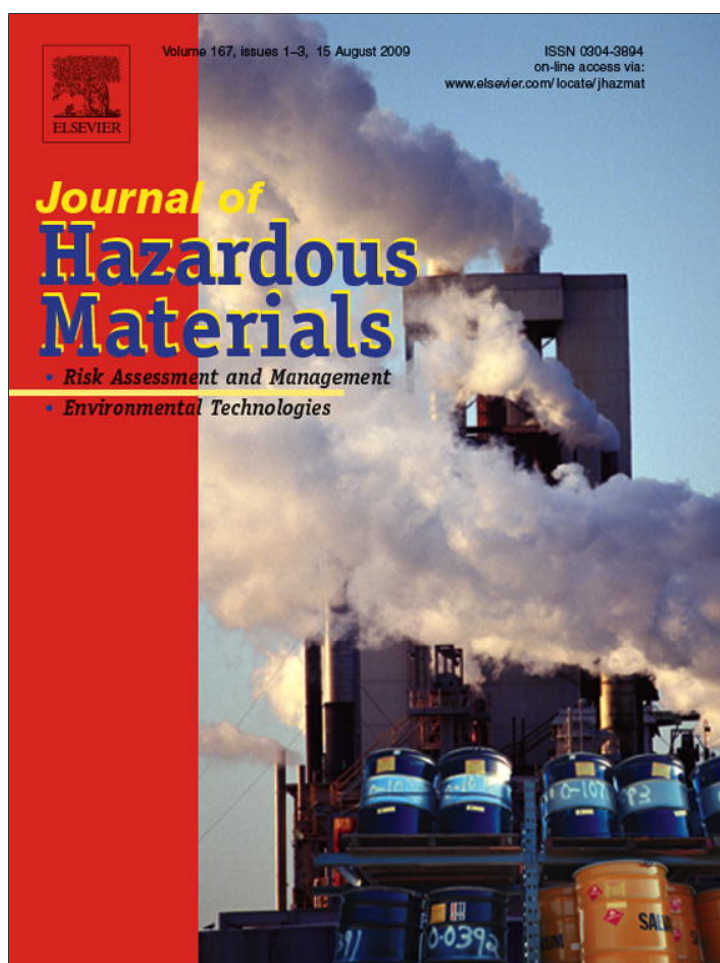


Provided for non-commercial research and education use.
Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

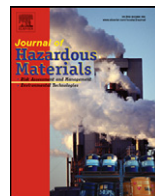
In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

<http://www.elsevier.com/copyright>



Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Trace mercury determination in drinking and natural water samples by room temperature ionic liquid based-preconcentration and flow injection-cold vapor atomic absorption spectrometry

Estefanía M. Martinis^a, Paula Bertón^a, Roberto A. Olsina^c,
Jorgelina C. Altamirano^{a,b}, Rodolfo G. Wuilloud^{a,b,*}

^a Laboratory of Environmental Research and Services of Mendoza (LISAMEN), (CCT – CONICET – Mendoza), Av. Ruiz Leal S/N Parque General San Martín, CC. 131, M 5502 IRA Mendoza, Argentina

^b Instituto de Ciencias Básicas, Universidad Nacional de Cuyo, Mendoza, Argentina

^c INQUISAL-CONICET, Departamento de Química Analítica, Facultad de Química, Bioquímica y Farmacia, Universidad Nacional de San Luis, San Luis, Argentina

ARTICLE INFO

Article history:

Received 6 August 2008

Received in revised form 18 December 2008

Accepted 7 January 2009

Available online 15 January 2009

Keywords:

1-Butyl-3-methylimidazolium

hexafluorophosphate

Ionic liquid

Mercury

Preconcentration

ABSTRACT

A liquid–liquid extraction procedure (L–L) based on room temperature ionic liquid (RTIL) was developed for the preconcentration and determination of mercury in different water samples. The analyte was quantitatively extracted with 1-butyl-3-methylimidazolium hexafluorophosphate ([C₄mim][PF₆]) under the form of Hg-2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (Hg-5-Br-PADAP) complex. A volume of 500 μ l of 9.0 mol L⁻¹ hydrochloric acid was used to back-extract the analyte from the RTIL phase into an aqueous media prior to its analysis by flow injection-cold vapor atomic absorption spectrometry (FI-CV-AAS). A preconcentration factor of 36 was achieved upon preconcentration of 20 mL of sample. The limit of detection (LOD) obtained under the optimal conditions was 2.3 ng L⁻¹ and the relative standard deviation (RSD) for 10 replicates at 1 μ g L⁻¹ Hg²⁺ was 2.8%, calculated with peaks height. The method was successfully applied to the determination of mercury in river, sea, mineral and tap water samples and a certified reference material (CRM).

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Mercury is one of the most harmful pollutants and it has become widespread into the environment mainly as a result of anthropogenic activities [1,2]. Mercury has no beneficial biological function, and its presence in living organisms is associated with cancer, birth defects, and other undesirable outcomes [3,4]. One of the routes of incorporation of mercury into the human body is drinking water [5]. Hence, control of mercury is becoming increasingly important, especially in water sources. Since mercury concentrations in waters are expected to be very low [6], powerful techniques are required and only few of them show enough sensitivity.

Different analytical techniques have been used for mercury determination at low concentrations including, cold vapor atomic absorption spectrometry (CV-AAS) [7], cold vapor atomic fluorescence spectrometry (CV-AFS) [8], flow injection-inductively coupled plasma optical emission spectrometry (FI-ICP-OES) [9],

and inductively coupled plasma mass spectrometry (ICP-MS) [10]. ICP-MS is used for the determination of mercury due to its high sensitivity, high selectivity, and high sample throughput. However, the cost of such instrumentation may still be prohibitive to many laboratories. Although ICP-OES and CV-AAS are the most used techniques for the determination of mercury, the low concentration level of mercury in water is not always compatible with the detection limit of these techniques. In order to achieve accurate, reliable and sensitive results, preconcentrations and separations are needed when the concentrations of analytes in the sample are too low to be determined directly by CV-AAS. The use of solvent extraction has been applied for determination of heavy metals at trace level prior to AAS detection [11]. These analytical approaches can effectively decrease the detection limit and eliminate matrix interference. However, the use of classical extraction method requires large amounts of high purity solvents, which may also result in environmental and safety problems due to high volatilization. Recently, considerable interest has been manifested in the use of room temperature ionic liquids (RTIL) as an alternative to regular solvents in a wide range of applications due to their unique chemical and physical properties [12–14]. Some of them are water stability, negligible vapor pressure, the fact that they remain liquid at room temperature, and their relatively favorable viscosity and density

* Corresponding author. Tel.: +54 261 5244064; fax: +54 261 5244001.

E-mail address: rwuilloud@lab.cricyt.edu.ar (R.G. Wuilloud).

URL: <http://www.cricyt.edu.ar/lisamen/> (R.G. Wuilloud).

characteristics [15]; what makes their use very attractive in separation processes [16].

The RTIL 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim][PF_6]$) has been proposed as a media for mercury extraction [17,18] as it forms a biphasic liquid system with water [19] and is therefore a suitable reagent for the extraction of metal ions from aqueous solution. However, the distribution ratio of Hg^{2+} between $[C_4mim][PF_6]$ and an aqueous phase is 0.84 [20,21]. In order to improve the extraction efficiency of a metal ion the use of a complexing reagent, such as 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) is an appropriate choice [9]. In fact, and to our current knowledge, the combination of $[C_4mim][PF_6]$ and 5-Br-PADAP chelating agent have not been used so far in an analytical extraction/preconcentration technique. Li et al. [22] developed an analytical extraction/preconcentration technique using 1-butyl-3-trimethylsilylimidazolium hexafluorophosphate for determination of mercury by a batch-type system CV-AAS. However, batch cold vapor generation methodology could suffer from some disadvantages, such as off-line analysis leading to high consumption of sample, as well as being time consuming. In addition, the risk of reagent and sample contamination is higher than using flowing injection-based analytical methodologies.

In this work, a novel application of the RTIL $[C_4mim][PF_6]$ as solvent for extraction and preconcentration of trace levels of mercury and further on-line determination by FI-CV-AAS is presented. Mercury was successfully extracted and preconcentrated under the form of Hg-5-Br-PADAP complex and later back-extracted into diluted hydrochloric acid. The feasibility of the proposed method was demonstrated by determining mercury at trace levels in real samples including, drinking, river and seawater matrices.

2. Experimental

2.1. Instrumentation

The experiments were performed using a PerkinElmer 5100PC atomic absorption spectrometer (PerkinElmer, Norwalk, USA) equipped with a flow injection analysis system (FIAS 200) and an AS-90 autosampler. A mercury electrodeless discharge lamp (PerkinElmer, Norwalk, USA) operated at a current of 210 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. Conditions for CV-AAS analysis were as follows: 0.2% (m/v) sodium borohydride (Merck, Darmstadt, Germany) at 5 mL min^{-1} , 3% (v/v) HCl (Merck, Darmstadt, Germany) at 8 mL min^{-1} , and 50 mL min^{-1} argon as a carrier. The sample injection volume was $250 \mu\text{L}$ in all experiments. Tygon type pump tubing was employed to carry sample, reagent and eluent.

2.2. Reagents

All the reagents were of analytical grade and the presence of mercury was not detected within the working range. A $1000 \mu\text{g mL}^{-1}$ Hg^{2+} stock solution was prepared from mercury(II) chloride (Merck, Darmstadt, Germany) in 0.1 mol L^{-1} nitric acid (Ultra pure grade, Figmay, Córdoba, Argentina). Lower concentrations were prepared by diluting the stock solution with 0.1 mol L^{-1} nitric acid. A $10^{-2} \text{ mol L}^{-1}$ 5-Br-PADAP (Aldrich, Milwaukee, WI, USA) solution was prepared in ethanol. Lower concentrations were prepared by serial dilution with ethanol. The buffer solution ($5 \times 10^{-2} \text{ mol L}^{-1}$) was prepared dissolving calcined sodium tetraborate (Merck) and taken to 1000 mL with ultrapure water. Sodium tetrahydroborate reagent was freshly prepared daily by dissolving the appropriate amount of $NaBH_4$ (Merck) in 0.05% (m/v) sodium hydroxide solution (Aldrich). After dissolution of the reagents, the solution was filtered through a Whatman No. 42 filter paper to

remove undissolved solids. Diluted HCl (Ultra pure grade, Figmay, Córdoba, Argentina) and NaOH (Merck) were used to adjust pH. A $NaNO_3$ (Merck) solution 2 mol L^{-1} was used in order to adjust ionic strength. Ultrapure water ($18 \text{ M}\Omega \text{ cm}$) was obtained from a Millipore Continental Water System. $[C_4mim][PF_6]$ was synthesized according with the method proposed by Huddleston et al. [23] and stored in contact with ultrapure water to equilibrate the water content in the RTIL [20].

2.3. Sample collection and conditioning

Tap water was allowed to run for 20 min and approximately 2000 mL of tap water was collected. River and seawater samples were collected in cleaned bottles rinsed three times with water sample prior to sample collection. A sample volume of 2000 mL was collected at a depth of 5 cm of the surface. Mineral water was a commercial product. The water samples were filtered through $0.22 \mu\text{m}$ pore-sized membrane filters immediately after sampling. They were irradiated for 3 h with a 150 W UV lamp in order to photooxidize organo-mercury compounds that could be present in water [9]. All material used for sampling activities was previously washed overnight with a 10% (v/v) HNO_3 water solution and rinsed with ultrapure water.

2.4. Extraction and preconcentration procedure

The extraction/preconcentration procedure was performed as follows: 0.5 mL of ethanol, $150 \mu\text{L}$ of $10^{-4} \text{ mol L}^{-1}$ 5-Br-PADAP solution, and 2 mL of buffer solution $5 \times 10^{-2} \text{ mol L}^{-1}$ (pH 9.2) were added to 20 mL of water sample in a centrifuge tube. For optimizing the preconcentration technique, 20 mL of $1 \mu\text{g L}^{-1}$ Hg^{2+} standard solution was used instead of the water sample. An amount of 0.7 g of $[C_4mim][PF_6]$ was added to the mix and the resulting system was shaken for 2 min with a vortex stirrer. In order to separate the phases, the turbid solution was centrifuged during 7 min at 3500 rpm ($1852.2 \times g$) and the aqueous phase was removed with a transfer pipet. The analyte was then back-extracted to an acidic aqueous phase by adding $500 \mu\text{L}$ of a 9 mol L^{-1} HCl solution, shaking it for 3 min and final centrifugation as it was mentioned before. Finally, a $250 \mu\text{L}$ aliquot of the resulting solution was analyzed by FI-CV-AAS. A schematic diagram of the preconcentration and determination system is shown in Fig. 1. Calibration was performed against aqueous standard solutions submitted to the same extraction procedure. Blank solutions were analyzed in the same manner as standard and sample solutions.

3. Results and discussion

3.1. Study of chemical vapor generation conditions

Cold vapor generation from the back-extracting acid solution was studied in order to reach the conditions for maximum sensitivity. The $NaBH_4$ concentration was an important parameter to be optimized due to the possible presence of organic compounds resulting during the back-extraction process from the RTIL phase. It was verified that the best signal to noise ratio was obtained with a reductant concentration of 0.2% (m/v). Consequently, this $NaBH_4$ concentration was adopted. The HCl concentration most suitable and compatible with the preconcentration and cold vapor generation system was also studied. The results obtained showed that HCl concentrations above 2% (v/v) allowed achieving the highest response for both systems. Hence, 3% (v/v) HCl was selected as the working concentration. The influence of $NaBH_4$ solution and HCl carrier solution flow rates on CV-AAS analytical response to mercury was studied in the intervals of $3\text{--}8 \text{ mL min}^{-1}$ and

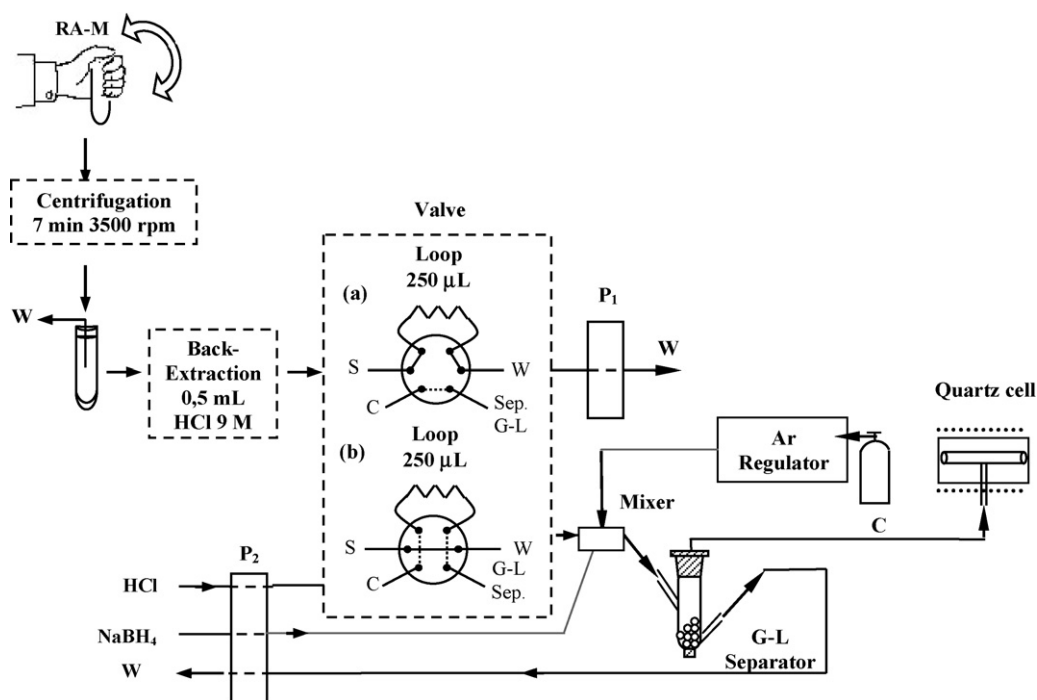


Fig. 1. Schematic diagram of the instrumental setup. RA-M: reagent adding and mixing, S: sample, C: carrier solution, W: waste, P₁ and P₂: peristaltic pumps, V: injection valve. Valve positions: (a) sample loading; (b) injection.

6–14 mL min⁻¹, respectively. Analytical signals increased with sample and reagent flow rates up to 5 mL min⁻¹ for NaBH₄ solution and 8 mL min⁻¹ for HCl solution. Higher flow rates for both reductant and acid did not lead to significant change in signals. Argon 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. This value was selected for further experiments.

3.2. Optimization of mercury extraction with RTIL

The study of the preconcentration variables was performed by modifying one variable at time, while keeping the others constant. This procedure allowed studying the individual effect of each variable on the extraction and preconcentration of the analyte by the RTIL phase. The sample acidity is a key factor in the chelation process of metal ions and subsequently affects the extraction efficiency of the system. Therefore, the effect of pH on analyte complexation and extraction of Hg-5-Br-PADAP was studied in the pH range of 1.5–13. The pH was varied by adding diluted HCl or NaOH solutions. Although stoichiometry of Hg-5-Br-PADAP is already known and reported by previous work [24], it was tested pH values in the acid range in order to investigate which 5-Br-PADAP species are extracted by the RTIL. The results illustrated in Fig. 2(a) show that the highest extraction efficiency was achieved between pH 8.5 and 12. Similar findings were obtained by the authors in a previous work [9] demonstrating that this pH interval is also optimal for Hg chelation with the 5-Br-PADAP reagent. Therefore, it can be concluded that the pH value of the media is rather defining the appropriate chemical form to be extracted than the extraction capabilities of the RTIL. Furthermore, a neutral 5-Br-PADAP chemical form is obtained within this pH interval as deduced from the dissociation constants of the reagent ($pK_{a1} = 0.1$, $pK_{a2} = 2.02$, and $pK_{a3} = 11.30$) [25]. The form of the complex at pH value higher than pK_{a3} is not efficiently extracted by the RTIL. Thus, a pH value of 9.2 was chosen for further experiments. The extraction phenomenon of the complex with the RTIL could be explained considering possible interactions through CH- π hydrogen bonds between the C₂H group of the imidazolium

ring and the aromatic structure of Hg-5-Br-PADAP. Likewise, interaction between hydrogen bond acceptor groups of 5-Br-PADAP and N-H-(imidazolium) hydrogen bonds could be also considered [26].

Ethanol was added to the sample solution in order to avoid the precipitation of the complexing agent and Hg-5-Br-PADAP complex in aqueous medium prior to their extraction. Therefore, ethanol concentration was studied in the range of 1.5–20% (v/v). This study showed that both the complexing agent and the complex remained in solution within the ethanol concentration range studied. The main effect of ethanol on the extraction process was observed on solubilization of the Hg-5-Br-PADAP complex and reagent in the initial aqueous media. No appreciable differences on the extraction kinetics were observed within that concentration range. However, it can be anticipated further solubilization of the [C₄mim][PF₆] RTIL for ethanol concentrations higher than 20% (v/v) [27] leading to a drop of the extraction efficiency and inefficient phase separation, and hence non-reproducible results. A 2.5% (v/v) ethanol concentration was chosen for further work as it allowed reaching high extraction efficiency while keeping the complex in solution.

The efficiency of the preconcentration process depends on the complexing reagent concentration. Thus, it is highly important to establish the minimal reagent-metal ion molar ratio that leads to achieve both total complexation of analyte and also the highest extraction. The 5-Br-PADAP/Hg²⁺ molar ratio was optimized in order to achieve the maximum extraction efficiency of Hg²⁺ by using the proposed preconcentration technique. The results are shown in Fig. 2(b). It can be observed that no signal variation took place for reagent to metal ion ratios higher than 75. The signal remained constant within a molar ratio the 75–400 range. A 5-Br-PADAP/Hg²⁺ molar ratio of 150 was selected for further experiments.

Sodium tetrahydroborate buffer was chosen as optimal to adjust the working pH at 9.2. The extraction system was studied within a sodium tetrahydroborate concentration range of 5×10^{-4} – 9.5×10^{-3} mol L⁻¹. The minimum buffer concentration for adjusting the working pH and achieving the best performance of the extraction system (maximum extraction efficiency;

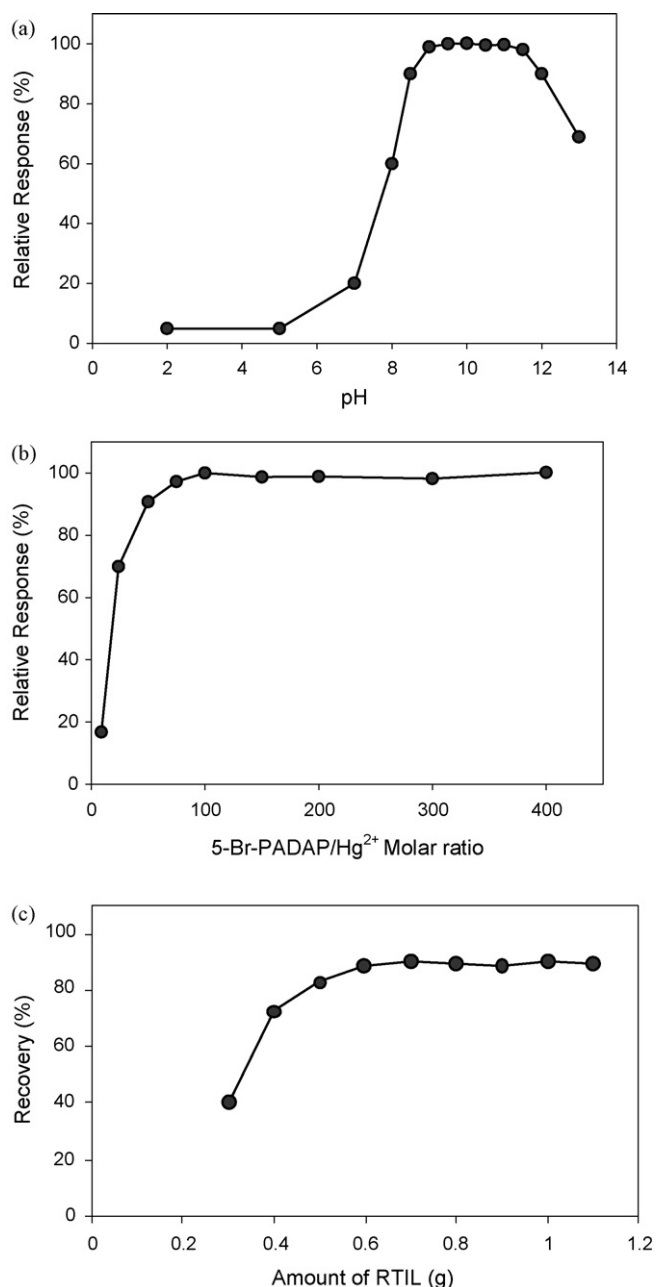


Fig. 2. Effect of different variables on the extraction efficiency of the system. (a) pH, (b) 5-Br-PADAP/Hg²⁺ molar ratio, and (c) amount of RTIL.

distribution ratio stability; lower equilibration time and easiness of phase separation) was $5 \times 10^{-3} \text{ mol L}^{-1}$. The effect of ionic strength on the performance of the extraction system was studied within $0\text{--}1 \text{ mol L}^{-1}$, adjusted with NaNO_3 . Higher salt concentrations were not assayed considering the simplicity of the sample analyzed in this work. However, it can be predicted some effect on the stability of Hg-5-Br-PADAP complex for high salt concentrations. This effect could be overcome by using an excess of 5-Br-PADAP reagent in order to force the equilibrium towards the formation of Hg-5-Br-PADAP complex.

The amount of RTIL that is used in this preconcentration procedure is a critical factor to obtain high recoveries of the analyte while obtaining a high volume ratio of the phases. Therefore, the extraction system was carefully studied in order to define the lowest RTIL phase mass necessary for achieving the highest preconcentration factor possible. The effect of the RTIL mass on the preconcentration

of Hg²⁺ was investigated in the range of 0.3–1.4 g. As it is shown in Fig. 2(c), a minimal RTIL mass of 0.6 g was required to reach optimal extraction efficiency. Lower RTIL masses lead to a reduction of the analytical response due to incomplete partitioning of the analytes towards the RTIL phase. Therefore, 0.7 g of RTIL was used in the proposed method.

The effectiveness of Hg²⁺ extraction under the influence of shaking and centrifugation processes was studied in this work. A 2 min shaking time and a 7 min centrifugation time at 3500 rpm ($1852.2 \times g$) were selected as complete separation occurred for this time and no appreciable improvements on analyte extraction were observed for longer times.

In order to obtain the best preconcentration factor, the extraction system was studied to allow the highest volume ratio between sample solution and RTIL phase. Thus, the effect of sample volume was examined up to 30 mL. As it is shown in Fig. 3, quantitative extraction was observed in a range of 5–20 mL. Higher sample volumes partially solubilized the RTIL phase, leading to non-reproducible results and a lower Hg²⁺ extraction. Therefore, a 20 mL sample volume was recommended to work with 0.7 g RTIL.

3.3. Optimization of mercury back-extraction from RTIL phase

It is already known that the presence of organic matter can negatively affect cold vapor generation reaction. Therefore, mercury had to be separated from the RTIL phase before CV-AAS determination. Transference of free Hg²⁺ ions from the RTIL phase into the aqueous phase could be effectively achieved by dissociation of Hg-5-Br-PADAP at low pH (Fig. 2(a)). Based on this consideration, various mineral acids and at different concentration levels were investigated for back-extracting Hg²⁺ from the RTIL phase, including nitric acid, hydrochloric acid and perchloric acid. It was noticed that the efficiency of the back-extraction process depends on the acid concentration. The effect of this variable was studied in the range of $0.5\text{--}10 \text{ mol L}^{-1}$ for the different mineral acids. The results showed that the recovery of Hg²⁺ from the RTIL phase was increased by increasing the concentration up to 9 mol L^{-1} for hydrochloric acid, 9.5 mol L^{-1} for nitric acid, and 5 mol L^{-1} for perchloric acid. The highest Hg²⁺ recoveries were then obtained with 9 mol L^{-1} hydrochloric acid. The minimal volume of acid solution that allowed achieving the best preconcentration factor was $500 \mu\text{L}$ of 9 mol L^{-1} hydrochloric acid solution.

The effectiveness of Hg²⁺ back-extraction under the influence of shaking and centrifugation processes was also studied. A 3 min shaking time and a 7 min centrifugation time at 3500 rpm

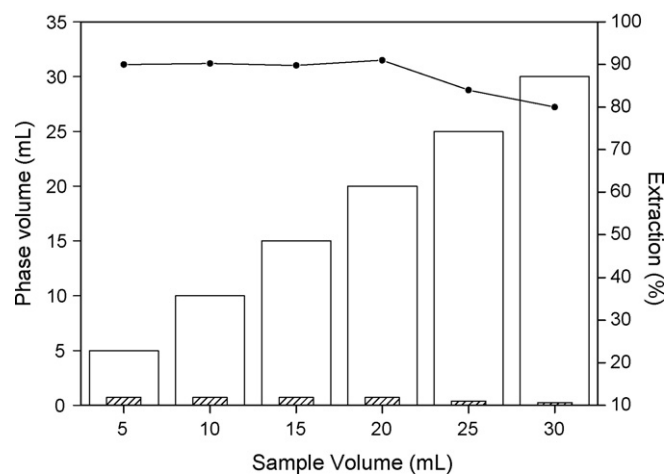


Fig. 3. Evaluation of Hg²⁺ extraction using different sample volume. (□) Sample volume, (▨) RTIL phase volume, and (●) Percentage of extraction or recovery.

Table 1
Characteristic performance data obtained by using the proposed method and other reported for Hg determination.

Method	LOD (ng L ⁻¹)	RSD (%)	Preconcentration factor	Sample consumption (mL)	Calibration range (ng L ⁻¹)	Analysis frequency (h ⁻¹)	Reference
Gold trap CV-AAS	7.6	2.2	7.1	1	n.r. ^b –1500	6.6	[29]
Activated carbon column CV-AAS	10	3.1	13	25	n.r. ^b –10 ⁶	22	[30]
^a CPE- ETAAS	10	4	22	1	n.r. ^b –16000	n.r. ^b	[31]
RTIL L-L CV-AAS	2.3	2.8	36	20	10–2500	30	Proposed method

^a Cloud point extraction (CPE).

^b Not reported.

(1852.2 × g) were found to be optimum since complete separation occurred for this time and no appreciable improvements on Hg²⁺ back-extraction were observed for longer times.

3.4. Interferences study

The effect of concomitant ions regularly found in water samples were studied on Hg²⁺ determination. The study was performed by analyzing 20 mL solutions containing 1 μg L⁻¹ Hg²⁺ and concomitant ions at the concentration levels at which they may occur in the sample. Thus, Cu²⁺, Zn²⁺, Pb²⁺, Ni²⁺, Mn²⁺ and Fe³⁺ could be tolerated up to at least 2500 μg L⁻¹. Commonly encountered concomitant ions such as alkali and alkaline earth elements do not form stable complexes with 5-Br-PADAP complexing agent at the working pH, and hence are not extracted from the aqueous solution. On the other hand, the amounts of anions usually present in natural water samples (S²⁻, CO₃²⁻, F⁻, SO₄²⁻, Cl⁻, PO₄³⁻) do not produce any interference. Analytical signal of the blank was not modified in the presence of the concomitant ions assayed.

3.5. Analytical performance

A 90% extraction was achieved for mercury when the procedure was developed under optimal experimental conditions. Therefore, the preconcentration factor obtained for a sample volume of 20 mL and a resulting RTIL phase volume of 500 μL was 36. The preconcentration factor was obtained as the ratio of the slopes of the calibration curves for Hg²⁺ with and without a preconcentration step. Consequently, a preconcentration factor of 36 was obtained with respect to conventional FI-CV-AAS analysis. The relative standard deviation (RSD) resulting from the analysis of 10

replicates of 20 mL solution containing 1 μg L⁻¹ Hg²⁺ was 2.8%. The calibration graph was linear between 10 and 2500 ng L⁻¹, with a correlation coefficient of 0.9997. The regression equation was $A = 0.490C + 0.0017$, where A is the absorbance and C is mercury concentration in μg L⁻¹. The limit of detection (LOD), calculated as the concentration of mercury required to yield a net peak equal to three times the standard deviation of the blank signal (3σ), was 2.3 ng L⁻¹ for the preconcentration of 20 mL of sample solution. Regarding the frequency of analysis, although preconcentration and back-extraction of the analyte for a single sample could take more than 15 min, it is possible to simultaneously treat as many samples as can be placed in the centrifugation and stirring equipment. For this work, it was possible to analyze 30 samples within an overall time of 1 h. A comparison of the proposed method with others reported in the literature for Hg determination is shown in Table 1. The proposed RTIL-based preconcentration method leads to a lower LOD, a higher preconcentration factor and higher frequency of analysis as compared to other alternatives. The method developed in this work is proposed as a suitable alternative to more expensive instruments for Hg determination at trace levels. This methodology does not require further instrumentation and it can be used with regular CV-AAS equipment. Thus, the RTIL-based analytical method could be of great interest especially for mercury determination in routine analytical laboratories.

3.6. Method validation

In order to demonstrate the validity of this method, 200 mL of each sample type (tap, mineral, sea and river water) were divided into portions of 20 mL each. The proposed method was applied to six portions and the average concentration of Hg²⁺ found was taken

Table 2
Method validation (95% confidence interval; $n = 6$).

Sample	Base value (μg L ⁻¹)	Quantity of Hg ²⁺ added (μg L ⁻¹)	Quantity of Hg ²⁺ found (μg L ⁻¹)	Recovery (%) ^a
Mineral water	–	–	0.14 ± 0.01	–
	0.14	0.5	0.66 ± 0.02	104
	0.14	1.0	1.12 ± 0.04	98
	0.14	1.5	1.66 ± 0.03	101
	0.14	2.0	2.14 ± 0.04	100
Tap water	–	–	0.11 ± 0.02	–
	0.11	0.5	0.60 ± 0.01	98
	0.11	1.0	1.13 ± 0.03	102
	0.11	1.5	1.53 ± 0.01	95
	0.11	2.0	2.17 ± 0.02	103
River water	–	–	0.05 ± 0.02	–
	0.05	0.5	0.53 ± 0.03	96
	0.05	1.0	1.07 ± 0.04	102
	0.05	1.5	1.54 ± 0.03	99
	0.05	2.0	2.03 ± 0.01	99
Seawater	–	–	0.06 ± 0.01	–
	0.06	0.5	0.54 ± 0.02	95
	0.06	1.0	1.11 ± 0.02	105
	0.06	1.5	1.61 ± 0.01	103
	0.06	2.0	2.08 ± 0.03	101

^a $100 \times [(\text{found} - \text{base})/\text{added}]$.

Table 3
Concentration of mercury in water samples (95% confidence interval; $n = 6$).

Sample	Concentration ($\mu\text{g L}^{-1}$)
1 ^a	0.14 \pm 0.01
2 ^a	0.10 \pm 0.02
3 ^a	n.d.
4 ^b	0.11 \pm 0.02
5 ^b	0.04 \pm 0.01
6 ^b	n.d.
7 ^c	0.05 \pm 0.02
8 ^c	0.04 \pm 0.01
9 ^c	0.06 \pm 0.01
10 ^d	0.06 \pm 0.02
11 ^d	0.08 \pm 0.01
12 ^d	n.d.

^a Mineral water.

^b Tap water.

^c River water.

^d Seawater.

as a base value. The remaining aliquots were spiked with increasing quantities of Hg^{2+} and were analyzed by the proposed method. The results shown in Table 2 demonstrate that mercury recoveries were acceptable and in the range of 95–105%. Additionally, the accuracy of the proposed methodology was evaluated by analyzing a certified reference material (CRM), QC METAL LL3 mercury in water, with a Hg^{2+} content of $6.48 \pm 0.51 \mu\text{g L}^{-1}$. Using the method developed in this work, the Hg^{2+} content found in the CRM was $6.42 \pm 0.02 \mu\text{g L}^{-1}$ (95% confidence interval; $n = 6$).

3.7. Determination of mercury in water samples

The method was applied for mercury determination in different water samples taken from San Juan and Mendoza provinces (Argentina) and Valparaíso (Chile). Mercury concentrations were in the range of 0.14 n.d. $\mu\text{g L}^{-1}$ for mineral water, 0.11 n.d. $\mu\text{g L}^{-1}$ for tap water, 0.06–0.04 $\mu\text{g L}^{-1}$ for river water and 0.08 n.d. $\mu\text{g L}^{-1}$ for seawater; 95% confidence interval ($n = 6$). The mean mercury concentration obtained for each kind of water sample is in good agreement with results reported by other authors [6,28]. The results are shown in Table 3.

4. Conclusion

In this work, a novel and sensitive analytical methodology for mercury preconcentration and determination in different water samples using $[\text{C}_4\text{mim}][\text{PF}_6]$ was developed. The use of RTILs biphasic systems as an alternative to conventional solvents offers several advantages including safety and high capacity to extract Hg^{2+} and other elements with high recoveries. $[\text{C}_4\text{mim}][\text{PF}_6]$ in combination with 5-Br-PADAP complexing reagent was successfully applied in this study for the extraction and preconcentration of Hg^{2+} . Likewise, a fast and quantitative back-extraction of the analyte from RTIL phase into aqueous phase was possible, allowing its further determination by FI-CV-AAS. It has to be pointed out that, although effective, RTIL-mediated extraction is mostly a batch process and further efforts focused on automating the extraction process using flow injection or sequential injection system need to be made to fully explore the advantages of RTIL-mediated extraction. The preconcentration method allowed mercury determination in sea, river, mineral and tap water samples at trace levels (ng L^{-1}) with high accuracy and reproducibility.

Acknowledgements

This work was supported by Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET); Agencia Nacional de Promo-

ción Científica y Tecnológica (FONCYT) (PICT-BID) and Universidad Nacional de San Luis, Argentina.

References

- [1] R. Eisler, Mercury hazards from gold mining to humans, plants, and animals, *Rev. Environ. Contam. Toxicol.* 181 (2004) 139.
- [2] E.G. Pacyna, J.M. Pacyna, J. Fudala, E. Strzelecka-Jastrzab, S. Hlawiczka, D. Panasiuk, Mercury emissions to the atmosphere from anthropogenic sources in Europe in 2000 and their scenarios until 2020, *Sci. Total Environ.* 370 (2006) 147.
- [3] A. Bhan, N.N. Sarkar, Mercury in the environment: effect on health and reproduction, *Rev. Environ. Health* 20 (2005) 39.
- [4] M. Valko, H. Morris, M.T.D. Cronin, Metals, toxicity and oxidative stress, *Curr. Med. Chem.* 12 (2005) 1161.
- [5] J.C. Clifton II., Mercury exposure and public health, *Pediatr. Clin. North Am.* 54 (2007) 237.e1.
- [6] J.Y. Song, M. Hou, L.X. Zhang, Determination of mercury at trace level in natural water samples by hydride generation atomic absorption spectrophotometry after cloud point extraction preconcentration, *Chin. Chem. Lett.* 17 (2006) 1217.
- [7] P. Rivaro, C. Ianni, F. Soggia, R. Frache, Mercury speciation in environmental samples by cold vapour atomic absorption spectrometry with in situ preconcentration on a gold trap, *Microchim. Acta* 158 (2007) 345.
- [8] W. Geng, T. Nakajima, H. Takanashi, A. Ohki, Determination of mercury in ash and soil samples by oxygen flask combustion method-Cold vapor atomic fluorescence spectrometry (CVAFS), *J. Hazard. Mater.* 154 (2008) 325.
- [9] J.C.A. De Wuilloud, R.G. Wuilloud, M.F. Silva, R.A. Olsina, L.D. Martinez, Sensitive determination of mercury in tap water by cloud point extraction pre-concentration and flow injection-cold vapor-inductively coupled plasma optical emission spectrometry 57 (2002) 365.
- [10] M.G. Minnich, D.C. Miller, P.J. Parsons, Determination of As, Cd, Pb, and Hg in urine using inductively coupled plasma mass spectrometry with the direct injection high efficiency nebulizer, *Spectrochim. Acta Part B At. Spectrosc.* 63 (2008) 389.
- [11] I. Kojima, A. Takayanagi, Selective extraction and one-drop flame atomic absorption spectrometric determination of trace amounts of silver in highly-pure copper and lead, *J. Anal. At. Spectrom.* 11 (1996) 607.
- [12] D. Wei, A. Ivaska, Applications of ionic liquids in electrochemical sensors, *Anal. Chim. Acta* 607 (2008) 126.
- [13] F. Du, X. Xiao, G. Li, Applications of room temperature ionic liquids in sample pretreatment, *Chem. Bull.* 70 (2007) 647.
- [14] H. Zhao, Innovative applications of ionic liquids as "green" engineering liquids, *Chem. Eng. Commun.* 193 (2006) 1660.
- [15] S.T. Handy, Room temperature ionic liquids: different classes and physical properties, *Curr. Org. Chem.* 9 (2005) 959.
- [16] X. Han, D.W. Armstrong, Ionic liquids in separations, *Acc. Chem. Res.* 40 (2007) 1079.
- [17] R. Germani, M.V. Mancini, G. Savelli, N. Spreti, Mercury extraction by ionic liquids: temperature and alkyl chain length effect, *Tetrahedron Lett.* 48 (2007) 1767.
- [18] S.X. Hua Zhao, Peisheng Ma, Use of ionic liquids as green solvents for extractions, *J. Chem. Technol. Biotechnol.* 80 (2005) 1089.
- [19] S. Carda-Broch, A. Berthod, D.W. Armstrong, Solvent properties of the 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid, *Anal. Bioanal. Chem.* 375 (2003) 191.
- [20] A.E. Visser, R.P. Swatloski, S.T. Griffin, D.H. Hartman, R.D. Rogers, Liquid/liquid extraction of metal ions in room temperature ionic liquids, *Separ. Sci. Technol.* 36 (2001) 785.
- [21] A.E. Visser, R.P. Swatloski, W.M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J. Davis J.H., R.D. Rogers, Task-specific ionic liquids for the extraction of metal ions from aqueous solutions, *Chem. Commun.* (2001) 135.
- [22] Z. Li, Q. Wei, R. Yuan, X. Zhou, H. Liu, H. Shan, Q. Song, A new room temperature ionic liquid 1-butyl-3-trimethylsilylimidazolium hexafluorophosphate as a solvent for extraction and preconcentration of mercury with determination by cold vapor atomic absorption spectrometry, *Talanta* 71 (2007) 68.
- [23] J.C. Huddleston, H.D. Willauer, R.P. Swatloski, A.E. Visser, R.D. Rogers, Room temperature ionic liquids as novel media for 'clean' liquid-liquid extraction, *Chem. Commun.* (1998) 1765.
- [24] D. Nonova, K. Stoyanov, Extraction-spectrophotometric determination of traces of copper(II), zinc(II), cadmium(II) and mercury(II) with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol, *Mikrochim. Acta* 82 (1984) 143.
- [25] D.A. Johnson, T.M. Florence, A study of some pyridylazo dyestuffs as chromogenic reagents and the elucidation of the nature of their metal complex spectra, *Talanta* 22 (1975) 253.
- [26] C.C. Cassol, A.P. Umpierre, G. Ebeling, B. Ferrera, S.S.X. Chiaro, J. Dupont, On the extraction of aromatic compounds from hydrocarbons by imidazolium ionic liquids, *Int. J. Mol. Sci.* 8 (2007) 593.
- [27] K.A. Fletcher, S. Pandey, Solvatochromic probe behavior within ternary room-temperature ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate + ethanol + water solutions 107 (2003) 13532.
- [28] E.L. Seibert, V.L. Dressler, D. Pozebon, A.J. Curtius, Determination of Hg in seawater by inductively coupled plasma mass spectrometry after on-line pre-concentration, *Spectrochim. Acta Part B At. Spectrosc.* 56 (2001) 1963.

- [29] E. Kopyś, K. Pyrzyńska, S. Garbos, E. Bulska, Determination of mercury by cold-vapor atomic absorption spectrometry with preconcentration on a gold-trap, *Anal. Sci.* 16 (2000) 1309.
- [30] N. Ferrúa, S. Cerutti, J.A. Salonia, R.A. Olsina, L.D. Martinez, On-line preconcentration and determination of mercury in biological and environmental samples by cold vapor-atomic absorption spectrometry, *J. Hazard. Mater.* 141 (2007) 693.
- [31] P.R. Aranda, R.A. Gil, S. Moyano, I.E. De Vito, L.D. Martinez, Cloud point extraction of mercury with PONPE 7.5 prior to its determination in biological samples by ETAAS, *Talanta* 75 (2008) 307.