Analytical Methods

PAPER

View Article Online
View Journal | View Issue

Cite this: *Anal. Methods*, 2015, 7, 1140

Hollow fiber supported ionic liquid membrane microextraction for speciation of mercury by high-performance liquid chromatography-inductively coupled plasma mass spectrometry†

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With an ionic liquid as the membrane liquid and dithizone as the carrier, a novel and simple hollow fiber supported liquid phase microextraction (HF-LPME) method was developed for the preconcentration and determination of monomethylmercury (MMHg) and inorganic mercury (IHg) in environmental water samples by high-performance liquid chromatography-inductively coupled plasma mass spectrometry (HPLC-ICP-MS). The parameters affecting the enrichment factors, including the type of ionic liquid membrane and carrier, the pH of the sample solution, the concentration of L-cysteine in the acceptor phase, stirring rate, extraction temperature and time, were optimized. With the optimal extraction conditions (ionic liquid membrane phase: $[C_4MIM][PF_6]$ with 0.02% (m/v) dithizone; acceptor phase: 25 μL, 1 g L^{-1} L-cysteine; extraction temperature: 50 °C; extraction time: 12 h), the obtained enrichment factors of MMHg and IHg were 1620 and 1540, and the detection limits for MMHg and IHg were 0.3 ng L^{-1} and 0.9 ng L^{-1}, respectively. There was no significant effect on the extraction efficiency in the presence of humic acid (0–25 mg L^{-1} dissolved organic carbon). The proposed method was applied to real water samples, and the spike recoveries obtained were in the range 90.8–108.2%. These results demonstrate that the proposed ionic liquid based HF-LPME-HPLC-ICP-MS method is a simple and sensitive technique for the determination of mercury species at trace levels in water samples, with a high reproducibility and accuracy.

Received 10th October 2014
Accepted 2nd December 2014

DOI: 10.1039/c4ay02408g

www.rsc.org/methods

Introduction

Mercury is known as a global contaminant, with high toxicity towards human beings and wildlife. The toxicity of mercury highly depends on its chemical form. Monomethylmercury (MMHg), the most toxic form of mercury, can be highly bioaccumulated and biomagnified in food webs, and can not be expelled from biological bodies.[1] It readily crosses the blood–brain barrier and causes severe damage to the central nervous system.[2] Inorganic mercury (IHg), Hg^{2+}, is believed to be the proximate toxic agent for all inorganic forms of mercury, which have the capacity to elicit idiosyncratic reactions.[2] Therefore, it is important to analyze the nature of the mercury species when assessing the toxicity and health risks of mercury, as well as their mobilities in the environment.[3] The concentration of mercury species in natural waters is very low.[4–6] Therefore, it remains a challenge to develop sensitive and reliable analytical techniques that are capable of measuring nanogram and picogram levels of mercury species.[7]

Due to very low levels of mercury species and the complexity of matrices in the environment, an effective pretreatment approach is of vital importance for the analysis of mercury species prior to quantitative chromatography-based techniques. In recent years, various sample enrichment and preparation procedures have been employed for the speciation of mercury, including solid-phase microextraction (SPME),[8–10] liquid–liquid microextraction (LLME),[11] single drop microextraction (SDME),[12] dual-cloud point extraction (dCPE)[13] and hollow fiber supported liquid phase membrane microextraction (HF-LPME).[14,15] Compared to other procedures, HF-LPME has many advantages, such as higher preconcentrations, sample clean-up, and the use of solvent-saving, simple and inexpensive equipment. Therefore, it has been widely applied as an alternative to conventional techniques for the enrichment of mercury species.[14–18]

To obtain efficient extraction, it is of great importance to select an appropriate organic membrane for the HF-LPME. Many organic solvents, which constituted the membrane in the

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ay02408g

hollow fiber in HF-LPME, have been applied, such as toluene, carbon tetrachloride, 1-octanol, undecane and cyclohexane *etc.*[15,19,20]

Ionic liquids (ILs) have been generally considered as "green solvents", based primarily on their negligible vapor pressures, and they have been used in liquid–liquid extraction (LLE), liquid phase microextraction (LPME), single drop microextraction (SDME) and solid phase microextraction (SPME), *etc.*[21–23] Although some ILs have recently been shown to be toxic to organisms,[24–26] they are still exceptional solvents due to their unique physicochemical properties, such as low melting points, broad liquid ranges, negligible vapor pressures, good thermal stabilities, good solubilities towards inorganic and organic compounds, and good extractabilities for various organic compounds and metal ions,[27,28] making them promising candidates as extraction media for a range of microextraction techniques. To the best of our knowledge, however, there are few reports on the application of ILs in HF-LPME for the speciation of mercury.[15,18–20,29] Previous studies[30,31] demonstrated that ILs could be firmly immobilized in the micropores of a supported membrane, and thus it is attractive to explore the use of ionic liquid-based hollow fiber liquid membrane extraction for the speciation of mercury.

In the present work, three-phase hollow fiber supported ionic liquid membrane microextraction was developed for the preconcentration and determination of trace levels of mercury species in environmental water samples by HPLC-ICP-MS. Parameters including the type of ionic liquid membrane and carrier, pH of the sample solution, concentration of L-cysteine in the acceptor phase, stirring rate, and extraction temperature and time, which may affect the preconcentration efficiency, were optimized. The method was applied for the extraction of mercury species in environmental water samples.

Experimental

Instrumentation

The HPLC system consisted of a Flexar LC pump (PerkinElmer, USA) and a Rheodyne model 7725i injector (Rheodyne, Cotati, CA, USA) equipped with a 20 μL sample loop. The mercury species separation was performed on a Shim-pack CLC-ODS column (15 cm × 6 mm × 5 μm, Shimadzu, Japan). Elemental determinations were performed on a NexION 300X (PerkinElmer, USA) ICP-MS. The HPLC system was connected to an ICP-MS instrument using a PEEK (0.1 mm I.D. × 1/16 mm O.D.) or a polytetrafluoroethylene (PTFE) tube (0.8 mm I.D. × 1.2 mm O.D.). The conditions of the HPLC-ICP-MS system are given in Table 1.

Reagents and materials

Stock solutions of inorganic mercury (100 mg L^{-1} as Hg) and methylmercury in methanol (76.6 ± 2.9 mg kg^{-1}) were purchased from the National Institute of Metrology, China. The stock solutions were stored in the dark at 4 °C. All diluted working solutions were prepared daily from the stock solutions using 10 mmol L^{-1} sodium thiosulfate.

1-Butyl-3-methylimidazolium hexafluorophosphate ([C_4MIM][PF_6]) (≥99.0%), 1-hexyl-3-methylimidazolium hexafluorophosphate ([C_6MIM][PF_6]) (≥99.0%) and 1-octyl-3-methylimidazolium hexafluorophosphate ([C_8MIM][PF_6]) (≥99.0%) were purchased from Chengjie Co., Ltd. (Shanghai, China). Dithizone and 1-(2-pyridylazo)-2-naphthol (PAN) were purchased from the Shanghai Chemical Factory (Shanghai, China). Trioctylphosphine oxide (TOPO) was purchased from J & K Technology Co., Ltd. (Shanghai, China). L-Cysteine was obtained from Beijing Solarbio Science & technology Co., Ltd. (Beijing, China). Terrestrial origin humic acid sodium salt with 35.1% of dissolved organic carbon (DOC) was purchased from Sigma-Aldrich (Steinheim, Germany). Deionized water produced by a Millipore ultra-pure water system (Millipore; Bedford, USA), 18.2 MΩ, was used for the preparation of reagents and standards. All chemicals were of analytical grade or better.

The acceptor phase, 1 g L^{-1} L-cysteine solution, was prepared daily by dissolving the appropriate amount of L-cysteine in deionized water. The membrane liquids were prepared by dissolving dithizone in various ILs.

The humic acid stock solution was prepared by dissolving the appropriate amount of terrestrial origin humic acid sodium salt in deionized water and shaking the resulting mixture on a rotator for more than 12 hours at room temperature. Finally, the solution was filtered through a 0.2 μm glass fiber filter. Working solutions were prepared by appropriate dilutions of the stock solutions with deionized water.

50/280 Accurel PP polypropylene hollow fiber tubing (50 μm wall thickness, 280 μm inner diameter, 0.1 μm pore size, 60% porosity) was obtained from Membrana (Wuppertal, Germany). A BD Micro-Fine Syringe (0.5 mL, with a needle of 0.3 mm outer diameter and 8 mm length, prepared for U-100 insulin injection) obtained from BD Consumer Healthcare (Franklin Lakes, NJ, USA) was used to fill the lumen of the hollow fiber with the acceptor for extraction and to flush out the acceptor.

Extraction procedure

The extraction and enrichment of mercury species in water samples was as follows: (1) the hollow fiber was cut into segments with lengths of 42 cm. The prepared extraction set-up had an effective length of 41 cm and the corresponding volume of acceptor was 25 μL. The fiber segment was cleaned with acetone by ultrasonication to remove any possible impurities and then directly dried in air; (2) the appropriate amount of dithizone, as the carrier, was dissolved in the ILs which were used as membrane liquids; (3) the deionized water was injected into the lumen of the fiber using a BD Micro-Fine Syringe. Then, the fiber was submerged in the membrane liquid for 2–3 minutes to fill the membrane pores of the hollow fiber wall. After that, the lumen of the fiber was slowly flushed and completely filled with the acceptor phase (whilst being careful to avoid any air bubbles). Then, the two ends of the fiber were folded and enveloped with aluminum foil. The looped fiber surface was carefully washed with deionized water to remove excess ionic liquid; (4) the prepared extraction device was submerged into the donor phase (400 mL) in a glass

Table 1 Optimized conditions of the HPLC-ICP-MS system for mercury speciation

Parameters	Optimized value
HPLC	
Column	Shim-pack CLC-ODS column (15 cm × 6 mm I.D. × 5 μm)
Mobile phase	1 g L^{-1} L-cysteine, 0.06 mol L^{-1} ammonium acetate
Flow rate of mobile phase	1.0 mL min^{-1}
Injection volume	20 μL
ICP-MS	
ICP-MS	PerkinElmer NexION 300X
Nebulizer	Meinhard nebulizer
Isotope	202
RF power	1500
Plasma gas flow rate	15.0 L min^{-1}
Auxiliary gas flow rate	1.35 L min^{-1}
Nebulizer gas flow rate	0.85 L min^{-1}
Dwell time	20 ms

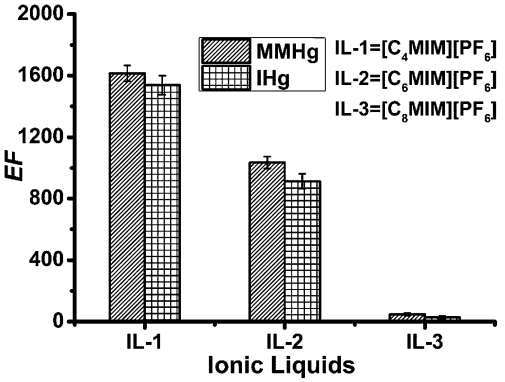

Fig. 1 Effect of the ionic liquid membrane on the extraction enrichment factors. Sample volume, 400 mL; carrier, 0.02% (m/v) dithizone; acceptor phase, 1 g L^{-1} L-cysteine solution; extraction temperature, 50 °C; extraction time, 12 h.

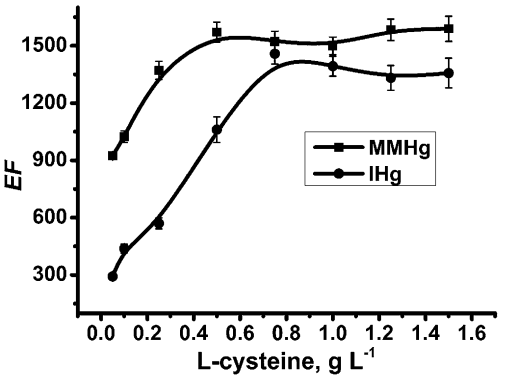

Fig. 2 The effect of L-cysteine concentration on the extraction enrichment factors. Sample volume, 400 mL; ionic liquid membrane, [C_4MIM][PF_6]; extraction temperature, 50 °C; extraction time, 12 h.

bottle with a screw cap. It is worth noting that the fiber must be fully immersed in the sample solution. The extraction and enrichment was carried out by stirring using a constant temperature magnetic stirrer (Jintan Zhongda Instrument Factory, Jiangshu, China) at 300 rpm. Meanwhile, the glass bottle was kept at 50 °C.

After the extraction was completed, the hollow fiber extraction device was taken out of the bottle. One of the sealed ends was carefully cut and connected to the needle of a BD Micro-Fine Syringe. Then, the other sealed end was cut, and the acceptor phase in the lumen was slowly blown into a conical glass tube. Finally, 20 μL of the acceptor solution was injected into the HPLC-ICP-MS system for analysis. A new fiber was used for each extraction in order to avoid memory effects in the extraction process.

Sample solutions spiked with 50 ng L^{-1} of MMHg and IHg were used to optimize the extraction parameters. All experiments were replicated three times and the mean values were obtained.

Calculation of enrichment factors

The concentration enrichment factor (EF) was introduced to evaluate the operation of the extraction in our experiments: $EF = C_A/C_D$. C_D and C_A are the initial analyte concentration in

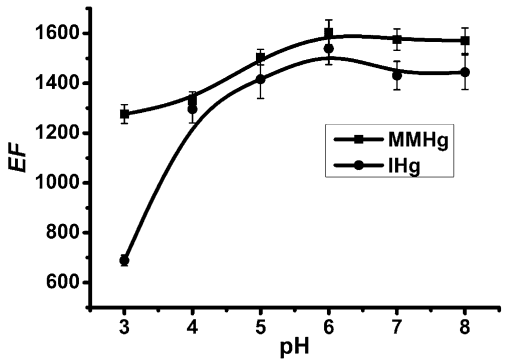

Fig. 3 Effect of the pH of the donor phase. Sample volume, 400 mL; ionic liquid membrane, [C_4MIM][PF_6]; acceptor phase, 1 g L^{-1} L-cysteine solution; extraction temperature, 50 °C; extraction time, 12 h.

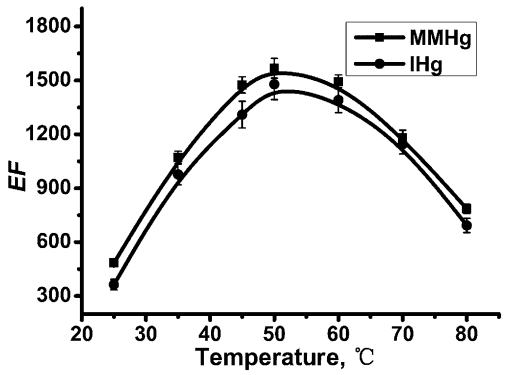

Fig. 4 Effect of extraction temperature on the extraction enrichment factors. Sample volume, 400 mL; ionic liquid membrane, [C_4MIM][PF_6]; acceptor phase, 1 g L^{-1} L-cysteine solution; extraction time, 12 h.

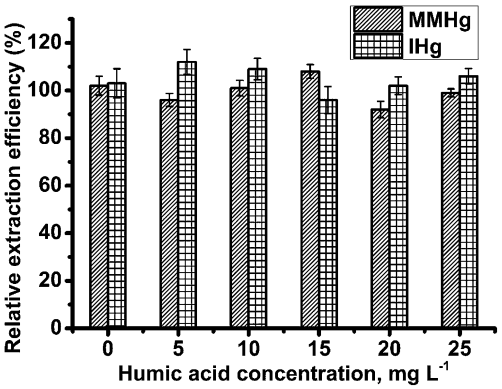

Fig. 5 Effect of humic acid concentration on the extraction enrichment factors. Sample volume, 400 mL; ionic liquid membrane, $[C_4MIM][PF_6]$; acceptor phase, 1 g L^{-1} L-cysteine solution; extraction temperature, 50 °C; extraction time, 12 h.

the donor phase and the final analyte concentration in the acceptor phase, respectively. All results are expressed as mean values of at least three replicates.

Sample collection and preparation

Tap water was collected in our laboratory after a flow time of about 5 min. River water was collected from the Jie river (Shandong, China). Waste water was obtained from a mine drainage system in Shandong, China. Sewage works effluent was collected from a local sewage treatment plant (Shandong, China). Before extraction, the acidic water samples were adjusted to about pH 6 with NaOH (1 M) and filtered through 0.25 μm micropore membranes.

Results and discussion

Selection of ionic liquid membrane

The nature of the liquid membrane in the pore of the hollow fiber is an essential factor for extraction. An appropriate membrane liquid should be immiscible with water, easily immobilized in the pores of the hollow fiber as a membrane barrier between the donor and the acceptor phase, and have a reasonably higher solubility for the analytes compared with the aqueous phase. Furthermore, it should have as low a toxicity as possible. ILs are considered as promising solvents for the replacement of traditional organic solvents, and have commonly been used as membrane liquids in HF-LPMEs.[27,28]

In this work, three ILs, including $[C_4MIM][PF_6]$, $[C_6MIM][PF_6]$ and $[C_8MIM][PF_6]$, were tested as membrane liquids. The results of the extractions are presented in Fig. 1. Out of the three ILs investigated, $[C_4MIM][PF_6]$ has the highest EFs for mercury species. This could be ascribed to the lower viscosity of $[C_4MIM][PF_6]$ as compared to the other ILs, allowing for the formation of a thinner membrane through which the analytes can more easily pass, resulting in the relatively higher mass diffusion rate of mercury species into the ionic liquid phase during extraction.[21,32] Thus, $[C_4MIM][PF_6]$ was finally selected for subsequent studies owing to its highest extraction efficiencies for mercury species.

Selection of the carrier in the ionic liquid membrane

In the HF-LPME methods reported, chelating reagents were used in the donor phase, forming a complex as the carrier or in the membrane liquid.[18,33] In this work, chelating reagents were dissolved in the ionic liquid, coordinating with mercury species and allowing the mercury species to easily pass through the membrane. Furthermore, the complex formed should be smoothly back extracted into the acceptor phase in the lumen of the hollow fiber. Three complexing reagents were investigated, including dithizone, trioctylphosphine oxide (TOPO) and 1-(2-pyridylazo)-2-naphthol (PAN) which have been commonly employed in the extraction of mercury species.[17–20,33,34] As seen from Fig. S1,† dithizone gave higher EFs for the extraction of IHg and MMHg as compared to PAN and TOPO in our experiments.

The concentration of dithizone in the membrane liquid was investigated in the range 0.001–0.08% (m/v) and the results are shown in Fig. S2.† The EFs of MMHg and IHg increased with an increase in the dithizone concentration in the range 0–0.02% (m/v) and then leveled off. Thus, 0.02% (m/v) dithizone was selected in the subsequent studies.

Effect of L-cysteine concentration in the acceptor phase

The mercury species extracted into the ionic liquid membrane in the pore of the hollow fiber coordinated with dithizone and formed complexes. A stronger ligand should be applied for the back extraction of mercury into the aqueous acceptor phase. L-Cysteine was selected due to its higher stability constants for its coordination compounds compared with those of dithizone, allowing it to easily displace mercury species from dithizone.[35] In addition, the acceptor phase containing L-cysteine can match with the HPLC eluent since L-cysteine was one of the main components of the HPLC eluent, which is conducive to the separation of mercury species.

The effect of the concentration of L-cysteine on the EFs was investigated in the range 0.05–1.5 g L^{-1} and the results are

Table 2 Analytical performance of the developed HF-LPME method

Compound	Linearity (ng L^{-1})	Linearity equation	Correlation coefficient	Detection limit (ng L^{-1})	RSD[a] (%)
MMHg	1–200	$y = 1615.23x + 1.41$	0.9996	0.3	2.1
IHg	3–200	$y = 1538.09x + 1.59$	0.9992	0.9	3.5

[a] Standard concentration, 0.1 μg L^{-1}, $n = 5$.

Table 3 Comparison of enrichment factors and detection limits for mercury species with other methodologies

Methods	Enrichment factors		LOD/ng L^{-1}		Sample volume/mL	Linearity/ng L^{-1}	Extraction Time/min	Repeatability/RSD, %	Reference
	IHg	MMHg	IHg	MMHg					
HF-LLLMME-CE-UV	103	265	800	1000	50	800–10^5	40	1.7–4.4	18
SPE-HPLC-ICP-MS	27.8	31.2	3	3	100	—	—	—	35
LPME-HPLC	—	120	—	3800	3.8	5×10^3–10^5	25	8.9	15
HF-LLLME-LVSS-CE-UV	—	2610	—	140	12	500–5×10^5	50	1.4–16.4	14
IL-DLLME-HPLC-ICP-MS	760	115	1.3	7.2	5	5–2000	2	2.3–7.4	36
DLLME-CV-AAS	310	200	30	400	10	500–10^5	5	4–6	43
DLLME-GC-MS	112	115	300	200	10	10^4–10^5	10	1–7	44
SPE-HPLC-AFS	1000	1000	800	4300	100–500	10^4–10^6	10	<6	45
HF-LPME-ICP-MS	20	—	3.3	—	2.5	20–3×10^4	15	10.2	46
HF-LPME-ET-AAS	270	—	60	—	30	200–3000	15	3.2	19
HF-LPME-HPLC-ICP-MS	48	27	110	230	10	—	20	<15	29
HF-LPME-HPLC-ICP-MS	1540	1620	0.9	0.3	400	1–200	720	2.1–3.5	This work

Table 4 Results of the water samples as determined using HF-LPME-HPLC-ICP-MS

Water sample	Concentration found (ng L^{-1})		Spike recovery[a] (%)	
	MMHg	IHg	MMHg	IHg
Tap water	ND[b]	9.4	95.7	90.8
River water	ND	17.6	98.3	93.1
Waste water	10.4	21.1	92.8	105.7
Sewage works effluent	9.7	12.8	102.1	108.2

[a] Concentration of each mercury species added was 50.0 ng L^{-1}. Each result represents the mean of three measurements. [b] ND, not detected.

shown in Fig. 2. The EF of MMHg increased with an increase in L-cysteine concentration in the range 0.05–0.5 g L^{-1} and then leveled off, while that for IHg increased up to 0.75 g L^{-1} and then leveled off. Considering the L-cysteine concentration of the HPLC eluent (1 g L^{-1}), 1 g L^{-1} of L-cysteine was chosen in the subsequent studies.

Effect of the pH of the donor phase

It was reported that the pH of the donor phase significantly affected the distributions, enrichment factors and recoveries of analytes.[20,36] In this work, the effect of the pH of the donor phase on the enrichment factors of MMHg and IHg was also investigated in the range 3–8. The pH of the donor phase was adjusted by using 0.01 M HNO_3 and 0.01 M NaOH solutions. The results (Fig. 3) showed that the MMHg and IHg EFs increased with an increase in pH in the range 3–6 and then slightly decreased with a further increase in pH. For IHg, at low pH there is only a limited amount of deprotonated dithizone for the formation of mercury–dithizonate, resulting in a very low concentration of mercury–dithizonate. Meanwhile, highly hydrophilic mercuric ions prefer to be partitioned in the aqueous phase and this results in a low extraction efficiency. In contrast, a high concentration of deprotonated dithizone at high pH leads to a high concentration of metal–dithizonate and results in a high extraction efficiency, due to the high solubility of mercury–dithizonate in the organic phase.[37] In addition, MMHg has a higher lipophilicity than inorganic mercury, which may be more easily extracted into the ionic liquid membrane. Therefore, high enrichment factors of MMHg were obtained even at relatively low pHs. Thus, pH 6 should be optimal for the obtainment of the highest enrichment factors.

Effect of the stirring rate

To accelerate extraction and reduce the time required to reach thermodynamic equilibrium, magnetic stirring was applied in our experiments. Under stirred conditions, the analytes in the donor phase can be quickly absorbed on the ionic liquid membrane, subsequently coordinate with the carrier and then be back extracted into the acceptor phase. The effect of the stirring rate on the EFs of the mercury species was investigated in the range 0–1000 rpm. The results are shown in Fig. S3.† The EF values of the mercury species slightly increased with an increase in the stirring rate from 0–300 rpm, and then decreased with further increases in the stirring rate. At an appropriate rate, magnetic stirring can accelerate the diffusion of the analyte and reduce the time to reach dynamic equilibrium in HF-LPME.[33] Above 300 rpm, however, the stirring may produce many bubbles on the surface of the hollow fiber, impeding the mass transfer of the mercury species, and causing loss of the membrane liquid, resulting in poor precision and possible experimental failure.[38] Thus, a 300 rpm stirring rate was selected in our subsequent experiments.

Effect of the extraction temperature

The extraction temperature plays an important role in the extraction. Just like the stirring rate, an elevated temperature in the extraction process can also accelerate the mass transfer and reduce the time to reach thermodynamic equilibrium. The extraction temperature in the experiment was optimized in the range from room temperature to 80 °C. As can be seen in Fig. 4, the EF values of MMHg and IHg increased with an increase in extraction temperature from 25 to 50 °C. The reason may be that

the viscosity of the IL decreased with the increase in temperature, which accelerated the mass transfer between the donor phase and the ionic liquid membrane below 50 °C, as well as between the ionic liquid membrane and the acceptor phase.[39]

The EFs of the mercury species decreased sharply with further increases in the extraction temperature. This may be explained by the fact that above 50 °C, the miscibility between the ionic liquid and the donor phase, as well as between the ionic liquid and the acceptor phase, increases with the increase in the extraction temperature, and the partition coefficients of the ionic liquid and water solution decrease.[40] On the other hand, the membrane on the hollow fiber surface is prone to be lost at higher extraction temperatures.

Selection of extraction time

Fig. S4† displays the effect of the extraction time on the equilibration of the mercury species. As can be seen, the extraction of mercury species reached equilibrium after 12 h. In most cases reported in the literature, extraction times for approaching equilibrium in order to maximize recovery in HF-LPME were typically in the range 10–90 min.[15,18,20,41] The reason for the longer equilibrium time in the present work can probably be attributed to the relatively high viscosity of the IL, which increases the membrane thickness and reduces mass transfer speed among the donor, liquid membrane and acceptor.[30,39] In addition, both L-cysteine and dithizone contain sulfur, and although the complex stability constant of L-cysteine is higher than that of dithizone, it is not easy for the acceptor phase to back extract mercury species from the liquid membrane,[35] which also prolongs the extraction time. Admittedly, while the extraction time seems relatively long, the repeatability of the extraction was much better than for those with shorter extraction times. Meanwhile, higher EFs (about 1400–1600) were obtained. Therefore, the extraction time of 12 h was selected in further experiments.

Matrix effect

Natural organic matter (NOM), which is ubiquitous in aquatic environments, is known to bind mercury species strongly, affecting their speciation, solubility, mobility and toxicity.[42] Thus, it is necessary to investigate whether NOM in the water samples affects the extraction efficiency. Humic acid (0–25 mg L^{-1} DOC), a common natural organic matter in the environment, was selected to study the matrix effect (Fig. 5). The relative extraction efficiency, which was calculated by the peak area normalization method, was introduced in order to investigate the matrix effect. Good relative extraction efficiencies of MMHg (92–108%) and IHg (96–112%) were obtained in the studied concentration range of humic acid. The results showed that there was no significant matrix effect on the extraction efficiencies of MMHg and IHg in the environmental water samples.

Method performance and real sample analysis

The analytical features of the present HF-LPME method for the enrichment of two mercury species under the optimized conditions are listed in Table 2. The enrichment factors based on 400 mL samples were calculated as 1620 and 1540 for MMHg and IHg, respectively. The linearity was in the range 1–200 ng L^{-1} for MMHg and 3–200 ng L^{-1} for IHg. The precisions (RSD) of the peak areas for five replicate injections of a mixture of 0.1 μg L^{-1} (based on Hg) of MMHg and IHg were 2.1% and 3.5%, respectively. The limits of detection (LODs) were calculated based on the signal-to-noise ratio of 3. The LODs for MMHg and IHg were 0.3 and 0.9 ng L^{-1}, respectively. Linear regression coefficients of MMHg and IHg were 0.9992 and 0.9996, respectively. A comparison of the LODs obtained for other liquid phase-based techniques for mercury speciation is given in Table 3. It can be seen that the LODs of this method are lower than or comparable with other techniques.

In order to validate the method, the proposed procedure was applied for the preconcentration and determination of MMHg and IHg in real water samples, including tap water, river water, waster water and sewage works effluent. The results are listed in Table 4. As can be seen, a relatively high concentration of MMHg was found in the sewage works effluent. These results indicate that great importance should be placed on mercury pollution in sewage works effluents. The water samples were then spiked with MMHg and IHg to evaluate the recoveries. The results show that the concentrations of mercury species obtained with the proposed method are in good agreement with the expected values.

Conclusions

A novel method of hollow fiber supported ionic liquid membrane microextraction for the enrichment and determination of trace levels of MMHg and inorganic mercury in environmental samples was developed. In this work, the ionic liquid membrane containing dithizone was immobilized in the pore of the hollow fiber and L-cysteine was used as the acceptor phase in the lumen. The present method provides high EFs and excellent reproducibility and linearity. With optimized conditions, the detection limits of MMHg and IHg in 400 mL water samples are 0.3 and 0.9 ng L^{-1}, respectively. The average recoveries of MMHg and IHg from spiked water samples were 97.2 ± 3.4 and 99.5 ± 7.6%, respectively. In addition, the ionic liquid as the membrane phase could not only provide good extractability for the mercury species but also forms an efficient barrier to exclude matrix interference in the environmental samples. Moreover, the hollow fiber supported ionic liquid membrane microextraction method is also expected to be applicable for the preconcentration of other metallic or organometallic compounds.

Acknowledgements

This work is jointly supported by the Projects of National Natural Science Foundation of P.R. China (21277084, 21207059), Promotive Research Fund for Young and Middle-aged Scientists of Shandong Province, China (BS2012HZ012) and Projects of Upgrade and Regeneration of Scientific Instruments of Shandong Province, China (2013SJGZ08). The support from the State Key Laboratory of Environmental Chemistry and Ecotoxicity, Research Center for Eco-

Environmental Science, Chinese Academy of Sciences (KF2011-17), Doctor Funds of Shandong Academy of Sciences, and Shandong Analysis and Testing Center are also appreciated.

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