

Analytical method development for arsenic monitoring in natural waters based on a polymer inclusion membrane system

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Abstract

A simple detection method for As inorganic species contained in natural waters is described based on the use of a polymer inclusion membrane (PIM) system. The membrane is made of a polymer (cellulose triacetate or polyvinyl chloride) and the ionic liquid Aliquat 336 (A336) as a carrier and it is placed in a special device to allow the transport of As from natural water (at $\mu\text{g L}^{-1}$ levels) to a 2 M NaCl solution. The preconcentration is possible due to the different volume ratio between feed and stripping solutions. Parameters related to PIM composition, effect of volumes, and transport kinetics, among others, has been studied. Finally, the method has successfully been applied to the analysis of different natural waters.

Keywords: Arsenic, polymer inclusion membranes, monitoring, natural waters.

1. Introduction

Arsenic is a well-known pollutant of natural origin, which is present in soil and water in different countries around the world. Its effects on human health due to continuous exposure have been widely reported. The World Health Organization (WHO) has estimated that over 130 million people are potentially exposed to arsenic in drinking water at concentrations above the guideline value of $10 \mu\text{g L}^{-1}$ (WHO 2011). Techniques such as atomic absorption spectroscopy (AAS), inductively coupled plasma-atomic emission spectrometry (ICP-AES) or inductively coupled plasma-mass spectrometry (ICP-MS) are used to measure the low levels of arsenic in waters but they are expensive, require trained personnel and they are not designed for on-site application. Some arsenic detection kits are commercially available but they suffer from interferences and they make use of harmful reagents. Therefore, as an alternative we have developed a device based on polymer inclusion membranes (PIM), which ensures the preconcentration of anionic arsenic species prior to their colorimetric determination as an alternative. Polymer inclusion membranes (PIMs) are a type of non-porous functionalized membranes that consists of a polymer, a plasticizer, and an extractant entrapped within the matrix. PIMs can be easily prepared, they are transparent, flexible, stable, and they have been applied in many fields, including the separation and preconcentration of inorganic

species and organic compounds (Almeida *et al.* 2012). Application of PIMs for arsenic monitoring purposes has been demonstrated by using a home-made device where the sample water is contacted with the membrane containing an anion-exchanger (methyl trioctylammonium chloride, Aliquat 336, A336). The transported species are released in the acceptor compartment inside the device which contains a NaCl solution (Fontàs *et al.* 2014). The driving force for the transport is a gradient of chemical potential of the test compound. The choice of appropriate acceptor composition and volumes of source and acceptor phase make it possible the preconcentration of the analyte for analytical purposes. Then, the concentration of the species found in the acceptor phase is proportional to the total concentration in the donor compartment. In the present work we have evaluated and optimized different parameters of the device design, including membrane composition, stripping phase characteristics, and membrane thickness in order to accomplish the preconcentration of arsenic species in a more convenient time scale and avoiding the matrix effect of the different natural waters.

2. Methods

2.1. Reagents and solutions

Stock solutions (100 mg L^{-1}) of As(V) were prepared from the solids $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Merck) and. Working solutions of arsenic in ultrapure water and well water were prepared by dilution of the corresponding stock solution. Sodium chloride (Fluka) was used to prepare the acceptor solution. 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 (A336), which is a mixture of quaternary alkylammonium chlorides, and the polymers polyvinyl chloride (PVC) and cellulose triacetate (CTA) were purchased from Fluka Chemie. A 0.5 M extractant solution in tetrahydrofuran or chloroform (Panreac, Spain), was used to prepare the polymeric films. For As(V) determination in well waters experiments, the molybdenum blue method was used. The colorimetric reagent solutions were prepared in accordance with the latest and improved version of the method (Fontàs *et al.* 2014). To account for the matrix effect, standard

Table1. Characteristics of the water samples used in this study.

	pH	Conductivity (μS)	[Na ⁺] (mg L^{-1})	[K ⁺] (mg L^{-1})	[Mg ⁺] (mg L^{-1})	[Ca ²⁺] (mg L^{-1})	[NO ₃ ⁻] (mg L^{-1})	[Cl ⁻] (mg L^{-1})	[SO ₄ ²⁻] (mg L^{-1})
Well water 1 (Pujarnol)	8.37	527	19	17	30	96	1.2	15.4	63.9
Well water 2 (Mongai)	7.76	470	10.7	8.4	14.9	68.9	9.5	15	38.3
Well water 3 (St. Hilari)	7.98	275	16.6	5.7	9	50	21.9	11.4	8.67
Well water 4 (Cerdanya)	7.5	423	11.4	7.7	13	71	0.3	4.29	2.53

solutions were prepared in both ultrapure water and 2 M NaCl.

2.2. Polymer inclusion membranes preparation

PIMs were prepared according to the procedure previously described (Fontàs *et al.* 2014). Briefly, 200 mg of CTA or 400 mg of PVC were dissolved in 20 mL CHCl₃ or THF, respectively. Then, the appropriate amount of extractant was added. The 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 2.5 cm² were cut from its central section and used in the experiments. PIMs composition is given in mass percentage of each component.

2.3. Preconcentration experiments

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 cm²). 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 or 50 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 or 2.5 mL) was immersed 1 cm in the sample solution in a vertical position. The water solution was continuously stirred to facilitate the transport. 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 analysis. Arsenic transport efficiency (TE) was determined by using Eq. (1):

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

where $[\text{As}]_{\text{strip}(t)}$ denotes the As concentration in the stripping compartment at the end of the contact time,

whereas $[\text{As}]_{\text{feed}(0)}$ is the initial As concentration in the water sample. The volume ratio between feed solution and stripping solutions is denoted by V_r . Duplicate experiments were performed, at minimum. All experiments were conducted at 22 ± 1 °C.

2.4. Apparatus

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

Arsenic concentration was also measured using a sequential inductively coupled plasma atomic emission spectrometer (ICP-AES) (Liberty RL, Varian, Mulgrave, Vic., Australia).

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

2.4. Water samples

Water samples were collected from different wells in the northeast part of Catalonia (Spain). The samples were analyzed and their concentration and location is depicted in Table 1.

3. Results and discussion

3.1 Effect of stripping composition

As(V) species present at typical pH of natural waters are anionic (mainly H₂AsO₄⁻ and HAsO₄²⁻) and can be extracted by the anion-exchanger A336 by means of the exchange of chloride anion of the extractant by the anionic species of As. For the same reason, a solution rich in chloride anions can revert the extraction reaction and allow the release of As. This is the basis of As transport thought the PIM containing A336. However, since the carrier is not selective, it can interact with all anions present in the sample, and, hence, it is necessary to ensure a chloride concentration high enough to not affect As transport. Thus, in our study, we have tested two different sodium chloride solutions as stripping phase for both ultrapure water and a spiked well water sample. We performed these experiments using a PIM made of 70%PVC-30%A336, based on our previous study (Fontàs *et al.* 2014) and let the experiment run for 24h. The obtained results are presented in Fig.1, where it can be observed that even though there was no significant difference in As(V) transport in

ultrapure water (around 65% efficiency), a 0.1 M NaCl solution only transported 30% of initial As present in well water. However, the increase of the concentration up to 2 M allowed overcoming the possible interferences of other anions contained in water. Thus, a 2 M NaCl solution was fixed as stripping for subsequent experiments.

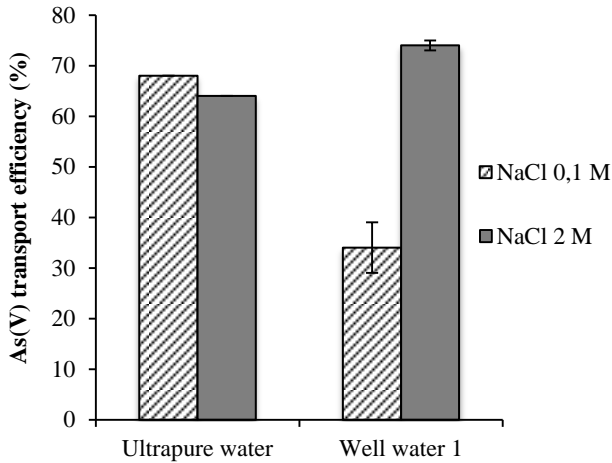


Figure 1. Effect of NaCl concentration used as stripping solution on As(V) transport in both ultrapure and well water (spiked at $100 \mu\text{g L}^{-1}$ As(V)). PIM: 70% PVC-30% A336; time: 24h; feed volume: 100 mL; stripping volume: 5 mL.

3.2 Optimization of experimental conditions for As transport

In order to improve the performance of the preconcentration system different experiments we done with the aim to shorten the length of the experiment. For that, we monitored As transport for experiments varying the volume of both feed and stripping solutions (keeping the volume ratio fixed at 20) and in different water matrix. Results are shown in Fig. 2, where it can be observed that 5 h extraction can be used with satisfactory results in terms of As(V) transport if a volume of 50 mL sample is used and 2.5 mL stripping phase.

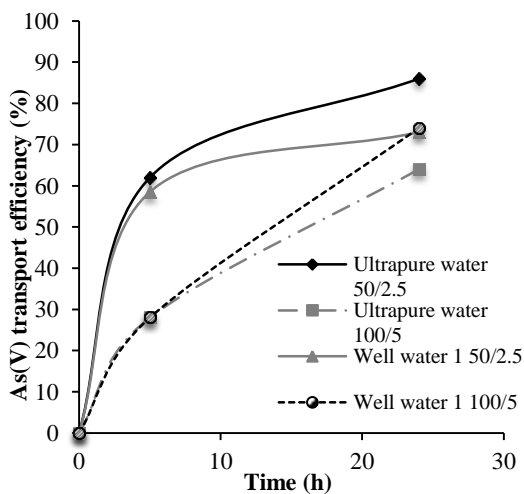


Figure 2. Transient profile of As(V) transport using the PIM device (70%PVC-30%A336) using different volumes of feed and stripping solutions (volume ratio fixed=20) in

both ultrapure and well water (spiked at $100 \mu\text{g L}^{-1}$ As(V)). Stripping solution: 2 M NaCl.

3.3 Effect of PIM composition and thickness

Different PIMs were prepared varying the polymer, A336 content, and membrane thickness. After 5 h of experiment As(V) transported to the stripping phase was determined. When comparing PIMs with the same A336 content but different polymer, it can be seen that no significant differences were found, as presented in Table 2. Surprisingly, membrane thickness did not affect As transport. PIMs from $96 \mu\text{m}$ to $25 \mu\text{m}$ gave similar As transport (about 45%). The following experiments were performed fixing a PIM composition of 50%CTA-50%A336. This membrane was fully characterized and both the homogeneity of the PIM (concerning its preparation) and the reproducibility of the system was investigated by running transport experiments using 3 different PIMs with the same composition and four replicates each PIM ($n=12$). The standard deviation of these different measurements was 2%.

3.4 Application to natural water samples

Finally, the proposed methodology was applied to the detection of As(V) contained at different levels ($30\text{-}100 \mu\text{g L}^{-1}$) in different well water samples (see chemical composition in Table 1). Results are collected in Table 3 in terms of As pre-concentrated in the stripping phase and transport efficiency. As it can be seen, after only 5 h experiment, As(V) was satisfactorily transported and the concentration was high enough to use a simple colorimetric method for its determination.

4. Conclusions

An effective methodology has been proposed using a simple device incorporating a PIM. Only a 5 hours contact of waters containing As(V) at ultra-trace levels with the PIM-device containing 2 M NaCl solution has allow a transport of 50-70% of the pollutant. No matrix effect has been observed for the four different well waters tested, and As has been quantified in the stripping phase by a simple colorimetric method, showing this new method as an attractive possibility to take into account for As monitoring studies.

Table 2. Effect of membrane composition and thickness on As(V) transport efficiency. Time: 5 h; Feed composition: $100 \mu\text{g L}^{-1}$ As(V) in well water 1 (50 mL); Stripping composition: 2 M NaCl (2.5 mL).

Polymer	PIM composition	Thickness (μm)	TE (%)
CTA	50%CTA-50%A336	45	53 ± 2
	70%CTA-30%A336	25	47 ± 2
PVC	50%PVC-50%A336	96	45 ± 5
	70%PVC-30%A336	39	42
	70%PVC-30%A336	60	58 ± 5
		30	47 ± 10

Table 3. As(V) detection in different natural waters by means of the proposed method. PIM: 50%CTA-50%A336; Time: 5h; Feed volume: 50 mL; Stripping composition: 2 M NaCl (2.5 mL).

	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	TE (%)
Well water 1	30	450	65 ± 5
	100	1060	53 ± 2
Well water 2	100	1300	65 ± 6
Well water 3	100	1440	72 ± 6
Well water 4	100	1320	66 ± 23

Acknowledgements

The financial support of the Spanish government through research projects CTM2013-48967-C2-2-P and CTM2016-78798-C2-2-P (AEI/FEDER/UE) is acknowledged. R. Vera acknowledges a grant from the Spanish Ministerio de Economía y Competitividad (ref. BES-2014-068314).

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