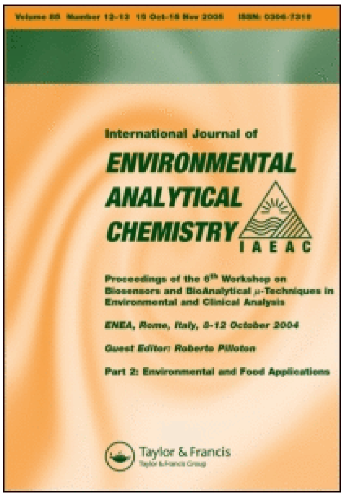

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Dispersive liquid-liquid microextraction based on ionic liquid and spectrophotometric determination of mercury in water samples

Maysam Gharehbaghi[a]; Farzaneh Shemirani[a]; Majid Baghdadi[a]
[a] School of Analytical Chemistry, University College of Science, University of Tehran, Tehran, Iran

To cite this Article Gharehbaghi, Maysam , Shemirani, Farzaneh and Baghdadi, Majid(2009) 'Dispersive liquid-liquid microextraction based on ionic liquid and spectrophotometric determination of mercury in water samples', International Journal of Environmental Analytical Chemistry, 89: 1, 21 — 33

To link to this Article: DOI: 10.1080/03067310802272994

URL: http://dx.doi.org/10.1080/03067310802272994

Intern. J. Environ. Anal. Chem.
Vol. 89, No. 1, 15 January 2009, 21–33

Taylor & Francis
Taylor & Francis Group

Dispersive liquid–liquid microextraction based on ionic liquid and spectrophotometric determination of mercury in water samples

Maysam Gharehbaghi, Farzaneh Shemirani* and Majid Baghdadi

School of Analytical Chemistry, University College of Science,
University of Tehran, Tehran, Iran

(*Received 31 January 2008; final version received 15 June 2008*)

A new simple and rapid dispersive liquid–liquid microextraction based on ionic liquid (IL) has been applied for the first time to preconcentrate trace levels of mercury as a prior step to its determination by spectrophotometric detection. In this method, small amount of an IL (1-hexyl-3-methylimmidazolium *bis*(trifluormethylsulfonyl)imid) as the extraction solvent was dissolved in acetone as the disperser solvent and the binary solution was then rapidly injected by a syringe into the water sample containing Hg cations which were complexed by 4,4′-*bis*(dimethylamino)thiobenzophenone (TMK) in the presence of sodium dodecyl sulphate as the anti-sticking agent. Thereby, a cloudy solution was formed and the Hg–TMK complex was extracted into the fine IL droplets. After centrifuging, the droplets of extractant were settled at the bottom of a conical test tube and the extracted phase was determined by spectrophotometry at 575 nm. Usually some parameters affect the complex formation and extraction, such as the type and volumes of extraction and disperser solvents, type and concentration of anti-sticking agent, salt concentration, pH and concentration of chelating agent, which have also been optimised for the presented method. Under optimum conditions, the enrichment factor of 18.8 was obtained from 10 mL of water. The detection limit of the method was found to be 3.9 $\mu g\,L^{-1}$ and the relative standard deviation ($n = 5$) for 50 $\mu g\,L^{-1}$ of mercury was 1.7%.

Keywords: ionic liquid; dispersive liquid–liquid microextraction; mercury; spectrophotometry

1. Introduction

Mercury is a naturally occurring metal as the result of the normal breakdown of minerals in rocks and soil from exposure to wind and water, and from volcanic activity. Mercury releases from natural sources have remained relatively constant in recent history, resulting in a steady rise in environmental mercury. However, it is also widely used in thermometers, fertilizers, pharmaceuticals and electronics. Waste incinerators and coal-fired utilities are a major source of mercury pollution [1].

Mercury may enter the aquatic environment from the weathering of rocks that contain Hg, factories or water treatment facilities that release water contaminated with mercury and incineration of municipal garbage that contains it. Also inorganic or organic

---

*Corresponding author. Email: shemiran@khayam.ut.ac.ir

ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310802272994
http://www.informaworld.com

compounds of mercury may be released to the water if mercury-containing fungicides are used.

This element may affect many different areas of the brain and their associated functions, resulting in a variety of symptoms. These include personality changes (irritability, shyness, and nervousness), tremors, changes in vision (constriction of the visual field), deafness, muscle incardination, loss of sensation and difficulties with memory [2].

The US Environmental Protection Agency determined that mercury chloride and methylmercury are possible human carcinogens. Therefore, the development of accurate and rapid determination methods for monitoring the levels of mercury in natural waters is necessary and essential. It should also be noted that in natural waters methylmercury levels are usually much lower than those of inorganic mercury [3].

Despite good developments in the modern analytical instruments, direct determination of trace analytes at low concentrations is often a problem for analytical chemists and, as a result, a sample-preparation step is required. The continuous quest for novel sample preparation procedures has led to the development of new methods, whose main advantages are their speed and negligible volume of solvents used. The solvent microextraction technique effectively overcomes these difficulties by reducing the amount of organic solvent as well as allowing sample extraction and preconcentration to be done in a single step. In comparing with conventional methods, solvent microextraction is faster and simpler, inexpensive, sensitive and effective for the removal of interfering matrices. Solvent microextraction is a form of solvent extraction with phase ratio values higher than 100 [4]. Compared with the conventional solvent extraction, microextraction may provide poorer analyte recovery; instead the concentration in the organic phase greatly enhances [5]. As a big advantage, the amount of the used organic solvent is highly reduced. In addition merely one step of operation is required, therefore, problems of contamination and loss of analytes vanish.

Dispersive liquid–liquid microextraction (DLLME) is a modified solvent microextraction method and its acceptor-to-donor phase ratio is greatly reduced comparing with the other methods [6–9]. In previous DLLME methods, the appropriate mixture of the common organic extraction and disperser solvents was rapidly injected by syringe into aqueous samples containing analytes. Thereby, a cloudy solution was formed and extraction occurred.

However, a problem still exists and that is continued reliance on using of toxic, hazardous, flammable and environmentally damaging organic solvents. Room temperature ionic liquids (RTILs) are being recently considered as replacement for these solvents in sample preparation, duo to their unique chemical and physical properties, among these, negligible vapour pressure, non-flammability, good extractability for various organic compounds and metal ions as a neutral or charged complex, as well as tuneable viscosity and miscibility with water and organic solvents.

Classical liquid–liquid extraction (LLE) based on ionic liquids (ILs) has been reported previously [10–18]. However, this method requires large amounts of IL, which is expensive. Single drop microextraction based on ILs was reported by Liu *et al.* [19]. But in this method the sensitivity was analyte dependent because of its different partition coefficient and the relatively large viscosity of IL.

The preconcentration and determination of Hg(II) in water samples has been studied in various extraction methods such as CPE and SPE. Spectrophotometric determinations of trace levels of mercury in water samples using dithizone in micellar medium have been reported [20,21]. The calibration graphs were linear in the range of 0.01–10 and 50–500 μg L^{-1}, respectively. However, the application of CPE for mercury determination is very limited and restricted to a few complex examples, mostly due to the peculiar characteristics of this element [22,23].

Also some SPE methods have been applied to extract and determine Hg ions in water samples. Alumina modified by dimethylsulfoxide has been used for the separation and preconcentration of Hg(II) with 98% recovery [24]. Column preconcentration of mercury as its tetraiodomercurate(II) ion using methyltrioctylammonium chloride–naphthalene adsorbent has been reported [25]. Generally, the amounts of eluent used in these methods are high, unfortunately. In 2008, Baghdadi developed a new method termed cold-induced aggregation microextraction which was based on the use of ILs in homogeneous liquid–liquid microextraction for extraction and preconcentration of mercury [26]. However, in this method two different ILs were used simultaneously and heating and cooling procedures were unavoidable.

For the first time in DLLME, very small amounts of a hydrophobic IL, namely, 1-hexyl-3-methylimmidazolium *bis*(trifluormethylsulfonyl)imid ([Hmim][Tf_2N]), were used as an extraction solvent, which is dissolved in acetone as the disperser solvent and then dispersed into the sample solution containing sodium dodecyl sulphate (SDS) as an anti-sticking agent to prevent sticking of IL to the test tube wall. After that, a cloudy solution of fine droplets of IL appeared. After centrifuging, the fine droplets of the extraction solvent sedimented at the bottom of a conical test tube.

The performance of DLLME based on IL is illustrated with the determination of mercury in water samples by using spectrophotometric detection. The effect of various experimental parameters on the extraction was investigated. This method is simple, rapid for extraction and preconcentration of Hg(II) from water samples and is superior against high content of salt and water-miscible organic solvents such as acetone compared with CPE. Further, in comparison with organic solvent extraction, it is much safer since only small amounts of IL are used which is being considered as a ‘green solvent’ for various separation processes. Another important capability of this method is that it can operate in flow-injection mode that our group is presently investigating.

2. Experimental

2.1 *Instrumentation*

A lambda 25 UV-VIS spectrometer from Perkin Elmer (Waltham, MA, USA) was used for recording the spectra and measuring the absorbance. A Universal 320R refrigerated centrifuge equipped with an angle rotor (6-place, 9000 rpm, Cat. No.1620A) was from Hettich (Kirchlengern, Germany).

2.2 *Reagents and solutions*

All reagents used were of analytical reagent grade. Doubly distilled water was used throughout the experiment. A stock solution of Hg(II) (1000 mg L^{-1}) was prepared by dissolving the appropriate amount of $HgCl_2$ (Merck, Darmstadt, Germany). Working standard solutions were prepared freshly by appropriate dilutions of the standard stock solution.

A 2×10^{-4} mol L^{-1}solution of 4,4′-*bis*(dimethylamino)thiobenzophenone (Merck, Darmstadt, Germany) was prepared by dissolving the appropriate amount in *n*-propanol (Merck, Darmstadt, Germany). This solution can be kept for 40 days in a dark place at room temperature.

A 1% (w/v) solution was prepared by dissolving the appropriate amount of SDS in doubly distilled water and a buffer solution (pH = 3.8, 1 mol L^{-1}) was prepared by mixing 88 mL of acetic acid (1 mol L^{-1}) and 12 mL of sodium acetate (1 mol L^{-1}).

Acetone as a disperser solvent, [Hmim][Tf$_2$N] as an extraction phase, SDS as the anti-sticking agent, acetic acid, sodium acetate, *n*-propanol, ethanol and sodium nitrate were purchased from Merck (Darmstadt, Germany).

2.3 *DLLME procedure*

A total of 500 µL of buffer (pH = 3.8, 1 mol L^{-1}), 250 µL of NaNO$_3$ 10% (w/v) and 250 µL of SDS 1% (w/v) were added into a 15 mL test tube with conical bottom containing mercury in the range of 12–140 µg L^{-1}. Then, 120 µL of 4,4′-*bis*(dimethylamino)thiobenzophenone (TMK) (2×10^{-4} mol L^{-1}) as chelating agent was added to the solution and the 10.00 mL total volume was adjusted with doubly distilled water. The pinkish complex of mercury was formed. Then, 500 µL of binary solution containing 60 mg of [Hmim][Tf$_2$N] (extraction solvent) and acetone (disperser solvent) was injected rapidly into the sample solution using a syringe and a stable cloudy solution (water, acetone and IL) was obtained. The Hg–TMK complex was extracted into the fine droplets of IL. The mixture was then centrifuged for 6 min at 5000 rpm. After this process fine droplets of [Hmim][Tf$_2$N] were joined together and sedimented at the bottom of the conical test tube. After removing the whole aqueous solution the extraction phase was diluted with 350 µL of ethanol (85%) and transferred to a 500 µL cell and the absorbance was measured at 575 nm.

3. Results and discussion

3.1 *Selection of IL*

ILs are composed of asymmetrically substituted nitrogen-containing cations (e.g. imidazole, pyrrolidine, pyridine, …) with inorganic anions (e.g. Cl^-, BF_4^-, PF_6^-, $(CF_3SO_2)_2N^-$, …). The range of available anion and cation combination could provide too many different ILs, so at first glance, perhaps it is difficult to select the desired IL but by considering the following conditions, the selection is not very difficult: IL has to be water-immiscible for analyte extraction. ILs containing Cl^-, BF_4^- and $CF_3SO_3^-$ are water-miscible and ILs containing PF_6^-, $(CF_3SO_2)_2N^-$ are water-immiscible. In addition, IL has to be liquid in experimental conditions and have extraction capability of the interested compounds and higher density than water for LLE. ILs containing an imidazolium cation was selected in this work. ILs containing $(CF_3SO_2)_2N^-$ and PF_6^- are hydrophobic and liquid in the experimental conditions.

Generally, selected IL has to be more immiscible in the sample solution to reduce extraction solvent consumption, moreover, IL must produce sedimented phase at appropriate amounts. Since the sample volume was 10 mL so if [Hmim][Tf$_2$N] was chosen as IL, about 34 mg of it will be dissolved in the sample, while water solubility of

[Hmim][PF_6] is 75 mg/10 mL. Therefore, in this work we selected [Hmim][Tf_2N] IL as the extraction solvent.

3.2 *Effect of pH*

Separation of metal ions by DLLME involves prior complex formation with sufficient hydrophobicity to be extracted into the small volume of the IL phase, whereby the desired preconcentration is obtained. pH plays a distinctive role on metal-chelate formation and subsequent extraction into IL phase. The effect of pH on the mercury complex extraction from water samples was studied in the range of 1.0–6.0. The results illustrated in Figure 1 reveal that the absorbance is initially increased by rising pH to 3 and then, after pH 4 absorbance starts to decrease. Thus, pH 3.8 seems a proper choice for both complexation and extraction.

3.3 *Effect of acetate/acetic acid buffer concentration and TMK concentration*

Absorbance as a function of the buffer concentration was studied in the range of 0.0–0.2 mol L^{-1}. Absorbance initially increased up to 0.01 mol L^{-1} of buffer and then approximately stayed constant. A concentration of 0.05 mol L^{-1} buffer was selected for subsequent experiments.

Also, the effect of TMK concentration was examined. As it is well expected, with accordance to a ML_2 stoichiometry of complex $[Hg_2\,(TMK)_4]^{2+}$ [27,28], the absorbance was increased by increasing TMK concentration. We investigated the TMK concentration in the range of 4.0×10^{-7}–3.6×10^{-6} mol L^{-1}. Maximum absorbance was obtained at a concentration of 1.6×10^{-6} mol L^{-1} and after that, absorbance approximately stays constant. A total of 2.4×10^{-6} mol L^{-1} was chosen as the optimum concentration of TMK.

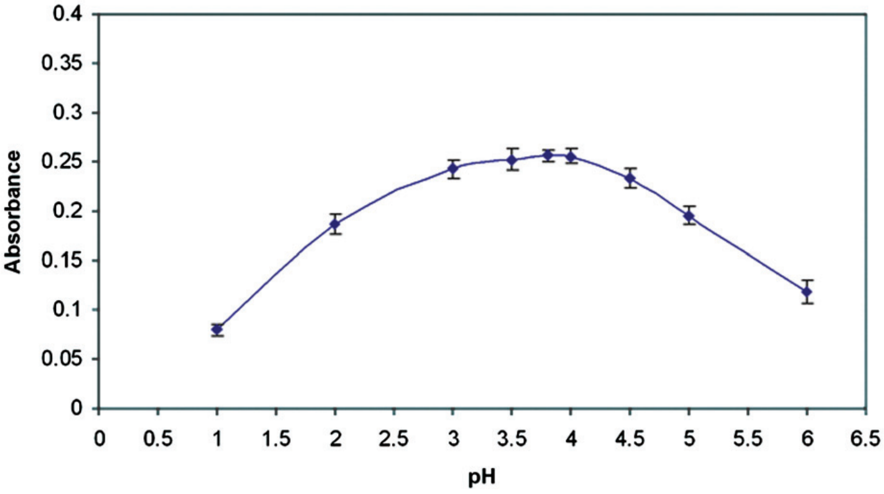

Figure 1. Effect of pH on the absorbance of Hg–TMK complex. (Utilised conditions: Mercury 50 μg L^{-1}, TMK 2.0×10^{-6} mol L^{-1}, $NaNO_3$ 0.02 mol L^{-1}, [Hmim][Tf_2N] 50 mg, Acetone 500 μL, Diluting agent 350 μL).

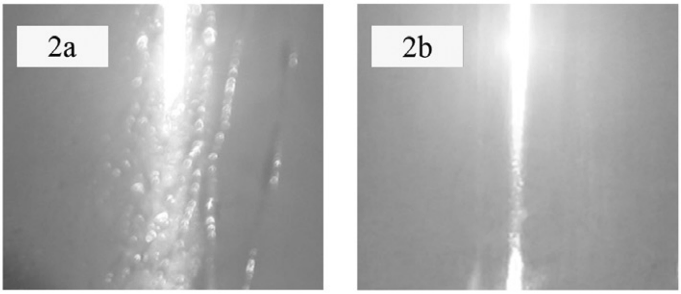

Figure 2. Effect of SDS as the anti-sticking agent [26]. (a) In the absence of SDS: enlarged view of the centrifuge tube wall that shows wall-stuck IL phase. (b) In the presence of SDS: enlarged view of the centrifuge tube wall that shows there is no IL phase on it.

3.4 *Selection of anti-sticking agent and effect of its concentration*

After centrifuging the sample solution containing fine particles of IL, some of the IL droplets have stuck on the wall of the test tube (Figure 2a) [26], so some extracted phase was lost. In order to overcome this problem, a surfactant was added into the sample solution. Therefore, during phase separation, molecules of surfactant surrounded fine particles of IL. Hence their interaction with the wall of the test tube decreased and consequently IL did not stick on it (Figure 2b) [26].

We have also investigated the effect of Triton X-114, Triton X-100 and SDS. The results showed that all these surfactants were helpful and in the presence of them the stickiness decreased clearly, but SDS was more effective than the others, perhaps due to its assisting on ion-pair extraction of the mercury cationic complex and/or its solubilising effect on complexation (the precipitation elimination).

In the presence of SDS, the absorbance initially increased up to 0.035% (w/v) and then decreased because of dissolving of IL. According to Figure 3, a concentration of 0.025% (w/v) SDS was chosen for subsequent experiments.

3.5 *Effect of amount of the extraction solvent*

To examine the effect of the extractant amount, solutions containing 500 μL of acetone and different amounts of IL in the range of 10–90 mg were subjected to the same procedures. According to Figure 4 that shows the curve of absorbance *versus* the amount of IL, with increasing IL concentration the absorbance initially increases up to 50 mg, then after 70 mg it starts to decrease. This drop off is due to the rise of the sedimented phase volume. The high sensitivity was obtained using 60 mg of [Hmim][Tf_2N] that was dissolved in 500 μL of acetone as the disperser solvent. The volume of the sedimented phase was determined using a microsyringe and was about 25 μL.

3.6 *Effect of type and volume of the disperser solvent*

The main criterion for the selection of disperser solvent is its miscibility in the extraction solvent and aqueous solution. In addition, the type of disperser directly influences the viscosity of the binary solvent. Thus, this solvent can control droplet producing and extraction efficiency. For studying this effect, two different solvents such as acetone and

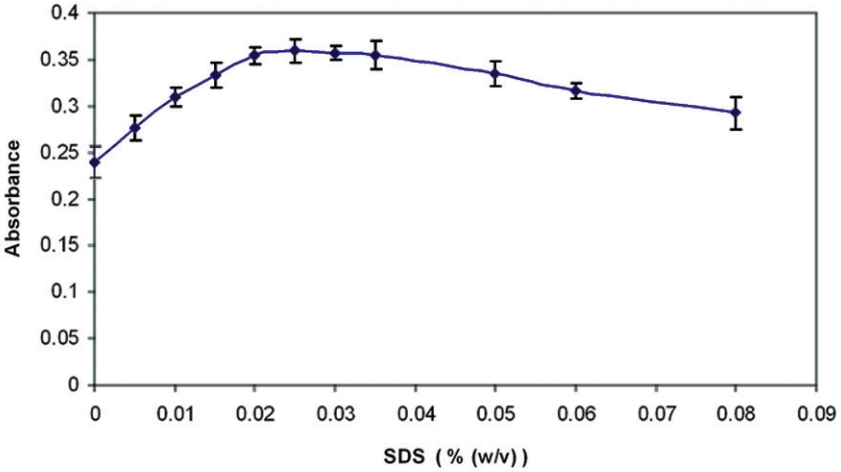

Figure 3. Effect of SDS concentration on the absorbance of HgTMK complex. (Utilised conditions: Mercury 50 μg L^{-1}, TMK 2.4×10^{-6} mol L^{-1}, Acetate/acetic acid buffer (pH = 4) 0.05 mol L^{-1}, $NaNO_3$ 0.02 mol L^{-1}, [Hmim][Tf_2N] 50 mg, Acetone 500 μL, Diluting agent 350 μL).

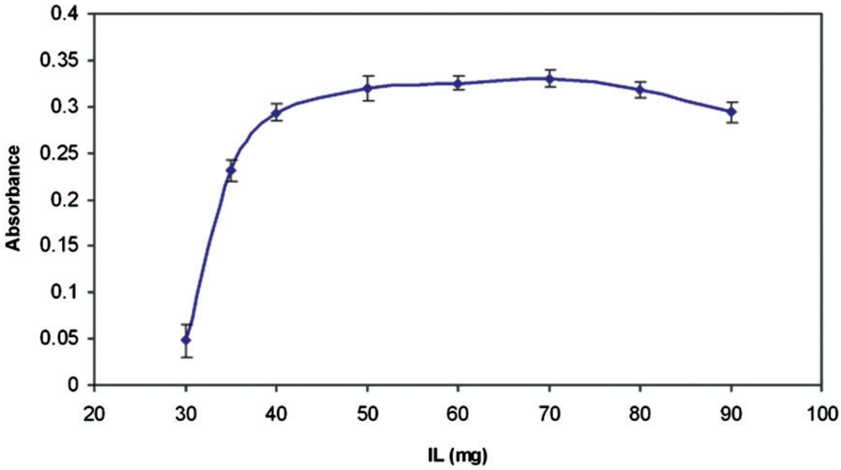

Figure 4. Effect of amount of IL on the absorbance of Hg–TMK complex. (Utilised conditions: Mercury 50 μg L^{-1}, TMK 2.4×10^{-6} mol L^{-1}, Acetate/acetic acid buffer (pH = 4) 0.05 mol L^{-1}, $NaNO_3$ 0.02 mol L^{-1}, SDS 0.025% (w/v), Acetone 500 μL, Diluting agent 350 μL).

ethanol were tested. A series of sample solutions were studied using 500 μL of each disperser solvent with 60 mg of the IL (extraction solvent). The obtained enrichment factors for these two dispersers show no statistical significant differences between them; however acetone was selected because it is more accessible than ethanol.

The effect of the volume of acetone on the extraction recovery was also studied. The different volumes of acetone up to 800 μL with addition of 60 mg of [Hmim][Tf_2N] were examined. At the first two tests, the droplets were big and the surface area was low, so the droplets rapidly settled at the bottom of the tube and low extraction efficiencies

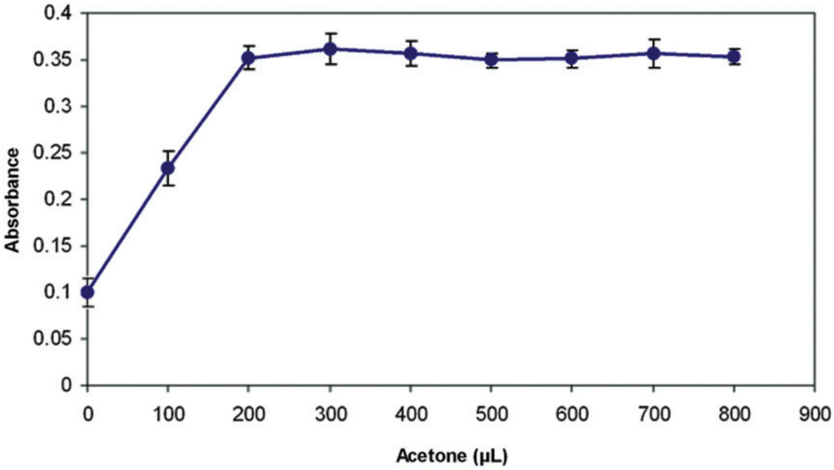

Figure 5. Effect of volume of acetone on the absorbance of Hg–TMK complex. (Utilised conditions: Mercury 50 μg L^{-1}, TMK 2.4×10^{-6} mol L^{-1}, Acetate/acetic acid buffer (pH = 4) 0.05 mol L^{-1}, $NaNO_3$ 0.02 mol L^{-1}, SDS 0.025% (w/v), [Hmim][Tf_2N] 60 mg, Diluting agent 350 μL).

were obtained. As it is shown in Figure 5, the absorbance increases up to 200 μL of disperser solvent volume and after that it approximately stays constant. Thus, 500 μL of acetone was chosen as the proper amount.

3.7 *Effect of salt concentration*

For studying the influence of ionic strength on the performance of DLLME, the $NaNO_3$ concentration in the range of 0.0–0.6 mol L^{-1} was investigated while other experimental conditions were kept constant. By increasing $NaNO_3$ concentration the extraction efficiency slowly increases due to the salting-out effect and then stays approximately constant. A concentration of 0.03 mol L^{-1} $NaNO_3$ was selected for subsequent experiments in order to increase the recovery.

3.8 *Effect of centrifuge conditions*

A series of solutions were tested at various rates of centrifugation. The rate of centrifugation was adjusted in the range of 1000–8000 rpm for 4 min. The absorbance slowly increases with increasing the rate to 5000 rpm and after that, it approximately stays constant. Therefore, 5000 rpm was selected as the best rate for centrifuging.

At the optimum rate, absorbance was investigated as a function of centrifugation time. Over 5 min, the absorbance was constant, indicating complete transfer of IL phase to the bottom of the centrifuge tube, so 6 min were selected as the optimum centrifugation time.

3.9 *Selection of the dilution agent for IL phase*

Dilution agent has to dissolve the IL and complex completely. We studied the effect of acetone (40–90%) and ethanol (60–100%). When one of these dilution agents was added in

Table 1. Effect of foreign ions on the recovery of mercury (50 µg L^{-1}).

Ion	Ion/Hg(II) ratio	Recovery (%)
Mn^{2+}	1000	104.8
Co^{2+}	1000	105.7
Zn^{2+}	1000	95.5
Ni^{2+}	1000	100.4
Cd^{2+}	1000	103.9
Ca^{2+}	1000	101.8
Pb^{2+}	1000	83.4
	500	96.2
Al^{3+}	500	110.6
	100	98.4
Cr^{3+}	500	111.5
	100	95.3
Cu^{2+}	100	104.5
Mg^{2+}	100	83.2
	50	104.1
Fe^{3+}	10	63.1
Fe^{3+}	100	97.3 [a]
Ag^{+}	1	93.4
Ag^{+}	1	100.8 [b]
Au^{3+}	1	103.9
Pd^{2+}	1	87.9
SO_4^{2-}	1000	102.0
PO_4^{3-}	1000	104.3
Cl^{-}	1000	95.2
F^{-}	1000	100.4
NO_2^{-}	10	104.3

Notes: [a] Fe^{3+} masked with 5.0×10^{-3} mol L^{-1} oxalate.
[b] Ag^{+} masked with 1.0×10^{-3} mol L^{-1} EDTA.

the various compositions, λ_{max} of complex was slightly shifted due to changes of solvent polarity. So in each composition of diluent, the absorbance was measured at related λ_{max} In 40% acetone the maximum absorbance was obtained but IL phase could not be dissolved completely, so the solution was turbid, but in the presence of 85% ethanol the sample was clear and maximum absorbance was acquired. Therefore, ethanol 85% was chosen as a diluting agent.

3.10 *Effect of coexisting ions*

The effects of coexisting ions in real water samples on the recovery of mercury were also studied. In these experiments, 10 mL of solutions containing 50 µg L^{-1} of mercury and various amounts of interfering ions were treated. A given species was considered to interfere if it resulted in a ±5% variation of the absorbance. The results obtained are given in Table 1.

As can be seen, most of the cations and anions examined did not interfere with the extraction and determination of mercury. However Ag^{+}, Pd^{2+} interfered at the same concentration as mercury and NO_2^{-} had adverse effect on the absorbance at 10 times

Table 2. Analytical characteristics of DLLME for determination of Hg.

Parameter	Analytical feature
Linear range ($\mu g\,L^{-1}$)	12–140
r^2	0.9998
Limit of detection ($\mu g\,L^{-1}$) ($3\sigma, n=5$)	3.9
Repeatability (RSD[a], %) ($n=5$)	1.7
Enhancement factor[b] (EF)	18.8
Sample volume (mL)	10
Extraction time (min)	<7

Notes: [a]RSD was obtained for $30\,\mu g\,L^{-1}$ concentration of Hg(II).
[b]Enhancement factor is the slope ratio of calibration graph after and before extraction.

higher than mercury. Interferences of Ag^+ and Fe^{3+} were eliminated in the presence of $1\times10^{-3}\,mol\,L^{-1}$ EDTA and $5\times10^{-3}\,mol\,L^{-1}$ oxalate, respectively.

Also TMK as well as its complexes are sensitive to oxidation/reduction. Hence, oxidising and reducing agents might interfere and since the drinking water system of Iran is disinfected by hypochlorite, which is oxidising agent, we could not determine mercury in the tap water.

3.11 *Figures of merit*

Table 2 summarises the analytical characteristics of the optimised method, including linear range, limit of detection, reproducibility and enhancement factor. The calibration graph was linear in the range of $12–140\,\mu g\,L^{-1}$ of mercury. The limit of detection, defined as $C_L = 3S_B/m$, where C_L, S_B and m are the limit of detection, standard deviation of the blank and slope of the calibration graph, respectively, was $3.9\,\mu g\,L^{-1}$. The relative standard deviation (RSD) for five replicate measurements of $50\,\mu g\,L^{-1}$ Hg(II) was 1.7%. The enhancement factor was obtained from the slope ratio of calibration graph after and before extraction, which was about 18.8. The equation of the calibration curve after the preconcentration procedure was given in Equation (1). Also the equation of the calibration curve before the preconcentration procedure was given at below in Equation (2).

$$A = 5.10\times10^{-3}\ C_{(Hg)} + 0.0508\ (r^2 = 0.9998,\ r = 0.9999) \tag{1}$$

$$A = 2.71\times10^{-4}\ C_{(Hg)} + 0.0268\ (r^2 = 0.9991,\ r = 0.9995) \tag{2}$$

These standard samples of mercury were chosen up to $400\,\mu g\,L^{-1}$ with execs TMK to measure their absorbance and obtain the equation of the calibration curve accurately.

3.12 *Analysis of water samples*

The proposed DLLME methodology was applied for the determination of mercury in different water samples. Mineral and river water samples were collected from the North of Iran and were analysed by DLLME as a prior step for spectrophotometric determination. No detectable levels of mercury in the river and mineral water samples were found.

Table 3. Determination and relative recovery of spiked Hg in different water samples.

Sample	Added Hg^{2+} ($\mu g\,L^{-1}$)	Found Hg^{2+} Mean ± SD[a] ($\mu g\,L^{-1}$)	Relative recovery (%)
Mineral water[b]	–	n.d.[c]	–
	25	25.2 ± 0.6	100.8
	50	50.9 ± 0.4	101.8
River water[d]	–	n.d.[c]	–
	25	24.7 ± 0.4	98.8
	50	46.1 ± 0.3	92.2
Saline serum[e]	25	25.2 ± 0.2	100.8
	35	35.8 ± 0.4	102.3
Synthetic sample[f]	25	25.8 ± 0.5	103.2
	35	34.8 ± 0.4	99.4

Notes: [a] Standard deviation ($n = 5$).
[b] Damavand mineral water, Iran.
[c] Not detected.
[d] Tajan river water, North of Iran.
[e] Produced by Daru Paksh Company for injection.
[f] Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, Mn^{2+} and Pb^{2+} 1000 $\mu g\,L^{-1}$ of each cation; Na^{+} and K^{+} 3000 $\mu g\,L^{-1}$ of each cation.

Moreover, the robustness of the proposed method was checked by performing recovery tests on a saline serum and a synthetic sample (no certified reference material was available). Each type of water was spiked with variable amounts of Hg^{2+} to assess matrix effects. The results are shown in Table 3. The relative recoveries of mercury from mentioned water samples at various spiking levels were between 92.2 and 103.2%. These results demonstrated matrices of these water samples, in our present context, had little effect on DLLME of mercury.

3.13 *Comparison to other methods*

Comparison of the present method with previously reported preconcentration methods is given in Table 4. In comparison with other reported methods, DLLME based on IL has low LOD (3.9 $\mu g\,L^{-1}$), good repeatability (RSD%) and short extraction procedure (less than 7 min). These characteristics are of key interest for routine laboratories in trace metal ion analysis. In addition, and as an innovation, an IL was applied as a 'green chemistry solvent' in DLLME for the first time to replace environmentally damaging organic solvents.

4. Conclusion

For the first time, the use of DLLME based on IL for preconcentration of mercury from real water samples is proposed as a prior step to their determination by spectrophotometric detection.

This method is simple, rapid, sensitive, low cost and has low toxicity since only very small amounts of an IL as a 'green extraction solvent' is used as a replacement of environmentally damaging organic solvents. Also the use of spectrophotometry as

Table 4. Characteristic performance data obtained by using DLLME and other techniques in determination of mercury.

Method	LOD[a]	RSD[b] (%)	Enhancement factor (EF)	Sample consumption (mL)	Time (min)	Calibration range ($\mu g\,L^{-1}$)	References
CPE-Spectrophotometry	14	4.8	6	50	>30	500–50	[21]
SPE-Spectrophotometry	4	2.5	100	1000	>500	0.0110–	[29]
SPE- Spectrophotometry	15	1.6	50	100	>8	90–2950	[30]
DLLME-Spectrophotometry	3.9	1.7	18.8	10	<7	140–12	This work

a detection system has a low operational cost in comparison with other methods such as FAAS and ICP/OES.

Acknowledgement

Financial support from the University of Tehran is gratefully acknowledged.

References

[1] D.M. Roundhill, J. Chem. Educ. **81**, 275 (2004).
[2] Agency for Toxic Substances and Disease Registry (ATSDR), *Toxicological Profile for Mercury* (U.S. Department of Health and Human Services, Public Health Service, Atlanta, GA, 2004).
[3] R.M. Blanco, M.T. Villanueva, J.E.S. Uria, and A.S. Medel, Anal. Chim. Acta **419**, 137 (2000).
[4] E. Carasek, J.W. Tonjes, and M. Scharf, Talanta **56**, 185 (2002).
[5] E.Z. Jahromi, A. Bidari, Y. Assadi, M.R.M. Hosseini, and M.R. Jamali, Anal. Chim. Acta **585**, 305 (2007).
[6] M. Rezaee, Y. Assadi, M.R.M. Hosseini, E. Aghaee, F. Ahmadi, and S. Berijani, J. Chromatogr. A **1116**, 1 (2006).
[7] S. Berijani, Y. Assadi, M. Anbia, M.R.M. Hosseini, and E. Aghaee, J. Chromatogr. A **1123**, 1 (2006).
[8] R.R. Kozani, Y. Assadi, F. Shemirani, M.R.M. Hosseini, and M.R. Jamali, Talanta **72**, 387 (2007).
[9] M. Gharehbaghi, F. Shemirani, and M. Baghdadi, Intern. J. Environ. Anal. Chem. **88**, 513 (2008).
[10] A.E. Visser, R.P. Swatloski, W.M. Reichert, S.T. Griffin, and R.D. Rogers, Ind. Eng. Chem. Res. **39**, 4596 (2001).
[11] A.E. Visser, R.P. Swatloski, S.T. Griffin, D.H. Hartman, and R.D. Rogers, Sep. Sci. Technol. **36**, 785 (2001).
[12] A.E. Visser, R.P. Swatloski, W.M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J.H. Davies, and R.D. Rogers, Environ. Sci. Technol. **36**, 2523 (2002).
[13] Z.J. Li, Q. Wei, R. Yuan, X. Zhou, H.Z. Liu, H.X. Shan, and Q.J. Song, Talanta **71**, 68 (2007).
[14] S. Chun, S.V. Dzyuba, and R.A. Bartsch, Anal. Chem. **73**, 3737 (2001).
[15] G.T. Wei, Z. Yang, and C.J. Chen, Anal. Chim. Acta **488**, 183 (2003).
[16] H. Luo, S. Dai, and P.V. Bonnesen, Anal. Chem. **76**, 2773 (2004).
[17] R. Germani, M.V. Mancini, G. Savelli, and N. Spreti, Tetrahedron Lett. **48**, 1767 (2007).
[18] N. Papaiconomou, J.M. Lee, J. Salminen, M.V. Stosch, and J.M. Prausnitz, Ind. Eng. Chem. Res. **47**, 5080 (2008).
[19] J.-F. Liu, Y.-G. Chi, G.-B. Jiang, C. Tai, J.-F. Peng, and J.-T. Hu, J. Chromatogr. A **1026**, 143 (2004).
[20] H. Khan, M.J. Ahmed, and M.I. Bhanger, Anal. Sci. **21**, 207 (2005).
[21] M. Garrido, M.S. Di Nezio, A.G. Lista, M. Palomeque, and B.S. Fernández Band, Anal. Chim. Acta **502**, 173 (2004).
[22] L.P. Yu, J. Agric. Food Chem. **53**, 9656 (2005).
[23] J.C.A. deWuilloud, R.G. Wuilloud, M.F. Silva, R.A. Olsina, and L.D. Martinez, Spectrochim. Acta Part B **57**, 365 (2002).
[24] E.M. Soliman, M.B. Shah, and S.A. Ahmed, Talanta **69**, 55 (2006).
[25] N. Pourreza and M. Behpour, Anal. Chim. Acta **481**, 23 (2003).
[26] M. Baghdadi and F. Shemirani, Anal. Chim. Acta **613**, 56 (2008).
[27] G.S. Matsibura, O.P. Ryabushko, and A.T. Pilipenko, Zh. Anal. Khim. **38**, 1008 (1983).
[28] Z. Marczenko, *Separation and Spectrophotometric Determination of Elements* (Ellis Hardwood, London, 1986).
[29] N. Rajesh and G. Gurulakshmanan, Spectrochim. Acta Part A **69**, 391 (2008).
[30] D. Kara and N. Tekin, Microchim. Acta **149**, 193 (2005).