Spectrochimica Acta Part B 66 (2011) 88–92

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

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

Analytical Note

Speciation of mercury in water samples by dispersive liquid–liquid microextraction combined with high performance liquid chromatography-inductively coupled plasma mass spectrometry

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ARTICLE INFO

Article history:
Received 6 June 2010
Accepted 6 December 2010
Available online 13 December 2010

Keywords:
Dispersive liquid–liquid microextraction (DLLME)
Methylmercury
Sodium diethyldithiocarbamate (DDTC)
Enrichment factors
HPLC-ICP-MS

ABSTRACT

The dispersive liquid–liquid microextraction (DLLME) combined with high performance liquid chromatography-inductively coupled plasma mass spectrometry for the speciation of mercury in water samples was described. Firstly methylmercury ($MeHg^+$) and mercury (Hg^{2+}) were complexed with sodium diethyldithiocarbamate, and then the complexes were extracted into carbon tetrachloride by using DLLME. Under the optimized conditions, the enrichment factors of 138 and 350 for $MeHg^+$ and Hg^{2+} were obtained from only 5.00 mL sample solution. The detection limits of the analytes (as Hg) were 0.0076 ng mL^{-1} for $MeHg^+$ and 0.0014 ng mL^{-1} for Hg^{2+}, respectively. The relative standard deviations for ten replicate measurements of 0.5 ng mL^{-1} $MeHg^+$ and Hg^{2+} were 6.9% and 4.4%, respectively. Standard reference material of seawater (GBW(E)080042) was analyzed to verify the accuracy of the method and the results were in good agreement with the certified values. Finally, the developed method was successfully applied for the speciation of mercury in three environmental water samples.

1. Introduction

Mercury species, usually present in natural water samples, are mercury (II) and methylmercury [1], and methyl mercury is considered to be the most toxic form of the elements. The environmental water sources can be polluted by mercury in two ways. One is that mercury was released into the air when coal, oil, or wood were burned or when mercury-containing wastes were incinerated; the other is the direct discharge of mercury-laden industrial or municipal waste. Thereby, monitoring the level of mercury, including each species in environmental water is of great importance to evaluate the risk of mercury exposure to human beings, in this case, accurate analytical methods are required.

There are many analytical techniques that can be used for the speciation of mercury, in summary, it can be classified into two general approaches: chromatographic methods and non-chromatographic methods as pointed out in articles [2,3]. Non-chromatographic methods for Hg speciation mostly determine only one species or one fraction rather than the simultaneous determination of all Hg species present. These methods are based on the different chemical or physical behavior of the Hg species [4–6]. However, chromatographic separation methods including capillary electrophoresis (CE) [7,8], gas chromatography [9,10], ion chromatography [11,12] and high performance liquid chromatography (HPLC) [13–16], which are combined with various spectroscopic detection techniques are able to determine all Hg species in a single step. In these studies, the powerful chromatographic systems were invariably adopted for the separation of mercury species, while inductively coupled plasma-mass spectrometry (ICP-MS) was preferred as the highly sensitive detecting technique. However, the amount of sample injection for chromatographic analysis is usually very tiny (tens of microlitres for HPLC or hundreds of nanolitres for CE), in this case, the coupling of the two techniques will inevitably weaken the detecting ability for the whole analytical method. Thus, for samples containing very low levels of species, preconcentration of analytes is desirable before column separation.

For mercury speciation, various enrichment methods, including flow injection microcolumn displacement sorption [17], hollow fiber liquid–liquid–liquid microextraction [18], "home made" C18 column solid phase extraction microcolumn [19], stir bar sorptive extraction [20], immersed-single drop microextraction (SDME) [21], ionic liquid-assisted head-space-SDME [22] and cloud point extraction [23,24] have been well used to couple with the above-mentioned analytical techniques in many previous studies. Each of these methods has its unique advantages, but commonly, all of them are mild, which means that no transformation of species occurs during the sample treatment. In addition, none of the target species should be lost, and the enrichment methods should be compatible with the subsequent analytical techniques.

In this work, we attempt to use dispersive liquid–liquid micro-extraction (DLLME) as a novel enrichment method, to combine with HPLC-ICP-MS for the speciation of mercury in environmental water

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doi:10.1016/j.sab.2010.12.003

samples. DLLME was first introduced by Assadi and his co-workers [25] in 2006, it used a binary mixture of a water miscible solvent, named disperser, and a high density one with very low water solubility, referred as the extractant, to extract the objective compounds from water samples [26]. It exhibits high performance such as rapid, inexpensive, high concentrating ability and low consumption of organic reagents, most importantly, it is suitable for batch analysis. Also, it is mild, and is compatible with the subsequent chromatographic separation. Up to the present, DLLME has been successfully applied for the enrichment of various organic compounds and inorganic metals in water samples [27–29]. However, there is no report on the use of this method as an effective enrichment technique prior to chromatographic separation coupled with atomic spectrometric detection for elemental speciation.

For the research purpose, CH_3Hg^+ and Hg^{2+} were chosen as the target species. Key factors such as the type of extractant and disperser and their volume, the amount of chelating reagent, pH, extraction time, salt effect and coexisting ions were investigated. To evaluate the feasibility of the method, spike test was carried out, and a standard reference material (GBW(E)080042, seawater) was analyzed.

2. Experimental

2.1. Apparatus

An X series II ICP-MS (Thermo Fisher Corp., USA) was used in this study. The instrument was operated in the time-resolved analysis (TRA) mode. The chromatographic system consisted of a Waters 626 pump and a rotary injection valve fitted with a 20 μL sample loop. Separation was achieved using an XBridge™ C18 column (150×4.6 mm id, 5 μm) (Waters, MA, USA). The outlet of the LC column was directly connected to the sample introduction system of ICP-MS via 50 cm of 0.18 mm i.d. Peek tubing. The optimized ICP-MS TRA parameters and chromatographic operating conditions are summarized in Table 1.

A centrifuge (model TDL-40B, China) was used to accelerate the phase separation during DLLME. The pH values were measured with a PHS-3 C pH-meter (Shanghai Precision &Scientific Instrument Co., Ltd, China).

2.2. Standard solutions and reagents

Ultrapure water (18.2 MΩ, prepared by Millipore, Simplicity 185) was used throughout the experiment. A stock standard solution of 1000 mg L^{-1} Hg^{2+} was purchased from CRM Information Center (Beijing, China). Stock standard solutions of methylmercury (1000 mg L^{-1}, as Hg) were prepared by dissolving CH_3HgCl in methanol, and CH_3HgCl was purchased from Dr. Ehrenstorfer (Augsburg, Germany). Working standard solutions were prepared by successive dilution of the stock solution. Standard reference material of seawater was obtained from National Standard Material Center (GBW(E)080042, Beijing, China).

Diethyldithiocarbamate (DDTC) as chelating agent was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and 0.05 mol L^{-1} DDTC was prepared by dissolving the compound in HPLC grade methanol (Fisher Scientific, USA). All other reagents, including carbon tetrachloride, chloroform and carbon disulfide as extraction solvent, ethanol and acetone as disperser solvent were at least of analytical grade.

Table 1
Operating conditions of HPLC-ICP-MS system.

Parameters	Value
ICP-MS system	
RF power/W	1500
Nebuliser gas flow/L min^{-1}	0.95
Auxiliary gas flow/L min^{-1}	0.80
Cooling gas flow/L min^{-1}	13.0
Sampling cone/mm	1.0, platinum cone
Skimmer cone/mm	0.7, platinum cone
Isotopes monitored	^{202}Hg
Dwell time/ms	200
Resolution	normal
Acquisition mode	Time resolved analysis
HPLC system	
Column	C18 reversed phase (150×4.6 mm i.d, 5 μm)
Mobile phase	0.06 mol L^{-1} ammonium acetate, 6% v/v methanol, 0.1% v/v 2-mercaptoethanol
Flow rate of the mobile phase	1.0 mL min^{-1}
Sample loop volume	20 μL

2.3. Sample preparation

Before DLLME, the tap, snow, and lake water samples were filtered through a membrane of 0.22 μm pore size, then it should be treated with the DLLME procedure immediately, if not, it should be kept in a refrigerator at 4 °C. For the standard reference material, ten-fold dilution was made prior to the analysis due to its high acidity.

2.4. Dispersive liquid–liquid microextraction procedure

A sample solution (5 mL) consisting of $MeHg^+$ and Hg^{2+} and 20 μL of DDTC (chelating agent) was placed into a 10 mL screw-cap glass test tube with conical bottom. A 500 μL of methanol (disperser solvent) containing 20 μL of carbon tetrachloride (extraction solvent) was injected rapidly into the sample solution. A cloudy solution was formed in the test tube. In this step, $MeHg^+$ and Hg^{2+} reacted with DDTC and were extracted into the fine droplets of carbon tetrachloride. The mixture was then centrifuged for 5 min at 3000 rpm, in this way, the dispersed fine droplets of carbon tetrachloride were sedimented at the bottom of the test tube. The sedimented phase (10 μL) was withdrawn by a microsyringe, and then it was transferred into a 1.5 mL polyethylene tube with a conical bottom. The sedimented phase volatiled rapidly in the air within 10 min (in order to prevent the Hg species from being lost, no heating and purging were used to evaporate the sedimented phase). Subsequently, 20 μL of the mobile phase was added to the polyethylene tube to dissolve the residue, and this solution was ready for the HPLC-ICP-MS separation and detection.

3. Results and discussion

3.1. Optimization of mobile phase for HPLC

The optimization of the mobile phase for HPLC was according to Wang's work [30]. First, a water solution containing 4% v/v methanol and 2% v/v acetonitrile was tried as the mobile phase, however, the retention time of $MeHg^+$ and Hg^{2+} was prolonged. Since the acetonitrile concentration higher than 5% v/v will cause the instability of the plasma, a mobile phase containing 6% v/v methanol, 0.1% v/v 2-mercaptoethanol, and 0.06 mol L^{-1} ammonium acetate (for pH adjustment to 6.8) was finally adopted. In comparison with Wang's work, the elution time of the Hg^{2+} was slightly reduced in this work, and baseline separation was also achieved.

3.2. Optimization of the DLLME procedure

Several key parameters, such as the type of extraction and disperser solvent and their volume, the amount of chelating agent, pH, extraction time and salt addition were investigated and optimized to obtain the best enrichment factor (EF), which is calculated as in the following equation.

$$EF = \frac{C_{sed}}{C_o} \quad (1)$$