Polymer-supported ionic liquid solid phase extraction for trace inorganic and organic mercury determination in water samples by flow injection-cold vapor atomic absorption spectrometry

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ABSTRACT

A simple and green technique named polymer-supported ionic liquid solid phase extraction (PSIL-SPE) was developed for mercury (Hg) species determination. Inorganic Hg (InHg) species was complexed with chloride ions followed by its introduction into a flow injection on-line system to quantitatively retain the anionic chlorocomplex ($HgCl_4^{2-}$) in a column packed with CYPHOS® IL 101-impregnated resin. The trapped InHg was then reduced with stannous chloride ($SnCl_2$) and eluted with the same flow of reducing agent followed by cold vapor atomic absorption spectrometry (CV-AAS) detection. Organic mercury species (OrgHg) did not interact with the impregnated resin and were not retained into the column. Total concentration of OrgHg was evaluated by difference between total Hg and InHg concentration. A 95% extraction efficiency was achieved for InHg when the procedure was developed under optimal experimental conditions. The limit of detection obtained for preconcentration of 40 mL of sample was 2.4 ng L^{-1} InHg. The relative standard deviation (RSD) was 2.7% (at 1 µg L^{-1} InHg and $n=10$) calculated from the peak height of absorbance signals (Gaussian-shape and reproducible peaks). This work reports the first polymer-supported IL solid phase extraction approach implemented in a flow injection on-line system for determination of Hg species in mineral, tap and river water samples.

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1. Introduction

In addition to natural inputs, anthropogenic sources of mercury (Hg) arise as the result of industrial, agricultural and pharmaceutical activities [1]. It is well-known that toxicity of Hg is highly dependent on its concentration, but more importantly, on its chemical form or species. In fact, organic Hg (OrgHg) species are generally more toxic than inorganic Hg (InHg) species [Hg(II)] as they can efficiently be adsorbed from the gastrointestinal tract and pass blood-brain and placenta barriers [2]. In order to obtain complete information about bioavailability and toxicological effects of Hg species, it is necessary to evaluate total concentration, and obtain both qualitative and quantitative data regarding speciation.

Several hyphenated techniques have been used for Hg species determination including gas chromatography (GC) [3,4] or high-performance liquid chromatography (HPLC) combined with a variety of detection techniques such as atomic absorption spectrometry (AAS) [5,6], atomic emission spectrometry (AES) [7,8], atomic fluorescence spectrometry (AFS) [9] or inductively coupled plasma mass spectrometry (ICP-MS) [10,11]. However, a preconcentration step is usually included in analytical methods because of the very low concentration of Hg species in unpolluted environmental samples. Thus, different approaches have been proposed for preconcentration of Hg species in water samples, such us liquid–liquid extractions (LLE) [4,12] and solid phase extractions (SPE) [13,14]. However, the use of classical extraction method requires large amounts of solvents, which may also result in environmental and safety drawbacks due to high volatilization. For this reason, a number of processes including encapsulation, co-polymerization or impregnation steps have been developed to immobilize the extractant in a suitable matrix [15,16]. The immobilization process not only reduces contamination risks but also makes the use of packed columns feasible for several applications.

Recently, considerable interest has been manifested in the use of ionic liquids (ILs) as an alternative to regular solvents producing

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volatile organic compounds. Ionic liquids display unique physico-chemical properties, including air and moisture stability, good thermal stability even at high temperatures, very low volatility, relatively favorable viscosity and miscibility with water and organic solvents, as well as good extractability for several ions [17]. In order to encourage the development of "green chemistry", ILs have been immobilized on different solid supports. Among ILs, 1-chlorovinyl-3-methylimidazolium chloride ([Nmim] [Cl]) ionic liquid have been immobilized onto not only PVC surface for retention of Cr(VI) [18], but also silica gel for preconcentration of 12 sulfonylurea herbicides [19]. Moreover, 1-hexyl-3-methylimid-azolium hexafluorophosphate ionic liquid ([C_6mim][PF_6]) has been immobilized on XAD-7 resin for determination of trace Hg [20]. Additionally, tetradecyl(trihexyl)phosphonium chloride (CYPHOS® IL 101) has been immobilized on XAD-7 resin and biopolymer capsules for recovery of Au [16], Pt [21] or Hg [15]. Nevertheless, CYPHOS® IL 101 has not been used for analytical applications as impregnation agent onto resins.

In this work, an on-line system was developed for selective retention of InHg, as $HgCl_4^{2-}$ anion, onto a column packed with a XAD polymeric resin impregnated with CYPHOS® IL 101. Subse-quently, the trapped InHg was reduced *in situ* with stannous chloride ($SnCl_2$) and displaced immediately from the column to the gas–liquid separator with the same stream of reducing agent. Finally, the volatilized Hg was measured by CV-AAS. Total Hg determination was performed by previous oxidation of OrgHg. Since OrgHg does not interact with the impregnated resin, it was deduced from total Hg and InHg concentrations. Retention mech-anisms of $HgCl_4^{2-}$ on different IL-impregnated resins, including Amberlite XAD-4, XAD-16 and XAD-1180, are discussed. To the best of our knowledge, this work reports the first analytical evidence that CYPHOS® IL 101-immobilized XAD resins can be highly efficient materials for Hg preconcentration under flow conditions.

2. Experimental

2.1. Instrumentation

The measurements were performed using a PerkinElmer 5100PC atomic absorption spectrometer (Norwalk, USA) equipped with a flow injection analysis system (FIAS 200) and an AS-90 autosampler. A Hg electrodeless discharge lamp (EDL) (PerkinElmer, Norwalk, USA) operated at a current of 170 mA and a wavelength of 253.7 nm with a spectral band pass of 0.7 nm was used. A deuterium background corrector was also used. Instrumental conditions used for Hg deter-mination were as shown in Table 1. Tygon-type pump tubing was employed to propel the sample, reagent and eluent. For the evalua-tion of InHg retention efficiency on different columns and XAD-1180 column adsorption capacity, a Perkin Elmer (Uberlingen, Germany) Model 5100ZL atomic absorption spectrometer equipped with a transversely heated graphite atomizer and a Zeeman-effect back-ground correction system was operated. A 20 μg of pre-reduced palladium as Pd(NO_3)$_2$ was employed for matrix modification. Finally, the following conditions for graphite furnace temperature program were selected: 110 °C (1 s ramp time/3 s hold time), 1000 °C (1 s ramp time/5 s hold time), 30 °C (5 s ramp time/20 s hold time), 110 °C (1 s ramp time/ 30 s hold time), 250 °C (pyrolysis temperature) (10 s ramp time/20 s hold time), 1300 °C (atomization temperature) (0 s ramp time/5 s hold time), 1800 °C (1 s ramp time/2 s hold time).

2.2. Reagents

All the reagents were of analytical grade and the presence of Hg was not detected within the working range. A 1000 mg L^{-1}

Table 1
Instrumental and experimental conditions for Hg species determination.

CV-AAS conditions	
EDL lamp current	170 mA
Slit width	0.7 nm
Analytical line: Hg	253.7 nm
HCl concentration	2.4 (mol L^{-1})
SnCl$_2$ concentration	5% (w/v)
SnCl$_2$ flow rate	6 mL min^{-1}
Carrier gas flow rate	50 mL min^{-1}
Column characteristics	
Length	5 cm
Internal diameter	2 mm
Filling material	Amberlite XAD-1180 impregnated with CYPHOS® IL 101
PSIL-SPE conditions	
Sample volume	40 mL
HCl concentration	3 mol L^{-1}
Sample loading flow rate	8 mL min^{-1}
Elution flow rate	6 mL min^{-1}

stock InHg standard was prepared from Hg(II) chloride (Merck, Darmstadt, Germany) in 0.1 mol L^{-1} nitric acid (Merck). Lower concentrations were prepared by diluting the stock solution with 0.1 mol L^{-1} nitric acid. Stock MeHg and PhHg solutions (1000 mg L^{-1}) were prepared from methylmercury chloride (Merck) and phenylmercury chloride (Merck) in pure ethanol and metha-nol (Merck), respectively. The organomercurial solutions were stored away from light at 4 °C to prevent decomposition. Finally, working standard solutions were prepared fresh daily. A SnCl$_2$ (Fluka, Buchs, Switzerland) solution was routinely prepared by dissolving 5 g of SnCl$_2$ in 20 mL of concentrated HCl and diluting to 100 mL with water. Hydrochloric acid (37%) (Ultra pure grade, Figmay, Córdoba, Argentina) was used. Purity of the Argon carrier gas was 99.99%. For chemical modification, a 1000 mg L^{-1} Pd solution was prepared by dissolving 62.7 mg Pd(NO_3)$_2 \cdot 2H_2O$ (Fluka, Buchs, Switzerland) in 25 mL 0.1% (v/v) HNO$_3$. Amberlite XAD-4, XAD-16 and XAD-1180 polymeric resins (Sigma-Aldrich, St. Louis, MO, USA) were assayed as filling materials for the micro-column. CYPHOS® IL 101 was kindly donated by Prof. Ullastiina Hakala (University of Helsinki, Finland) and provided by CYTEC Industries Inc. (Canada). Ultrapure water (18 MΩ cm) was obtained from a Milli-Q Academic A-10 Millipore Water Purification System (Billerica, MA, USA). All bottles used for storing samples and standard solutions and the glassware used in the experiments were cleaned with pure water, then soaked in 10% (v/v) HNO$_3$ solution at least for 24 h and thoroughly rinsed 5 times with ultrapure water before use.

2.3. Preparation of CYPHOS® IL 101-impregnated XAD resins

Before impregnation, Amberlite XAD-4, XAD-16 and XAD-1180 polymeric resins were purified with successive aliquots of water, 10% (v/v) HCl solution and ethanol in order to remove inorganic impurities and monomeric materials. Finally, resins were dried at room temperature. The impregnation of the resins with CYPHOS® IL 101 was performed by contact of 1 g of conditioned Amberlite XAD resin with a solution containing 500 mg of IL in 5 mL of ethanol for 6 h. Subsequently, the solvent was removed by filtra-tion with 0.45 μm pore size PTFE membrane filters (Millipore Corporation, Bedford, MA, USA) and the resultant IL-impregnated resin was dried at 50 °C for 30 min, followed by drying at room temperature during 24 h for complete evaporation of the solvent.

2.4. Sample collection and conditioning

For tap water samples collection, domestic water was allowed to run for 20 min and approximately a volume of 1000 mL was collected in a HDPE bottle. The manipulation and analysis of tap water samples was developed immediately after sampling. River water samples were collected in cleaned nitric acid-washed HDPE bottles rinsed 3 times with water sample prior to collection. A sample volume of 1000 mL was collected at a depth of 5 cm below the surface. Immediately after sampling, the 1000 mL water aliquots were filtered through 0.22 μm pore size PTFE membrane filters (Millipore Corporation) and stored at 4 °C. All sampling materials were previously washed overnight with a 1.5 mol L^{-1} HNO$_3$ solution and then rinsed with ultrapure water. The manipulation and analysis of the samples were developed in a regular clean laboratory.

2.5. Preconcentration and determination of InHg species

A schematic diagram of the preconcentration and determination system is shown in Fig. 1. In order to determine InHg, the whole preconcentration procedure was performed as follows: 40 mL of sample or a 0.5 μg L^{-1} InHg standard solution (for optimization) in 3 mol L^{-1} HCl medium were prepared in a 50 mL volumetric flask to form anionic chlorocomplexes. Before loading, the column was conditioned for preconcentration at the correct pH with 3 mol L^{-1} HCl, with valve (V) in the load position (a). Subsequently, the pre-treated aqueous sample solution was loaded into the column at a flow rate of 8 mL min^{-1}. After the loading time, the sample still present in the lines and the column was removed by further washing with 3 mol L^{-1} HCl solution. Then, valve (V) was switched to the injection position (b) and the retained metal complex was not only reduced with 5% (w/v) SnCl$_2$ in 2.4 mol L^{-1} HCl but also eluted with the same stream of the reducing agent at a flow rate of 6 mL min^{-1} directly into the gas–liquid separator of CV-AAS instrument. Calibration was performed against aqueous standard solutions submitted to the aforementioned extraction procedure.

2.6. Determination of total Hg and OrgHg species

For determination of total Hg, and before sample analysis, 40 mL-aliquots of sample were irradiated for 3 h with a 15 W UV lamp in order to photooxidize OrgHg species. In fact, the use of UV lamps has been previously reported by other authors for decomposition of OrgHg species [22,23]. In our work, oxidation process based on the utilization of UV irradiation was selected because it requires no addition of chemical oxidants, thus simplifying the procedure and reducing sample contamination. Afterwards, the same procedure described before was applied for total Hg determination. Finally, the concentration of OrgHg species was deduced by the difference between total Hg and InHg concentration.

3. Results and discussion

3.1. Impregnation of XAD resins with CYPHOS® IL 101 and Hg retention

According to International Union of Pure and Applied Chemistry (IUPAC), XAD resins under study are considered as mesoporous materials, with pore diameters ranged between 20 and 500 Å [24]. Table 2 shows the main properties of resins [25–27]. Specifically, Amberlite XAD-4 can be acknowledged as a hydrophobic polyaromatic resin; XAD-16 resin shows an equal dipole moment than XAD-4, while XAD-1180 resin is less polar than XAD-4. Therefore, different impregnation results were expected depending on the type of resin.

In the present work, retention capacity of IL-impregnated XAD resins was studied under flow or dynamic conditions. Home-made columns packed with the proposed IL-impregnated XAD resins were designed. Since each resin showed distinct properties, they were individually examined in order to analyze their retention capacity towards InHg. Thus, a study to compare the retention capacity of InHg by XAD-4, XAD-16 and XAD-1180 resins was developed. Initially, 50 mL of 25 μg L^{-1} InHg solution in 3 mol L^{-1} HCl were loaded onto the different columns and the effluent was subsequently analyzed with electrothermal atomic absorption
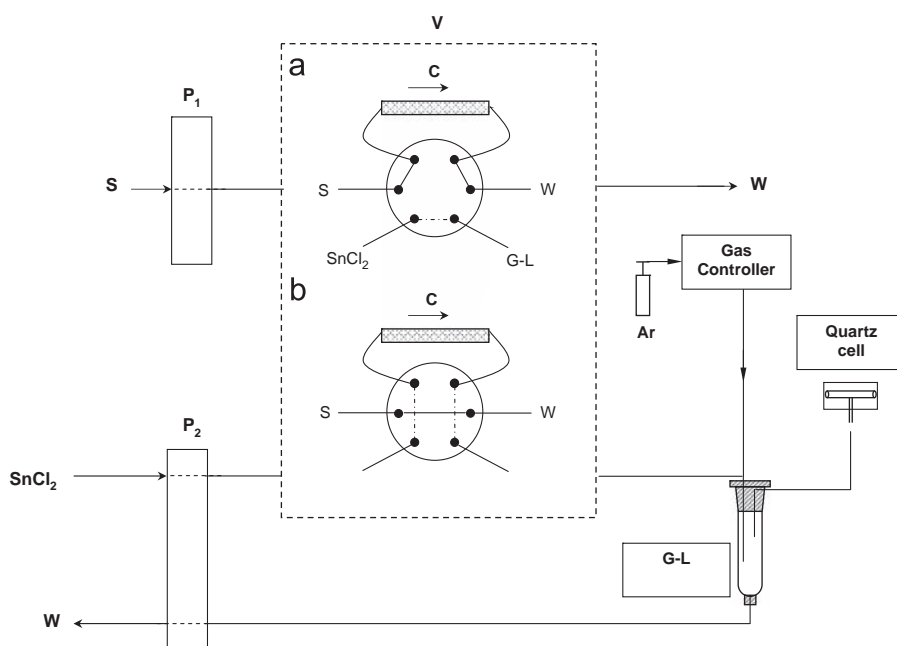

Fig. 1. Schematic diagram of the on-line PSIL-SPE set-up. S: sample (flow rate: 8 mL min^{-1}); SnCl$_2$: reducing-elution agent (flow rate: 6 mL min^{-1}); W: waste; P$_1$ and P$_2$: peristaltic pump; V: injection valve; C: column filled with IL-impregnated XAD resin; G–L: gas–liquid separator. Valve positions: (a) sample loading; (b) injection.

Table 2
Physical properties and retention performance of IL-impregnated XAD resins.

Property	Resin		
	XAD-4	XAD-16	XAD-1180
Particle size (mm)	0.49–0.69	0.56–0.71	0.35–0.6
Surface area ($m^2 g^{-1}$)	≥725	≥800	≥500
Porosity ($mL mL^{-1}$)	≥0.50	≥0.55	≥0.60
Pore diameter (Å)	40	100	140
Pore volume ($mL g^{-1}$)	0.98	1.82	1.68
Impregnation load with CYPHOS® IL 101 ($mg g^{-1}$ resin)	168	205	302
InHg retention (%)	50	73	95

spectrometry (ETAAS). It could be observed that XAD-4 resin exhibited the lowest retention efficiency, being 50% only. On the other hand, XAD-16 resin showed 73% retention towards InHg. Finally, the best results were obtained using XAD-1180 resin with 95%-retention of the analyte onto the solid phase material under the experimental conditions mentioned in Table 1.

Considering the dissimilar properties of XAD resins, it was expected to find some differences related to the amount of CYPHOS® IL 101 impregnated on each solid support. Thus, the amount of CYPHOS® IL 101 immobilized on the resin (q_{IL}) was evaluated following a procedure described by Arias et al. [28]. Basically, a known amount of impregnated resin was weight and mixed with ethanol for 24 h to dissolve the IL. Subsequently, the solvent was separated from the resin by decantation. Finally, the resin was dried at 50 °C for 24 h for complete solvent evaporation. The mass difference between impregnated (XAD$_{IL}$) and washed resin (XAD) was hence useful to calculate the mass of extractant immobilized on the resin (q_{IL}).

$$q_{IL} = XAD_{IL} - XAD$$

It was observed that XAD-4, XAD-16 and XAD-1180 resins supported 165, 228 and 302 mg CYPHOS® IL 101 g^{-1} of resin, respectively. Since microcolumns are normally filled with approximately 300 mg of resin, the use of these little volumes of extractant turns the proposed PSIL into a convenient and green SPE technique, in which the extractant agent is impregnated onto a polymeric solid support.

Fig. 2 shows that InHg retention was closely linked with the amount of IL impregnated on the resin. Thus, a linear relationship between both variables was obtained, with a correlation coefficient of 0.9965. Finally, Amberlite XAD-1180 could be impregnated not only with the highest amount of IL but also led to the highest retention of InHg on the resin. On the other hand, physical properties shown in Table 2 could be linked with the amount of impregnated IL and analyte retention. Thus, the influence of several properties of XAD resins, including particle size, surface area, porosity, pore diameter and pore volume, was considered. On the one hand, particle sizes of the three Amberlite resins under study are not significantly different, thus suggesting that this property would not have influence on neither the impregnation of the IL onto the resin pores nor the retention of InHg. On the other hand, although surface area and pore volume vary depending on each resin, no logical relations could be established between the results of this study and these two properties. Furthermore, the effect of resin porosity on analyte retention capacity was examined. The mass of CYPHOS® IL 101 IL impregnated onto XAD resins could be related with the specific porosity of each resin. Thus, Amberlite XAD-1180 shows the highest porosity and hence the highest number of hollows to be impregnated by the IL. Additionally, the influence of pore diameter on InHg retention was analyzed. Amberlite XAD-4 resin exhibits the lowest pore diameter while XAD-16 has a medium pore diameter. Finally, XAD-1180
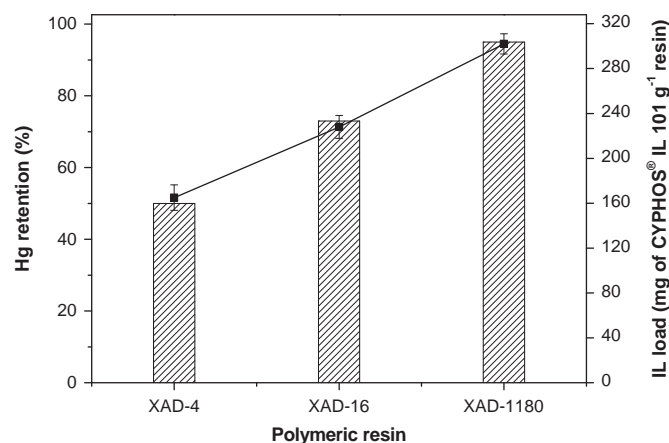

Fig. 2. InHg retention (%) using the IL-impregnated XAD resins under study (bar graph). Amount (mg) of CYPHOS® IL 101 g^{-1} of XAD-4, XAD-16 or XAD-1180 resin, respectively (line graph).

resin displays the highest pore diameter. Therefore, pore diameter can also be related with the mass of impregnated CYPHOS® IL 101 and subsequent InHg retention. The higher the pore diameter of the resin, the higher amount of CYPHOS® IL 101 is expected to be impregnated in the solid support. Subsequently, higher retention of the analyte onto XAD resin can be expected too.

Once InHg retention was evaluated, the retention of OrgHg species onto the columns was studied. Thus, 50 mL of 25 µg L^{-1} OrgHg solution in 3 mol L^{-1} HCl were loaded onto the different columns and effluent was also analyzed by ETAAS. No retention of OrgHg species was observed with any of the IL-impregnated XAD resins. The lack of affinity of these impregnated materials for OrgHg species could be attributed to the fact that these compounds form neutral complexes with chloride ions [29,30], thus avoiding the formation of ion pairs with CYPHOS® IL 101 and their retention onto the column. Additional discussion is provided later on in this work. As XAD-1180 resin showed the best performance for retention of the analyte, it was chosen as the filling material.

3.2. Column design and performance

The effect of different parameters such as column internal diameter and length on analyte retention was evaluated. It was observed that a minimal column length of 5 cm was the best choice for optimal retention of the anionic InHg chlorocomplex. Shorter columns did not show efficient retention as $HgCl_4^{2-}$ was not fully retained on the IL-impregnated resin. Further increases in length did not lead to any improvement in InHg retention. Likewise, the inner diameter was another variable to be considered. It is already known that inner diameter has an important effect on signal dispersion generated in an on-line preconcentration

system [31]. Therefore, the effect of different inner diameters of the microcolumn on analyte dispersion was evaluated. A reduced inner diameter was preferred in order to achieve low dispersion, allowing analyte elution in a minimal volume of eluent. A 2-mm inner diameter was found to be effective for anionic complex retention. The high back pressure built-up inside the flow injection system limited the application of columns with lower inner diameter.

3.3. Source and concentration of chloride ions

It has to be pointed out that an increase of experimental errors could be feasible when chloride ions originated from salts are used as they have to be weighted, solubilized and transferred to a volumetric flask. For this reason, HCl was preferred as source of chloride ions for $HgCl_4^{2-}$ complex formation. Concentration of HCl was evaluated in the interval of 0.5–5 mol L^{-1}. As shown in Fig. 3(a), the best results were achieved with concentration of 3 mol L^{-1}. Therefore, 3 mol L^{-1} was selected. This large excess of chloride ions ensured the occurrence of the analyte only in the form of $HgCl_4^{2-}$ complex [32]. In accordance with Guibal et al. [15]. $HgCl_4^{2-}$ anion would probably interact with tetradecyl(trihexyl)phosphonium cation bound to CYPHOS® IL 101, exhibiting an ion exchange

mechanism between $HgCl_4^{2-}$ present in sample solution and Cl^- originated from CYPHOS® IL 101. Moreover, this would also explain the inability of OrgHg neutral complex to be retained on the IL-impregnated XAD resins. Other authors have suggested the possibility that an ion-pairing mechanism could be involved in the retention of $HgCl_4^{2-}$ on IL-impregnated resins [21].

3.4. Sample solution flow rate

The sample loading flow rate through the column is a very important parameter, since this is one of the steps that mainly controls the time of analysis. Moreover, this variable is critical to achieve high retention of InHg anionic complex. The solution was passed through the column with loading flow rates adjusted in the range of 1–12 mL min^{-1}. No major changes on the relative response were observed between 3 and 8 mL min^{-1}, while it diminished at flow rate values higher than 8 mL min^{-1} (Fig. 3 (b)). This decrease on the analytical signal could be attributed to insufficient contact time between the analyte and CYPHOS® IL 101 phase. A flow rate of 8 mL min^{-1} was chosen for further experiments.

3.5. Cold vapor generation and elution conditions

The removal of InHg from CYPHOS® IL 101-impregnated polymer resin has been previously evaluated [15]. The highest desorption (97%) was obtained with nitric acid (HNO_3 6 M). However, this stage was assayed in a batch mode, as 2 h were needed in order to reach the desorption equilibrium. In our work, the elution of the analyte was studied under flow conditions and using HNO_3 was assayed at concentrations between 1 and 5 mol L^{-1}. Non Gaussian-shape elution peaks and low analytical recovery (25%) were obtained, most probably due to insufficient contact time for optimal InHg recovery from the column under on-line conditions. Alternatively, a stream of reducing solution, using $SnCl_2$ in HCl medium was evaluated as elution agent. It could be observed that the aforementioned solution was effective for both reduction and elution steps. The fast elution of Hg from the microcolumn can be explained considering the high kinetic of Hg vapor generation reaction and release from the IL phase. Thus, optimization of CV generation and elution conditions was jointly developed.

The concentration of the reducing agent was an important parameter to be assayed. The best signal-to-noise ratio was obtained with a concentration of 5% (w/v) $SnCl_2$ (Fig. 4(a)). Higher concentrations of the reducing agent did not lead to significant differences of Hg signals. Additionally, HCl concentration in the reducing solution was studied in detail. As shown in Fig. 4(b), 2.4 mol L^{-1} HCl was the most suitable concentration for CV generation. A 5% (w/v) $SnCl_2$ solution with 2.4 mol L^{-1} HCl concentration guaranteed the displacement of the volatilized analyte to the gas–liquid separator since the InHg reduction step is practically instantaneous [33]. The effect of flow rate of the reducing-elution agent was also studied. The effect of elution flow rate is illustrated in Fig. 4(c), from which it can be observed that an elution flow rate of about 6 mL min^{-1} was optimal. Furthermore, Ar was used as carrier gas in this work. It was found that 50 mL min^{-1} of Ar allowed an efficient separation and transport of volatile species to the absorption cell.

3.6. Interference study

The effects of potential interfering species on Hg determination were assayed. The study was performed by loading into the column 40 mL of solutions containing 1 µg L^{-1} InHg and concomitant ions at the concentration levels at which they may occur in
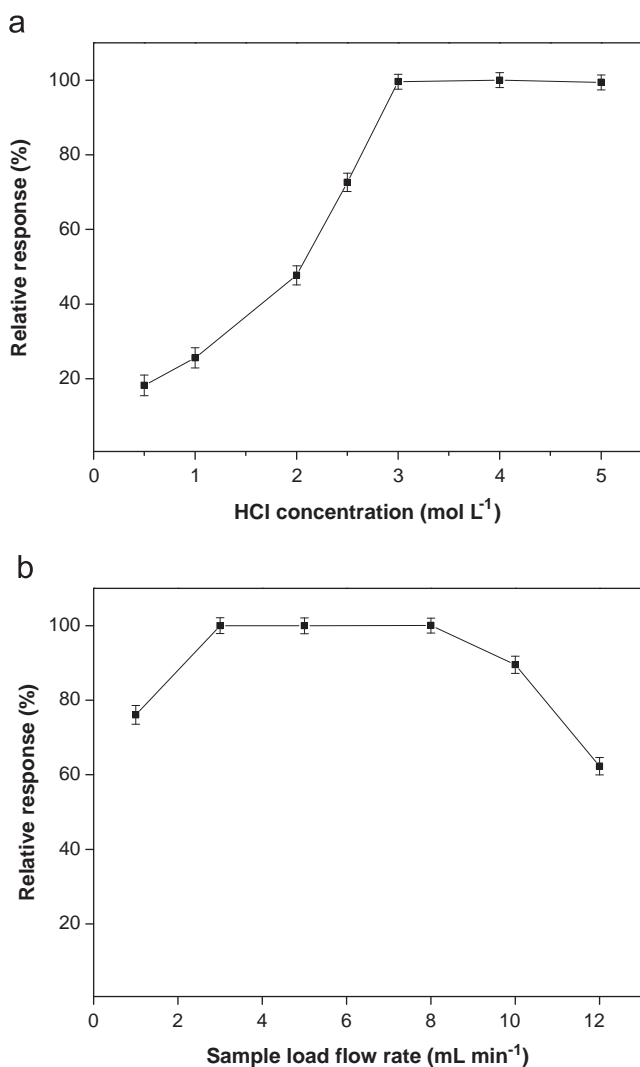

Fig. 3. (a) Effect of HCl concentration (mol L^{-1}) on $HgCl_4^{2-}$ complex formation and retention, and (b) Influence of sample load flow rate (mL min^{-1}) on analytical response.
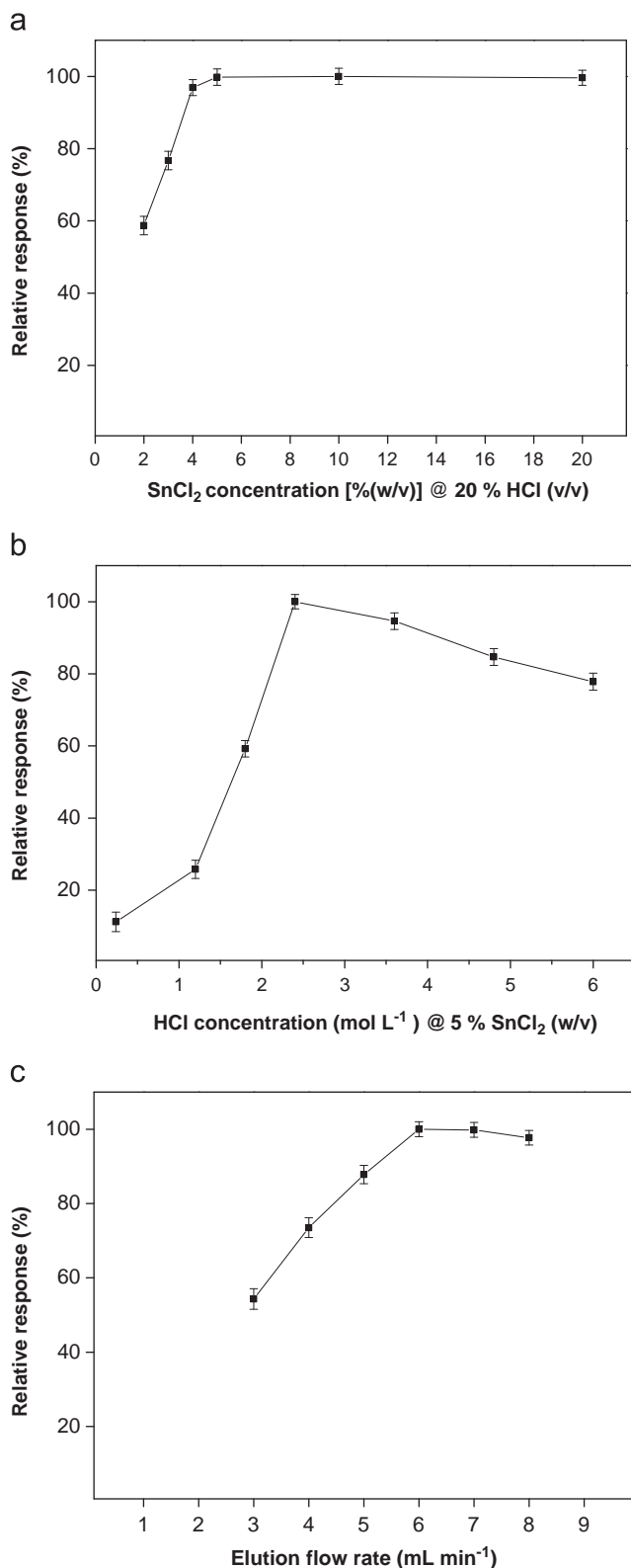
Fig. 4. (a) Effect of SnCl$_2$ concentration, (b) HCl concentration and (c) flow rate (mL min^{-1}) on cold vapor generation and elution of Hg.

the samples or even higher. It was necessary to evaluate the individual effect of potential interfering ions on HgCl$_4^{2-}$ formation, such as Fe^{3+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Tl^{3+} and NH$_4^+$. The results indicated that the efficiency of InHg retention was not affected by the presence of a high concentration of matrix ions. It was observed that Fe^{3+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+} and Mn^{2+} could

be tolerated up to at least 5 mg L^{-1}. Moreover, NH$_4^+$ and Tl^{3+} cations did not interfere up to at least 1 mg L^{-1}. The high concentration of chloride ions was enough to ensure total complexation of the analyte even in the presence of the interfering cations. Likewise, the effect of typical anions such us F$^-$, SO$_4^{2-}$, CO$_3^{2-}$, PO$_4^{3-}$ and NO$_3^-$ which might occur in the samples under study was examined. It was observed that these anions did not interfere with the accurate Hg determination up to at least 500 mg L^{-1}. Moreover, absorbance signals of the blanks were not modified by the concomitant ions assayed in this work.

3.7. Performance of preconcentration system

The time necessary for preconcentration of 40 mL of water sample was about 5.5 min which can be itemized into the following steps: 5 min at 8 mL min^{-1} for loading, 10 s at 6 mL min^{-1} for elution and 20 s at 8 mL min^{-1} for washing. Thus, the sample throughput was about 11 samples per hour which is significantly higher than that obtained in previous works were 4 samples per hour was reported [34–36]. On the other hand, the capacity to reuse the column was assessed by monitoring the change in the recoveries of analyte throughout several adsorption and elution cycles. An aliquot of 5 mL of 10% (v/v) HNO$_3$ was used to regenerate the column after each cycle. In presence of this mineral acid, the column keeps stable without either deterioration or decrease in analyte retention. This novel technique showed the ability to use the column filled with CYPHOS® IL 101-impregnated XAD-1180 resin for at least 300 preconcentration cycles with no decrease in column performance.

Flow or dynamic adsorption capacity of the microcolumn was evaluated as it determines the amount of sorbent required to quantitatively retain the analyte from sample solution [37]. In this work, a 20 mg L^{-1} InHg solution was passed through the column at 8 mL min^{-1}. An aliquot of 500 μL of the effluent was sampled every 15 s. Finally, Hg was determined in all the aliquots by ETAAS. The highest retention capacity was reached only when 25 mL of a 20 mg L^{-1} InHg solution was loaded into the microcolumn, turning this novel CYPHOS® IL 101-immobilized solid support into an excellent alternative for Hg determination.

3.8. Analytical figures of merit

Extraction efficiency, limit of detection, linearity, correlation coefficient and sensitivity enhancement factor (EF) were determined in this work. A 95% extraction efficiency of InHg was achieved under optimal experimental conditions (Table 1). Moreover, a 51-fold EF was obtained (for 40 mL of sample) with respect to conventional FI-CV-AAS analysis when the preconcentration method was applied. The calibration graph was linear in the range of 0.01–2.30 μg L^{-1}, with a correlation coefficient of 0.9994. The relative standard deviation (RSD) for ten replicate measurements at 1 μg L^{-1} of InHg was 2.7%. Finally, the LOD, calculated based on the signal at intercept and three times the standard deviation about regression of the calibration curve [38], was 2.4 ng L^{-1} InHg.

In order to demonstrate the strengths of the proposed method, a comparison with other methods reported in the literature is shown in Table 3. As can be observed, some of the previous methods reported a high consumption of ILs, which makes these techniques more expensive. In contrast, the proposed methodology is able to use the microcolumn filled with IL-impregnated resin for at least three hundred cycles, turning this method into a cost-effective alternative. Although the method proposed by Chen et al. showed very low consumption of IL, sampling frequency was lower than that obtained by our work. Thus, the proposed method exhibits important analytical advantages such as low detection limit and high sample throughput. All in all, the proposed PSIL-SPE

Table 3
Analytical methods reported for metal preconcentration using SPE with supported-IL sorbents.

Method	IL	Analyte	Speciation analysis	LOD (ng L^{-1})	RSD (%)	Sample consumption (mL)	IL consumption (mg)/application yield	Sampling frequency (h^{-1})	Refs.
SPE-FAAS	[C$_4$mim][PF$_6$][a]	Bi	No	2300	2.3	500	2000/7 cycles	2	[35]
SPE-ICP-AES	[(Tesp)mim][Cl][b]	Fe	No	480	1.7	150	n.r.[c]	1	[36]
SPE-ETAAS	[Nmim][Cl][d]	Cr	Yes	3.0	2.9	2	0.045[e]/300 cycles	9	[18]
SPE-AAS	[C$_6$mim][PF$_6$][f]	Pb–Cd	No	1610	1.4	50	13.33/sample	n.r.[c]	[40]
SPE-CV-AAS	[C$_4$mim][PF$_6$]	Cd	No	4.6	2.2	200	10/3 cycles	3	[34]
PSIL-SPE-CV-AAS	CYPHOS®IL 101	Hg	Yes	2.3	2.7	40	302/at least 300 cycles	11	This work

[a] [C$_4$mim][PF$_6$] IL: 1-butyl-3-methylimidazolium hexafluorophosphate.
[b] [(Tesp)mim][Cl]: N-3-(-3-triethoxysilylepropyl)-3-methylimidazolium chloride.
[c] n.r.: not reported.
[d] [Nmim][Cl]: 1-chlorovinyl-3-methylimidazolium chloride.
[e] Data reported in mL.
[f] [C$_6$mim][PF$_6$] IL: 1-hexyl-3-methylimidazolium hexafluorophosphate.

Table 4
Determination and recovery study of InHg and OrHg in drinking and natural water samples (95% confidence interval; $n=6$).

Sample	Spiked Hg as		InHg		OrHg	
	InHg (µg L^{-1})	OrgHg (µg L^{-1})	Found (µg L^{-1})	Recovery (%)[a]	Found (µg L^{-1})	Recovery (%)[a]
Mineral water	0	0	0.04 ± 0.01	–	< LOD	–
	1.00	0	1.02 ± 0.02	98.2	< LOD	–
	0	1.00	0.04 ± 0.01	–	1.00 ± 0.05	100
	1.00	1.00	1.05 ± 0.02	101	0.98 ± 0.05	98.5
Tap water	0	0	0.06 ± 0.01	–	< LOD	–
	1.00	0	1.09 ± 0.03	103	< LOD	–
	0	1.00	0.14 ± 0.01	–	1.01 ± 0.05	101
	1.00	1.00	1.05 ± 0.02	99.6	1.00 ± 0.05	100
River water	0	0	0.07 ± 0.01	–	0.03 ± 0.02	–
	1.00	0	1.08 ± 0.03	101	0.04 ± 0.02	–
	0	1.00	0.06 ± 0.01	–	1.01 ± 0.04	98.1
	1.00	1.00	1.03 ± 0.02	96.2	1.00 ± 0.04	97.3

[a] 100[(Found-base)/added].

technique using CYPHOS® IL 101 and combined with CV-AAS is an excellent analytical tool for the determination of Hg species in real water samples. A previous work about determination of mercury in water samples has been published by our research group [23]. In that method, 700 mg of IL had to be used for analysis of one sample only. On the other hand, the immobilization process allows the use of 90.6 mg of IL (amount of IL on column filled material) for at least 300 preconcentration cycles, turning the proposed PSIL-SPE technique into a green and cost-effective alternative.

3.9. Mercury speciation analysis in water samples

To assay the reliability of the proposed method, different samples including mineral, tap and river water were analyzed in this work. A recovery study was developed on water samples spiked with InHg and OrgHg (as equimolar concentrations of MeHg and PhHg) at known concentration levels. Recoveries for spiked Hg species ranged between 96.2% and 103% (Table 4). Regarding total Hg determination, the accuracy of the proposed method was evaluated by analysis of a certified reference material (CRM), QC Metal LL3 Mercury in water, with a declared Hg concentration of 6.48 ± 0.51 µg L^{-1}. Since the certified concentration value in the CRM was higher than the upper limit of the linear range achieved by this method, a 4-fold dilution had to be implemented prior to the analysis. Using the method developed in this work, Hg concentrations in the CRM was found to be

6.45 ± 0.03 µg L^{-1} (95% confidence interval; $n=6$), thus indicating an acceptable accuracy of the analytical method.

Finally, the method was applied for Hg species determination in different water samples. Concentrations found in mineral water samples were in the range of 0.03–0.05 µg L^{-1} for InHg, while OrgHg was generally not detected. Concentrations in tap water were between 0.04 and 0.06 µg L^{-1} for InHg, meanwhile OrgHg was not detected. On the other hand, concentrations found in river water samples were in the range of 0.05–0.08 µg L^{-1} for InHg and not detected – 0.04 µg L^{-1} for OrgHg (95% confidence interval; $n=6$). It must be stated, that mean concentration values of Hg species obtained for each type of water sample were similar to results obtained by other authors for the same kind of samples [1,39].

4. Conclusions

A novel and sensitive analytical methodology for Hg species preconcentration and determination in several water samples using non-volatile extraction solvents, such us ILs, has been presented in this work. The results demonstrate the possibility of using CYPHOS® IL 101-impregnated Amberlite XAD-1180 resin for efficient preconcentration and determination of Hg species. Moreover, an important advantage from the use of ILs as impregnation agents is that the overall consumption is minimal in comparison with their use in conventional LLE techniques. Thus, at least three hundred preconcentration cycles are feasible using

the same IL-impregnated microcolumn, while in classical LLE just a few analyses could be developed with an equivalent volume of IL. Finally, the IL-impregnated XAD resin showed high capacity to retain InHg. In conclusion, a green, simple, sensitive and cost-effective determination of total Hg and its inorganic and organic fractions has been successfully achieved with the proposed PSIL-SPE technique.

Acknowledgments

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