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The Use of a Polymer Inclusion Membrane for Arsenate Determination in Groundwater

Ruben Vera, Enriqueta Anticó and Clàudia Fontàs *

Department of Chemistry, University of Girona, C/Maria Aurèlia Capmany 69, 17003 Girona, Spain;
ruben.vera@udg.edu (R.V.); enriqueta.antico@udg.edu (E.A.)
* Correspondence: claudia.fontas@udg.edu; Tel.: +34-648426341

Received: 6 July 2018; Accepted: 9 August 2018; Published: 17 August 2018

Abstract: A polymer inclusion membrane (PIM) containing the ionic liquid methyltrioctylammonium chloride (Aliquat 336) as the carrier has been used satisfactorily for the preconcentration of arsenate present in groundwater samples, allowing its determination by a simple colorimetric method. The optimization of different chemical and physical parameters affecting the membrane performance allowed its applicability to be broadened. The transport of As(V) was not affected by the polymer used to make the PIM (cellulose triacetate (CTA) or poly(vinyl chloride) (PVC)) nor the thickness of the membrane. Moreover, the use of a 2 M NaCl solution as a stripping phase was found to allow the effective transport of arsenate despite the presence of other major anions in groundwater. Using the PIM for the analysis of different groundwaters spiked at 100 μg L^{-1} resulted in recoveries from 79% to 124% after only 5 h of contact time. Finally, the validated PIM-based method was successfully applied to the analysis of waters containing naturally occurring arsenate.

Keywords: arsenate; polymer inclusion membranes; Aliquat 336; groundwater

1. Introduction

Arsenic is a well-known pollutant that is present in high levels in soil and water in different countries around the world [1]. The World Health Organization (WHO) has set an upper limit of 10 μg L^{-1} in a guideline for concentrations in drinking water [2]. Due to the high toxicity of arsenic even at low concentrations, it is of paramount importance to perform routine analyses to monitor this pollutant in waters. Of the different separation techniques, functionalized membranes have attracted considerable attention as a valuable technology for many analytical purposes in recent years. This is the case of polymer inclusion membranes (PIMs), which are non-porous functionalized membranes that consist of a polymer, a plasticizer, and an extractant. These membranes are transparent, flexible and stable, and have been used in many applications such as sensing, both ion-selective electrodes (ISE) and optodes, sample pre-treatment (separation and pre-concentration), and electro-driven extraction. PIMs have also been used as passive samplers deploying the membrane device for a 7-day period without reporting any drawback due to membrane fouling [3–5]. With the proper selection of the carrier, these membranes can effectively transport different species, such as inorganic pollutants [5], organic compounds [6] and metallic species [7].

In a previous study [8], a PIM made of cellulose triacetate (CTA) as the polymer and Aliquat 336 as the carrier was used for the transport of arsenate from aqueous natural samples to an 0.1 M NaCl stripping solution. Arsenate was transported through the membrane by the formation of the ion-pair $[(R_3R'N^+)_2HAsO_4{}^{2-}]$, which was released in the stripping compartment by exchanging arsenate with the chloride present in this phase [8]. Under neutral pH conditions, inorganic As(III) transport was negligible since it is mainly present as a neutral species and, thus, the developed PIM allowed the quantitative separation of both inorganic As species. Moreover, it was found that even though other anions present in natural waters were also transported (e.g., chloride, phosphate, nitrate, sulphate and carbonate), As(V) transport efficiency was not hampered. The developed PIM-based separation system was later implemented in a special device, incorporating a PIM made of 69% (*w*/*w*) poly(vinyl chloride) (PVC) as the base polymer and 31% (*w*/*w*) Aliquat 336 as the carrier, which allowed the preconcentration of arsenate, thus providing easy arsenate detection by means of the formation of a blue complex [9]. This method provided a working range from 20 $\mu g L^{-1}$ to 120 $\mu g L^{-1}$ As(V) in ultrapure water, and a limit of detection (LOD) of 4.5 $\mu g L^{-1}$ after 24 h of contact time using 5 mL 0.1 M NaCl as the stripping phase. It was successfully applied in the analysis of different waters from the Pyrenees region with low conductivity values. These two previous works allows us to establish the conditions for the effective transport of inorganic As(V) in a transport cell (without preconcentration) [8], and to apply the membrane system in a PIM-based device to allow As(V) preconcentration and detection with good results after 24 h contact time for water samples bearing low conductivity [9].

In the present study, in order to extend the applicability of this separation system, we have evaluated and optimized the chemical and physical parameters that can affect the PIM-based device, such as membrane composition, stripping phase characteristics, and membrane thickness, in order to accomplish the preconcentration of arsenic species in a more convenient timescale and to broaden the applicability of the method to more complex groundwater (GW) samples.

2. Methods

2.1. Reagents and Solutions

Stock solution (100 mg L^{-1}) of As(V) was prepared from solid Na_2HAsO_4. 7 H_2O purchased from Merck (Darmstadt, Germany). Working solutions of arsenate in ultrapure water and GW were prepared by dilution of the corresponding stock solution. Sodium chloride, obtained from Fluka (Bern, Switzerland), was used to prepare the stripping solution. Calibration standards of arsenic were prepared using the Spectrascan standard solution for atomic spectroscopy (Teknolab, Drшbak, Norway).

The extractant Aliquat 336 and the polymer PVC were purchased from Sigma-Aldrich (Steinheim, Germany) and CTA from Acros Organics (Geel, Belgium). The organic solvents tetrahydrofuran (THF) and chloroform ($CHCl_3$) (Panreac, Castellar del Vallès, Spain) were used to prepare the polymeric films.

Simulated groundwater (SGW) was prepared by dissolving 0.17 g of $NaHCO_3$, 0.22 g of $CaCl_2 \cdot 6H_2O$ (Panreac, Castellar del Vallès, Spain) and 0.07 g of Na_2SO_4 (Merck, Darmstadt, Germany) in 1 L of ultrapure water.

All reagents and solvents were of analytical reagent grade. Ultrapure water from a MilliQ Plus water purification system (Millipore Ibérica S.A., Madrid, Spain) was used to prepare all solutions.

2.2. Colorimetric Detection of As(V)

The determination of As(V) preconcentrated in the stripping phase was performed using the molybdenum blue method, which is based on the formation of an arsenomolybdate complex. The reagent solutions were prepared in accordance with the latest, improved version of the method [10]. Ammonium molybdate was prepared by dissolving 5.2 g of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Scharlau, Barcelona, Spain) and 8.8 mg of potassium antimonyl tartrate, $K(SbO)C_4H_4O_6 \cdot 0.5H_2O$ (Merck, Darmstadt, Germany) in 30 mL of 9 M sulphuric acid and diluted with deionized water to 50 mL in a volumetric flask. A solution 10% (w/v) of ascorbic acid (Panreac, Castellar del Vallès, Spain), which was used as a reductant, was prepared daily. The reagents were added to As(V) samples or standard solutions in accordance with the recommended procedure. To account for the matrix effect, standard solutions were prepared both in ultrapure water and 2 M NaCl.

2.3. Polymer Inclusion Membrane (PIM) Preparation

PIMs were prepared by dissolving either CTA (200 mg) or PVC (400 mg) and the appropriate volume of a 0.5 M Aliquat 336 solution in chloroform or in THF, respectively. The solution was poured into a 9.0 cm diameter flat-bottom glass Petri dish which was set horizontally and covered loosely. The solvent was allowed to evaporate over 24 h at room temperature and the resulting film was then carefully peeled off the bottom of the Petri dish and circular 2.5 cm^2 pieces were cut from its central section and used in the experiments. PIMs of different thicknesses were prepared by reducing proportionally the total mass of polymer and Aliquat 336.

All PIM compositions are given in mass percentages for each component.

2.4. Preconcentration Experiments and Calibration Curve

The schematics and the whole set-up of the PIM-based device used in the preconcentration experiments are described elsewhere [11]. The device incorporates the PIM with an area of 2.5 cm^2 and contains the stripping solution. This device is immersed 1 cm in a vertical position in 100 or 50 mL of a water sample containing arsenic and placed on a magnetic stirrer. After a predetermined contact time, the device was removed from the solution and a selected volume of the stripping solution (usually 2 mL) was taken for the colorimetric analysis.

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

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

where $[As]_{strip(t)}$ denotes the arsenic concentration in the stripping compartment at the end of the contact time, whereas $[As]_{feed(0)}$ is the initial arsenic concentration in the water sample. The volume ratio between the feed solution and stripping solutions is denoted by Vr.

The calibration curve for the preconcentration method was prepared by using the final selected conditions in accordance with the TE results (50 mL of aqueous feed solution, 2.5 mL of 2 M NaCl as the stripping phase and 5 h contact time).

All experiments were conducted at 22 ± 1 °C, and were done per duplicate as minimum. Standard deviation (SD) is shown for each case with the corresponding number of replicates (n).

2.5. Apparatus

A Cary ultraviolet-visible (UV-Vis) (Agilent Technologies, Tokyo, Japan) instrument was used to measure the absorbance of As(V) complex at $\lambda = 845$ nm.

Arsenic concentration in the source solution of two GW samples with naturally occurring arsenic was measured using an inductively coupled plasma optical emission spectroscopy system (Agilent 5100 Vertical Dual View ICP-OES, Agilent Technologies, Tokyo, Japan).

PIM thickness was measured using a Digimatic Micrometer 0–25 mm (Mitutoyo, Takatsu-ku Japan).

The pH and conductivity values were determined with a Crison Model GLP 22 pH meter and Ecoscan, Entech Instruments, portable conductimeter, respectively. A magnetic multistirrer 15 (Fischer Scientific, Hampton, NH, USA) was also used.

2.6. Water Samples

Seven GW samples were collected from different locations in north-east Catalonia (Spain). Table 1 indicates the location of the different sampling spots as well as the main chemical characteristics of the different waters. GW samples 1–5 do not contain As and were used to study the effect of the water matrix by adding arsenate at different concentrations. GW samples 6 and 7 contained naturally occurring arsenic. All waters were used without any treatment (filtration or pH adjustment) except for sample GW7, which was brought to neutral pH by adding HCl.

Table 1. Characteristics and georeferences of the water samples used in this study.

Samples	Georeferences of Sampling Point (Coordinates)	pH	Conductivity (μS cm^{-1})	Ions (mg L^{-1})							Arsenic Concentration (μg L^{-1})
				[NO_3^-]	[Cl^-]	[SO_4^{2-}]	[HCO_3^-]	[Na^+]	[Mg^+]	[Ca^+]	
GW1 (Pujarnol)	42°6′16.907″ N Lat., 2°42′34.64″ E Long.	7.21	684	1.2	15.4	63.9	269	19.0	30.1	96.1	n.f.
GW2 (Mongai)	41°47′59.047″ N Lat., 0°57′38.832″ E Long.	7.76	470	9.5	15	38.3	n.m.	10.8	14.9	68.9	n.f.
GW3 (St. Hilari)	41°53′16.46″ N Lat., 2°31′11.867″ E Long.	7.98	275	21.9	11.4	8.7	172	16.6	9.0	50.0	n.f.
GW4 (Cerdanya)	42°21′16.059″ N Lat., 1°42′17.742″ E Long.	7.5	423	0.3	4.3	2.5	349	11.4	13.2	70.7	n.f.
GW5 (Setcases)	42°22′22.208″ N Lat., 2°18′3.026″ E Long.	7.56	110	3.3	0.9	8.0	88	3.7	2.7	23.6	n.f.
GW6 (Cerdanya)	42°22′16.393″ N Lat., 1°40′41.159″ E Long.	7.5	236	2.2	2.7	12.4	140	n.m.	n.m.	n.m.	67.1
GW7 (Cerdanya)	42°22′12.595″ N Lat., 1°40′54.456″ E Long.	9.69	185	0.4	2.2	11.8	n.m.	n.m.	n.m.	n.m.	70.4
SGW	-	7.5	459	n.a.	71	47.0	123	70.2	n.a.	40.3	n.a.

n.m.: not measured; n.a.: not added; n.f.: not found.

3. Results and Discussion

3.1. Parameters Affecting the Preconcentration System

3.1.1. Stripping Composition

As reported in our previous study [9], As(V) transport through the PIM containing Aliquat 336 is based on an anionic exchange in which the chloride present in the striping phase is the driving force behind the up-hill transport of the arsenate anion. Despite other anions such as sulphate or nitrate also being transported through the PIM, the effectiveness of the system was not affected as long as the total concentration of anions in GW did not exceed the chloride concentration in the stripping solution. However, the applicability of the method was severely hampered in the case of water samples with high conductivity. Thus, to broaden the application of this PIM-based preconcentration system, we tested the use of a 2 M NaCl solution instead of 0.1 M NaCl, maintaining all the other experimental parameters (e.g., PIM: 69% PVC–31% Aliquat 336 (*w*/*w*), time: 24 h, feed volume: 100 mL and stripping volume: 5 mL). The results are presented in Figure 1 as As(V) transport efficiency for both ultrapure water and GW1 and the two stripping solution compositions tested. It is worth mentioning that the conductivity of GW1 (648 µS) is between 2–6 times higher than the conductivity of natural waters studied in our previous work (in the 120–194 µS range) [9]. As can be observed, As(V) transport efficiency is dramatically affected if 0.1 M NaCl is used as the stripping phase, since only 34% of arsenate is transported. TE for GW1 increases up to 70% when the concentration of NaCl in the stripping phase is increased to 2 M. Similar results were observed in the work of Garcia-Rodríguez et al. [12], where the same PIM device was used for the monitoring of sulfamethoxazole (SMX) in natural waters, where a 2 M NaCl solution allowed a more efficient mass transfer across the membrane than an 0.5 M NaCl solution. Hence, a stripping phase consisting of a 2 M NaCl solution was fixed for subsequent experiments.

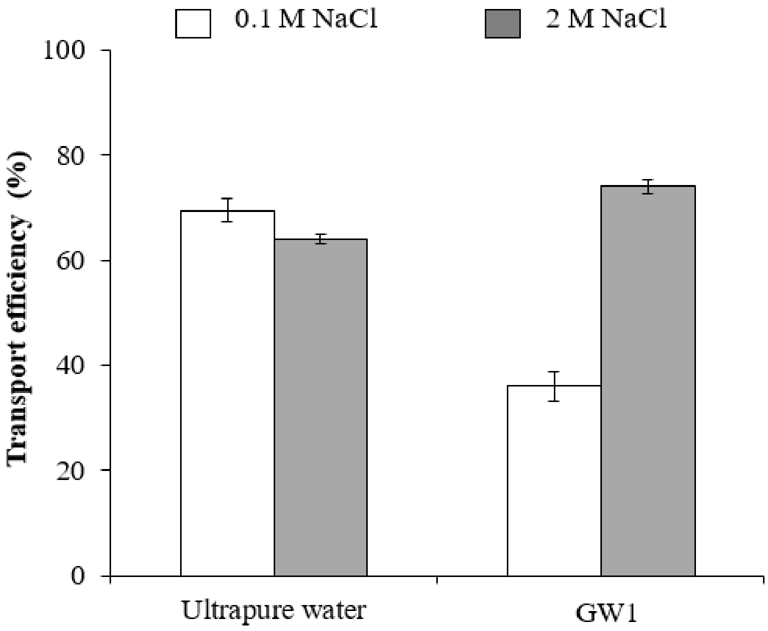

Figure 1. The effect of NaCl concentration used as a stripping solution on As(V) transport in both ultrapure and groundwater GW1 (spiked at 100 µg L^{-1} As(V)). Polymer inclusion membrane (PIM): 69% poly(vinyl chloride) (PVC)–31% Aliquat 336 (*w*/*w*); time: 24 h; feed volume: 100 mL; stripping volume: 5 mL (n = 2).

3.1.2. Contact Time and Sample and Stripping Volume

As(V) transport was assessed by varying the volume of both feed and stripping solutions (volume ratio fixed at 20) and using two different water samples, ultrapure and GW1. As shown in Figure 2, better transport efficiencies are obtained for both water samples tested, when 50 mL volumes for the feed and 2.5 mL for the stripping solution (50/2.5) were used in the PIM-based device system after 24 h contact time.

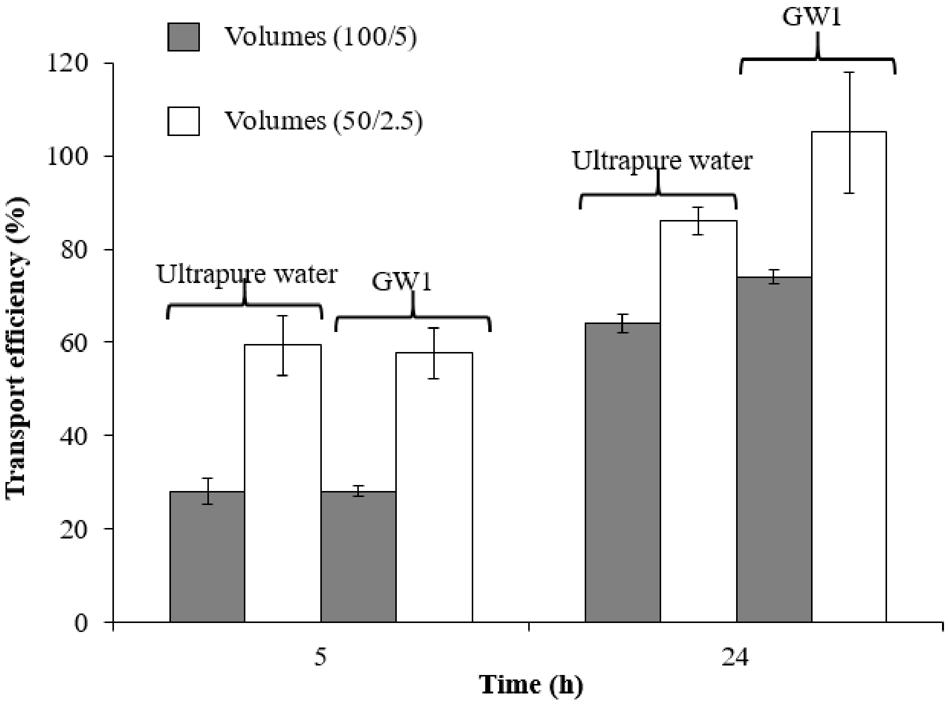

Figure 2. As(V) transport efficiency using a PIM-device with different volumes as feed and stripping solutions in both ultrapure and GW1 (spiked at 100 μg L^{-1} As(V)), after 24 h (a) and 5 h (b) contact time (n = 2). PIM composition was 69% PVC–31% Aliquat 336 (*w*/*w*) and 2 M NaCl was used as the stripping phase.

Moreover, As(V) transport efficiencies at 5 h and 24 h are compared in the same figure. It can be observed that TE are higher when the contact time is 24 h but satisfactory results, around 60% of TE, are also obtained at a time as short as 5 h. In our previous work [9], at a contact time of 5 h and using 0.1 M NaCl as the stripping phase and the 100/5 volumes, the TE obtained was around 20%. Besides, at 5 h contact time, the difference in terms of As(V) transport between the two different water samples is negligible. Therefore, 50/2.5 volumes for feed and stripping solutions and a contact time of 5 h were selected for further experiments.

3.1.3. Membrane Characteristics

As reported by other authors [8,12], transport efficiency can be affected by both the amount of extractant in the PIM and the nature of the polymer. Therefore, various membrane compositions with different thickness were studied in terms of arsenate preconcentration in the stripping phase, after a 5 h contact time. As can be seen in Table 2, there was only slight variation for the different PIM compositions even though different polymers were employed. These results are in concordance with other publications where similar results were obtained with PIMs prepared with the two polymers, CTA and PVC [13,14].

Table 2. Effect of membrane composition and thickness on As(V) preconcentration in the stripping phase (n = 3). Feed composition: 100 µg L^{-1} As(V) in GW1 (50 mL).

Polymer	PIM Composition (*w*/*w*)	Thickness (µm)	[As] Stripping (µg L^{-1}) (± SD)
Poly(vinyl chloride) (PVC)	69% PVC–31% Aliquat 336	60	1160 (± 58)
		30	940 (± 94)
	50% PVC–50% Aliquat 336	96	900 (± 45)
		39	840 (± 53)
Cellulose triacetate (CTA)	70% CTA–30% Aliquat 336	38	880 (± 18)
	52% CTA–48% Aliquat 336	45	1060 (± 85)
		25	940 (± 19)

Additionally, different authors have reported the great influence of PIM thickness when metal transport is rate-limited by the diffusion of the metal across the membrane [15–17]. However, the reduction of the membrane thickness, using the PIM-based device under the selected conditions, did not enhance the As(V) preconcentration, which can be explained by diffusion through the membrane not being the only rate-limiting factor as diffusion in the acceptor solution is also involved [11].

The fact that only slight differences are obtained in terms of arsenate preconcentration using different PIMs composition highlights the great sturdiness of the system under these experimental conditions. PIM with a composition of 52% CTA–48% Aliquat 336 (*w*/*w*) and a thickness of 45 µm was used in further experiments since the amount of reagents necessary to prepare PIMs made of CTA is smaller than PIMs based on PVC.

It should be noted that the preconcentration system provides an arsenate enrichment of around 10 times the initial concentration in the feed solution, which is a clear improvement in facilitating the detection of arsenate in polluted GW samples at low levels.

3.2. Analytical Application of the PIM-device

3.2.1. Effect of Water Matrix

The matrix composition of the calibration standards must be considered for the application of the PIM-based preconcentration system in the determination of As(V) as this is a critical point which can affect the TE and, consequently, the sensitivity of the method. For this reason, different water samples, GW1 to GW5 and SGW, were tested (see Table 1 for composition) under the selected experimental conditions. As(V) transport efficiencies are compared in Table 3, where values ranging from 53% up to 72% for GW1–4 and a value of 81% for GW5 are presented. The highest TE of GW5 is clearly related to the lowest conductivity value, which enables higher arsenate transport across the PIM. Our results support the hypothesis that the accuracy of the method might be compromised by the matrix composition used for the preparation of the calibration standards and the conductivity of the target water sample. As SGW presents an intermediate TE between GW1 and GW5, this is finally selected for the calibration and validation of the PIM-based device method.

Table 3. Comparison of the different GW samples on arsenate transport efficiency with the proposed PIM-based method (n = 2).

Water Sample	Conductivity (µS cm^{-1})	Amount of As(V) Added (µg L^{-1})	TE (%) (± SD)
GW1	684	100	53 (± 8)
GW2	470	100	65 (± 6)
GW3	275	100	72 (± 6)
GW4	423	100	66 (± 23)
GW5	110	100	81 (± 11)
SGW	459	100	63 (± 8)

3.2.2. Analytical Parameters

Under selected conditions, the proposed PIM-based method was applied to standards containing As(V) in the range of 10 µg L^{-1} to 150 µg L^{-1} in SGW. Figure 3 shows the absorbance measured for each standard plotted versus known concentrations of As(V) in the initial feed phase, and a straight line was fitted to measured points by the least-square method. Parameters of the resulting calibration curve are also included in Figure 3. The fact that the regression coefficient was higher than 0.99 indicates a good linearity throughout the studied working range. It is worth mentioning that the LOD of 7 µg L^{-1} is in concordance with the maximum permitted in drinking waters set at 10 µg L^{-1} by the WHO [2], and acceptable relative standard deviation (RSD) values (below 20%) at two different levels (i.e., 10% at 30 µg L^{-1} and 13% at 100 µg L^{-1}) are also obtained.

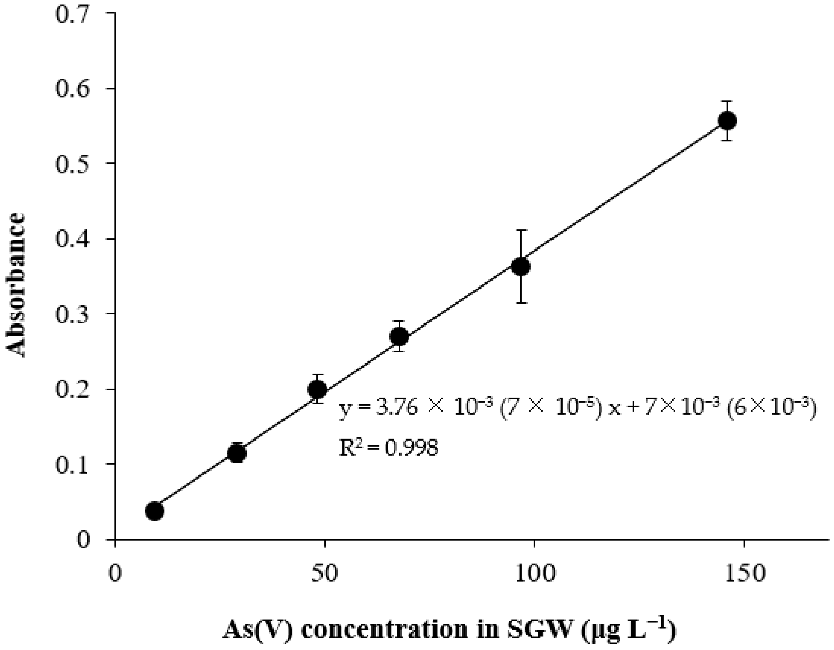

Figure 3. Calibration curve obtained with the PIM-based method. PIM, 52% CTA–48% Aliquat 336 (w/w) (n = 3). Feed solution, 50 mL of different As(V) concentrations in simulated groundwater (SGW); stripping solution 2.5 mL 2 M NaCl.

Recovery values of the proposed PIM-based method were calculated taking into account the calculated As(V) content based on the concentration found in the stripping and using the equation shown in Figure 3, in relation to the spiked level of different GW with 100 µg L^{-1} As(V). The results are collected in Table 4, where it can be seen that recovery values range from 79% up to 124% with the highest recovery corresponding to GW5.

Table 4. Effect of water sample on As(V) recovery (n = 2).

Water Sample	As(V) Recovery (%) (± SD)
GW1	79 (± 13)
GW2	98 (± 10)
GW3	109 (± 9)
GW4	100 (± 35)
GW5	124 (± 17)

All recovery values and standard deviations obtained using our proposed PIM-based device method can be considered satisfactory taking into account the μg L^{-1} concentration level, as reported in the guidelines for standard method performance requirements [18].

3.3. Application to Contaminated Groundwater (GW) Samples

The proposed method was used to analyse two naturally occurring arsenate GW samples from Catalonia (north-east Spain). A comparison between the direct analysis of the water sample by inductively coupled plasma optical emission spectroscopy (ICP-OES) and the proposed PIM-based device method is presented in Table 5. The good agreement shows that the method is suitable for the determination of As(V) in GW samples.

Table 5. As(V) concentration in GW samples determined by the ICP-OES reference method and the proposed PIM-based device method (n = 2).

Water Sample	**As Concentration Measured (μg L^{-1}) (± SD)**	
	ICP-OES	**PIM-Based Device**
GW6	67 (± 2)	82 (± 2)
GW7	70 (± 3)	67.4 (± 0.5)

4. Conclusions

An effective and simple methodology has been proposed employing a device incorporating a PIM made of 52% CTA–48% Aliquat 336 (*w*/*w*) and using the volumes of 50 mL and 2.5 mL for the feed and stripping solutions, respectively. The selection of a 2 M NaCl solution as the stripping phase and 5 h contact time resulted in TE around 53–81%. The type of polymer and the membrane thickness do not seem to influence the transport results under the studied experimental conditions. The use of an SGW as a matrix for the preparation of calibration standards enabled an improvement of the analytical parameters for the determination of As(V) in GWs with different chemical compositions.

The results obtained for the PIM-based method of two GW samples naturally containing As(V) is in concordance with the ICP-OES analysis. Hence, it is demonstrated that the proposed method can be used as an attractive alternative for the determination of arsenate within a range of different aqueous matrices with different conductivities.

Author Contributions: R.V. conducted the experimental work as a Ph.D. student under the supervision of C.F. and E.A., and was the responsible of writing the manuscript. C.F. and E.A. contributed to propose the research, the discussion of the results, data interpretation and the revision of the manuscript.

Funding: This research was funded by the Spanish government through research project CTM2016-78798-C2-2-P (AEI/FEDER/UE).

Acknowledgments: R. Vera acknowledges a grant from the Spanish Ministerio de Economía y Competitividad, ref. BES-2014-068314.

Conflicts of Interest: The authors declare no conflict of interest.

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