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System for mercury preconcentration in natural waters based on a polymer inclusion membrane incorporating an ionic liquid

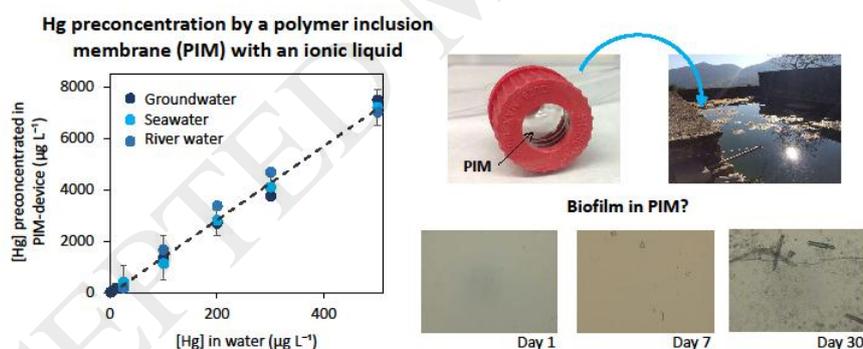
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Graphical abstract



Highlights:

- A PIM made of CTA, TOMATS and NPOE allows Hg transport.
- A diluted cysteine solution enables Hg elution from the PIM.
- The PIM-device allows Hg preconcentration from any type of natural water

- Biofouling does not significantly affect the transport of Hg at least until day seven

Abstract

In this study, we have evaluated two different ionic liquids (IL) as extractants based on the same cation (trioctylmethylammonium) but bearing the anion thiosalicylate (TOMATS) or salicylate (TOMAS). Both IL have been incorporated as carriers in polymer inclusion membranes (PIMs), and mercury (Hg) has been preconcentrated using a special device. Results show that among the tested IL, TOMATS has given better results. A PIM made of 50% cellulose triacetate, 30% TOMATS and 20% nitrophenyl octyl ether as a plasticizer enabled the effective transport of Hg to a 10^{-3} M cysteine solution used as a stripping phase. This novel and simple PIM-device system allows the transport of Hg at low concentration levels in different types of natural waters such as rivers, groundwater and seawater without any previous treatment. Since no matrix effect was observed on Hg transport efficiency with different waters, this newly developed PIM-system could be used as a global detection system for this metal. The effect of biofilm growth on the surface of PIMs has been investigated for the first time, and no significant differences on Hg transport have been found when using a fresh PIM and a PIM deployed for 7 days in a pond.

Keywords: Mercury; Polymer Inclusion Membranes; ionic liquid; natural waters

1. Introduction

Mercury (Hg) is a toxic metal naturally present in the environment, and is considered a global pollutant given that it has been released into atmospheric, aquatic and terrestrial ecosystems as a result of human activity [1]. Hg occurs in the environment in different chemical forms, but the mercuric ion (Hg^{2+}) is the one that presents high cell toxicity [2] and can be transformed into methylmercury (MeHg^+) that tends to bioaccumulate and biomagnify through aquatic trophic chains [3]. Given its high toxicity and hazardous effects on wildlife and human health [4], monitoring it in aquatic ecosystems has become a requirement for environmental purposes. In this sense, different international regulations have become aware of it, such as the European Water Framework Directive (WFD) [5] which has identified Hg and its compounds as a priority hazardous

substance, or the Minamata Convention on Mercury [6], which is the best prospect seen so far for reducing risks from direct and indirect exposure to Hg at a global level.

The use of extractants, which are able to interact with metals, can be used to facilitate their analysis [7,8]. In this sense, ionic liquids (IL) can be employed as heavy metal extracting agents [9–11]. ILs are a class of organic non-molecular solvents that are liquid at room temperature (and under 100°C). They are formed by an organic cation, which contains N or P atoms, and an organic or inorganic anion, and possess unique properties that makes them a good alternative for green chemistry [9]. The application of ILs as extracting agents for efficient removal of metal ions can be manipulated by proper selection of the anion, which is supposed to bind to the respective metal ions. Trioctylmethylammonium chloride (Aliquat 336) or trihexyl(tetradecyl)phosphonium chloride (Chypos IL 101) are common sources of cations to form new ILs derivatives [9,10,12–14] as shown in [15] where novel thiosalicylate-based ionic liquids from Aliquat 336 and Cyphos IL 101 are prepared and investigated as heavy metals extractants.

The thiol-containing IL trioctylmethylammonium thiosalicylate (TOMATS) shows a high affinity to extract Hg. This reagent has successfully been used to impregnate activated carbon for Hg removal through a batch-adsorption technique [16]. TOMATS was found to effectively remove Hg from synthetic aqueous solutions at pH 6-8 with a maximum adsorption capacity of 83.33 mg/g. However, the desorption process was not possible. This IL has also been incorporated into a polymeric matrix of cellulose triacetate (CTA) to form a polymeric sorbent used as a binding phase in a Diffusive Gradient of Thin Films (DGT) device for Hg monitoring in river water [17]. Moreover, this CTA-TOMATS sorbent was also investigated to extract Hg from different natural water samples to facilitate its detection by EDXRF [18]. It was found that the extraction of Hg was not affected by the type of water tested (river, sea, tap, and groundwater) and, remarkably, that its content in the polymeric sorbent was stable up to 6 months after extraction. This fact reveals the great stability of the complex formed within TOMATS and Hg.

As a step forward in these recent investigations, it seems appropriate to use polymeric films incorporating TOMATS as functionalized membranes to allow not only the extraction of the metal, but its transport and release to a receiving solution to preconcentrate the metal. These membranes are known as polymer inclusion

membranes (PIMs). Besides the extractant and the polymer, PIMs can also incorporate a plasticizer to enhance the mechanical properties of the film as well as to facilitate the diffusion of the extracted species [19,20]. These components are held inside the polymer matrix by a combination of physicochemical interactions [21] and the process of polymer entanglement [22]. Generally, PIMs are stable, homogeneous and dense films, with the absence of pores in their structure, and exhibit good mechanical properties (e.g., strength and flexibility). These membranes are not currently commercially available but can be easily prepared. It is important to point out that the specificity of the membrane relies on the characteristics of the extractant (called carrier when incorporated in the PIM) [23]. The carrier reactively interacts with the compound of interest, acting as the phase-transfer agent and thus extracting the compound from the aqueous phase (or feed phase) into the membrane phase by forming a hydrophobic ion-pair or a complex, which is finally released into a receiving solution (stripping phase) [24]. PIMs have allowed the separation and transport of different species such as metals, metalloids, ions and small organic compounds [19,24]. Moreover, when PIMs are incorporated in a special device containing a small reservoir for the receiving phase, the target analyte can also be preconcentrated into an adequate solution to facilitate its analysis, as is the case of As in groundwater [8], Cd in seawater [25] or the antibiotic sulfamethoxazole [26] in natural waters. The same PIM-based device has also been successfully used as a passive sampler to monitor Zn [27] or ammonia [28].

In the present study, we have taken the opportunity to use this PIM-based device for the preconcentration of Hg from different natural water samples to facilitate its detection. The IL TOMATS has been chosen as a carrier, based on its good performance for extracting Hg. We have also tested trioctylmethylammonium salicylate (TOMAS), with a similar chemical structure to TOMATS, but bearing an alcohol group instead of a thiol (SH-) group. This IL has shown to be a good extractant for some metals such as Cu(II) and Cd(II) [29], but it can also interact with Hg when incorporated in an electrode designed for the potentiometric determination of Cd(II) [30].

With this aim, we have first prepared and characterized both ILs to produce, afterwards, PIMs with TOMATS and TOMAS as carriers to investigate Hg extraction and elution. A device incorporating PIMs has been used for the transport and preconcentration of Hg from different environmental waters with the purpose of obtaining a low-cost and simple system to facilitate Hg monitoring in the environment.

2. Materials and methods

2.1. Reagents, solutions and apparatus

TOMATS and TOMAS were prepared using the commercial reagent Aliquat 336 (Sigma-Aldrich, UEA), chloroform stabilized with ethanol (Panreac, Spain), and the sodium salts of thiosalicylate (TCI, Japan) and salicylate (Fluka, Switzerland), respectively. The polymer cellulose triacetate (CTA) (Fluka, Switzerland), and the plasticizer nitrophenyl octyl ether (NPOE) (Sigma-Aldrich, UEA) were used to prepare PIMs.

Simulated natural water (SNW) with a composition 2 mM NaHCO₃, 1 mM CaCl₂·H₂O, 0.5 mM Na₂SO₄ was prepared by dilution of sodium nitrate, sodium bicarbonate, calcium chloride hexahydrate (Panreac, Spain) and sodium sulphate (Merck KGaG, Germany) in Milli-Q water (18.2 MΩ cm). Working mercury solutions were prepared daily by the appropriate dilution of Hg standard of ICP 1000 mg L⁻¹ ± 2 mg L⁻¹ c(HNO₃)= 12% w/w (Fluka, Switzerland) in the tested water. Milli-Q water used in this work was obtained by a Milli-Q Plus system (Millipore, France). L-Cysteine (Merck KGaA, Germany) and ethylenediaminetetraacetic (EDTA) (Panreac, Spain) were used for elution experiments.

Hg content in the different aqueous samples was measured using an inductively coupled plasma optical emission spectrometer (Agilent Technologies, Agilent 5100 Vertical Dual View ICP-OES) for Hg concentration in the range of 25 – 7000 µg L⁻¹ (λ= 253.652 nm). For lower Hg concentrations (1 – 200 µg Hg L⁻¹) an inductively coupled plasma mass spectrometry (ICP-MS) system (Agilent Technologies, Agilent 7500c ICP-MS) was employed. The isotope ²⁰²Hg was selected since it is the most abundant. In both cases, standards were specially prepared with the corresponding matrix to avoid the possibility of interferences during sample analyses.

An optical microscope BX-40 (Olympus, Japan) was used to observe the surface of PIMs in biofouling studies.

2.2. IL preparation and characterization

ILs were prepared by exchanging the chloride anion present in the formulation of Aliquat 336 by the thiosalicylate or the salicylate anion, for TOMATS and TOMAS preparation, respectively [18,31]. In this study, 3 g of sodium thiosalicylate or salicylate were added for 5 g of Aliquat 336. The chemical structure of ILs is represented in Fig. 1.

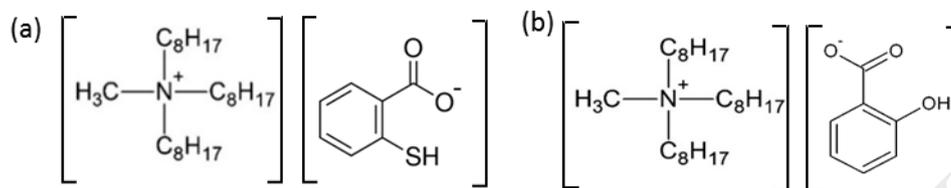


Figure 1. Chemical structure of TOMATS (a) and TOMAS (b).

ILs were characterized by elemental analyses with a Perkin Elmer EA2400 instrument and results are shown in Table 1 which shows that the experimental values of N, C, H and S are similar to the expected ones, indicating that this procedure is a simple way to obtain the desired ILs.

Table 1. Elemental analysis (N, C, H, and S, in %) of both ILs prepared (n=2).

Element	TOMATS		TOMAS	
	Theoretical	Analysed	Theoretical	Analysed
N	2.70	2.54 ± 0.01	2.80	2.67 ± 0.04
C	73.60	72.16 ± 0.37	75.90	75.38 ± 0.01
H	11.30	11.76 ± 0.16	11.70	12.69 ± 0.15
S	6.00	6.02 ± 0.13	0.00	0.82 ± 0.09

In addition, proton nuclear magnetic resonance (¹H NMR 400 MHz Bruker) was performed for both ILs, using deuterated chloroform (CDCl₃) as a reference. The corresponding description of the spectrums confirmed the expected results and can be found in Supplementary Material (S1).

2.3. PIM preparation

PIMs with a composition of 50% CTA - 50% IL (% in mass) were prepared by the solvent casting method as described in [23]. For PIMs with a composition of 50% CTA - 30% IL - 20% NPOE, the same amount of CTA (200 mg) was used, but 120 mg of IL

and 80 mg of plasticizer were added. The stability of the PIM was studied in terms of mass loss, which is related with the loss of the carrier [32]. For that, pieces of PIM about 4 cm² were immersed in 25 mL of Milli-Q water, sea water or 10⁻³M cysteine solution, with agitation during 24 h. PIMs were weighted before and after the experiment, and the mass loss was then calculated.

2.4. PIM extraction and elution experiments

To evaluate the effectiveness of IL incorporated in PIMs, some experiments were conducted by contacting 4 cm² pieces of tested PIMs with 25 mL of 1 mg L⁻¹ Hg in SNW under orbital agitation at a constant rate (basic KS250 multiple stirrer Ika, Labortechnik, Germany). Extraction efficiency (EE) was evaluated by Equation 1,

$$EE (\%) = \frac{([Hg^{2+}]_i - [Hg^{2+}]_f)}{[Hg^{2+}]_i} \times 100 \quad (Eq. 1)$$

where $[Hg^{2+}]_i$ denotes the Hg initial concentration in the aqueous phase and $[Hg^{2+}]_f$ is the final Hg concentration in the water sample after contacting with the PIM.

The same procedure was conducted to evaluate the possibility of recovering the extracted metal. To this end, PIMs loaded with Hg were contacted with 25 mL of the tested eluent during 24 hours under orbital stirring. Recovery efficiency (RE) was calculated using Equation 2,

$$RE (\%) = \frac{[Hg^{2+}]_{aq}}{[Hg^{2+}]_i - [Hg^{2+}]_f} \times 100 \quad (Eq. 2)$$

where $[Hg^{2+}]_{aq}$ denotes the Hg concentration in the eluent after the deployment time of the loaded membrane and $[Hg^{2+}]_i$ and $[Hg^{2+}]_f$ are the initial and final Hg concentration in the initial aqueous solution, respectively.

2.5. PIM-preconcentration experiments

Figure 2 shows the scheme of the PIM-device used in this work [33]. This system consists of a glass tube with a bottom opening that contains a circular piece of PIM fixed with a screw cap especially designed to expose 1.5 cm² of membrane to the feed solution. The glass tube is then filled with 5 mL of receiving phase and the top opening is closed with a standard screw cap. To carry out the experiments using the device, 100 mL of water spiked with Hg (1-500 µg L⁻¹) were poured into a glass beaker and placed

on a magnetic stirrer Multistirrer 15 (Fisher Scientific, USA). As a receiving phase, 5 mL of 10^{-3} M cysteine or 5 mL 10^{-2} M EDTA were investigated.

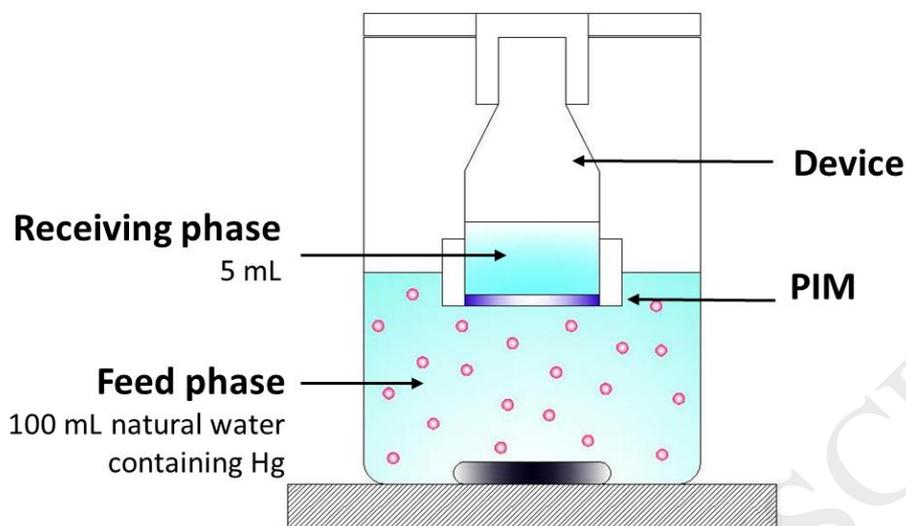


Figure 2. Scheme of the PIM-device system used for Hg(II) pre-concentration experiments.

After 24 h of deployment time, the PIM-device was removed from the feed solution and the receiving phase was taken for analysis. The performance of the system was studied in terms of transport efficiency (TE) calculated following Equation 3,

$$TE(\%) = \left(\frac{V_s}{V_f} \right) \left(\frac{[Hg^{2+}]_{rec(t)}}{[Hg^{2+}]_{feed(0)}} \right) \times 100 \quad (Eq. 3)$$

where $[Hg^{2+}]_{rec(t)}$ denotes the Hg concentration in the receiving phase at time t , $[Hg^{2+}]_{feed(0)}$ is the initial Hg concentration in the water sample and V_s and V_f are the volume of stripping and feed solution, respectively.

2.6. Water samples

To evaluate the effect of water composition on Hg transport, several natural water samples with different chemical composition were tested. Samples were collected at different locations in Catalonia (NE Spain): groundwater (GW) was collected from Pujarnol (Pla de l'Estany, Girona), seawater samples from the Mediterranean Sea (Tossa de Mar, Girona), and river water was sampled from the Ter River (Girona). For application purposes, hot spring water from Caldes de Malavella (Girona) and bottled

mineral water from Viladrau (Girona) were also included. The chemical composition of these samples is shown in Table 2.

The ionic 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 values were determined with a Micro pH 2002 (Crison, Spain), and conductivity was obtained with a hand-held Eutech instrument TDS 6+. Total organic carbon (TOC) was determined by a Shimadzu TOC-V CSH (230V) analyzer.

Table 2. Chemical characteristics of the water samples used for this study (concentrations are expressed in mg L⁻¹ and conductivity in $\mu\text{S cm}^{-1}$). * Data from [20].

Source	pH	conductivity	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	NO ₃ ⁻	TOC
GW*	8.3	527	17.92	17.12	30.10	96.10	15.43	63.86	268.5	1.17	0.22
River*	7.2	462	11.78	3.09	14.91	119.54	16.52	26.19	460	7.57	1.15
Sea*	8.1	66100	11764.13	427.87	1411.86	442.95	21075.16	2919.51	145.26	<0.02	4.82
SNW	7.45	459	70.18	0	0	40.25	71.19	47.35	120	0	0
Hot spring	7.36	3500	1190	2.7	8.8	24.4	570.1	41.4	1998.5	<0.02	nt
Mineral	7.3	242	12.2	nt	4.2	28.5	6.0	11.2	114	nt	nt

nt: not tested

2.7. Biofouling studies

To evaluate possible grow of biofilm on PIM's surface, different membranes were deployed for 7 and 30 days (Spring 2017) in a pond of a farm located in Pujarnol (Girona), where GW is sampled (chemical characteristics depicted in Table 2). This pond contains natural freshwater algae floating and growing underwater on rocks and mud.

PIMs were observed by means of an optical microscope before and after the deployment exposure time and, afterwards, membranes deployed for 7 days were used for Hg transport experiments using 100 mL of SNW with 100 μL^{-1} Hg as a feed phase and 5 mL of 10⁻³ M cysteine as a receiving solution.

3. Results and discussion

3.1. PIM with TOMATS or TOMAS: extraction and elution experiments

The effectiveness of TOMATS incorporated in a polymeric matrix was demonstrated in our previous studies, where a PIM with a composition of 50% CTA-50% TOMATS extracted Hg from natural waters [17,18]. In the present study, with the aim of comparing the extraction efficiency of both IL, we used PIMs containing 50% TOMATS or 50% TOMAS to test their ability to extract Hg from a SNW sample. Experiments were designed in order to ensure that PIMs had enough extraction capacity to completely extract the Hg present in the solution. Results are presented in Fig. 3, which shows that even though TOMATS is the most efficient IL, allowing a quantitative extraction of Hg, the derivative incorporating the salicylate anion is also able to extract more than 50% of the metal initially present in the solution. In the study by Zhang et al. [34] using the IL tricarpylmethylammonium 2-(methylthio)benzoate, in which the S atom is bearing a methylene group instead of the H of TOMATS, it was reported that the extraction of Hg(II) occurred via an interaction of the metal with the S atom along with the contribution of the carboxylate group.

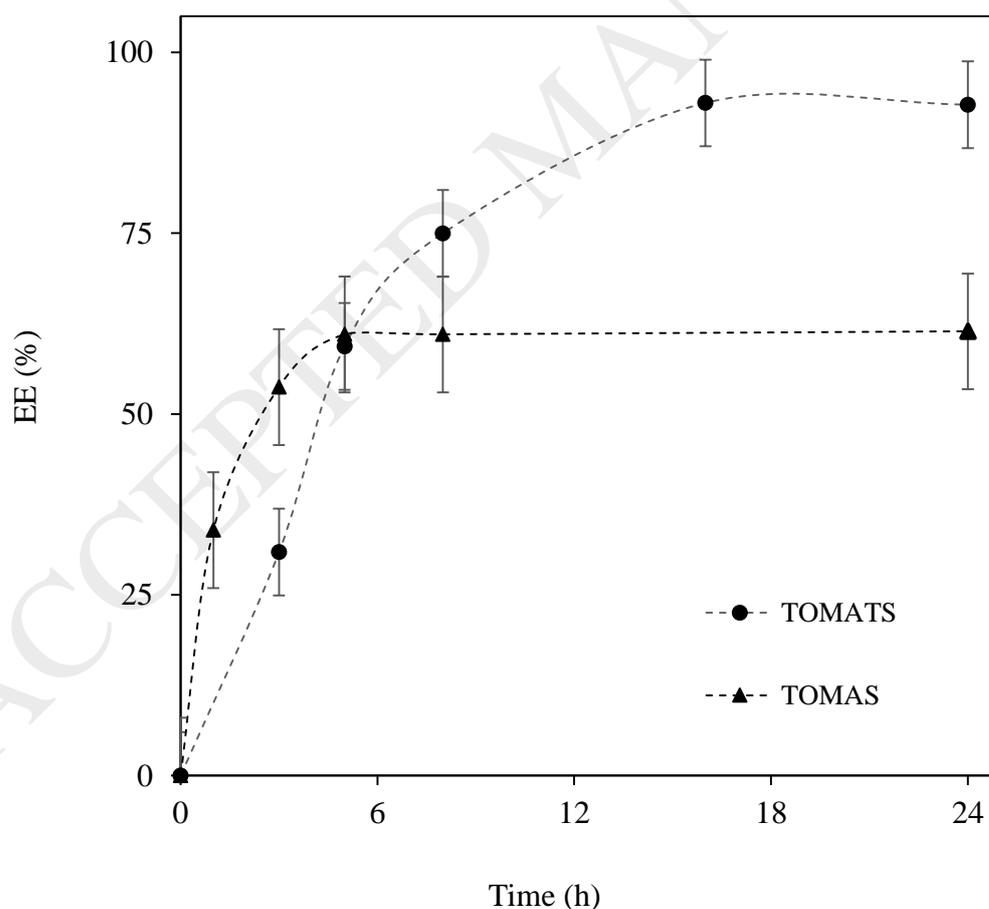


Figure 3. Hg extraction efficiency vs. time with PIMs made of 50% CTA-50% IL (25 mL of SNW 1000 $\mu\text{g L}^{-1}$ Hg; n = 5).

In the case of TOMAS, it is reported in [30] that the extraction of Cd(II) is based on the chelating effect of the carboxylate group in addition to the formation of metal hydroxylates that forms a coordinate interaction between TOMAS and the metal ion. Given this, a similar extraction mechanism can be proposed for the extraction of Hg with this IL.

The fact that the value of %EE is higher for the PIM incorporating the derivative bearing a thiol group instead of the alcohol is in agreement with the well-known high affinity of Hg for S-containing reagents. However, it is important to consider that the formation of very stable complexes can hamper further elution, if the extracted metal needs to be recovered in an aqueous solution.

Hg-loaded PIMs were used to investigate the elution efficiency (in terms of recovery, RE) using chelating agents such as EDTA, which form stable complexes with many metals, and cysteine, bearing both a thiol and a carboxylic acid group. Results are presented in Table 3. It could be observed that, no matter whether the concentration of cysteine was 10^{-3}M or 0.1M, it allowed the recovery of the extracted Hg for both IL with good efficiencies. However, the fact that 69% of metal extracted with the PIM with TOMAS could be eluted using a 0.01 M EDTA solution, compared to only 6.6% for TOMATS, revealed that the complex formed between Hg ions and TOMAS was probably weaker than the complex formed with TOMATS.

Table 3. Hg recovery efficiencies (RE, %) using Hg-loaded PIMs (50% CTA + 50% IL).

	Hg recovery efficiency (%)	
	TOMATS	TOMAS
0.01 M EDTA	6.6	69.0
0.1 M cysteine	100	71.5
10^{-3} M cysteine	76.8	nt

nt: not tested

3.2. Hg preconcentration using a PIM-device

3.2.1. Optimization of PIM composition

When a PIM is used for transport purposes, first the metal has to be extracted from the feed phase, followed by its facilitated transport through the membrane, and the final release of the metal to the receiving solution. All these steps take place simultaneously, and, therefore, a proper receiving solution is needed to avoid the accumulation of the metal in the membrane that turns into a decrease in efficiency. Likewise, in transport experiments, the composition of the PIM is of paramount importance since not only does the metal have to be extracted but also the complex (carrier and metal) must diffuse through the polymeric matrix. Given this, we tested different membrane compositions as well as receiving solutions to evaluate Hg transport using the PIM-device (Fig. 2). For both IL we tested membranes with and without a plasticizer, and also, in the case of TOMATS, PIMs with different amounts of the three components were also investigated. It is worth mentioning that all the formed membranes were dense, with no pores in the structure (as shown in [23] and in Fig. S2), and that their characterization by means of FT-IR spectrometry revealed the typical bands of the main components of the PIM (see Fig. S3).

As a receiving phase for the PIM-device, an EDTA solution was only tested for PIMs with TOMATS, whereas cysteine was investigated for membranes with both IL. Even though a 0.1M cysteine solution gave high recovery values in batch experiments, for transport experiments we only tested a 10^{-3} M solution of this reagent, since it is known that organic compounds at quite high concentration can be transported to a small degree across functionalized membranes by passive diffusion. This fact leads to a decrease in the efficiency of the separation system [35].

Table 4 shows the effect of both PIM and receiving solutions composition on Hg TE(%) after 24 h of experiment. In the case of TOMATS, when the membrane was made with only the polymer and the IL (70/30 or 50/50 CTA/TOMATS), the transport was very low. Even though the PIM with 50% TOMATS exhibited a very good extraction performance [23], it was not effective for transport purposes. Hence, we also tested PIMs with a plasticizer. It is known that the addition of a plasticizer increases the fluidity and plasticity of a PIM, improving its permeability due to the plasticization effect [20,36]. NPOE is one of the most commonly used plasticizers in PIMs [19,37]. Accordingly, PIMs containing 20% or 40% NPOE were investigated in the case of

TOMATS. As can be observed in Table 4, the presence of NPOE dramatically increased Hg TE(%), with similar values for both NPOE content.

In the case of PIMs containing 50% TOMAS, the transport of Hg was ineffective in either EDTA or cysteine solutions. The addition of the plasticizer in the membrane increased the TE(%), but only reaching a value of 34%.

Consequently, PIM with a composition 50% CTA-30% TOMATS-20% NPOE was fixed for further experiments. To ensure the homogeneity of this PIM, five different replicates of transport experiments were done using membranes prepared on different days, and the relative standard deviation (RSD, %) of the TE(%) was 8, demonstrating the precision of this methodology. Moreover, this PIM composition was found to result in a stable membrane, since an insignificant mass loss was found for each solution tested (1.4% for milli-Q water, 1.8% for a 10^{-3} M cysteine solution and 2.5% for sea water). These results are in agreement of those reported in [17] where a mass loss of 2.4% was found for a PIM made of 50%CTA-50% TOMATS immersed in 0.1 M NaCl solution.

Table 4. Effect of PIM composition and receiving phase on Hg transport efficiencies (TE, %). Feed phase: 100 ml of SNW, spiked value=500 $\mu\text{g L}^{-1}$ Hg (n=2 and n=5 for *).

	PIM composition			Receiving phase	TE (%)
	CTA (%)	IL (%)	NPOE (%)		
TOMATS	70	30	-		4 \pm 5
	50	50	-	10^{-3} M cysteine	38 \pm 2
	50	30	20		84 \pm 7*
	30	30	40		80 \pm 5
TOMAS	50	50	-	10^{-3} M cysteine	9 \pm 0
	50	30	20	10^{-3} M cysteine	34 \pm 6
	50	50	-	0.1M EDTA	2 \pm 1

3.2.2. Water matrix effect

The presence of other components existing in natural waters can negatively affect the efficiency of the membrane. On the one hand, some major ions could compete with the target species for the active sites of the carrier, becoming an interference. This effect was observed when studying the transport of As(V) using a PIM-device containing the IL Aliquat 336, since hot spring water samples, bearing high conductivity values (3,450

μS), hampered the transport of arsenate [8]. On the other hand, some of these major ions can act as complexing agents and affect metal speciation. In the case of Hg, different species can be found in natural waters depending on chloride concentration at a neutral pH. Taking into account the pH and both chloride and hydrogencarbonate anions content in each water (shown in Table 2) we calculated the predominance species of Hg (at a value of $500 \mu\text{g L}^{-1}$) using the MINTEQ software. It was found that the predominant species in river, SNW and groundwater were neutral or cationic, whereas in seawater the predominant inorganic species was the anionic complex HgCl_4^{2-} . These differences may influence Hg extraction and transport depending on the carrier. For instance, if the ion exchanger Aliquat 336 is used, Hg can only be extracted if it is present as an anionic form [38] and, therefore, can be useful for seawater or high salinity water samples, but not for GW or river water samples, for example.

With the aim of testing whether TOMATS can provide a wider use in different natural waters, transport experiments were performed using river, GW and seawater, as well as SNW, and results are presented in Fig.4. As shown, despite the different species' dependence on the water's characteristics, no statistical significant differences ($p > 0.05$) were observed on transport efficiency for the different waters tested. This fact reveals the great robustness of the detection method based on a PIM incorporating TOMATS as a carrier.

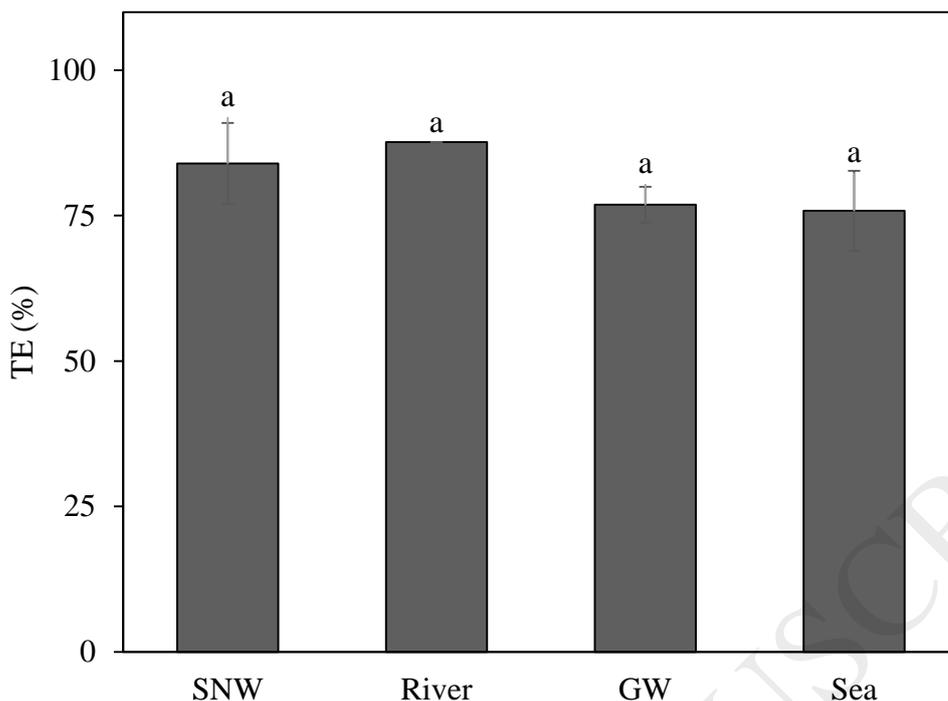


Figure 4. Matrix effect on Hg TE using the PIM-device system. Feed phase: 100 mL $500 \mu\text{g L}^{-1}$ Hg ($n = 3$). Different letters within the graph indicate significant differences.

3.2.3. Calibration

The effect of metal concentration in different natural waters was investigated in a range of $25 - 500 \mu\text{g L}^{-1}$ for both river and seawater while the range for GW was $1 - 500 \mu\text{g L}^{-1}$. Also, three replicates using milli-Q water as a feed phase (with no Hg added) were done to calculate the limit of detection (LOD) and quantification (LOQ) of the PIM-system by analysing the receiving phase by ICP-MS. Then, LOD was found to be $0.29 \mu\text{g L}^{-1}$ and LOQ was $0.74 \mu\text{g L}^{-1}$. Fig. 5 shows the calibration curves obtained for the analysis of Hg concentrated in the receiving phase plotted vs. the initial Hg present in the water sample. As shown in Fig. 5a, a straight line was fitted to measured points by the least-square method. Parameters of the resulting calibration curve are also included in Fig. 5a. The fact that the regression coefficient was higher than 0.99 in all cases indicates good linearity throughout the working range, whereas similarities within the slopes of the regression lines reveal the lack of matrix effect within the waters studied. Fig. 5b depicts the calibration curve obtained for GW containing Hg in the range 1 to $10 \mu\text{g L}^{-1}$. As shown, good linearity is also obtained, and the value of the slope (14.5) is in concordance with the calibration curves obtained with a higher amount of Hg.

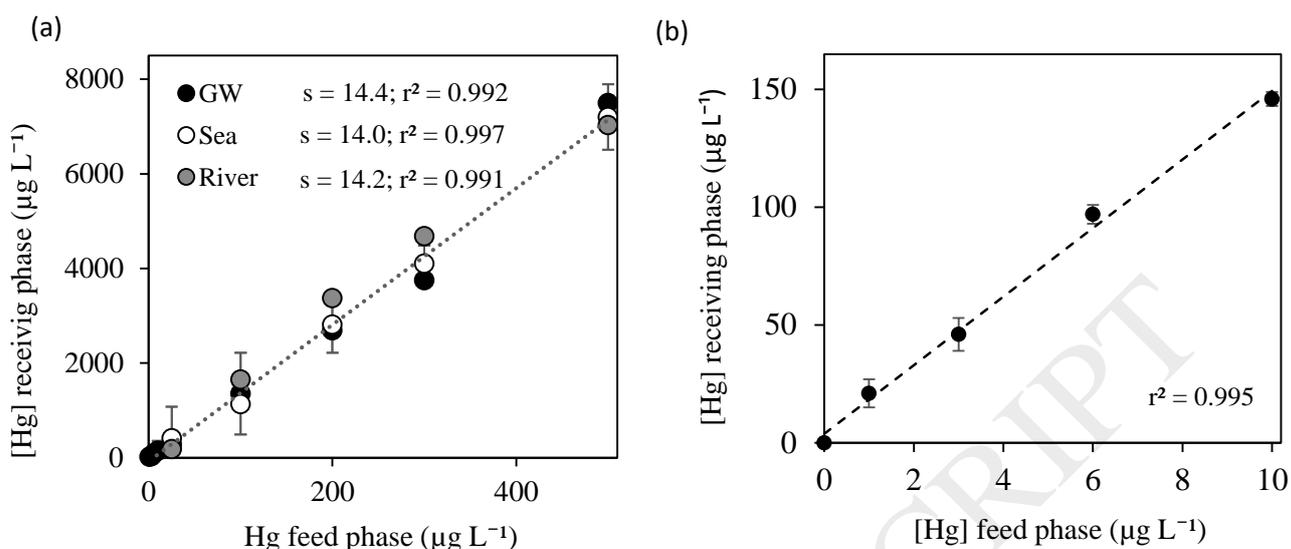


Figure 5. Calibration curves obtained with PIM-device using different natural waters (n=2). (a) Feed phase: 100 mL water with 25 - 500 µg L⁻¹ Hg and (b) 100 mL of GW 1 - 10 µg L⁻¹.

These results are highly noteworthy since they demonstrate that a single calibration curve is enough to determine the initial amount of Hg present in natural water, after its preconcentration by the PIM-device.

3.3. Hg determination using the PIM-device

The PIM-device was used to determine the amount of Hg in natural waters spiked with 5 µg L⁻¹ of metal (Table 5). To this end, Hg preconcentrated in the receiving phase was interpolated in the calibration curve in Fig. 5(b) and the Hg initially present in water samples was determined. As shown in Table 5, a good agreement was found between both the spiked level and the Hg content using the PIM-device. It is worth mentioning that even though the metal was present at a very low content in such complex samples (e.g. hot spring water, seawater), the use of this methodology enabled its detection.

Table 5. Application of the PIM-device to determine Hg content in natural waters (n=3).

Sample	[Hg] added (µg L ⁻¹)	[Hg] in the receiving phase (µg L ⁻¹)	[Hg] found* (PIM-device) (µg L ⁻¹)
Spring	5	78 ± 5	5.1 ± 0.2

Mineral	5	89 ± 5	5.8 ± 0.3
Groundwater	5	78 ± 6	4.8 ± 0.2
Sea	5	74 ± 4	5.1 ± 0.3

* Calculated from calibration curve of Fig. 5

3.4. PIM biofouling characteristics and effect on Hg transport

Taking into account the good performance exhibited for this PIM system, and with the aim of using this device as a passive sampler to facilitate Hg monitoring in water bodies in possible future studies, we also tested (for the first time) the possible biofouling growth on the surface of the membrane. Biofouling is the colonization by bacteria and various flora and fauna that can form a biofilm which can damage the surface of the membrane [39] and can even affect the transport of the compounds of interest, as happens in DGT devices [39,40].

PIMs were observed by an optical microscope before and after deployment in the controlled water reservoir. Two different deployment times were investigated: 7 days, which is a normal time for passive sampling studies with PIM devices [27], and 37 days, to better investigate whether or not the biofilm could grow. PIMs surface images are shown in Fig. 6. It can be seen that PIMs immersed for 7 days were not colonized by biofilm, but after a month of deployment, some diatoms appeared on the surface of the membrane, the main orders being *Naviculate* and *Pennate*. After 7 days of deployment, the transport of Hg in the PIM was investigated and compared with new PIMs. No statistical differences ($p > 0.05$) were found for the TE(%) values. However, further experiments should be performed at longer deployment times to better establish the likely role of biofilm growth on PIMs.

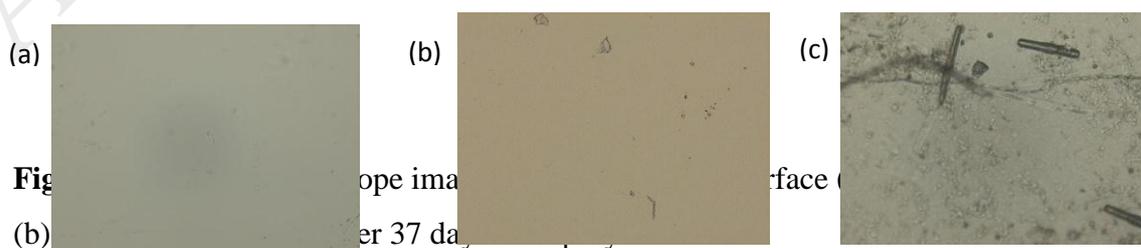


Fig. 6. Optical microscope images of the PIM surface (a) before deployment, (b) after 7 days of deployment, and (c) after 37 days of deployment.

4. Conclusions

This novel, low-cost and simple method to facilitate mercury determination presented here is based on a PIM containing CTA as a polymer, TOMATS as a carrier, and the plasticizer NPOE, with an optimized composition of 50%CTA-30%TOMATS-20%NPOE. Since the efficiency of the system was not affected by the composition of the waters tested, this method may be a suitable global solution when dealing with Hg monitoring in natural waters. Furthermore, since no biofilm growth was observed for about a week of deployment in the field, the PIM-system would appear to be a very promising tool for the design of a suitable passive sampler device for eutrophic freshwaters.

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