapted from a previous study (Yang et al. 1999). Calibration standards of As were prepared using the Spectrascan standard solution for atomic spectroscopy (Teknolab). All reagents and solvents were of analytical reagent grade and distilled water was purified by a Milli-Q Plus system (Millipore).

The extractant Aliquat 336, which is a mixture of quaternary alkylammonium chlorides, and the polymer polyvinyl chloride (PVC) were purchased from Fluka Chemie. A 0.5 M Aliquat 336 solution in tetrahydrofuran (THF) (Panreac, Spain), was used to prepare the polymeric films.

For the molybdenum blue method, the colorimetric reagent solutions were prepared in

accordance with the latest and improved version of the method of Tsang et al. (Tsang et al. 2007). A solution of ammonium molybdate was prepared by dissolving 5.2 g of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (Scharlau) and 8.8 mg of potassium antimonyl tartrate, $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6\cdot 0.5\text{H}_2\text{O}$ (Merck), in 30 ml of 9 M sulphuric acid and diluted by deionized water to 50 ml in a volumetric flask. Ascorbic acid is used as a reductant and a solution 10% (w/v) of ascorbic acid (Panreac) was prepared daily. The reagents were added to As(V) samples or standard solutions according to the recommended procedure (Tsang et al. 2007). To account for the matrix effect, standard solutions were prepared in both Milli-Q water and 0.1 M NaCl.

2.2. Polymer inclusion membranes preparation

PIMs were prepared according to the procedure previously described (Güell et al. 2011a). Briefly, 400 mg of PVC were dissolved in 20 mL THF and adding the appropriate amount of the Aliquat 336 solution in THF. This mixture was poured into a 9.0 cm diameter flat bottom glass Petri dish which was set horizontally and covered loosely. The solution was allowed to evaporate over 24 hours at room temperature. The resulting film was then carefully peeled off the bottom of the Petri dish and circular pieces with an area of 11.6 cm^2 or 2.5 cm^2 were cut from its central section and used in the transport or preconcentration experiments, respectively.

2.3. Transport and preconcentration experiments

Preliminary experiments to optimize the transport system were performed in a two compartment membrane cell described elsewhere (Güell et al. 2010), where 190 mL of both feed and stripping solutions (0.1 M NaCl) were used.

The device designed for preconcentration purposes (PIM-device) consists of a glass tube with two openings, one at the top (0.9 cm diameter) and another one at the bottom (1.8 cm diameter). The PIM was placed at the bottom opening and fixed with a screw cap specially designed to expose the maximum membrane area to the sample solution (2.5 cm^2). The opening at the top was closed with a standard screw cap and was used to fill the device with the appropriate volume of stripping solution.

To carry out the experiments using this device, 100 ml of arsenic containing water were poured into a glass beaker placed on a magnetic stirrer. The device incorporating the membrane and stripping solution (5 mL 0.1M NaCl) was immersed 1 cm in the sample solution in a vertical position. To better facilitate As transport the water solution was continuously stirred. After a predetermined contact time the device was removed from the solution and a selected volume of the stripping solution (usually 4 or 2 mL) was taken for analysis.

Arsenic transport efficiency (TE) was determined by using Eq. (1):

$$TE(\%) = \frac{[As]_{strip(t)}}{[As]_{feed(0)}} \frac{1}{Vr} \times 100 \quad (1)$$

where $[As]_{strip(t)}$ denotes the As concentration in the stripping compartment at the end the contact time, whereas $[As]_{feed(0)}$ is the initial As concentration in the water sample. The volume ratio between feed solution and stripping solutions is denoted by Vr . For the two-compartment cell $Vr = 1$, and for the PIM device $Vr = 20$.

As a minimum, duplicate experiments were performed. All experiments were conducted at 22 ± 1 °C.

2.4. Apparatus

An HP- Diode Array instrument was used to measure the absorbance of the arsenic complex at $\lambda = 820$ nm. Absorbance measurements were carried out for method validation once all the experimental parameters were optimized.

A sequential inductively coupled plasma atomic emission spectrometer (ICP-AES) (Liberty RL, Varian, Mulgrave, Vic., Australia) was used to determine the arsenic concentration in the aqueous stripping solutions. Measurements were conducted at $\lambda=228.812$ nm. Major cations like Na, Ca, Mg and K were also measured with this instrument.

For arsenic concentrations at the $\mu\text{g L}^{-1}$ level, a quadrupole-based ICP-MS system (Agilent 7500c, Agilent Technologies, Tokyo, Japan) equipped with an octapole collision reaction cell was employed. The isotope ^{75}As was selected and special conditions in the reaction cell ($3 \text{ mL min}^{-1} \text{ H}_2 + 0.5 \text{ mL min}^{-1} \text{ He}$) were employed to avoid spectral interferences due to the presence of chloride in water samples.

The anionic composition of the water samples was determined by an ion chromatograph (IC) DIONEX IC5000 equipped with an autosampler AS-AP, a conductivity detector, and a IonPac® AS18 anion-exchange column (4x250mm) with the AG Guard column (4x50 mm).

The pH and conductivity values were determined with a Crison Model GLP 22 pH meter and Ecoscan, Entech Instruments, portable conductimeter, respectively.

2.5. Water samples

Water samples containing arsenic naturally occurring and others without arsenic were collected in the north part of Catalonia (Spain). The samples were analysed and their composition is depicted in Table 1. Lles and Setcases are villages located close to the Pyrenees Mountains, and three different wells were sampled in each place. At Caldes the water was collected from a hot spring. Additionally, tap water from Girona city was also collected to study possible anions interferences in the arsenate transport.

3. Results and discussion

3.1. Efficiency of the PIM system for inorganic As transport

3.1.1. Composition of the membrane

Normally PIMs consist of a polymer which provides mechanical strength, a carrier, which is the responsible for the extraction process, and sometimes a plasticizer can be used to provide elasticity or a modifier to vary the membranes properties. In our previous work (Güell et al. 2011a), a PIM made of CTA as the polymer and Aliquat 336 as the carrier exhibited a very good performance in terms of inorganic As(V) transport. In this study, however, we wanted to explore the use of the polymer PVC for As transport. It has been reported that PIMs made of PVC and Aliquat 336 are very efficient for the transport of different species such as thiourea (Sakai et al. 2000), Cd in chloride media (Xu et al. 2004) or Cr(VI) (Gherasim et al. 2011). Moreover, Pereira *et al.* (Pereira et al. 2009) have studied the compatibility of this polymer and Aliquat 336, and showed that this combination resulted in successful membranes. The stability of a PIM made of 60%(w/w) PVC and 40%(w/w) Aliquat 336 has also been investigated by Kagaya et al. (Kagaya et al. 2012) who have suggested that though PIMs are

capable of losing membrane liquid phase, this loss leads to a stable membrane composition with minimal further loss of membrane liquid phase.

From our preliminary study on inorganic As(V) transport using PVC-based PIMs, it was observed that better results were obtained when the PIM did not contain any plasticizer (Fontàs et al. 2012). Thus, in the present work, we investigated PIMs containing only PVC and 20%(w/w) or 31%(w/w) Aliquat 336. The transient concentration curves corresponding to these two membrane compositions are depicted in Fig.1. As it can be observed, the PIM with the lower concentration of Aliquat 336 allowed the transport of As but only with a 30% transport efficiency in 300 min (Fig. 1(a)). However, the PIM containing 10% more Aliquat 336 (Fig. 1(b)) allowed the quantitative transport of As for the same period of time. Thus, a PIM composition of 69%(w/w) PVC and 31%(w/w) Aliquat 336 was selected for the subsequent experiments.

3.1.2. Transport of inorganic As(III)

As stated above, the transport of inorganic As(III) species at neutral pH is not favourable using anion-exchangers as carriers. Therefore, for total inorganic As (*i.e.* As(III) and As(V)) analysis, a preliminary oxidizing step is required to ensure that all inorganic As species are in the arsenate form. In the literature, different approaches are proposed for oxidizing As(III) to As(V), such as the use of hydrogen peroxide, activated carbon or titanium dioxide (Yang et al. 1999). In the present work, we investigated the photolytic oxidation reaction assisted by hydrogen peroxide as a simple and cost-effective method to allow total As transport. In this method 0.5 mL of the commercial H₂O₂ solution were added to 200 mL of 10 mg L⁻¹ As(III) solution. The solution was exposed to sun light for 40 min and then pH was adjusted to 7. The complete oxidation of As(III) to As(V) was verified by the molybdenum blue method. After this treatment, the resulting solution was used as a feed solution in the PIM separation system. Fig. 2 shows the transport profiles for inorganic As(III) solutions with and without an oxidizing pretreatment step. This pretreatment step resulted in the quantitative transport of inorganic As(III) as As(V), thus allowing total inorganic As measurement with the proposed PIM system. In the absence of an oxidizing pretreatment step only inorganic As(V) can be measured. Therefore, measurements with and without the pretreatment step will allow the quantification of both arsenate and arsenite in the water samples analysed.

3.2. Arsenic preconcentration using the PVC-based device

To demonstrate that the preconcentration of arsenate was possible using the PIM system, different PIM-devices were contacted with 100 mL solution of $100\ \mu\text{g L}^{-1}$ inorganic As(V) in Milli-Q water for 24 hours under constant agitation. After this period of time, the arsenic content in the stripping solution was analyzed. Results for 4 different experiments using different membrane pieces from the same original membrane or from different membranes were obtained and it was found that arsenate was effectively concentrated in the stripping phase, with concentrations varying from 1340 to $1530\ \mu\text{g L}^{-1}$. The determination of As(V) in the stripping phase was then conducted by the colorimetric molybdenum blue method, while direct measurement of As(V) was not possible in the original $100\ \mu\text{g L}^{-1}$ solution. Under these conditions, we obtained a transport efficiency of 68-76% calculated by Eq.(1) and a variation coefficient of 5%. These results led to further investigation of the suitability of the proposed device as an analytical tool for As monitoring.

Moreover, the kinetics of the transport is an important issue to take into account since it will determine the time needed for the whole procedure. Thus, different PIM-devices were mounted (to stop them at the desired time) and were immersed in 100 mL milli-Q water with $100\ \mu\text{g L}^{-1}$ inorganic As(V). Fig. 3 illustrates the kinetics of the arsenate preconcentration where it can be seen that the maximum transport efficiency was achieved after 17 h of contact under agitation. However, for practical considerations, we fixed 24 h for the subsequent experiments.

3.2.1 Effect of feed composition

The influence of the feed pH and matrix composition on the device performance was studied. The effect of feed pH on arsenate transport was discussed in detail by us in a previous study involving PIMs (Güell et al. 2011a). These membranes exhibited the fastest transport for inorganic As(V) in the pH range between 5 and 7. This pH range overlaps with the pH range of most natural waters. The same optimal pH range for the transport of inorganic As(V) was observed for the PVC based PIM used in the present study indicating that there was no need of pH adjustment of natural waters prior to their inorganic As analysis with the proposed PIM based device.

Considering that the PIM transport mechanism is based on anionic exchange, it is well known that not only arsenic species but also other anions present in natural water samples can be transported through the membrane, and, thus, these anionic species can potentially interfere with the preconcentration of the target analyte. Natural water may have a very different composition (e.g. Table 1). To evaluate matrix effect we tested arsenic transport for natural waters containing arsenic as well as tap water from Girona spiked with arsenate. The transport efficiencies for these natural waters are compared in Table 2 with that for milli-Q water. Even though the conductivity of the waters studied as well as their initial arsenic concentration was different, similar transport efficiencies were obtained except for the hot spring where no As transport was observed. In the case of spiked tap water sample, we also determined the percentage of other anions transported to the stripping phase. It was found that 75% of sulphate and 27% of nitrate were also co-transported along with arsenate. These results indicate that arsenate is preconcentrated, even in the presence of other anionic species, if the total concentration of anions does not exceed the chloride concentration in the stripping solution needed to ensure the chemical pumping. This condition was not fulfilled in the case of the hot spring water from Caldes, where the high chloride content of the sample hampered the efficient transport of arsenate. The conductivity of a water sample can be used as an indicator of the suitability of the membrane system for inorganic As analysis.

3.3. Analytical figures of merit

The proposed preconcentration method was applied to standards containing As(V) in the range 20 to 120 $\mu\text{g L}^{-1}$ in Milli-Q water with the molybdenum blue method used for measuring the concentration of As(V) in the stripping solution. Fig.4 shows the calibration curves obtained for the analysis of the As(V) standards by the molybdenum blue method with and without preconcentration using the PIM-device. From the slope of each calibration curve it can be stated that the sensitivity of the method using the PIM-based device is 17 times higher than that of the direct analysis. Possible variations due to matrix effects were examined by constructing calibration curves in the natural water Setcases 1 (see Table 1 for composition). The resulting calibration curves presented very similar parameters (slope value: 0.0053 (SD=0.0002) for milli-Q water and 0.0055 (SD=0.0003) for Setcases 1 water).

The limit of detection (LOD) was calculated for signal equal to three times the standard deviation of a solution containing $20 \mu\text{g L}^{-1}$ As (V). An LOD of $4.5 \mu\text{g L}^{-1}$ was obtained. This value is lower than the regulated value from the WHO.

Inter-day repeatability was evaluated at two concentration levels, $20 \mu\text{g L}^{-1}$ ($n = 5$) and $100 \mu\text{g L}^{-1}$ ($n = 3$). The standard deviation (SD) for these measurements is $2 \mu\text{g L}^{-1}$ and $8 \mu\text{g L}^{-1}$, respectively.

3.4. Application to natural water samples

The proposed method was used to analyze natural waters from the Pyrenees region containing arsenic. The results obtained are compared with those obtained with ICP-MS in Table 3. The good agreement obtained shows that As in the water samples is present as As(V) and that the developed method is suitable for As detection.

4. Conclusions

A simple device for arsenic preconcentration based on the use of a 69%(w/w) PVC and 31%(w/w) Aliquat 336 PIM is proposed where the measurement of the preconcentrated As in the stripping solution is done by the molybdenum-blue colorimetric method. The PIM- device is easy to operate and uses a non-toxic stripping reagent (i.e. sodium chloride solution). An LOD of $4.5 \mu\text{g L}^{-1}$ was obtained showing that the proposed method is suitable for the determination of arsenic in ground waters to be used as a source of drinking water. The performance of the PIM-device has been evaluated and very good agreement has been achieved between results obtained by the proposed method and by ICP-MS. Moreover, PIM-device has successfully been used for the analysis of naturally occurring arsenic waters with low conductivity. Considering both the simplicity and the use of non toxic reagents, this new method can be viewed as an attractive alternative to existing methods for As monitoring.

Acknowledgements

Dena Desarrollos S.A. is acknowledged for the financial support of this research.

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Figure captions

Figure 1. Transient concentration curves of inorganic As(V) transport experiments in a two compartment cell, $V_r = 1$. A PIM made of 80% PVC-20% Aliquat 336 (w/w) (a) and 69% PVC-31% Aliquat 336 (w/w) (b) were used. Feed solution: 10 mg L^{-1} inorganic As(V), pH=7; Stripping solution: 0.1 M NaCl.

Figure 2. Transient concentration curves of inorganic As(III) oxidation/transport experiments in a two compartment cell, $V_r = 1$ (PIM: 69% PVC-31% Aliquat 336 (w/w); Feed solution: 10 mg L^{-1} inorganic As(III), pH=7; Stripping solution: 0.1 M NaCl.

Figure 3. Kinetics of As(V) transport using the PIM-device ($V_r = 20$). PIM: 69% PVC-31% Aliquat 336 (w/w); Feed solution: 100 mL of $100 \text{ } \mu\text{g L}^{-1}$ inorganic As(V) at pH=7; Stripping solution: 5 mL 0.1 M NaCl.

Figure 4. Calibration curves obtained with (PIM-device, $V_r = 20$) and without the PIM preconcentration step. PIM: 69% PVC-31% Aliquat 336 (w/w). Feed solution: 100 mL of different inorganic As(V) concentrations in milli-Q water at pH=7; Stripping solution: 5 mL 0.1 M NaCl (SD direct measurement: 0.002 A.U.; SD PIM-device: 0.003 A.U.; $n=4$ in both cases).

Figure 1

(a)

(b)

Figure 2

Figure 3

Figure 4

Table 1. Characteristics of the water samples used for this study. Concentrations are given in mg L⁻¹, except for As, which is in µg L⁻¹. Conductivity is in µS cm⁻¹.

Sample	conductivity	pH	Ca ²⁺	Mg ²⁺	Na ⁺	Cl ⁻	SO ₄ ²⁻
NO ₃ ⁻	HCO ₃ ⁻	As (µg L ⁻¹)*					
Lles 1	164	8.60	10.5	1.1	38.6	2.8	13.6
2.1	140	80					
Lles 2	190	8.66	15.3	2.6	40.1	2.9	12.4
2.3	116	59					
Lles 3	188	7.26	23.5	3.7	32.6	nd	nd
nd	160	48					
Setcases 1	110	7.56	23.6	2.6	3.7	0.9	8.0
3.3	811	nd					
Setcases 2	120	7.55	27.2	2.5	3.1	1.0	15.0
0.7	874	45					
Setcases 3	94	7.78	21.1	2.2	1.9	1.1	4.5
0.8	523	2					
Caldes	3450	7.14	33.1	9.0	>700	570.0	41.0
<LOQ 2040	59						
Tap water	394	7.80	60.2	11.0	23.4	32.0	52.2
8.0	182	2					

nd: not detected

*Determined with ICP-MS under the conditions specified in the text.

Table 2. Effect of water conductivity on arsenic transport efficiency of the PIM-device (described in section 2.3, $V_r = 20$). PIM: 69% PVC-31% Aliquat 336 (w/w).

Water sample	Water conductivity (μS)	[As] initial ($\mu\text{g L}^{-1}$)	[As] stripping ($\mu\text{g L}^{-1}$)	Transport efficiency (%)
Milli-Q*	-	100	1420	71
Girona tap water*	394	116	1750	75
Lles 1	164	70	966	69
Setcases 2	120	55	778	70
Caldes	3450	59	0	0

* spiked samples

Table3. Comparison of As concentration measured by ICP-MS and using the proposed method (PIM: 69% PVC-31% Aliquat 336 (w/w)). The standard deviation is expressed in parentheses.

Sample	Arsenic concentration ($\mu\text{g L}^{-1}$)	
	ICP-MS (n =2)	PIM-based device (n = 3)
Lles 1	80 (1)	72 (3)
Lles 2	59 (1)	63 (5)
Lles 3*	48	42
Setcases 2	45 (1)	58 (5)
Setcases 3	5 (2)	7 (1)

* n = 1

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Title:

A novel low-cost detection method for screening of arsenic in groundwater

Date:

2014-10-01

Citation:

Fontas, C., Vera, R., Batalla, A., Kolev, S. D. & Antico, E. (2014). A novel low-cost detection method for screening of arsenic in groundwater. ENVIRONMENTAL SCIENCE AND POLLUTION RESEARCH, 21 (20), pp.11682-11688. <https://doi.org/10.1007/s11356-014-2917-5>.

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