Development of Ionic Liquid-based Magnetic Nanoparticle-supported Dispersive Liquid Liquid Microextraction Technique for Mercury Preconcentration Prior to Hydride Generation Atomic Absorption Spectrometry in Aqueous Samples

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ABSTRACT

A simple and efficient ionic liquid-based magnetic nanoparticle-supported dispersive liquid liquid microextraction (IL-mDLLME) method was developed to enrich mercury before its determination by flow injection-hydride generation atomic absorption spectrometry. In this experiment, imidazolium hexafluorophosphate ionic liquid, having different cationic groups as 1-allyl/butyl/methyl, was used to extract mercury-4-(2-pyridylazo) resorcinol complex from aqueous samples into fine droplets. After adding of Fe_3O_4 MNPs to the extraction media, enriched mercury was separated from the aqueous solution using an external magnet. Some analytical parameters influencing the efficiency of the proposed (IL-mDMME) method, such as pH, amount of

IL, ligand concentration, extraction time, amount of Fe_3O_4 MNPs, sample volume and matrix effect, were optimized.

Under the optimized conditions, good linearity was obtained with correlation coefficients (r) greater than 0.9938. The repeatability and reproducibility of the proposed method were found to be good, and the limits of detection ranged from $0.18 \mu\text{g L}^{-1}$ to $0.54 \mu\text{g L}^{-1}$ for the studied ionic liquids. The accuracy of the proposed method, was assessed by standard addition method calculated by relative standard deviations in the range of 100-110% for tap water and 97-100% for mineral water. Within this extraction technique, fast, green, and efficient enrichment of mercury was achieved by centrifugation steps using environmentally friendly ionic liquids and obtaining high enrichment factors.

fore, new strategies have been adopted to DLLME by using portable, economical, and effective external magnetic nanoparticles (MNP) (14) for easy separation of trace amounts of metal ions such as Cr, Cu, and Pb or herbicides, uric acid, etc., from aqueous samples (15, 16) and to reach equilibrium in a short time. This results in mass transfer of the analytes from the aqueous phase to the organic phase (17, 18).

In this study, mercury (Hg), one of the most toxic heavy metals, was preconcentrated using ionic liquid-based magnetic nanoparticle-supported DLLME prior to its determination by flow injection-cold vapor atomic absorption spectrometry (FI-CVAAS). Mercury can cause dangerous cumulative effects to the central nervous system, respiratory failure, hypertension, chromosomal disorders, cerebral palsy, even death (19). In addition, chronic exposure to Hg(II) causes renal damage and morphological changes, renal tubular damage, regeneration of the tubular epithelium, and proximal tubular necrosis (20). The tolerable limit of inorganic mercury in drinking water is $6 \mu\text{g L}^{-1}$ (21). Because of its high toxicity and the bioaccumulation factor, mercury determination is very important in environmental and biological samples such as soil, sediment, wastewater, and groundwater (22-24).

In this study, three imidazolium-based ionic liquids of different cationic groups (allyl, butyl, and methyl) were studied and compared.

INTRODUCTION

In recent years, new approaches to analytical chemistry have focused on the miniaturization and simplification of the sample preparation steps. Dispersive liquid liquid microextraction (DLLME) has become the most preferred technique due to the large surface area of the extractant and high extraction recovery within a short time (1-5). Ionic liquids have been used

as a green extractant in DLLME since 2008 (4, 6) because of their efficient chemistry, using low toxic media, vapor pressure, and having adjustable viscosity, etc. (7-11). Zhang et al. (12) used 1-hexyl-3-methylimidazolium hexafluorophosphate for the preconcentration of triazole herbicides, and Tuzen and Pekiner (13) used 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide for speciation of selenium. In some cases, ionic liquids (ILs) have caused some disadvantages when used with dispersive solvents such as methanol, acetone, acetonitrile, decanol, 2-propanol, etc. There-

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Within the developed technique, the enriched mercury phase was collected onto the magnetic Fe(III) oxide (Fe_3O_4) nanoparticles, separated with an external magnet, and directly analyzed. Thus, in the centrifugation step no extraction process was applied, the analysis was performed, and application of the MNPs in the ionic liquid-based DLLME was found to be a rapid, effective, and green microextraction technique.

EXPERIMENTAL

Instrumentation

For synthesis of AMIM- PF_6 , a Buchi rotary evaporator (Flawil, Switzerland), Selecta 2001 pH meter (Barcelona, Spain), ultrasonic bath (Nuve, Turkey), and Labconco FreezeZone Freeze-Dryer 2.5 (Labconco Corporation, USA) were used.

Spectrum BX-II FTIR (PerkinElmer, Inc., USA), Philips X'Pert Pro XRD (X'Celerator detector), FEI Tecnai G² Spirit Biotwin TEM, Shimadzu UV-1800 spectro-photometer (Kyoto, Japan), and Varian Cary Eclipse spectrofluorometer (Palo Alto, CA, USA) were used for the characterization studies of the synthesized ionic liquid and the prepared Fe_3O_4 magnetic nanoparticles.

Quantitative analysis of mercury was performed using the AAnalystTM 700, equipped with a FIASTM 100 hydride generation system (PerkinElmer, Inc., USA). A Hg-EDL lamp was used. The instrumental parameters are summarized in Table I.

Chemicals, Reagents, and Standard Solutions

Analytical grade ionic liquids 1-allyl-3-methylimidazolium chloride (AMIM-Cl), 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM- PF_6), 1-benzyl-3-methylimidazolium hexafluorophosphate (BeMIM- PF_6), and ammonium hexa-

fluorophosphate ($\text{NH}_4\text{-PF}_6$) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and Alfa Aesar (Haverhill, MA, USA).

Dichloromethane, ethanol ($\text{C}_2\text{H}_5\text{OH}$), hydrochloric acid (HCl), nitric acid (HNO_3), acetic acid, pH buffer solutions and Fe(II)/Fe(III) chloride, sodium borohydride, potassium permanganate (KMnO_4), sodium acetate, sodium hydroxide (NaOH), Triton[®] X-100, sodium dodecyl sulfate, hexadecylcetyltrimethyl ammonium bromide were purchased from E. Merck, Sigma-Aldrich or Alfa Aesar. Deionized water was obtained with a Milli-Q[®] water purification system (Millipore Corporation, USA).

The individual stock standard solution of mercury (1000 mg/L) was purchased from PerkinElmer, Inc. (Shelton, CT, USA). The working solutions were prepared daily by dilution of the stock standard solution of mercury. All working and stock solutions were stored in a refrigerator at +4 °C.

1-allyl-3-methylimidazolium hexafluorophosphate was prepared as reported in the literature (25). Briefly, 0.02 moles of AMIM-Cl and 50 mL of dichloromethane were mixed in a flat bottom flask. Then, 0.02 moles of $\text{NH}_4\text{-PF}_6$ was added and reacted by stirring for 24 hours at room temperature. Later, the pre-

cipitated ammonium bromide was filtered and discharged. The organic phase was evaporated and 1-allyl-3-methylimidazolium hexafluorophosphate (AMIM- PF_6) was obtained.

For characterization of AMIM- PF_6 , the FTIR and ¹H-NMR spectra were recorded and the results are given as follows:

FTIR (cm^{-1}): 3100-3050 (aromatic=C-H stretching), 2950-2850 (aliphatic symmetric and asymmetric C-H stretching), 1570-1560 (C=N stretching), 1460-1450 (C=C stretching vibrations), 1330-1280 and 1168-1050 (C-H stretching and C-C stretching), 847-719 (aromatic = C-H out-of-plane bending).

¹H-NMR (CDCl_3): 8.39 ppm (s, 1H, NCHN), 7.03 ppm (d, 2H, $\text{NCH}_2\text{CHCH}_2$), 5.6 ppm (m, 5H, $\text{NCH}_2\text{CHCH}_2$), 5.0 ppm (m, 2xCH, NCHCHN), 4.42 ppm (d, 2H, $\text{NCH}_2\text{CHCH}_2$), 3.52 ppm (s, 1H, NCH_3).

Preparation of Fe_3O_4 Magnetic Nanoparticles

For the preparation of Fe_3O_4 MNP, 11.6 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved with 200 mL ultrapure water for 5 minutes in an ultrasonic bath. Then, 4.3 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was added and stirred at 80 °C for 15 minutes under a N_2 stream, ultra-

TABLE I
Instrumental Operating Conditions

AAnalyst 700 FAAS	
Wavelength	253.7 nm
Slit dimension	0.7 nm
EDL current	185 mA
Flow rate of argon	100-110 mL/min
FIAS 100	
Carrier	HCl (3%, v/v)
Reductant	NaBH_4 (0.2%, w/v) in 0.05% (w/v) NaOH
Stabilization	KMnO_4 (5%, w/v)
Cell temperature	100 °C

sonically. Then, 40 mL of NH_3 (25%, v/v) was added with a funnel. After the ammonia addition, a black solid precipitate was formed (magnetic nanoparticle suspension), stirred for 15 minutes ultrasonically, and separated by the application of an external magnet, then washed with water, and finally dried with a freeze dryer (26).

The characteristic infrared bands of Fe_3O_4 MNP are shown in Figure 1a. The Fe-O-Fe stretching vibration was observed at $600\text{--}550\text{ cm}^{-1}$ (27) and the Fe-O-Fe characteristic vibration at 588 cm^{-1} . Also, the peak at 1629 cm^{-1} is assigned to the O-H bending (28). For XRD characterization of Fe_3O_4 MNP, all characteristics at 20° were recorded in Figure 1b. The characteristics at 20° are seen at $30.3, 35.7, 43.1, 53.8, 57.1, 62.7$ corresponding to (220), (311), (400), (422), (511), (440) peaks, respectively (29).

Ionic Liquid-based Magnetic DLLME Method

Five milliliters of aqueous solution containing $40\text{ }\mu\text{g L}^{-1}$ of Hg (II), $10 \times 10^{-6}\text{ mol L}^{-1}$ of PAR, 2 mL of pH 7 buffer and 4% (v/v) of the BMIM- PF_6 were placed in a test tube and completed to 10 mL with ultrapure water. Then 50 mg of Fe_3O_4 was added to the tube. The mixture was ultrasonically shaken for 120 sec-

onds. A magnet was subsequently held around the test tube to collect the nanoparticles at the bottom of the test tube. The upper aqueous phase was removed and 500 μL of 3% (w/v) HCl was added to the enriched phase. Then, the solution was vortexed for 30 seconds to desorb the IL as well as the Hg(II) from the MNPs.

Finally, the nanoparticles were isolated from the solution with a magnet, and the rich phase was diluted to 5 mL with 3% (w/v) HCl before spectroscopic analysis.

Samples

Optimized extraction conditions were applied to tap water and mineral water samples. The water sample was collected directly at the laboratory and allowed to stand for 30 minutes, while the mineral water sample was degassed ultrasonically for 15 minutes. All samples were filtered through $0.45\text{ }\mu\text{m}$ pore-sized disc filters prior to extraction and analysis.

RESULTS AND DISCUSSION

Optimization of Extraction Parameters

The optimization parameters were studied for pH, surfactant, ionic liquid, magnetic nanoparticle, and extraction time. Determination

of the optimum extraction value of all steps, percentage of extraction recovery (E %) was calculated using the following equation:

$$E(\%) = \frac{C_{\text{sed}}}{C_0} \times \frac{V_{\text{sed}}}{V_0} \times 100$$

where,

C_{sed} = concentration of the analyte in the sedimented phase, C_0 = initial concentration of the analyte in the aqueous sample, V_{sed} = volume of the sedimented phase, and V_0 = volume of the aqueous phase.

pH of Complexation

The ligand of PAR (4-(2-Pyridylazo)resorcinol) forms strong complexes with metal ions through the heterocyclic nitrogen group, azo group, and o-hydroxyl group in its structure. The PAR molecule is a dibasic acid and the complex formation is directly dependent on the pH of the solution medium. For this reason, the pH of the extraction media was determined at first using buffer solutions with pH values ranging from 3, 4, 5, 5.5, 6, 7, 8, to 9. The obtained results in Figure 2 show that highest extraction recovery was obtained around pH 6.

Effect of Surfactant

Surfactant selection is a factor that affects the efficiency of pre-

Fig. 1. Characterization of Fe_3O_4 MNP : (a) FTIR spectrum, (b) XRD spectrum.

concentration in the extraction and is effective in dissolving the water-immiscible extraction solvent in the aqueous sample. Experiments were conducted with aqueous solutions of sodium dodecyl sulfate (SDS), Triton® X-100 (TX-100), and cetyl trimethylammonium bromide (CTAB) at 1×10^{-5} M concentrations to investigate the surfactant effect on mercury preconcentration. As shown in Figure 3, addition of the surfactant did not have an effect on the recovery of mercury for BMIM-PF₆ and BeMIM-PF₆, while the addition of CTAB caused an increase on the extraction recovery for AMIM-PF₆.

Therefore, the effect of CTAB amount was studied as the next optimization step only for AMIM-PF₆. For this, CTAB was added at different concentrations from 2×10^{-6} M to 1.5×10^{-5} M for four levels into the aqueous solution. As seen in Figure 3, the extraction yield increased up at 5×10^{-6} M and became maximum at 1×10^{-5} M. For subsequent studies, AMIM-PF₆ was performed with 1×10^{-5} M of CTAB.

Effect of Amount of PAR

In the IL-based extraction method applied in this study, it is necessary to form the hydrophobic complex of the analyte before adding the ionic liquid to the extraction medium. For this, the

type and amount of chelating agent are the key factor. PAR is a widely used ligand for many applications, such as metal extraction, spectrophotometric and chromatographic metal ion analysis, forming many metal-colored complexes. In the structure, a strong heterocyclic nitrogen group, metal groups containing an azo group and o- is a ligand that forms complexes (30-32).

In order to get high extraction yield, the required amount of PAR was investigated from 0.5×10^{-6} M to 20×10^{-6} M. With a PAR from 0.5 to 2×10^{-6} M, the extraction recovery increased from 20% to 60% for AMIM-PF₆. For BMIM-PF₆, the effect of PAR amount affected the recovery by dynamically increasing to 1×10^{-5} M. After that amount, extraction recovery was almost stable.

While adding 0.5×10^{-6} M of PAR to BeMIM-PF₆ media, the extraction recovery was optimal at 60%, though adding the higher amount of PAR decreased the extraction recovery. Following, the extraction recoveries obtained were evaluated for all three ionic liquids. The highest extraction was obtained at concentrations of 2×10^{-6} M PAR for AMIM-PF₆, 1×10^{-5} M PAR for BMIM-PF₆, and 0.5×10^{-6} M PAR for BeMIM-PF₆ (Figure 4).

Effect of Amount of Ionic Liquid

To optimize the amount of ionic liquid, the experiments were carried out for varying amounts of AMIM-PF₆, BMIM-PF₆ and BeMIM-PF₆ ionic liquids. For this, different concentrations of the ionic liquids used from 2% to 10% (v/v for AMIM-PF₆ and BMIMPF₆, w/v for

Fig. 2. Effect of pH. Conditions: 10 mL of working solution; 40 µg/L of Hg(II); 1×10^{-5} M PAR; 25 mg of Fe₃O₄; 5 min extraction time.

Fig. 3. Effect of surfactant. Conditions: 10 mL of working solution; 40 µg/L of Hg(II); pH 6; 1×10^{-5} M PAR; 25 mg of Fe₃O₄; 5 min. extraction time.

Fig. 4. Effect of PAR. Conditions: 10 mL of working solution; 40 µg/L of Hg(II); pH 6; 25 mg of Fe₃O₄; 5 min. extraction time.

BeMIM-PF₆) were added to the aqueous solution containing 40 µg L⁻¹ of mercury. The optimized amount for each ionic liquid was determined as 6%, 4%, and 3% for AMIM-PF₆, BMIM-PF₆, BeMIM-PF₆, respectively (Figure 5).

Effect of Fe₃O₄ MNP

Compared to conventional micron-sized adsorbents, MNPs offer high extraction capacity, fast extraction dynamics, and high extraction efficiency. Satisfactory results can therefore be obtained with lower amounts of these adsorbents. For this, the effect of MNP on the enrichment of mercury by IL-mDLLME was examined with different amounts of Fe₃O₄ with MNPs ranging from 10 to 100 mg. As seen in Figure 6, while the MNP amount increased to 25 mg for AMIM-PF₆ and 50 mg for BMIMPF₆/BeMIM-PF₆, the extraction recoveries were increasing from 25% to 60, 70, nearly 100% for each ionic liquid, respectively. After these amounts, the extraction recoveries decreased. Thus, the optimized amount for highest extraction recoveries was found to be Fe₃O₄ MNP as 25 mg for AMIM-PF₆ and 50 mg for BMIM-PF₆ and BeMIM-PF₆.

Effect of Desorption Solution

In this IL-mDLLME extraction process, desorption of enriched

mercury from loaded Fe₃O₄ MNP including IL is an important step. For this, different acidic and/or alcoholic solutions and their mixtures like ethanol, HCl (3%, v/v), HNO₃ (65%, w/v), C₂H₅OH:HNO₃ (1:1, v/v), C₂H₅OH:HCl (1:1, v/v) were studied. From the results obtained, the best desorption was achieved using C₂H₅OH:HNO₃ (1:1, v/v) for AMIM-PF₆, 3% HCl(w/v) for BMIM-PF₆, and BeMIMPF₆, representing 69.3% and 100.0%.

Effect of Extraction Time

Extraction time is one of the most important factors of the IL-mDLLME method. Extraction time is defined as the time from the injection of the dispersive and the extraction solvent mixture to centrifugation. It is also known to be an effective way to improve mass

transfer from the aqueous phase to the extraction phase in the case of inclusion of the vortex mixing process. In this study, the effect of extraction time was controlled between 30 and 300 seconds. As shown in Figure 7, highest recovery was found in the range of 60 to 180 seconds. As can be seen from the graph, the optimized extraction recovery was reached at 60 seconds for AMIM-PF₆ and BMIM-PF₆, 180 seconds for BeMIM-PF₆.

Interference Studies

In the present study, PAR was selected as complexing agent for mercury in aqueous samples. It can also react with other metal ions to form their complexes that may cause the interferences on mercury. Thus, some metal ions (Al³⁺, Cu²⁺, Fe³⁺, Mn²⁺, Ni²⁺, Pb²⁺, Zn²⁺, etc.)

Fig. 5. Effect of ionic liquid. Conditions: 10 mL of working solution; 40 µg/L of Hg(II); pH 6; 25 mg of Fe₃O₄; 5 min. extraction time.

Fig. 6. Effect of Fe₃O₄. Conditions: 10 mL of working solution; 40 µg/L of Hg(II); pH 6; 5 min. extraction time.

Fig. 7. Effect of extraction time. Conditions: 10 mL of working solution; 40 µg/L of Hg(II); pH 6.

commonly determined in water samples were studied on the extraction. Beside this, the complexation behavior of the ionic species by anionic forms (Cl^- , NO_3^- , etc.) may influence the efficiency of the extraction. Under optimized conditions according to the proposed method, the effect of some foreign ions such as Pb(II) , Mn(II) , Ni(II) , and Fe(III) in the determination of Hg(II) at $40 \mu\text{g L}^{-1}$ was investigated. The interfering ions and the recovery values are given in Table II.

Most of the cations and anions are tolerated up to high levels (up to $25 \mu\text{g L}^{-1}$). A species resulting in more than 10% variation in the recovery of the target analyte is considered as an interfering agent 90-95%. This could be reduced by adding some suitable masking agents to the extraction medium.

Analytical Figures of Merit of the IL-mDLLME Method

The calibration data of mercury were obtained using an HG-AAS system after the preconcentration step. Besides this, the linear range and correlation coefficient (R^2) were determined. Also, the limit of

detection (LOD) was calculated by 10 blank measurements as 3xS . The precision of the method was determined for intra- and inter-day as relative standard deviation (%RSD). Applicability of the method was evaluated by analyzing tap water and mineral water samples using the developed method. Accuracy studies were accomplished by calculating the relative standard deviation from the added or known amount of mercury to the water samples and investigated by the recovery experiments of the samples. For the optimum extraction conditions, the enrichment factor (EF) was calculated for AMIM-PF₆, BMIM-PF₆, and BeMIM-PF₆ ionic liquids depending on the ratio of the concentration of Hg(II) in the enriched phase to the initial concentration of Hg(II) in the aqueous sample. All analytical parameters for each ionic liquid-based mDLLME method are given in Table III.

Sample volume for an analysis is an important factor due to the low concentration of mercury in water samples. To survey the effect of sample volume on the recovery, different volumes of sample solutions (5, 10, 20, 30, 40, and 50 mL)

were studied at $40 \mu\text{g L}^{-1}$ Hg concentration and keeping other parameters constant. The recovery values of Hg(II) affected by sample volume above 20 and 30 mL for AMIM-PF₆, BMIM-PF₆, and 15 mL for BeMIM-PF₆ resulted in decreases of extraction recoveries. Above these sample volumes, the recovery was affected decreasingly.

Analysis of Samples

In this study, the developed microextraction method for the enrichment of mercury was applied to real water samples with BMIM-PF₆ under optimum conditions. In the tap water and mineral water samples, mercury was not detected. For this, unspiked tap water and mineral water samples and their spiked samples at two concentration levels of $10 \mu\text{g L}^{-1}$ and $50 \mu\text{g L}^{-1}$ were analyzed by using the developed IL-mDLLME method ($n=3$). The results are listed in Table IV. The relative recoveries at three concentration levels were in the range of 97.6–107.6%, with RSDs within the range of 1.3–2.8%, demonstrating that the proposed method can be used for the determination of trace Hg(II) in real environmental water samples. The performance of the developed method was evaluated with other DLLME methods for inorganic mercury. As shown in Table V, the developed method for preconcentration of mercury had

TABLE II
Interference Effect

Ion	Conc. ($\mu\text{g L}^{-1}$)	Extractn. %Recov.	Ion	Conc. ($\mu\text{g L}^{-1}$)	Extractn. %Recov.
Pb^{2+}	5	94	Fe^{2+}	10	90
Mn^{2+}	5		Cu^{2+}	10	
			Pb^{2+}	10	
Pb^{2+}	10	92	K^+	1000	95
Mn^{2+}	10		Na^+	1000	
			Mg^{2+}	1000	
Ni^{2+}	5	93	Ca^{2+}	1000	
Co^{2+}	5				
Zn^{2+}	5		NO_3^-	1000	95
			Cl^-	1000	
Co^{2+}	25	91	SO_4^{2-}	1000	
Al^{2+}	25				
Fe^{2+}	25				

TABLE III
Analytical Parameters

Parameters	Ionic Liquids		
	AMIM-PF ₆	BMIM-PF ₆	BeMIM-PF ₆
Linear range ($\mu\text{g L}^{-1}$)	2-100	5-250	2-200
R^2	0.9942	0.9954	0.9938
LOD ($\mu\text{g L}^{-1}$)	0.44	0.18	0.54
Intra-day RSD (%)	1.52 ^a	3.37 ^b	6.73 ^c
Inter-day RSD (%)	8.66 ^a	4.52 ^b	5.94 ^c
EF	31.6	38.3	46.1

^aFor $10 \mu\text{g L}^{-1}$, $n=3$;

^bFor $5 \mu\text{g L}^{-1}$, $n=3$;

^cFor $2 \mu\text{g L}^{-1}$, $n=3$.

TABLE IV
Recovery Results of Sample Analysis (n = 3)

Sample	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	ER $\pm$ RSD (%)
Tap water	-	ND*	-
	10	10.1 $\pm$ 0.3	101.4 $\pm$ 2.8
	50	53.8 $\pm$ 3.4	107.6 $\pm$ 1.5
Mineral water	-	ND*	-
	10	9.8 $\pm$ 0.5	97.6 $\pm$ 1.7
	50	49.9 $\pm$ 2.8	99.8 $\pm$ 1.3

*ND: Not detected.

small LOD values, high accuracy levels, and good linear range.

CONCLUSION

In the present work, a dispersive liquid liquid microextraction methodology based on the use of Fe_3O_4 magnetic nanoparticles supported with imidazolium ionic liquid was developed to enrich mercury in tap water and mineral water samples. The use of nanoparticles in this system offer a rapid extraction without any centrifugation steps. Further, this method combines the advantages of the DLLME technique with the use of ionic liquid as a green extractant in small amounts. The whole analytical procedure, including pH, complexation, MNP amount, extraction time were optimized for all three ionic liquids. There was no significant difference observed when changing the cationic groups for ionic liquids. This method was successfully applied to the preconcentration of inorganic mercury in real natural waters achieving accuracy between 97.6–107.6% for 10 $\mu\text{g L}^{-1}$ and 50 $\mu\text{g L}^{-1}$ standard additions.

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TABLE V
Comparison of Proposed Method With Other DLLME Methods for Hg(II)

Method	Sample	Linear Range ($\mu\text{g L}^{-1}$)	LOD ($\mu\text{g L}^{-1}$)	Spiked Recov. (%)	Ref.
Traditional DLLME	Water	10.0–300.0	2.8	93.6–104.0	(32)
Ion pair-based surfactant-assisted DLLME	Fish	20–20000	9	98.1–100.5	(33)
IL-DLLME	Blood	0.15–8.50	0.03	96–103	(34)
DLLME	Water	1–1000	0.62	86.6–95.1	(35)
IL-mDLLME	Tap & mineral water	5–250	0.18	97.6–107.6	This work

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