Talanta 78 (2009) 537–541

Contents lists available at ScienceDirect

Talanta

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

Speciation of mercury by ionic liquid-based single-drop microextraction combined with high-performance liquid chromatography-photodiode array detection

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ARTICLE INFO

Article history:
Received 4 September 2008
Received in revised form
24 November 2008
Accepted 2 December 2008
Available online 6 December 2008

Keywords:
Mercury speciation
Ionic liquid
Single-drop microextraction
Liquid chromatography

ABSTRACT

Room temperature ionic liquids can be considered as environmentally benign solvents with unique physicochemical properties. Ionic liquids can be used as extractant phases in SDME, being compatible with chromatographic systems. A single-drop microextraction method was developed for separation and preconcentration of mercury species ($MeHg^+$, $EtHg^+$, $PhHg^+$ and Hg^{2+}), which relies on the formation of the corresponding dithizonates and microextraction of these neutral chelates onto a microdrop of an ionic liquid. Afterwards, the separation and determination were carried out by high-performance liquid chromatography with a photodiode array detector. Variables affecting the formation and extraction of mercury dithizonates were optimized. The optimum conditions found were: microextraction time, 20 min; stirring rate, 900 rpm; pH, 11; ionic liquid type, 1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6MIM][PF_6]$); drop volume, 4 μL; and no sodium chloride addition. Limits of detection were between 1.0 and 22.8 $\mu g\,L^{-1}$ for the four species of mercury, while the repeatability of the method, expressed as relative standard deviation, was between 3.7 and 11.6% ($n=8$). The method was finally applied to the determination of mercury species in different water samples.

1. Introduction

Mercury is considered a highly toxic element because of its accumulative and persistent character in the environment. It exists in a large number of different chemical and physical forms with a wide range of properties. Organometallic species of mercury are considerable more toxic than inorganic mercury, because of their high affinity to SH group of proteins and lipid tissues, which leads to accumulation of organomercury species in superior organisms [1]. Among these species, methylmercury is the most hazardous, being formed in the aquatic environment by biotic and/or abiotic processes [2]. Industrial use of inorganic and organometallic species in different activities, mainly pharmaceutical, paper, electrochemical and agriculture industries, accounts for the main anthropogenic sources [3].

Separation of mercury species before their determination is generally carried out by gas chromatography (GC) or high-performance liquid chromatography (HPLC). HPLC displays the possibility to separate a great variety of organomercury compounds (i.e. volatile and non-volatile). The detection systems used along with HPLC can be broadly divided into three approaches: photometry, plasma techniques (ICP-MS, ICP-AES) and cold vapour atomic absorption and fluorescence spectrometry (CV-AAS, CV-AFS) [4]. Application of HPLC to speciation studies of Hg has been reviewed by Harrington [5].

Owing to the low levels of mercury species in environmental samples, a preconcentration technique is usually necessary before their determination. Single drop microextraction (SDME) [6] is a simple, low-cost, fast and environmentally friendly preconcentration technique based on a great reduction of the extractant phase-to-sample volume ratio. SDME can be operated in two different modes: headspace-single-drop microextraction (HS-SDME), when the extractant drop is exposed to the headspace of the sample, and Direct-single-drop microextraction (Direct-SDME), when analytes are extracted from the bulk aqueous phase onto a microdrop of extractant phase by immersion of the drop in a stirred aqueous sample solution. SDME is not an exhaustive technique, and only a small fraction of analytes is extracted/preconcentrated for analysis. One of the most important parameters that should be selected carefully when SDME is used is the extractant phase. The choice of extractant should be based on comparison of selectivity, extraction efficiency, incidence of drop loss, rate of drop dissolution and level of toxicity [7]. Moreover, the extractant phase should be compatible with the analytical technique ultimately employed. There are two

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doi:10.1016/j.talanta.2008.12.003

possibilities to select the extractant phase when the immersed-SDME mode is used: organic solvents and ionic liquids. Although organic solvents are mainly employed, the use of ionic liquids (ILs) is increasing because of their particular physicochemical properties, being environmentally friendly extractant phases [8]. 1-alkyl-3-methylimidazolium hexafluorophosphates ([C_nMIM][PF_6], n = 4, 6, 8) have been used for SDME applications in both direct immersion and headspace modes for extraction. Analytes include of polycyclic aromatic hydrocarbons [9], chlorobenzenes [10,11], phenols [12,13], chloroanilines [14], trihalomethanes [15], BTEX (benzene, toluene, ethylbenzene, and xylene) [16], benzophenone-3 [17], formaldehyde [18] and 45 typical environmental pollutants [19] including BTEX, polycyclic aromatic hydrocarbons, phthalates, phenols, aromatic amines, herbicides, organotin and organomecury. As can be seen above, ILs have been used in SDME almost as a whole in the organic field.

Two papers have been published so far, where SDME is employed for extraction and preconcentration of mercury species. Gil et al. [20] employed Headspace-SDME in combination with ETAAS for determination of methylmercury after its derivatization with $NaBH_4$ by using a microdrop of Pd(II) as both extractant and matrix modifier in the furnace. A 40-fold enrichment factor was achieved in only 2 min of microextraction. Liu et al. [19] studied the extractability of five organomercury compounds (methylmercury, ethylmercury, phenylmercury, dimethylmercury and diethylmercury) by SDME in its immersed mode combined with CV-AFS using two ILs, 1-alkyl-3-methylimidazolium hexafluorophosphate ([C_nMIM][PF_6], n = 4, 8). Enrichment factors between 4 and 40 were achieved.

The aim of this study was to develop a new method for extraction and preconcentration of mercury species as dithizonates onto an ionic liquid microdrop using immersed-SDME in combination with HPLC with a photodiode array detector. Optimisation of variables such as type of ionic liquid, pH of the sample, microdrop volume, stirring rate, microextraction time and salt content in the sample were studied, and the optimized procedure was applied to determine mercury species in aqueous samples.

2. Experimental

2.1. Standard solutions and reagents

A stock standard solution of mercury (II) (1000 mg L^{-1}) was prepared by dissolving the corresponding amount of mercury (II) chloride from Fluka (Steinheim, Germany) in a 1% HNO_3 solution. Stock standard solutions of methylmercury and ethylmercury (1000 mg L^{-1} (as Hg)) were prepared by dissolving CH_3HgCl and C_2H_5HgCl, both from Riedel-de Haën (Seelze, Germany) in methanol. The stock standard solution of phenylmercury 1000 mg L^{-1} (as Hg)) was prepared by dissolving C_6H_5HgCl (Riedel-de Haën, Seelze, Germany) in ethanol. Standard solutions were prepared daily by appropriate dilutions with methanol. All solutions were stored in the dark at 4 °C.

Methanol, ethanol, acetonitrile and acetic acid were HPLC-grade, being obtained from Scharlau Chemie (Barcelona, Spain). HPLC-grade Tetrahydrofuran was purchased from Scharlau Chemie (Barcelona, Spain) and Sigma Aldrich (Steinheim, Germany).

De-ionized water (resistivity ≥18 MΩ cm) obtained from a water purification system (Milli-Q Biocel A10) supplied by Millipore (Billerica, MA, USA) was used to prepare the mobile phase in the LC system.

Dithizone was obtained from Merck (Darmstadt, Germany) and used without further purification. The reagent solution was prepared weekly by dissolving 20.0 mg of dithizone in 100 mL of acetonitrile.

1-butyl-3-methylimidazolium hexafluorophosphate [C_4MIM][PF_6] and 1-octyl-3-methylimidazolium hexafluorophosphate [C_6MIM][PF_6] were purchased from Merck (Darmstadt, Germany), while 1-hexyl-3-methylimidazolium hexafluorophosphate [C_6MIM][PF_6] was obtained from Green Solutions (Vigo, Spain).

Sodium chloride from Merck (Darmstadt, Germany) was used to study the effect of ionic strength on the microextraction of mercury species. Analytical reagent-grade sodium acetate (99%) and ethylenediaminetetraacetic acid disodium salt (EDTA) were obtained from Aldrich (Steinheim, Germany) and Scharlau Chemie (Barcelona, Spain), respectively.

2.2. Water samples

Tap water from the main area water-supply network of San Vicente del Raspeig (Alicante, Spain), river water from Turia river (Valencia, Spain) and wastewater (Alicante, Spain) from a municipal wastewater treatment plant were used as water samples for recovery studies.

2.3. Apparatus

A Hamilton Gastight syringe (Model 1702 Hamilton Bonaduz AG, Bonaduz, Switzerland; length: 5.1 cm, i.d.: 0.015 cm) was used to suspend the drop of ionic liquid and inject it into the HPLC system.

A Waters LC system equipped with a Waters 600E high-pressure pump and a Waters 996 photodiode array detection (PDA) system set at 475 nm (Milford, MA, USA) was employed. A personal computer equipped with a Milenium 32 Waters program for LC system was used to process all chromatographic data.

A 7725i Rheodyne injector (Rohnert Park, CA, USA) and a Phenomenex C-18 (150 × 4.60 mm i.d., 3 μm particle size) column from Phenomenex (Torrance, CA, USA) were also used for injection and separation, respectively.

A Crison (Alella, Spain) micropH 2000 pH meter was used for pH measurements.

2.4. Procedure

A 12 mL aqueous sample solution containing $MeHg^+$, $EtHg^+$, $PhHg^+$ and Hg^{2+} was added into a 20-mL amber vial, the pH value was adjusted to 11 with 1.5 mL of 0.1 mol L^{-1} HPO_4^{2-}/PO_4^{3-} and a few drops of 0.1 mol L^{-1} NaOH. Then, 1.5 mL of dithizone solution (20 μg mL^{-1} in acetonitrile) was added to the sample to form the corresponding dithizonates. The mixture was magnetically stirred for 3 min and degassed for 5 s before microextraction in order to remove the bubbles attached to the stirrer formed because of the mixture between the water sample and the acetonitrile, since bubbles can disturb the stability of the drop during the microextraction process. After that, the blunt tip of the needle of a 25-μL Hamilton Gastight syringe was sheathed with a 3-mm long polytetrafluoroethylene (PTFE) tube (0.8 mm i.d. and 1.6 mm o.d.) to expose a 4 μL drop of [C_6MIM][PF_6] to the sample. After stirred extraction at 900 rpm for 20 min, the remaining ionic liquid was withdrawn back into the microsyringe and then injected into the HPLC system for determination, where THF/MeOH/(0.1 M HAc/AcNa pH 4.0 + 50 μM EDTA) (36/32/32%) at 0.8 mL min^{-1} flow rate was selected as mobile phase, based on a previous work [21]. EDTA was added to the mobile phase in order to eliminate the interference of other metal ions on Hg speciation [21].