



Facilitating inorganic arsenic speciation and quantification in waters: Polymer inclusion membrane preconcentration and X-ray fluorescence detection

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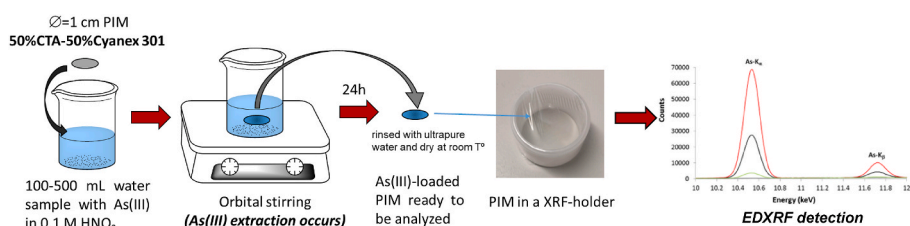
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HIGHLIGHTS

- A PIM composed of 50 % CTA and 50 % Cyanex 301 selectively extracts As(III).
- As(III) is extracted into a PIM and analyzed via EDXRF spectrometry.
- As(V) is reduced to As(III) using a $\text{Na}_2\text{SO}_3 + \text{KI}$ solution prior to extraction.
- The LOD of the combined PIM extraction and EDXRF analysis is $0.6 \mu\text{g L}^{-1}$.
- Successful As speciation in As-contaminated waters is achieved.

GRAPHICAL ABSTRACT



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ABSTRACT

Background: Arsenic, classified as a priority pollutant and human carcinogen by the IARC, is subject to stringent regulatory limits in food and water. Among various arsenic species found in water samples, arsenite (As(III)) is identified as the most toxic form. Given the limitations of conventional spectroscopic techniques in speciation analysis, there is a crucial need for innovative and sustainable methodologies that enable arsenic speciation. Simplifying these methodologies is essential for widespread applicability and effective environmental monitoring.

Results: This study proposes a simple and cost-effective analytical methodology for speciating inorganic arsenic in water samples. The method involves extracting As(III) into a polymer inclusion membrane (PIM) containing the extractant Cyanex 301 (bis(2,4,4-trimethylpentyl) dithiophosphinic acid), followed by analysis using energy dispersive X-ray fluorescence (EDXRF) spectrometry. The concentration of arsenate was measured after a reduction step using a thiosulfate/iodide mixture. This simple methodology allows a limit of quantification for trivalent arsenic ($2 \mu\text{g L}^{-1}$), which is well below the World Health Organization's recommended maximum permissible level of As in drinking water ($10 \mu\text{g L}^{-1}$). The method that is developed allows the determination of As at trace levels in waters with naturally occurring arsenic.

Significance and novelty: This study represents a significant advance in the field, providing a novel and efficient methodology for arsenic speciation analysis in water samples. By combining the advantages of polymer inclusion membrane (PIM) extraction with energy dispersive X-ray fluorescence (EDXRF) spectrometry, this study offers a cost-effective and environmentally friendly approach to address the critical issue of arsenic contamination in water sources, thereby contributing to enhanced environmental monitoring and public health protection.

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1. Introduction

Arsenic exists in various forms in the environment, originating from both natural processes, including weathering and leaching of volcanic rocks, minerals, and geothermal waters, as well as industrial activities such as fossil fuel processing and mining operations, with gold exploration being particularly noteworthy [1,2]. Arsenic in water can be found in different chemical species, with the specific composition being influenced by factors such as pH, redox potential, and environmental conditions [3]. The inorganic arsenic species, arsenite (As(III)) and arsenate (As(V)), are widely recognized as being more toxic than their organic counterparts, such as monomethylarsenate (MMA) and dimethylarsenate (DMA). Moreover, among the inorganic forms, arsenite is notably more soluble, mobile, and, consequently, more toxic than arsenate [4]. Recognized as a priority pollutant by regulatory agencies such as the EPA and classified as a human carcinogen by the IARC [5], arsenic is subject to strict regulatory limits in food and water [6]. Therefore, trace-level speciation analysis is crucial for assessing potential arsenic toxicity and meeting regulatory standards.

The determination of trace levels of As in water samples can be done with instrumental techniques, including inductively coupled plasma-mass spectrometry (ICP-MS) [7] and atomic absorption spectroscopy with hydride generation (HG-AAS) [8]. However, direct determination can be limited by insufficient sensitivity and potential interference from the sample matrix and, furthermore, atomic spectroscopy is not suitable for direct speciation analysis of As. The instrumentation necessary for As speciation analysis is complex and costly and is based on hyphenated techniques such as HPLC-ICP-MS [9].

To enhance the analysis and speciation of As, there is a pressing need for the development of efficient and environmentally friendly methods for arsenic extraction and determination that are in line with Green Chemistry principles [10,11]. This is the case of microextraction procedures [12–14], which require fewer reagents but may pose challenges in handling. In contrast, polymer inclusion membranes (PIMs), a subtype of functionalized membranes, offer significant advantages, such as simplicity, cost-effectiveness, and customization for specific analytes. PIMs consist of an extractant, which interacts with the target analyte, and a polymer, that forms a film that is easy to handle and use [15–17]. The extractants used in PIMs are derived from conventional liquid-liquid extraction techniques. However, these techniques have drawbacks, including the cost and toxicity of the reagents, as well as the use of high toxicity solvents and flammable substances [18]. Therefore, PIMs offer a greener alternative by reducing the quantity of reagents required and providing unique capabilities for both preconcentration and speciation.

In our research group, we have successfully developed PIMs made of cellulose triacetate (CTA) as the polymer and Aliquat 336 as the extractant for the preconcentration of As(V) in different water samples [19–21]. Aliquat 336 is a quaternary ammonium salt that is capable of interacting with anionic species through the formation of an ion pair that can be extracted into the membrane. This mechanism is particularly suitable for As(V), as it predominantly exists in anionic forms over a wide pH range, including the pH of natural water. In contrast, for As(III), the predominant species in the same pH range is the neutral species H_3AsO_3 , which makes it unable to be extracted. The same PIM is used in a study [22] for the separation of As(III) and As(V) through the extraction of the latter prior to analysis by AAS. In all these studies, the quantity of As(III) is determined by the difference between the total As and the As(V) transported with the membrane.

However, unlike As(V), As(III) can interact with thiol groups by forming an As(III)-thiolate bond [23]. This strong affinity of arsenite for thiol-ligands can be utilized to selectively extract and separate it from As(V). This principle underlies the use of Cyanex 301 (bis(2,4,4-trimethylpentyl)dithiophosphinic acid) for extracting As(III). In their study, Gupta et al. [24] demonstrated that Cyanex 301 exhibited a high extraction capacity for As(III) in acidic media, while As(V) was not extracted. It was suggested that the extractant acted as a solvating

molecule, forming the extracted species AsO^+Cl^- -Cyanex 301 in HCl medium. Similarly, Iberhan et al. [25] reported effective extraction of As(III) using Cyanex 301 in sulfuric acid media in solvent extraction experiments.

Cyanex 301 has been effectively incorporated into PIMs and extensively investigated for the transport of metals such as La(III), Ce(III) [26], and Am(III) [27] or base metals [28]. However, there is currently a lack of research on PIMs focusing on the extraction of As(III). Therefore, this study presents a novel investigation as we assess, for the first time, the incorporation of Cyanex 301 extractant into a PIM for the selective extraction of As(III).

Moreover, in order to avoid the elution of arsenic from the loaded membrane, which is a mandatory step when the analysis is done by the aforementioned atomic spectroscopy techniques, we have investigated the possibility of directly determining arsenic species by energy dispersive X-ray fluorescence (EDXRF) spectrometry after membrane preconcentration procedure. Even though EDXRF is not widely used for the detection of pollutants in natural water samples, because of its low sensitivity for the analysis of liquids, it can be successfully used in combination with a suitable preconcentration procedure [29]. Considering that EDXRF operates best on solid samples, and gives optimal sensitivity and accuracy for thin and homogeneous targets, preconcentration procedures leading to solid thin targets are ideal for use in combination with this technique.

Therefore, the combination of PIM preconcentration and XRF detection results in a more sustainable, simpler, and potentially more efficient analytical approach. This methodology has successfully been used in previous studies in the detection of Hg [30] and Cr(VI) [31], among others. In the case of As, determination and speciation studies using EDXRF spectrometry have successfully been achieved by the preconcentration of As(V) in a mixed-matrix membrane incorporating metal organic frameworks (MOF) [32], or multiwalled carbon nanotubes impregnated with Aliquat 336 [33]. Nakamura and co-workers developed a method based on the use of XRF after in situ preconcentration of As through a hydrophilic polytetrafluoroethylene filter placed on a Zr and Ca loaded cation-exchange disk. However, it was necessary to form As(III)-pyrrolidine dithiocarbamate complex to ensure its retention [34].

The present study aims to develop a more environmentally sustainable method for the extraction of As(III) and As speciation studies in natural waters using a PIM preconcentration and direct determination through EDXRF.

2. Experimental section

2.1. Reagents and solutions

As(III) and As(V) stock solutions (150 mg L^{-1}) were prepared by weighing the corresponding amounts of NaAsO_2 (Fluka, Germany) and $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Merck, Germany). Working solutions were prepared by dilution of stocks in 0.1 mol L^{-1} nitric acid (Panreac, Spain). Sodium thiosulfate and potassium iodide (Panreac, Spain) were used for the preparation of 1 % (w/v) and 0.5 % (w/v) solutions, respectively, which were both employed for the As(V) reduction. Calibration standards of As were prepared by dilution of a 1000 mg L^{-1} commercial As stock ICP solution purchased from Sigma Aldrich.

Cellulose triacetate purchased from Fluka (Germany) was used to prepare the polymer inclusion membrane, and it was dissolved in chloroform. The extractant Cyanex 301 (bis(2,4,4-trimethylpentyl)dithiophosphinic acid) was kindly supplied by Cytec (New Jersey, USA) and was used as received.

2.2. Polymer inclusion membrane preparation

Membranes were prepared by the solvent casting method using 200 mg of CTA and the same amount of Cyanex 301 to have PIMs with a

composition 50 % CTA-50 % Cyanex 301 (mass, %) following the procedure described in Ref. [30].

The resulting PIM is shown in Fig. 1(a), while Fig. 1(b) shows the SEM image of the membrane's cross section. As can be observed, membranes are dense, with a homogeneous structure, transparent and without pores.

2.3. Evaluation of the ability of PIMs to extract As

Preliminary extraction experiments were performed in order to evaluate the ability of PIMs to extract arsenic. The experiments were carried out at ambient temperature of 22 ± 1 °C using a PIM 50 % CTA-50 % Cyanex 301 with an area of 4 cm^2 put in contact with 25 mL of 10 mg L^{-1} As(III) or As(V) in 0.1 mol L^{-1} HNO_3 and orbitally stirred for the desired time. This procedure was also applied to natural water samples (well water and mineral water) spiked with 10 mg L^{-1} of As(III) at $\text{pH} = 1$ (0.1 mol L^{-1} HNO_3). Arsenic content in the liquid sample before and after the extraction process was measured by means of ICP-OES. The extraction efficiency was calculated as:

$$\text{Extraction Efficiency (\%)} = \frac{[\text{As}]_i - [\text{As}]_f}{[\text{As}]_i} \times 100 \quad (1)$$

Where $[\text{As}]_i$ and $[\text{As}]_f$ are the initial and final concentrations of arsenic in the aqueous solution before and after the extraction, respectively.

2.4. As-PIM preconcentration and analysis

In order to achieve a higher amount of As per area of membrane, a smaller area of the PIM (circular segments of 1 cm diameter) was used. Membranes were put in contact with different volumes (100–500 mL) of aqueous solutions containing from 1 to $100 \text{ } \mu\text{g L}^{-1}$ of As(III) at $\text{pH} = 1$ (HNO_3) through orbital stirring for 24h. During this step, trivalent As was extracted into the membrane. Subsequently, the membranes were removed from the solution, rinsed with ultrapure water, and allowed to dry at room temperature.

These membranes were ready to be measured by XRF spectrometry without any further treatment (following the conditions described in section 2.8). Fig. 2 shows the schematic diagram of the described methodology.

2.5. Studies into As(V) reduction

Two different solutions were tested to reduce As(V) to As(III): 1 % (w/v) sodium thiosulfate and 0.5 % (w/v) potassium iodide. In both cases, 1 mL of the target reducing solution was added to 100 mL of an aqueous standard containing $200 \text{ } \mu\text{g L}^{-1}$ of As(V) at $\text{pH} = 1$. After 30 min, the PIM was added, and the extraction process was performed following the procedure described in section 2.4.

2.6. Speciation studies

Speciation studies were carried out using solutions containing mixtures of As (III) and As (V) at different concentration ratios. Two different experimental approaches were used, which are represented in Fig. 3. In Method 1, the aqueous sample was divided into two beakers. In the first one, a PIM was added to extract only arsenic in the trivalent form. In the second one, the extraction was carried out after a reduction step and it allowed the determination of the total arsenic present in the solution (As(III) + As(V)). The amount of As(V) was calculated as the difference between the total arsenic and the As(III) concentration. In Method 2, the experiment was conducted in the same beaker. First, a PIM was added to extract As (III). After 24 h, the membrane was removed, the reducing agent was added, and a second membrane was inserted in order to perform the extraction of As (V).

2.7. Application to natural waters containing arsenic: analysis of real samples

The developed analytical method was initially validated using natural water samples without arsenic, which were spiked. These samples included mineral waters as well as a well water sample from Pujarnol (Girona, Spain). Moreover, the methodology was used for the detection and quantification of As species in two different natural waters with naturally occurring As: the spring water of Caldes de Malavella (Girona, Spain) and the groundwater of Lles de Cerdanya (Cerdanya, Spain). Caldes de Malavella is a town that is rich in springs, located between the Pyrenees and the Costa Brava in the province of Girona, in Catalonia. This water presents a pH of 7.3 and a high conductivity of $3500 \text{ } \mu\text{S cm}^{-1}$, with a high contribution of sodium, chloride and hydrogen carbonate ions. Lles de Cerdanya is a Pyrenean village in the province of Girona. In this case, the pH is 8.6 and the conductivity is $190 \text{ } \mu\text{S cm}^{-1}$.

2.8. PIM analysis by EDXRF

For EDXRF measurements, PIMs were arranged between two $4.0 \text{ } \mu\text{m}$ thick prolene X-ray foils (purchased from Chemplex Industries, Inc., Palm City, US) placed in Teflon cups of 3.4 cm, which incorporate a snap-on ring at the end of the cells for the attachment of thin-film supports. A boric acid pellet with a height of 1.5 cm was placed on the top of the cell as a back stopper. Then, samples were introduced into the sample holder of the equipment for EDXRF analysis.

A touch-control S2 RANGER EDXRF system (Bruker AXS, GmbH, Germany) with a Pd X-ray tube (max. power of 50 W) and an XFLASH™ Silicon Drift Detector (SDD) with a resolution of 129 eV at Mn- K_{α} was used. The instrument, which is equipped with nine primary filters that can be selected to improve measuring conditions for elements of interest, can operate under vacuum conditions. An additional advantage of this instrument is the low operating cost given that it does not require cooling media to function. Detailed information about the specific features of the S2 RANGER spectrometer can be found elsewhere [35].

For As determination in the membranes, the X-ray tube was set at 40

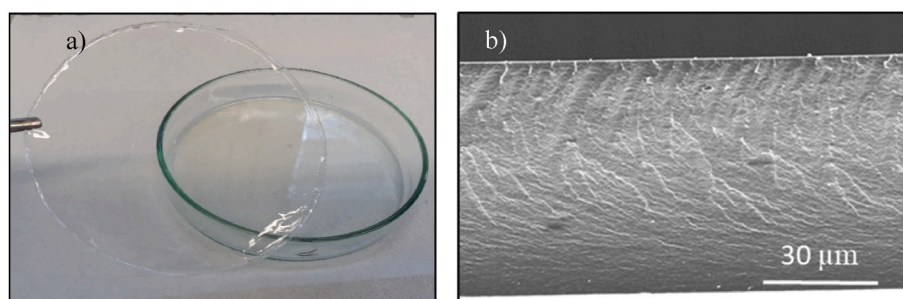


Fig. 1. (a) PIM made by 50 % CTA-50 % Cyanex 301; (b) SEM cross section.

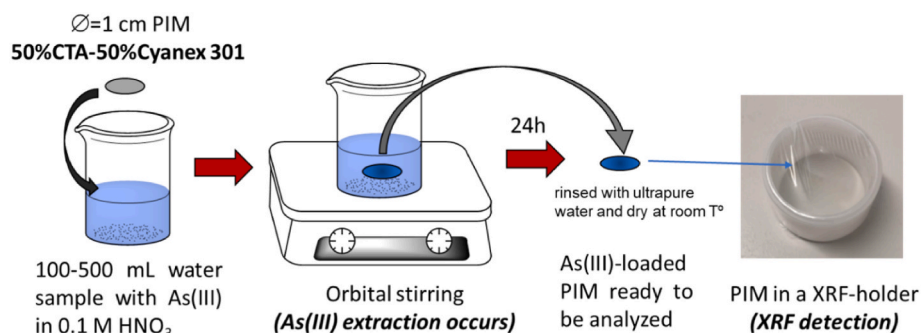


Fig. 2. Schematic representation of As(III)-PIM extraction for further XRF analysis.

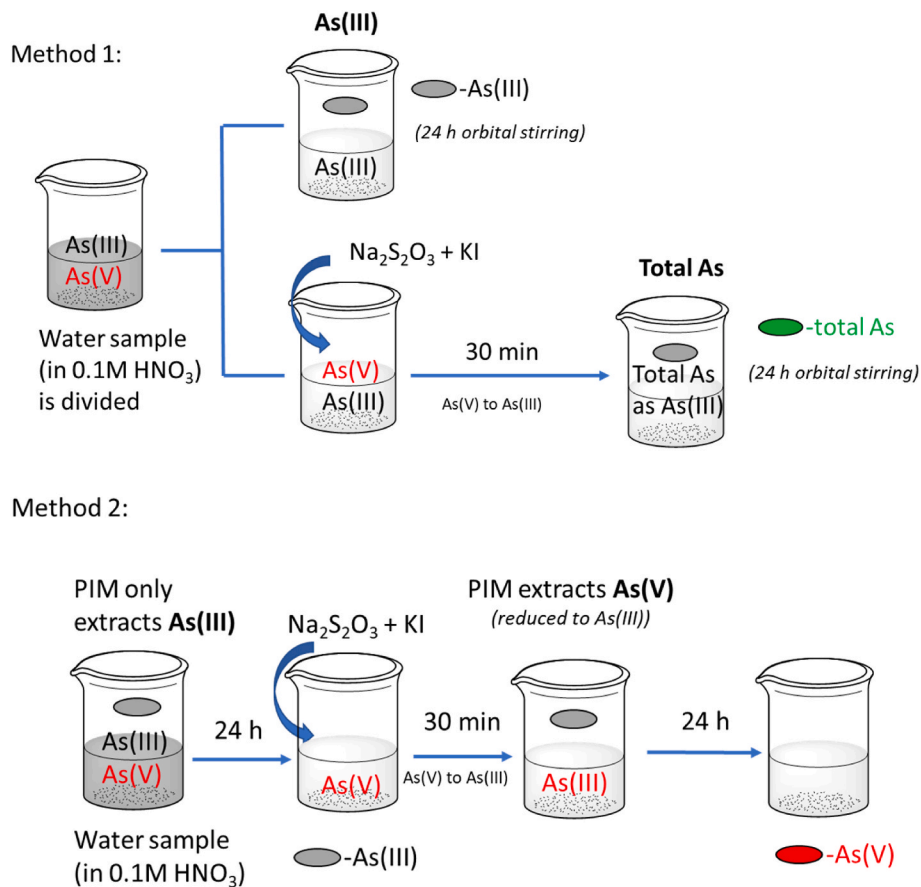


Fig. 3. Schematic representation of Method 1 and Method 2 for As speciation studies.

kV and the intensity was adjusted to 250 μA to obtain a maximum count rate of 100 kcounts/s. In order to get the best signal-to-noise ratio and the best analytical response for As measurement, an Al foil of 500 μm thickness was employed as a primary filter. In an earlier study, we demonstrated the suitability of this primary filter to improve analytical performance for elements with energy emission lines of up to 10–12 keV (As- K_{α} : 10.551 KeV) [36]. The measurement time was set at 200s as a trade-off between an acceptable repeatability of measurements and the total analysis time.

2.9. Instruments

The total content of As in waters and extraction studies was determined by an inductively coupled plasma optical emission spectroscopy spectrometer system (Agilent Technologies, Agilent 5100 Vertical Dual View ICP-OES, Agilent Technologies, Japan) at $\lambda = 193.696$ nm.

A scanning electron microscope (SEM) from (Zeiss DSM 960 Germany) was used to acquire cross section images of the PIMs.

3. Results and discussion

3.1. Evaluation of a PIM containing Cyanex 301 as a sorbent for As extraction

First, the ability of the PIM to extract As(III) and/or As(V) was investigated using a 10 mg L^{-1} solution of each species in 0.1 M HNO_3 in contact with the PIM for 24 h. The analysis of the solution after the extraction process revealed a quantitative extraction of As(III), while As(V) was not extracted. These results agree with those on solvent extraction of As using Cyanex 301 [24,25], where only arsenite was extracted.

To assess the feasibility of extraction from natural waters, we

investigated the effect of a water matrix using both well water and mineral water with 10 mg L^{-1} As(III) and pH 1 (with HNO_3). Different experiments were run and the extraction efficiency was calculated after 3, 6 and 24 h of contact. The results are shown in Fig. 4 next to the extraction of As(III) in ultrapure water and 0.1 M HNO_3 for comparison purposes. The extraction was successful in all water matrices, although extraction efficiency was slightly lower in natural waters at 3 and 6 h compared to ultrapure water. After 24 h, however, As(III) was quantitatively extracted in all samples, demonstrating that, despite the presence of other ions in natural waters, the PIM is effective for application in such waters. Therefore, a contact time of 24 h was chosen for future experiments. The extraction of As(III) from well water samples was also tested at pH 0, pH 2 (adjusted with nitric acid) and the natural pH of 8.37 of this water. Results for the two acidic solutions showed similar trends to those at pH 1 (0.1 M HNO_3). However, extraction efficiency decreased to 30 % at the natural water pH. Thus, subsequent experiments were conducted at pH 1 (0.1 M HNO_3).

3.2. Testing the ability of PIMs to perform As determination by EDXRF

After confirming the efficiency of the PIM containing Cyanex 301 as a sorbent for As(III) extraction in aqueous samples, the potential to use this analytical approach in combination with EDXRF detection was tested. In order to enhance the preconcentration of As on the membrane, smaller segments of the membrane were used (circular pieces of PIM with a diameter of 1 cm) with larger sample volumes, typically 500 mL. The first experiment was conducted by contacting the membrane with both 500 mL 0.1 M nitric acid (blank) and the same volume of a solution of $100 \text{ } \mu\text{g L}^{-1}$ of As(III) in 0.1 M HNO_3 . After 24 h in agitation, the membranes were withdrawn, rinsed with ultrapure water, and left to dry at room temperature prior to their analysis. The resulting EDXRF spectra are shown in Fig. 5. As can be seen in both spectra, there are appreciable peaks of P and S from the organothiophosphorus extractant Cyanex 301 used, confirming the effective incorporation of this compound into the PIM matrix. In addition, other peaks appear in the resulting spectra, including some from the elastic and inelastic scattering of the primary Pd X-ray source and small peaks of Fe, Cu and Zn that can presumably be attributed to the instrument components themselves. Nevertheless, as can be seen in the region where As- K_{α} is placed, there are no spectral overlaps and the As peak can be properly fitted in the PIM contacted with a solution containing $100 \text{ } \mu\text{g L}^{-1}$ of As(III). The analytical response obtained to As was so high that it suggested the potential sensitivity of the proposed method for the determination of low amounts of As.

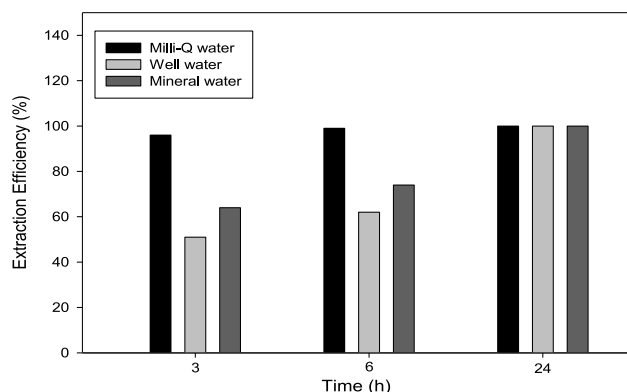


Fig. 4. As(III) extraction efficiency vs time. Experimental conditions: 25 mL of a 10 mg L^{-1} As (III) solution in 0.1 M HNO_3 , PIM composition: 50 % CTA- 50 % Cyanex 301.

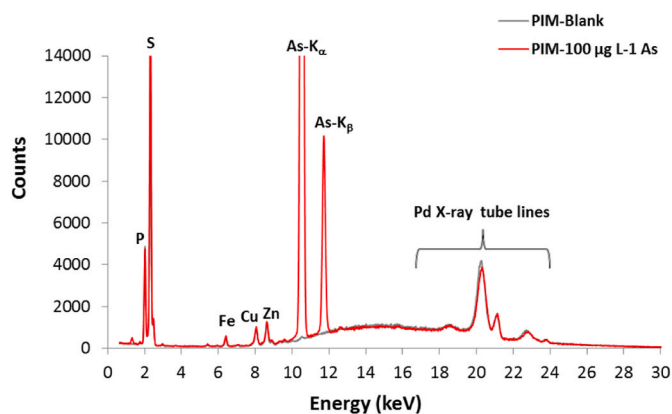


Fig. 5. EDXRF spectra for the analysis of PIMs contacted (during 24h) with 0.1 M nitric acid (blank) and with an aqueous solution containing $100 \text{ } \mu\text{g L}^{-1}$ of As (III).

To further explore this possibility, the same methodology was used to extract lower concentrations of As (10 and $50 \text{ } \mu\text{g L}^{-1}$ As-arsenite). As shown in Fig. 6, even for the lowest concentration investigated, the As peak is clearly detected. Moreover, the results obtained indicate that there is a significant relationship between the As peak area obtained for each membrane and the initial As(III) content in the aqueous solution, which could be further tested as a calibration approach for quantitative analysis.

3.3. Analytical figures of merit of the developed method

Once the best experimental conditions for the extraction and determination of arsenic had been established, analytical figures of merit for the combined methodology were taken into account. Firstly, the possibility of obtaining a calibration curve was investigated using 500 mL of aqueous solutions with As(III) concentrations in the range of 1 – $150 \text{ } \mu\text{g L}^{-1}$. These water samples were taken throughout the whole proposed methodology (as detailed in Fig. 2) and were measured by EDXRF. It is important to point out that in this case it was not necessary to correct either the matrix or the thickness, unlike what is commonly the case in EDXRF analysis of solid samples. In this case, due to the organic nature of the PIM matrix, the attenuation of the incident primary and emergent secondary spectral line radiation is almost negligible and, therefore, the As intensity is proportional to its concentration. Thus, by plotting the intensities of the analytical line (As- K_{α}) of As-loaded PIM versus the corresponding concentration of As in aqueous solutions, a calibration curve was obtained ($y = 3.4595x - 1.7231$) with a determination coefficient of 0.998.

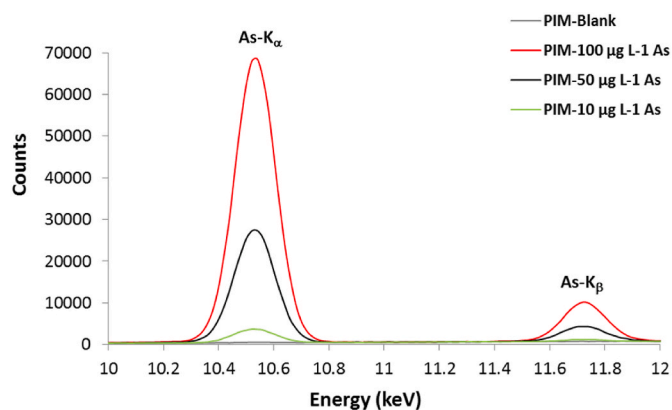


Fig. 6. EDXRF spectra of PIMs contacted with aqueous solutions containing different As (III) concentration levels.

The detection limit (LOD) of the methodology was determined by analyzing a PIM exposed to a $20 \mu\text{g L}^{-1}$ As(III) aqueous solution at acidic pH, applying the 3σ criterion (three times the square root of the spectrum background [37]). This yielded a minimum detectable concentration of $0.6 \mu\text{g L}^{-1}$. The limit of quantitation (LOQ) was calculated as 3.3 times the LOD, resulting in $2 \mu\text{g L}^{-1}$. Given that the legal limit for arsenic in drinking water is $10 \mu\text{g L}^{-1}$, the proposed methodology is well-suited for compliance with regulatory standards.

Moreover, as shown in Table 1, the LOD and linear range for As determination using the PIM-EDXRF approach are comparable to, or better than, those achieved with other XRF methods for As speciation, including high-power WDXRF systems [33,37,38]. It is also noteworthy that using PIM as an extraction method simplifies the sample preparation stage compared to other published analytical strategies (see Table 1).

Moreover, the precision of the PIM-EDXRF method was investigated at two levels of As(III) concentration: $10 \mu\text{g L}^{-1}$ and $100 \mu\text{g L}^{-1}$. In both cases, the volume of the sample was 500 mL and extraction experiments were done in quintuplicate. The overall precision obtained was good, showing RSD values of 5.60 % and 5.77 % for $10 \mu\text{g L}^{-1}$ and $100 \mu\text{g L}^{-1}$, respectively.

3.4. As(V) determination

As stated in section 3.1, As(III) is the only species extracted by the PIM. Therefore, the determination of As(V) to both performing As speciation studies and As(V) quantification requires a preliminary step to reduce As(V) to As(III), followed by the determination of this last species. Among the different reducing agents that have been used for the reduction of As(V), sodium thiosulfate is generally used since it allows for fast and complete reduction at room temperature, and the subsequent determination of As(III) can be carried out in the presence of the excess thiosulfate [41,42]. Gupta et al. used this reagent to reduce As(V) to As(III) prior to its extraction by Cyanex 301 [24]. Additionally, some studies have utilized a combination of sodium thiosulfate and potassium iodide as reducing agents. For instance, in Ref. [43], 1 mL of 1 % (w/v) sodium thiosulfate and 1 mL of 0.5 % (w/v) potassium iodide were added to an As(V) solution to pre-reduce arsenic(V) to arsenic(III) prior to the coprecipitation procedure using a nickel-pyrrolidine dithiocarbamate complex.

Therefore, in our study, we evaluated both 1 % (w/v) thiosulfate (TS), and the mixture of thiosulfate/iodide (TS + KI) (1 %: 0.5 %, w/v) to reduce As(V) to As(III), to then be able to extract this species by the

Table 1

Recent published methods based on the use of preconcentration and XRF detection for inorganic As speciation in water samples.

Sample preparation	XRF system	LOD ($\mu\text{g L}^{-1}$)	Linear range ($\mu\text{g L}^{-1}$)	Water type	Ref.
SPE + pellet preparation	WDXRF (4 kV)	0.23	10–100	Spiked drinking water	[38]
Formation of As-APDC complex + SPE	WDXRF (4 kV)	2	10–100	Well water samples	[39]
SPE disk (Ti Zr-CD)	WDXRF (4 kV)	0.8	10–100	Well water samples	[34]
DMSPE using $\text{Al}_2\text{O}_3/\text{GO}$ nanocomposite	EDXRF (9W)	0.02	2–50	Mineral, tap water	[40]
3 phase-HF-LPME	TXRF (50 W)	0.03	0.5–200	Spiked mineral, tap and ground water	[12]

SPE: solid phase extraction, APDC: ammonium pyrrolidinedithiocarbamate, DMSPE: dispersive micro solid phase extraction, GO: graphene oxide, HF-LPME: hollow fibre liquid phase microextraction.

PIM. The concentration of arsenate can then be estimated as the difference between the total As concentration (resulting from As extraction after the reduction step), and initial As(III), using the extraction methodology directly in the water sample (as described in Fig. 2).

All experiments were performed using 100 mL of a $200 \mu\text{g L}^{-1}$ As(V) aqueous solution at pH = 1, adding 1 mL of the reducing solution (TS or TS + KI). After the extraction process, the membranes were analyzed by EDXRF. Fig. 7 shows the effect of the reducing agent on As(V) determination in terms of the sensitivity of the signal obtained when analysing the PIM after the extraction. For comparison purposes, results obtained for the determination of As(III) and As(V) in solutions at the same concentration levels, but without applying the reduction step, are also displayed.

As can be observed, both reducing agents tested effectively reduced As(V). However, the thiosulfate/iodide mixture demonstrated slightly better performance. Therefore, this mixture was selected for subsequent pre-reductions.

3.5. Speciation studies

After confirming the feasibility of reducing As(V) to As(III), speciation investigations were conducted to determine the potential presence of As(V) in natural water samples using PIM extraction and EDXRF detection. For this purpose, an aqueous solution containing $20 \mu\text{g L}^{-1}$ As(III) and $100 \mu\text{g L}^{-1}$ As(V) in ultrapure water at pH = 1 was prepared. Two different experimental approaches were tested. Method 1 (see Fig. 3, top) involved the use of two aliquots of the sample, while in Method 2 (see Fig. 3 bottom), the detection was done in the same aliquot of sample. In Fig. 8, a comparison of the results obtained from the two methods is presented. Arsenic concentrations were determined from the radiation intensity value of As and by means of the corresponding calibration curve (section 3.3).

As shown, no significant differences were observed between the results obtained. Therefore, Method 2 was selected for further experiments due to its simplicity and the reduced sample volume required.

Given the potential variation in As(III)/As(V) concentration ratios across different water samples, we investigated the effect of As(V) concentration on As(III) determination using the developed methodology. To do this, several aqueous standards and spiked mineral water samples containing different concentration ratios of As(III) and As(V) species were prepared and analyzed using the PIM-EDXRF method. The results obtained (see Table 2) indicate that inorganic speciation at trace levels is possible independently of the As(III)/As(V) ratio present in the aqueous sample. Moreover, recovery values of around 100 % were

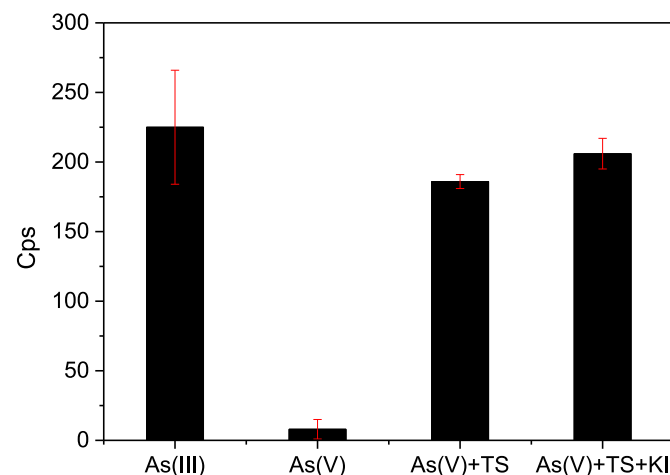


Fig. 7. Effect of the reducing agent on As(V) reduction (see experimental details in the main text). TS: thiosulfate, TS + KI: mixture of thiosulfate/iodide (n = 3).

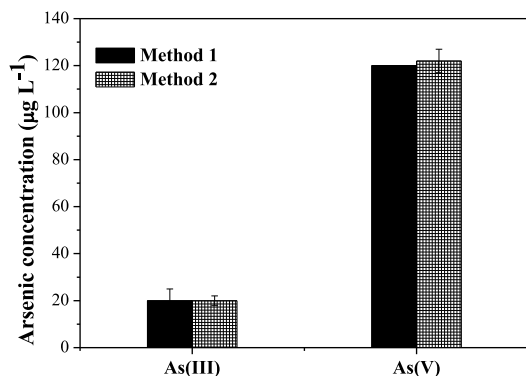


Fig. 8. Results obtained for As determination in a mixture of 20 $\mu\text{g L}^{-1}$ As (III) and 100 $\mu\text{g L}^{-1}$ As (V) in ultrapure water at pH = 1 using reduction methods 1 and 2 (see additional details in section 2.6, and Fig. 3).

obtained for both ultrapure and mineral waters, indicating the absence of matrix effects on As (III) determination.

3.6. Application of the PIM-EDXF methodology for the determination of As species in natural waters

The PIM-EDXF methodology was applied to determine As(III) and As (V) species in various types of water samples, including spring and groundwater. As shown in Table 3, arsenate was the predominant form of arsenic present, with concentrations of As(III) below the quantification limit (LOQ) in both cases. Additionally, the total As content in the water samples was determined by ICP-OES for comparison purposes. Moreover, acceptable agreement was found between the sum of As (III) + As (VI) concentrations determined by PIM-EDXF method and the total As determined by ICP-OES. This fact demonstrates the potential of the method for monitoring inorganic As species at trace levels in natural water samples.

4. Conclusions

The novel methodology developed here, which is based on the combined use of a PIM containing Cyanex 301 with EDXRF spectrometry, enables the determination of As (III) at low $\mu\text{g L}^{-1}$ levels in natural waters. To date, most PIMs that have been designed have involved the selective extraction of As (V) even though this inorganic species is less toxic than the trivalent one. One of the key advantages of this novel method is its efficiency and cost-effectiveness. The PIM performs dual functions by extracting and preconcentrating arsenic while also serving as the support for direct analysis. This approach eliminates the need for complex elution steps or additional treatments, reduces the consumption of chemical reagents, and minimizes environmental impact. Moreover, the method has demonstrated its efficacy in detecting arsenic in naturally polluted waters, highlighting its applicability for environmental monitoring and management purposes. The achieved limit of quantification for trivalent arsenic (2 $\mu\text{g L}^{-1}$) falls below the World Health Organization's recommended maximum permissible level for drinking water (10 $\mu\text{g L}^{-1}$), demonstrating the method's sensitivity and reliability for regulatory compliance and public health protection. Overall, this study represents a significant step in developing sustainable methods for arsenic speciation analysis, enhancing environmental monitoring and ensuring water resource safety.

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Table 2

Determination of As (III) species in spiked ultrapure and mineral water samples containing mixtures of As (III) and As (V). Results are expressed in $\mu\text{g L}^{-1}$ as mean values \pm standard deviations (n = 3).

Water type	Added		Found	Recovery (%)
	As(III)	As(V)	As(III)	As(III)
Ultrapure water	20	100	20 \pm 5	100
	100	20	116 \pm 18	116
Mineral water	20	100	19.6 \pm 0.9	98
	60	60	62 \pm 8	103
	100	20	111 \pm 1	111

Table 3

Detection of arsenic species (PIM-EDXRF method) and total arsenic (ICP-OES) in natural water samples. Results are expressed in $\mu\text{g L}^{-1}$ as mean values \pm standard deviations (n = 3).

Sample	PIM-EDXRF method		ICP-OES
	As (III)	As (V)	As (Total)
Spring water	<2	44 \pm 4	49 \pm 6
Ground water	<2	55 \pm 3	68 \pm 3

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CRedit authorship contribution statement

Donatella Chillè: Methodology, Investigation, Data curation. **Eva Marguè:** Writing – review & editing, Writing – original draft, Supervision. **Enriqueta Anticó:** Writing – review & editing. **Claudia Foti:** Writing – review & editing. **Clàudia Fontàs:** Writing – review & editing, Writing – original draft, Supervision, Resources, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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