Exploring preconcentration procedures based on trioctylmethylammonium thiosalicylate (TOMATS) to facilitate mercury detection in natural waters

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ABSTRACT

Mercury, Hg, is a hazardous contaminant that is present in the environment because of natural and anthropogenic sources. Due to its high toxicity and its presence in aquatic systems, it is important to develop methodologies to control its existence in the environment.

In this study we have developed preconcentration procedures using the Task Specific Ionic Liquid (TSIL) trioctylmethylammonium thiosalicylate (TOMATS) to facilitate the detection of mercury in natural waters. Two different approaches have been investigated: the incorporation of TOMATS in a polymer inclusion membrane and its use to impregnate solid sorbents.

In the case of PIMs, we first investigated the effect of membrane composition. For that, different membranes were prepared using cellulose triacetate (CTA) or polyvinylchloride (PVC) as polymers, TOMATS as a carrier, and different plasticizers bearing long aliphatic chains, and were incorporated in a special device to perform Hg preconcentration. 50% CTA+ 30% TOMATS+ 20% NPOE membrane was used for the following studies.

The effect of other metals on Hg transport was evaluated. It was observed that all metals were transported through the PIM and were preconcentrated in the stripping phase. Using this PIM-device an application with different natural waters showed that it is a good procedure to preconcentrate Hg.

Also, novel sorbents based on silicon dioxide (SiO_2) nanoparticles and cellulose powder were modified with TOMATS in order to design extraction studies and elution with cysteine. They were compared with non-impregnated sorbents and it was observed that in both cases the extraction was really efficient, showing that the impregnation was done successfully. It was observed that its kinetics is fast. These experiments were also performed with less amount of impregnated sorbent and different volumes in order to calculate their capacity of mercury extraction. The impregnated sorbents were also studied, in terms of extraction and elution, incorporated in a gel of agarose, the binding gel of the DGT technique, without losing extraction efficiency towards mercury.

RESUM

El mercuri, Hg, és un contaminant perillós que es troba al medi ambient tant per causes naturals com antropogèniques. Degut a l'alta toxicitat d'aquest metall i la seva presència en sistemes aquàtics, és de gran requeriment desenvolupar metodologies per tal de controlar la seva existència al medi ambient.

En aquest estudi, hem desenvolupat procediments de preconcentració utilitzant el tiosalicilat de trioctilamoni (TOMATS) com a *Task Specific Ionic Liquid* (TSIL) per facilitar la detecció de Hg en aigües naturals. S'han investigat dos enfocs diferents: la incorporació de TOMATS en una membrana d'inclusió polimèrica i el seu ús per impregnar sorbents sòlids.

En el cas de les PIMs, primer hem investigat l'efecte de la composició de la membrana. Per a això, es van preparar diferents membranes utilitzant acetat de cel·lulosa (CTA) o clorur de polivinil (PVC) com a polímers, TOMATS com a transportador, i diferents plastificants amb cadenes alifàtiques llargues, i es van incorporar en un dispositiu especial per preconcentrar el mercuri. La membrana de composició 50% CTA + 30% TOMATS + 20% NPOE es va utilitzar per als estudis posteriors.

L'efecte d'altres metalls sobre el transport de Hg es va avaluar. Es va observar que tots els metalls van ser transportats a través de la PIM i es van preconcentrar a la fase receptora. Usant aquest dispositiu, es va portar a terme una aplicació amb diferents aigües naturals on es va demostrar que, aquests dispositius amb PIMs que contenen TOMATS, són útils per a la preconcentració de Hg.

Així mateix, es van modificar nous sorbents, basats en nanopartícules de diòxid de silici i pols de cel·lulosa, amb TOMATS per dissenyar estudis d'extracció i elució amb cisteïna. Es van comparar amb els mateixos sorbents no impregnats i es va constatar que en ambdós casos l'extracció era realment eficaç, demostrant que la impregnació es va fer amb èxit. Es va observar que la seva cinètica d'extracció és ràpida. Aquests experiments també es van realitzar amb menys quantitat de sorbent impregnat i diferents volums de fase aquosa per tal de calcular la capacitat d'extracció de mercuri. També es va estudiar l'extracció i l'elució d'aquests sorbents impregnats incorporats en un gel d'agarosa, el gel d'unió de la tècnica DGT, que no va perdre l'eficiència d'extracció cap al mercuri.

RESUMEN

El mercurio, Hg, es un contaminante peligroso que se encuentra en el medio ambiente tanto por causes naturales como humanes. Debido a la gran toxicidad de este metal i su presencia en sistemas acuáticos, es de gran importancia desarrollar metodologías para controlar su presencia en el medio ambiente.

En este estudio, hemos desarrollado procedimientos de preconcentración utilizando el tiosalicilato de trioctilamonio (TOMATS) *Task Specific Ionic Liquid* (TSIL) para facilitar la detección de Hg en aguas naturales. Se han investigado dos enfoques diferentes: la incorporación de TOMATS en una membrana de inclusión de polimérica y su uso para impregnar sorbentes sólidos.

En el caso de las PIMs, primero investigamos el efecto de la composición de la membrana. Para eso, se prepararon diferentes membranas usando acetato de celulosa (CTA) o cloruro de polivinilo (PVC) como polímeros, TOMATS como transportador, y diferentes plastificantes con largas cadenas alifáticas, y se incorporaron en un dispositivo especial para realizar la preconcentración de Hg. Se utilizó una membrana de composición 50% de CTA + 30% de TOMATS + 20% de NPOE para los siguientes estudios.

El efecto de otros metales sobre el transporte de Hg fue evaluado y se observó que todos los metales se transportaron a través de la PIM y se preconcentración en la fase de extracción. Al usar este dispositivo PIM, una aplicación con diferentes aguas naturales demostró que es un buen procedimiento para preconcentrar Hg.

Además, los nuevos sorbentes basados en dióxido de silicio (SiO_2) y polvo de celulosa se modificaron con TOMATS para diseñar estudios de extracción y elución con cisteína. Se compararon con los mismos sorbentes no impregnados y se constató que en ambos casos la extracción fue realmente eficiente, demostrando que la impregnación se realizó con éxito. Se observó que su cinética es rápida. Estos experimentos también se realizaron con menos cantidad de sorbente impregnado y diferentes volúmenes de fase acuosa para calcular su capacidad de extracción de mercurio. También se estudió la extracción y la elución de estos sorbentes impregnados incorporados en un gel de agarosa, el gel de unión de la técnica DGT, que no perdió la eficiencia de extracción hacia el mercurio.

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1. INTRODUCTION

1.1. Mercury in the environment

Mercury is a hazardous environmental contaminant. Mercury is released from natural sources by erosion and volcanism, as well as by anthropogenic activities, such as mining, hydroelectric and paper industries. Nevertheless, fossil fuel combustion is the main contributor to Hg in the environment. Mercury is ubiquitous in the environment and it is present in several chemical species, both organic and inorganic.[1,2,3]

The environmental mobility and toxicological effects of mercury are strongly dependent on the chemical species present. All Hg compounds are toxic to human and animals, but organic forms (particularly monomethyl mercury and dimethylmercury) have the highest toxicity. These organic forms are the most common in aquatic systems where metallic Hg and inorganic mercury can be found. Inorganic mercury (Hg^{2+}) can be methylated to MeHg by sulphate-reducing bacteria[1,2]. These chemical species may cause high levels of Hg contamination in fish from even very low concentrations of MeHg in water and highly bioaccumulate throughout the aquatic food chain. This compound reaches human bodies after the ingestion of contaminated seafood, and may lead to several diseases.[1,4] Mercury is neuro and immunotoxic, and has been designated by the World Health Organization as one of the most dangerous chemicals to public health. It has been shown that the half-life of inorganic Hg in human brains ranges from several years to several decades.[5]

1.2. Chemical preconcentration procedures for sample treatment

Usually, metals are determined in environmental samples by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) or an Inductively Coupled Plasma Mass Spectrometry (ICP-MS). In the specific case of Hg it can also be determined by cold vapor atomic absorption spectrometry (CVAAS), atomic fluorescence spectrometry (AFS), direct analysis by thermal decomposition or direct mercury analyzer (DMA), which integrates thermal decomposition, gold amalgamation preconcentration, followed by atomic absorption spectrometry.[6]

However, metals are present in environmental samples at very low concentration or are in complex matrix that hamper its detection. For that, from an analytical point of view,

there is a great interest in the development of preconcentration processes that will facilitate the determination of the target metals in different complex samples.[7]

1.2.1. Ionic liquids and their application as extractants

Ionic Liquids (IL) are a class of organic non-molecular solvents that are normally liquid below 110ºC. In general, they consist of an organic cation containing nitrogen or phosphorus and an organic or inorganic anion. The ionic bond is usually stronger than the Van der Waals forces between the molecules of ordinary liquids. For that reason, common salts tend to melt at higher temperatures than other solid molecules. Properties, such as melting point, viscosity and solubility of starting materials and other solvents are determinate by the substituents of the organic component and by the counter-ion. The absence of volatility is one of the most important advantages of ionic liquids, offering a much lower toxicity as compared to low-boiling-point solvents.[8,9].

Tricaprylmethylammonium chloride (Aliquat 336) is a common used ionic liquid. It is composed of a large organic cation associated with a chloride ion. Due to its quaternary ammonium structure, it has a permanent positive charge which can form salts with anions over a wider pH range than other amines. Therefore, Aliquat 336 finds applications in environments from acid to slightly alkaline pH.

In addition, if a functional group is incorporated to the IL, a task-specific IL (TSIL) is obtained. This modification implies an improvement of the affinity from de IL to the compound of interest. In this sense, Aliquat 336 is an inexpensive IL showing easy procedures for TSIL synthesis. [10,11]

The thiol-containing TSIL trioctylmethylammonium thiosalicylate (TOMATS), contain no fluorine and it is absolutely stable against hydrolysis. Therefore, it is non-corrosive, and is much easier to dispose. The low toxicity of the cation is known from related compounds like trioctylmethylammonium chloride Aliquat 336 (a phase transfer catalyst) and thiosalicylic acid.[12]

1.2.2. Polymer Inclusion Membranes (PIM)

Polymer inclusion membranes are a type of functionalized membranes that contain a specific ligand (called carrier) that can interact with the species of interest. Besides the carrier, PIMs are formed by a base polymer (usually cellulose triacetate (CTA) or polyvinylchloride (PVC)), and also a plasticizer can be added.[13] CTA is a polar polymer with a number of hydroxyl and acetyl groups that is capable of forming highly orientated hydrogen bonding, which gives CTA a crystalline structure. All the components are mixed in order to be entrapped within the base polymer matrix by a combination of physicochemical interactions.[14]

PIMs usually appear as flexible, thin and stable films that are simple and cheap to prepare. Moreover, they possess good mechanical properties (e.g. strength and flexibility) and are also versatile considering the diversity of target compounds that they can extract.[15] It is important to point out that the carrier has the central role in the PIM extraction process. It reactively complexes with the compound of interest, acting as the phase-transfer agent and thus extracting the compound from the aqueous phase into the membrane phase by forming a hydrophobic ion-pair or a complex. For example, Aliquat 336 has extensively been used as a carrier in PIMs forming suitable membranes in either CTA or PVC polymers.[16] PIMs incorporating Aliquat 336 have shown to effectively transport anionic species in a wide range of applicability since they are suitable to transport organic compounds such as antibiotics,[17] inorganic anions[18,19] or metallic species like Cd or Cr,[20,21] among others.

When PIMs are incorporated in a special device, they can be used for preconcentration purposes. A PIM made of CTA and Aliquat 336 was used in a previous work to detect As inorganic spices contained in groundwater (Fontàs C. et. al[22]). Also, the same device containing a PIM made of CTA, TOMATS as a carrier and NPOE as a plasticizer has been recently used to preconcentrate Zn, Cd, Pb and Ni from different natural waters[23].

1.2.3. Uses of TOMATS in separation systems for Hg

Mercury extraction efficiency was evaluated using a PIM made of CTA and TOMATS.[24] In this work, also transport studies were done using PIM containing TOMATS in PIM-devices with 5 mL of Cysteine 10^{-3} M as receiving phase. G. Elias et al. developed a simple methodology based on a PIM containing TOMATS in combination with Energy

Dispersive X-ray Fluorescence (EDXRF) spectrometry to enable the extraction and determination of Hg at low µg L^{-1} level from natural waters.[6] This IL has also proven its efficiency in terms of mercury extraction when used to impregnate activated carbon. Mercury-removal values achieved with modified activated carbon were higher than those of virgin activated carbon due to the increase in the number of thio groups on the surface of the modified activated carbon.[25] This activated carbon modified with TOMATS was used as a novel composition for the removal of mercury from aqueous solutions.

2. OBJECTIVES

The main objective of this study is to develop preconcentration procedures based on IL trioctylmethylammoniumthiosalicylate (TOMATS) to facilitate mercury detection in natural waters.

Within this main objective we have the following secondary aims:

- To incorporate TOMATS in PIMs and optimize membrane composition in terms of Hg transport.

- To study the effect of water composition and presence of other metals on the efficiency of PIM towards Hg.

- Application of the developed PIM system for the preconcentration of Hg from natural waters.

- To impregnate sorbents of different nature with TOMATS to be used to extract mercury.

3. EXPERIMENTAL SECTION

3.1. Reagents and solutions

All working aqueous solutions with mercury were prepared with the appropriate amount of Hg standard for ICP 1000 ± 2 mg L^{-1} $c(HNO_3)$ (Fluka, Switzerland) added to different waters tested. Furthermore, in one of the experiments Cd, Ni and Pb corresponding to ICP stock solutions 1000 ± 2 mg L^{-1} were also added to water samples. A dilution of L-Cysteine (Cys) (Merck KGaA, Germany) was used to prepare elution solutions.

Reagents used for preparing PIMs were polymers cellulose triacetate (CTA, chemical structure in Figure 1a) (Fluka, Switzerland), and polyvinylchloride (PVC, chemical structure in Figure 1b). Chloroform was used to dissolve CTA whereas THF was used to dissolve PVC. TOMATS (chemical structure in Figure 1c), used as a carrier, was prepared from the commercial reagent trioctylmethylammonium chloride (Aliquat 336) (Sigma-Aldrich, UEA) and sodium thiosalicylate (TCI, Japan) (see section 3.4 for its preparation).
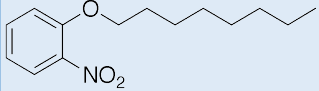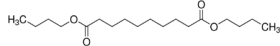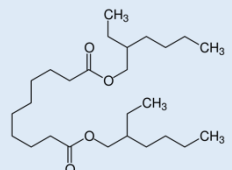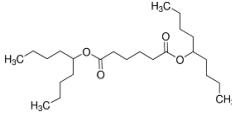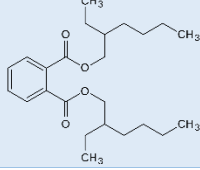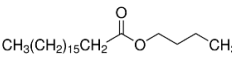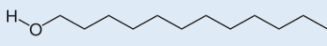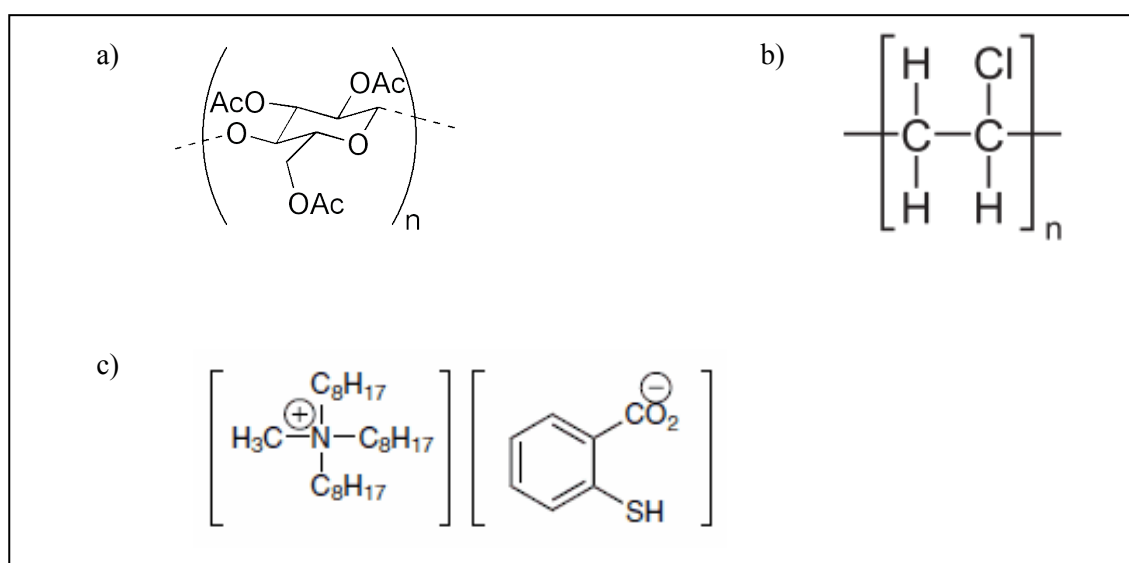

Fig. 1: Chemical structure of (a) CTA, (b) PVC, (c) TOMATS.

Different plasticizers were tested and their chemical structure and characteristics are sown in Table 1:

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Table 1: Chemical structure and characteristics of all plasticizers used in this work.

	Chemical structure	Viscosity (cP)	Dielectric Constant (ε_r)	Density (g/mL)	MW
NPOE		11.1 (25ºC)[b]	24 (25ºC)[b]	1.04	251.32
DBS		9.5[b]	4.5 (20ºC)[b]	0.936	314.46
DOS Bis (2-ethylhexyl) sebacate		16.7[b]	3.9[b]	0.914	426.67
BBPA Bis (1-bentylpentyl) adipate		14[a]	4[a]	0.91	398.62
BEHP Bis (2-ethylhexyl) phtalate		78[a]	5[a]	0.985	390.56
BTS Butyl stearate		nf	nf	0.861	340.58
Dodecanol		nf	5.82 (30ºC)[b]	0.83	186.34

nf: not found

[a] Fontàs, C. et al. (2007) Polymer inclusion membranes: The concept of fixed site membrane revised. *Journal of Membranes Science, 290*, 62-72.

[b] Ines, M.; Almeida, G. S. et al. (2012) Recent trends in extraction and transport of metals using PIMs. *Journal Membrane Science 415-416*, 9-23.

For the impregnation of sorbents (sorb) with TOMATS (sorb-TOMATS) experiments, two different materials were used (Aldrich Chemistry), and their characteristics are shown in Table 2. As it can be seen, SiO_2 was a sorbent at a nanoparticle (NP) size, whereas cellulose was at the micro particle (P) range.

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Table 2: Characteristics of the sorbents.

Sorbent	Particle size	Molecular weight	Abbreviation
Silicon dioxide (SiO_2)	10-20 nm	8.3	Si(NP)
Cellulose	20 µg	527	Cel(P)

Furthermore, agarose (Fisher BioReagents, Belgium) was also used to prepare gels including the impregnated sorbents prepared.

3.2. Water composition

Some of experiments were performed using a simulated natural water that was prepared by diluting sodium bicarbonate (2mM $NaHCO_3$), calcium chloride hexahydrate (1mM $CaCl_2 \cdot H_2O$) and sodium sulfate (0.5mM Na_2SO_4) in Milli-Q water (Millipore).

Moreover, other natural waters such as groundwater (Pujarnol, Girona), sea water (Pals, Girona), mineral water (Viladrau) and spring water (Caldes de Malavella, Girona), were also used. They were already characterized. (see Table 3 for chemical composition):

Table 3: Chemical composition of water samples used in this work.

	Simulated natural water	Groundwater	Mineral water	Sea water	Spring water
pH	7.45	8.3	7.9	8.1	7.36
Conductivity ($\mu S\ cm^{-1}$)	459	527	237	66100	3500
Ca^{2+} ($mg\ L^{-1}$)	40.25	96.10	28.5	442.95	24.4
SO_4^{2-} ($mg\ L^{-1}$)	47.35	63.86	11.2	2987	41.4
HCO_3^- ($mg\ L^{-1}$)	122	269	114	140	269
Cl^- ($mg\ L^{-1}$)	71.19	15.43	6	21075.16	570.1

3.3. Material and equipment

For Hg determination, two instruments have been employed depending on metal concentration. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) Agilent 5100 Synchronous Vertical Dual View (Agilent Technologies, USA) (25-9000 µg L^{-1}) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) Agilent 7500c

(Agilent Technologies, USA) (1-200µg L^{-1}). For the analysis of stripping and eluted solution, standards of 10^{-3} M cysteine were used, whereas standards of 0.1 M HNO$_3$ were used for the analysis of feed and aqueous solution.

The analytical balance used, model Cobos ATX224, was manufactured by Shimadzu (Japan). An orbital shaker, model KS250 basic, purchased from IKA (Germany) was used. Also, two magnetic stirrers were used: OVAN (Trallero and schelee, Spain) and a Multistirrer 15 (VELP scientifica, Italy). The water for the dilutions was obtained from Mili-Q Direct Water Purification System (Milipore Iberica S.A., Spain). A pHmeter microH 2001 (Crison, Spain) was used for the adjustment of the solutions.

Moreover, a microwave and an oven at 90ºC, were employed for the gels preparation. These gels were prepared using two glasses of 17 x 7 cm.

3.4. TOMATS preparation

The TSIL TOMATS was synthesized using commercial reagents: Aliquat 336 as a source of the cation and sodium thiosalicylate as a source of the anion. First, 5 g of Aliquat 336 was dissolved in 50 mL CHCl$_3$. Then, 2.8 g of sodium thiosalicylate was slowly added and the solution was stirred for 5 hours.

We assume that an exchange process occurs as shown in Eq. (1):

$$A^+Cl^-(org) + TS^-_{(org)} \leftrightarrow A^+TS^-_{(org)} + Cl^- \qquad (1)$$
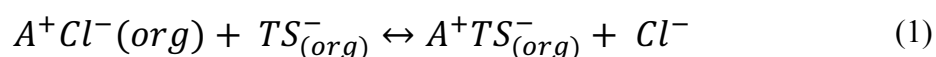
Where A$^+$Cl$^-$ is Aliquat 336 (tricaprylmethylammonium chloride) and TS$^-$ is thiosalicylate.

Afterwards, the solution was poured in a separatory funnel and rinsed with deionized water (Milli-Q) to remove the excess of sodium thiosalicylate and the formed sodium chloride. Magnesium sulfate was added to eliminate possible remaining water and the solution was filtered. Finally, chloroform was evaporated using a rotary evaporator under reduced pressure until a brownish viscous liquid was obtained. Physical Characteristics of TOMATS are shown in Table 4:

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Table 4: Physical characteristics of TOMATS.[10]

Appearance	Olive Green, viscous liquid
Relative Molecular Mass	521.89 g/mol
Empirical Formula	$C_{32}H_{59}NO_2S$
Solubility	Soluble in alcohol ethyl acetate, THF, acetonitrile, acetone, dichloromethane, DMSO; insoluble in water, hexane
Melting point	< 30º C
Leaching into aqueous phase	< 100 ppm

3.5. Polymer Inclusion Membranes (PIM) preparation

PIMs were prepared by dissolving a specific amount of polymer (CTA or PVC) in 20 mL chloroform if CTA was used as a polymer, or in 15 mL THF if PVC was used as a polymer. After 5 hours stirring, a specific volume of TOMATS and plasticizer were added to the solution that still remained stirring for a couple of hours. Then, the solution was drowned into a flat-bottom Petri dish, which was covered. The solvent was evaporated after 24 h at room temperature, and the resulting membrane was carefully peeled off the bottom of the Petri dish. The resulting membranes (Fig. 2) were used for the different experiments designed. PIMs with different composition were prepared (see in Table 5).

Table 5: Composition of PIMs design in this work (% composition in mass).

PIM	Polymer	Ionic Liquid	Plasticizer
M1			20% NPOE (80 μL)
M2			20% BBPA (80 μL)
M3	50% CTA (200 mg)	30% TOMATS (120 mg)	20% BEHP (80 μL)
M4			20% BTS (80 μL)
M5			20% Dodecanol (80 μL)
M6	50% PVC (400 mg)	50% TOMATS (400 mg)	0%
M7		30% TOMATS (240 mg)	20% NPOE (160 μL)

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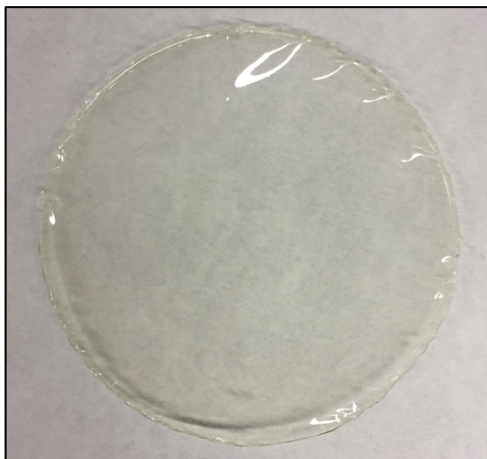

Fig. 2: Image of a PIM with composition 50% CTA 30% TOMATS and 20% NPOE.

3.6.   PIM transport studies

PIMs transport studies, were done using a preconcentration home-made device (PIM-device), that consists of a shaped glass tube with two openings and fixed with a screw cap especially designed to expose the maximum membrane area to the sample solution (2.5 cm^2). The opening at the top was closed with a standard screw cap and was used to fill the device with 5 mL stripping solution (10^{-3} M cysteine). As shown in Figure 3, the device hung into the feed solution of 100 mL in a way that the PIM was in contact with both the stripping and feed solution.
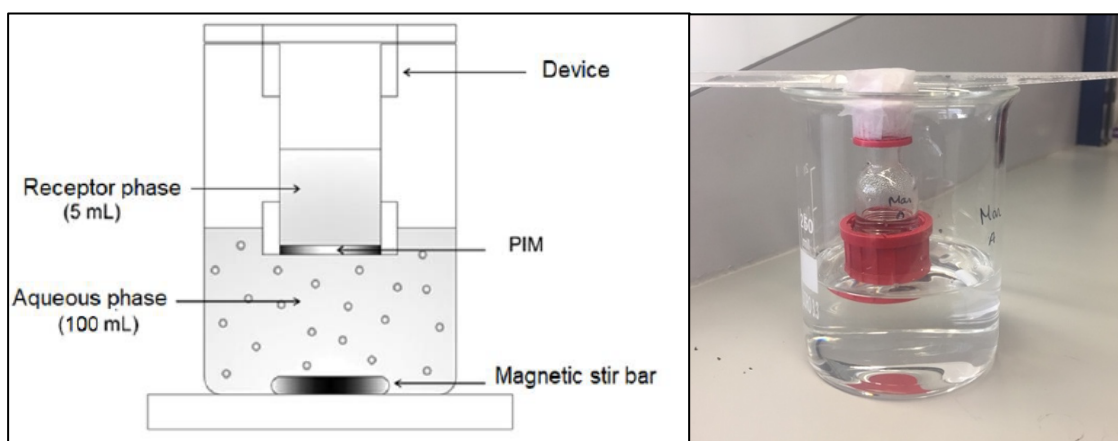

Fig. 3: PIM device used in the present study. Left: experimental scheme.[17] Right: home-made PIM device.

The experiment lasts 24 hours while continue stirring the feed solution. Then, stripping phase was analyzed in the ICP-OES, depending on the concentrations of the samples. Transport efficiency (TE (%)) was calculated using Eq. (2):

$$TE\ (\%) = \frac{[Hg]_{strip\ (f)}}{[Hg]_{feed\ (i)}} \cdot \frac{1}{V_r} \cdot 100\% \tag{2}$$

where $[Hg]_{strip\ (f)}$ denotes mercury concentration in the stripping compartment at the end of the contact time. The volume ratio between feed solution and stripping solutions is denoted by V_r. For the preconcentration PIM device, V_r is 20.

Moreover, the effect of other metals on the Hg transport was studied on sea water and groundwater. This experiment was designed in PIM devices using M1. It was stirring 24 hours at room temperature. The feed phase used was composed of 100 mL of both sea water and groundwater 5 μg L^{-1} of Hg and 100 μg L^{-1} of Cd, Ni and Pb, and the stripping phase was composed by 5 mL of 10^{-3} M cysteine. The solutions were analyzed in the ICP-MS.

Using this device an application was studied. For that, spiked solutions containing 100 mL of groundwater, sea, mineral or spring water 5 μg L^{-1} of Hg as feed solution, and 5 mL 10^{-3} M cysteine as stripping phase were used. Result solutions were analyzed in the ICP-MS.

All the experiments were carried out during 24 h at room temperature, using M1.

3.7.   Preparation of impregnated sorbents with TOMATS

To impregnate Cel(P) and Si(NP) with TOMATS, 300 mg of this TSIL were weighted and dissolved in 50 mL of EtOH under magnetic agitation until complete dissolution. Afterwards, 0.1g of sorbent was added to the solution and agitated in the orbital shaker for at least 2 hours.

After all, it was let to evaporate for one week, obtaining the sorb-TOMATS as a result (see Figure 4, left: Si(NP)-TOMATS; right: Cel(P)-TOMATS).
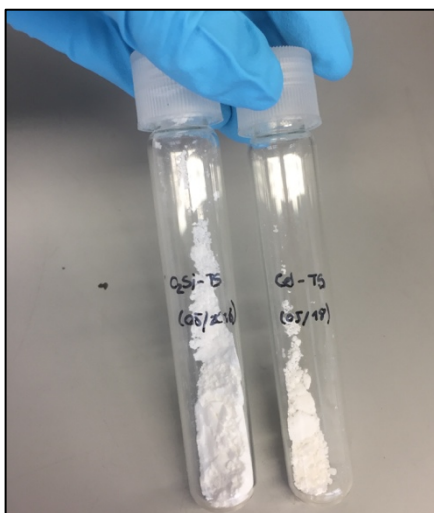
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Fig. 4: Image of sorb-TOMATS obtained.

3.8. Preparation of gels incorporating sorb-TOMATS

We prepared an agarose gel 1.5% incorporating sorb-TOMATS using a couple of glasses (17cm x 7cm) separated by a Teflon cut of 0.05 cm thick in the form of U.

First of all, 0.12 g (1.5%, wt fraction) of agarose were weighted. Then 0.12 g (1.5%, wt) of sorb-TOMATS were added, and the mixture was in contact with in 8 mL of Milli-Q water (17 x 7 x 0.5 = 6mL). To dissolve the agarose, it was brought to the boiling point using a microwave. Immediately, the solution was introduced into the oven at 90 ºC to avoid jellification. Also, glasses were kept at this temperature. The agarose solution was poured with a micropipette between the two glasses (Fig. 5 left), and then it was let cool down for about 30 minutes.

Once we have the 17 x 7 x 0.5 cm gel has been obtained, circular pieces with a 5.3 cm^2 of area were cut and kept in a 0.01 M NaNO$_3$ solution (Fig. 5 right).
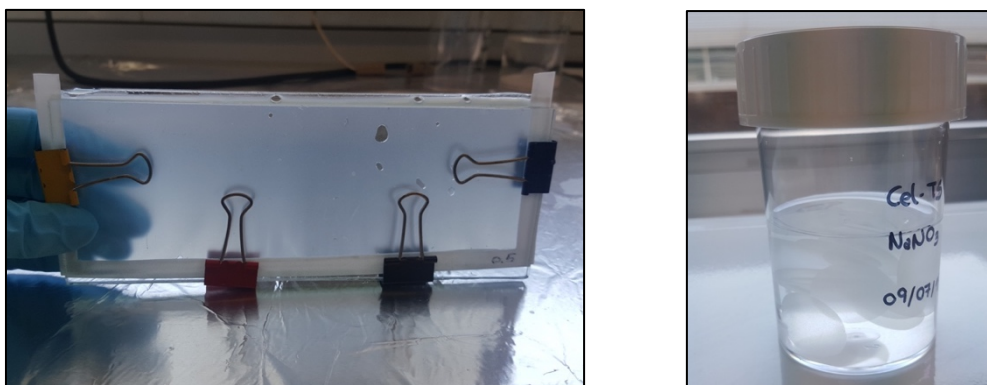

Fig. 5: Left: image of 17 x 7 x 0.05 cm^2 Si(NP)-TOMATS gel. Right: circular pieces of Cel(P)-TOMATS gel kept in 0.01M NaNO3 solution.

3.9. Hg extraction studies with impregnated sorbents

To study Hg extraction with impregnated sorbents different experiments were done:

- 0.02 g of sorb-TOMATS was in contact with 25 ml of simulated natural water containing 500 µg L^{-1} of Hg, and aqueous samples were withdrawn at regular periods of time (10, 20, 40 min). The aqueous solution was filtered by cellulose acetate syringe filters (0.45 µm pore size, 25mm diameter) and was analyzed to determine the extraction following the equation (3):

$$E\ (\%) = \frac{[Hg]_{aq.sol\ (i)} - [Hg]_{aq.sol.(f)}}{[Hg]_{aq.sol\ (i)}} \cdot 100\% \qquad (3)$$

where $[Hg]_{aq.sol.(i)}$ denotes mercury concentration in the aqueous solution before the experiment and $[Hg]_{aq.sol.(f)}$ denotes mercury concentration in the aqueous solution after the experiment.

- 0.01 g of sorb-TOMATS in 25 or 100 mL of simulated natural water 1 mg L^{-1} of Hg, and aqueous samples were withdrawn after 3 hours.

The elution was done by the cellulose acetate syringe filter used for the aqueous phase, with 5 mL of 10^{-3}M cysteine. Elution was calculated using eq. (4):

$$Elution\ (\%) = \frac{[Hg]_{eluted\ (f)}}{[Hg]_{aq.sol.(i)}} \cdot \frac{1}{V^r} \cdot 100\% \qquad (4)$$

where $[Hg]_{eluted(f)}$ denotes mercury concentration in the eluted solution after the experiment. For impregnated sorbent experiments, V_r is 5.

This experiment allowed to calculate the extraction Hg capacity following the eq. (5):

$$Capacity = \frac{mgHg}{g\ sorbent} \qquad (5)$$

Where *mgHg* are the mg of mercury extracted and *g sorbent* is the amount of impregnated sorbent used (0.001g).

All solutions where analyzed in the ICP-OES.

3.10. Hg extraction studies with gels incorporating sorb-TOMATS

A circle piece of gel incorporating sorb-TOMATS was added to 25 mL of simulated natural water containing 500 µg L^{-1} of Hg. Next, it was under orbital stirring and aqueous samples were withdrawn at regular periods of time (1, 5 and 8 hours). Therefore, the extraction could be calculated using the equation (3).

As the higher extraction was at t = 8h, these gels were eluded during 12 hours in 5 mL 10^{-3}M cysteine to recover the Hg of the extractant, and the elution was calculated following the equation (4). The solutions were analyzed in the ICP-OES.

4. RESULTS AND DISCUSSION

4.1. Transport studies with PIMs

4.1.1. Optimization of PIM composition

The extraction and transport of Hg through the membranes depends on several phenomena. These are basically the amount of polymer and the plasticizer used in the design of the PIM. For that, in this study we tested two different polymers, (CTA and PVC) as well as different plasticizers (see PIMs composition in Table X), to evaluate the transport of Hg. Results are presented in Table 6, where it can be seen that only PIMs prepared with CTA as a polymer allowed a significant transport. The analysis of the final feed phase revealed that for PIMs made of PVC (M6 and M7) the extraction was almost complete, but no transport occurred. Hence, Hg was collected on the membrane. However, in the case of PIMs made of CTA all metal extracted was transported to the stripping phase.

Table 6: Effect of PIM composition on Hg transport (SD for n=2 and *n=5).

PIM	TE (SD) (%)
M1*	84 (7)
M2	72 (2)
M3	77 (1)
M4	73 (0)
M5	70 (2)
M6	2,6 (0.1)
M7	5 (2)

It is of significance that even though the plasticizers exhibited very different chemical characteristics (dielectric constant, viscosity or chemical nature) very similar TE was obtained (in the range 70-84%). These plasticizers were chosen considering the length of the aliphatic chains, which is a new parameter to consider as a possible factor to influence the metal transport. Plasticizers with long chains may better separate the polymer chains and, probably, affect the formation of appropriate channels where the species metal-carrier can diffuse. In a previous work done in the research group it was observed that

plasticizers such as 2-fluorophenyl 2-nitrophenyl ether (without any aliphatic chain) only allowed a 29% of metal transport, whereas tributyl phosphate (only chains of 4 carbons) gave a 39 % TE. Hence, considering the results from this study, it seems that plasticizers with long aliphatic chains facilitate the transport of Hg through a CTA matrix.

Further experiments were done fixing M1 as a PIM composition.

4.1.2. Effect of other metals on Hg transport

In a recent work done in the research group, it was found that M1 was also capable to transport Cd, Ni, Pb and Zn, using a receiving solution of 0.1 M EDTA (for the first three metals) or 0.1 M HNO_3 for Zn. For that, we wanted to investigate if the presence of these metals in a larger amount than Hg could hamper TE for Hg. These experiments were run using as a feed phase both spiked sea water and ground water at 5 μg L^{-1} for Hg and 100 μg L^{-1} for the other metals. After 24 h, the stripping phase (10^{-3} M cysteine) was analyzed to determine the concentration of all metals. Results are presented in Fig. 7. As it can be seen, even though Hg was present at very low concentration, and despite the complexity of the water matrix, especially in the case of sea water, the TE was very effective in both water samples (77% for sea water and 98% for groundwater).
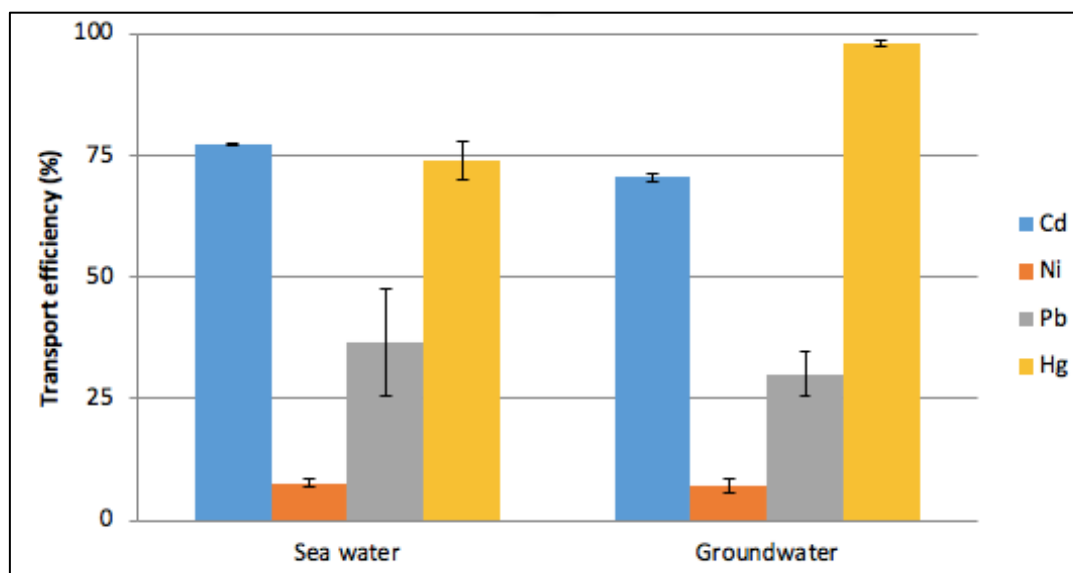

Fig. 7: Effect on Hg transport including other metals in sea water and groundwater samples.

Moreover, it was observed that all other metals were also transported through the PIM and were preconcentrated in the stripping phase (see table 7), with a significant efficiency in the case of Cd. Given this, we want to highlight, on the one hand, the wide possibilities of this PIM-device with membrane M1 for the monitoring of metallic contaminants in natural waters. And, on the other hand, that Hg transport is not significantly affected by the presence/transport of other metals present at a concentration 20 times higher.

Table 7: Concentration of Hg and other metals in the stripping phase (μg L^{-1}) (SD, n=2).

	[Hg] stripping (SD) (μg L^{-1})			
	Cd	**Ni**	**Pb**	**Hg**
Sea water	1548 (5)	151 (17)	731 (220)	74 (4)
Groundwater	1410 (15)	141 (28)	602 (90)	98 (1)

4.1.3. Application of the developed PIM-device for Hg detection in different natural waters

Finally, this system was used to preconcentrate spiked samples (at 5μg L^{-1}) of different natural water. We choose samples of different complexity such as a spring water (with a high conductivity value) as well as two drinking water samples. Results are found in Table 8 in terms of Hg concentrated in the stripping phase. As it can be seen, in all cases Hg was preconcentrated and hence, facilitating its analysis.

Table 8: Hg preconcentration using the PIM-device (SD, n=2).

Tested water	[Hg]$_{stripping}$ (SD) (μg L^{-1})
Spring	78 (5)
Mineral	89 (5)
Groundwater	78 (16)

4.2. Extraction studies with sorbents impregnated with TOMATS

To explore new preconcentration systems using the TSIL TOMATS we investigated the possibility of impregnating different sorbents with this extractant. For that, we choose two different materials, an organic (Cel) and inorganic (Si) and we compared the extraction efficiency of Hg using both impregnated and not impregnated sorbents. Results are presented in Fig. 8, where the extraction efficiency was determined at different times.
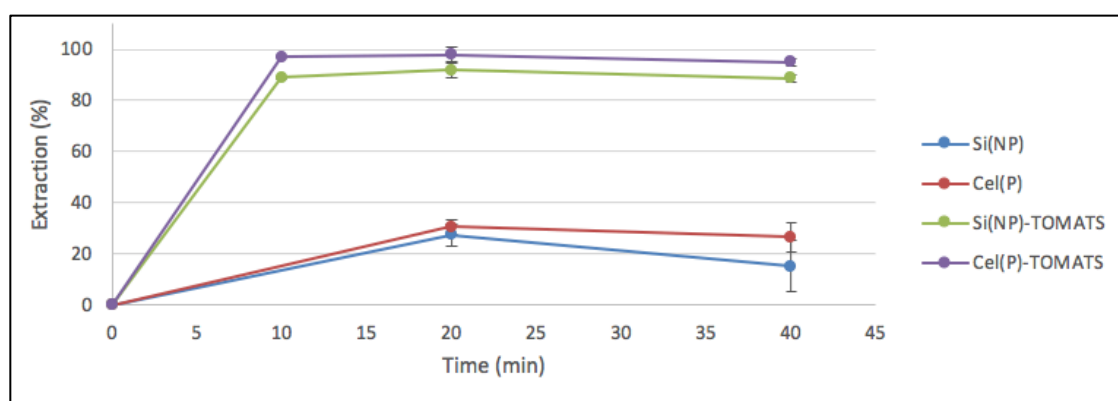

Fig 8: Hg extraction (%) using sorbents and sorb-TOMATS vs. time. Solution: 25ml simulated natural water with 500 μg L^{-1} Hg; sorbent: 0.01 g; orbital agitation; SD for n=2.

As it can be seen, the extraction of Hg was very effective for both impregnated sorbents, showing that the impregnation procedure was successful, and that was independent on the material used. Moreover, the extraction was very fast, being quantitative in only 10 min of contact. When using sorbents without TOMATS about a 20% of extraction was observed. Furthermore, was the elution was done successfully.

In order to obtain the capacity value of the sorb-TOMATS another experiment was performed using smaller amount of material (0.01 g) and higher amount of Hg (25 or 100 ml of 1 mg L^{-1} metal). After 3 h of contact, the solution was filtered and analyzed. Results are shown in Table 9 where it can be observed that the prepared material present similar capacity independent on the nature of the sorbent.

Table 9: Sorb-TOMATS capacity of Hg extraction. Solution: 25 or 100 mL of simulated natural water with 1 mg L^{-1} of Hg; sorbent 0.01 g; orbital agitation (SD for n=2).

	Volume (mL)	Extraction(%) (SD)	Capacity (mg Hg/ g sorbent)
Si(NP)-TOMATS	25	100 (0.5)	---
	100	93 (2)	9.4
Cel(P)-TOMATS	25	100 (0.4)	---
	100	96 (2)	9.7

To evaluate the possibility to elute the extracted Hg, 5 ml of 10^{-3}M cysteine were carefully passed through the syringe filter where the loaded sorbent (0.01 g contacted with 25 mL 500 µg L^{-1}) was retained. In the case of Si(NP)-TOMATS a 72% (SD=4) of elution was obtained whereas in the case of Cel(P)-TOMATS the elution was 30% (SD=17). The high SD for the elution of C(P)-TOMATS is due to the handling of the experiment. However, we want to point out the simplicity of the elution procedure that allows the recovery of 70% extracted metal using Si(NP)-TOMATS.

4.2.1. Impregnated sorbents incorporated in a gel

These new materials can be seen as a possible Hg binding phases to be used in Diffusive Gradients in Thin Films (DGT) technique, which have a wide application as a passive sampler. For that, we evaluated the possibility to include the impregnated sorbents in a gel matrix and test their extraction efficiency. As indicated in the experimental section, agarose was used to form the gel phase, since this material is used in the DGT technique. For comparison purposes, the same experiment was run using the same amount of impregnated sorbent as the one included in the gel, but directly in contact with the aqueous solution. Results can be seen in Fig. 9 where the extraction efficiency is shown vs. time for both sorbents contained in a gel or as free particles. Even though the sorb-TOMATS is embedded in a gel matrix, the extraction efficiency is very high and the kinetics of extraction follows a similar trend than the free particles extraction. These are very promising results in terms of using this new material as binding phase in DGTs for mercury monitoring.

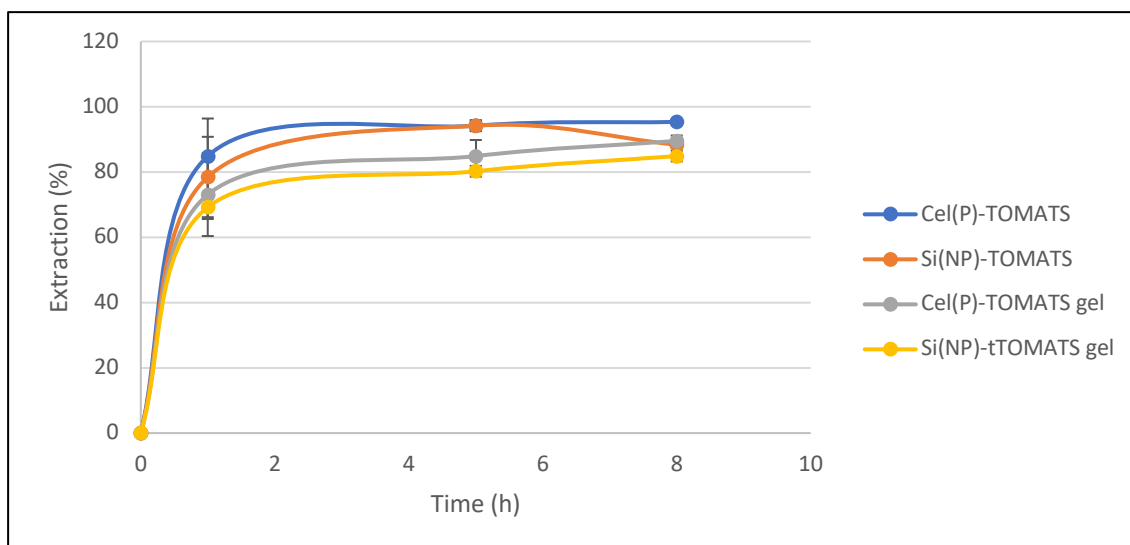Exploring preconcentration procedures based on TOMATS to facilitate mercury detection in natural waters

Fig 9: Comparison of gels and sorbents extraction (%). Solution: 25 mL simulated natural water with 500 µg L^{-1} Hg 0.004 g; orbital agitation (SD for n=2).

Also, the elution was investigated. For the gel sorbents, they were contacted 8h with 5 ml of 10^{-3} M cysteine while for the free sorbent we followed the same procedure described above. The obtained results are shown in Figure 10, where it can be seen that good recovery values are obtained for both gels, which is similar than the one obtained for free Si(NP)-TOMATS (due to problems with the sample it was not possible to test the elution of Cel(P)-TOMATS).
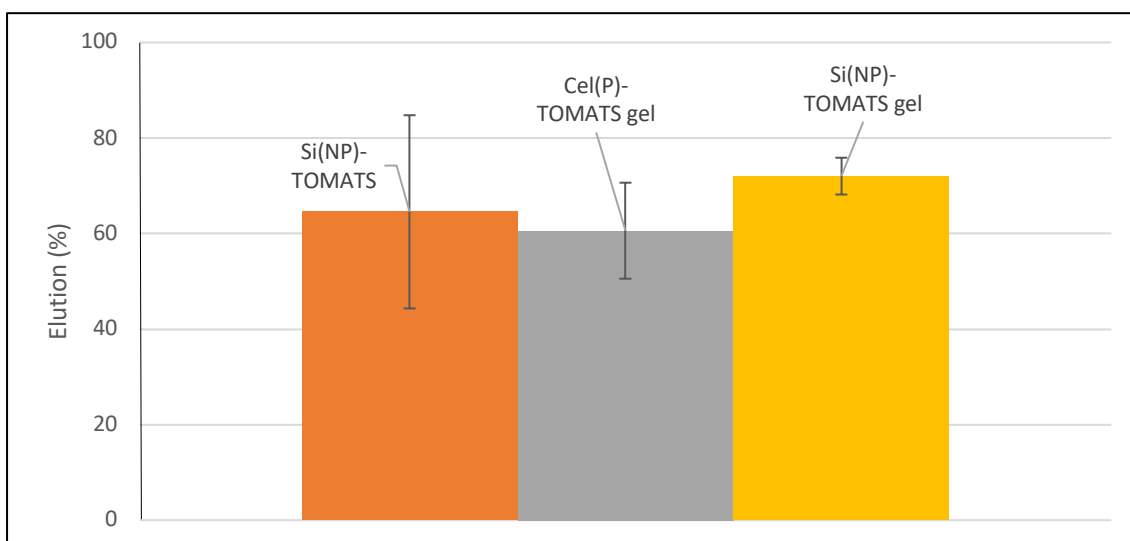

Fig 10: Comparison of gels and sorbents elution (%) for 8h experiments. Solution: 5 mL 10^{-3}M cysteine (SD for n=2).

4.3. Ethical and sustainability criteria

For the elaboration of this work, different ethical and sustainability criteria have been considered:

- Safety has been considered at all times to reduce the risk of accidents, using nitrile gloves and a gown in the laboratory.
- The manipulation of the solutions and the treatment of the waste has been done considering the criteria of sustainability that apply to the chemical analysis laboratory.
- The generated waste has been delivered to suitable waste protocols according to the instructions of the Faculty of Sciences and according to their chemical characteristics.

5. CONCLUSIONS

The main conclusions of this study are:

- PIMs made of CTA, TOMATS and plasticizers with long aliphatic chains allow the effective preconcentration of Hg from different natural waters, without an important effect on water matrix or presence of other metals.

- Novel sorbents based on SiO_2 nanoparticles and cellulose powder have been successfully prepared by impregnation of TOMATS. The impregnated sorbents have a higher capacity for extracting Hg than the original materials.

- Impregnated sorbents incorporated in a gel of agarose does not lose extraction efficiency towards Hg.

- A cysteine solution is able to elute the extracted metal in both systems using TOMATS: PIM and impregnated sorbents

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