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Online anion exchange column preconcentration and high performance liquid chromatographic separation with inductively coupled plasma mass spectrometry detection for mercury speciation analysis

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HIGHLIGHTS

- Hg^{+}, MeHg, EtHg and Hg^{2+} were enriched by the SAX column preconditioned with sodium 3-mercapto-1-propanesulfonate.
- The enrichment factors of 1025–1108 were obtained using 6 mL sample in a 1.5-min enrichment procedure.
- Rapid separation was achieved within 5 min on a 50-mm C_{18} column using 0.5% (v/v) 2-mercaptoethanol as the mobile phase.
- MeHg, EtHg and Hg^{2+} concentrations at sub ng L^{-1} to sub μg L^{-1} levels were detected in the water.

GRAPHICAL ABSTRACT

This work demonstrated the online mercury preconcentration by a strong anion exchange guard column, followed by high performance liquid chromatographic separation and inductively coupled plasma mass spectrometry detection. The mercury species were enriched by around 1000-fold using 6 mL sample in a 1.5-min enrichment procedure.

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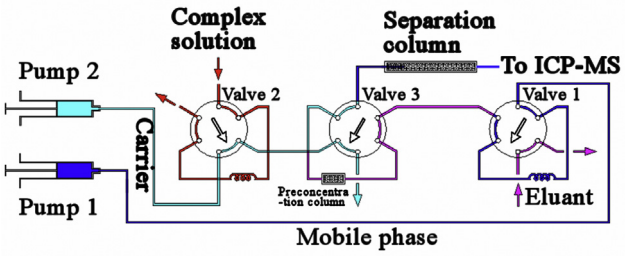

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ABSTRACT

A hyphenated method for mercury speciation analysis by the coupling of high performance liquid chromatography and inductively coupled plasma mass spectrometry with the online strong anion exchange column (SAX) preconcentration was developed. The Hg analytes (Hg^{+}, MeHg, EtHg and Hg^{2+}) were absorbed on the SAX column preconditioned with sodium 3-mercapto-1-propanesulfonate, and then rapidly eluted (less than 16 s) by 5 μL 3% (v/v) 2-mercaptoethanol. The enrichment factors of 1025 for Hg^{+}, 1084 for MeHg, 1108 for EtHg and 1046 for Hg^{2+} were obtained using 6 mL sample in a 1.5-min enrichment procedure. Rapid separation of the four mercurial compounds was achieved within 5 min on a 50-mm C_{18} column using 0.5% (v/v) 2-mercaptoethanol as the mobile phase. The detection limits for Hg^{+}, MeHg, EtHg and Hg^{2+} were 0.015, 0.010, 0.009 and 0.016 ng L^{-1}, each, and the relative standard deviations of peak height and peak area (5 ng L^{-1} for each Hg species) were all below 5%. Mercury speciation in three freshwater, two drinking water and two seawater samples were then analyzed by the proposed method. MeHg and Hg^{2+} concentrations down to 0.14 and 0.56 ng L^{-1} were detected in the drinking waters.

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1. Introduction

Mercury is the most poisonous element and now a global pollutant because of natural existence and extensively anthropogenic input and global transport. The toxicity of mercury is highly dependent on its chemical form [1,2]. Owing to their lipophilic nature, organomercury compounds (*e.g.*, mono- and dimethyl mercury (MeHg and DMeHg), ethylmercury (EtHg), phenylmercury (PhHg), *etc.*) are more toxic than inorganic mercury species (Hg(I) and Hg(II)). They can easily permeate biological membranes and interfere with many biochemical processes by binding to biomolecules containing thiol groups [1]. For the purposes of health risk assessment and biogeochemical cycling research of mercury species, it is highly desirable to develop accurate and sensitive analytical methods to determine the chemical form of mercury rather than total mercury in various sample matrices.

A chromatographic separation followed by an element specific detector constitutes most commonly used methods. The coupling of high performance liquid chromatography (HPLC) and inductively coupled plasma mass spectrometry (ICP-MS) is predominately adopted due to its simple interface and excellent sensitivity. The hyphenated HPLC–ICP-MS technique has been well applied for mercury speciation analysis in environmental samples (water [3–10], sediment [10,11], soil [12–14], *etc.*), food [5,15–26], biological fluids and tissues from human [27–35], animals [36,37] and plants [38–40], and cosmetic samples [41]. The detection limits offered by the above HPLC–ICP-MS methods without any offline or online preconcentration were downscaled to 4 ng L^{-1} for Hg(II) [38], 3 ng L^{-1} for MeHg [38], 5 ng L^{-1} for EtHg [32] and 32 ng L^{-1} for PhHg [3]. However, the concentrations of mercury species in unpolluted environmental samples are normally at trace and even ultra-trace levels. For example, the concentration of total mercury is below 1 ng L^{-1} in the open ocean water, and in the ranges of 0.5–5 ng L^{-1} in the estuarine water and 1–5 ng L^{-1} in the freshwater [42]. Hence, it is an arduous task to determine mercury species in these samples directly by the combination of HPLC and ICP-MS. In these cases, offline and/or online preconcentration of analytes before their chromatographic separation is desirable.

A wealth of preconcentration techniques including flow injection displacement sorption (FIDS) [43], liquid–liquid microextraction (LLME) [8,41,44,45], stir bar sorptive extraction [46], single drop micro-extraction [47,48], cloud point extraction (CPE) [6,29], solid phase (micro-) extraction (SPE and SPME) [4,7,9,10,34,49–52] have been utilized for enriching mercury species. Among the above enrichment techniques, solid phase (micro-) extraction is simple and inexpensive, free of toxic organic reagent, and feasible of online application in HPLC. In the SPE or SPME applications for mercurial compounds, reversed-phase material such as C_{18} [4,7,34,49–52] and cation exchange columns [9,53] as well as polyurethane foam immobilized with complexing reagent [10] have been employed as the adsorbent. However, to the best of our knowledge, the application of mercury preconcentration by an anion exchange column has not been reported.

In this work, a hyphenated method for mercury speciation analysis was developed by reversed phase high performance liquid chromatographic separation and ICP-MS detection after online anion exchange column preconcentration. After preconditioning with sodium 3-mercapto-1-propanesulfonate, the strong anion exchange guard column could retain mercury species in the flow-through sample due to the complexing reaction between mercurial compounds and the mercapto group. The enriched analytes were eluted out of the SAX column by 3% (v/v) 2-mercaptoethanol and then separated by a 50-mm reversed phase C_{18} column followed by ICP-MS detection. The preconcentration conditions including the type, concentration and volume of the eluent, the sample volume and flow rate, and the matrix effect were investigated. The mobile phase composition as well as its flow rate was further optimized. To validate this method, the analysis of certified reference materials of freshwater (GBW(E) 080041) and seawater (GBW(E) 080042) and spike recovery tests were also performed. Finally, the proposed method was applied in the speciation analysis of mercury in real water samples.

2. Materials and methods

2.1. Chemicals and reagents

All reagents used were of analytical or chromatographic grade. A stock standard solution of 1000 mg L^{-1} Hg^{2+} (Hg(II)) in 5% nitric acid was obtained from National Standard Material Center (GSBG 62069-90, Beijing, China). Mercurous nitrate was purchased from Aladdin Chemistry (Aladdin Chemistry Co., Ltd., Shanghai, China) to prepare the stock standard solution of 1000 mg L^{-1} Hg^{+} (Hg(I)) in 1% nitric acid. Methylmercury chloride (≥95%) and ethylmercury chloride (≥95%) were both purchased from Alfa Aesar (A Johnson Matthey Company, MA, USA). Stock standard solutions of MeHg and EtHg at 1000 mg L^{-1} (as Hg) were prepared by individually dissolving appropriate amounts of methylmercury chloride and ethylmercury chloride in methanol, respectively. All these stock solutions were stored in amber glass bottles and kept at 4 °C in the dark. Work standard mixture solutions containing the four mercury species were prepared by successive dilution of the above stock solutions in the ultrapure water. 1000 mg L^{-1} bismuth stock solution prepared by dissolving bismuth(III) nitrate pentahydrate from Sigma–Aldrich (St. Louis, MO, USA) in 1% HNO_3 was employed to prepare the internal standard solution (5 μg L^{-1}) [20]. Sodium 3-mercapto-1-propanesulfonate (MPS) from Aladdin Chemistry Co., Ltd., (Shanghai, China) was used to prepare the complexing solution (50 mM MPS). 2-mercaptoethanol (ME, ≥98%) purchased from Alfa Aesar (Ward Hill, MA, USA) was employed to prepare the mobile phase (0.5% (v/v) ME in ultrapure water) and the eluent (3% (v/v) ME in ultrapure water). High-purity nitric acid (Jiangyin Chemical Regent, Jiangyin, China) was used in the experiment. Certified reference materials (CRM) of freshwater (GBW(E) 080041) and seawater (GBW(E) 080042) from National Standard Material Center (Beijing, China) were used to validate the accuracy for mercury speciation analysis in water samples. All solutions were filtered through a membrane of 0.45 μm pore size before analysis. Ultrapure water with a resistivity of 18.2 MΩ cm, obtained from a Milli-Q Plus water purification system (Millipore, Bedford, MA, USA) was used throughout the experiment. Ultrapure water was newly prepared by the Millipore purification system just before every use to inhibit the possible mercury contamination during the storage. Extreme attention must be paid to all the reagents for obtaining low blank mercury values, *e.g.*, MPS and ME solutions were checked before everyday use in term of mercury concentration. Once contaminated, they were prepared again and even re-purchased from the suppliers. All the utensils were soaked in 20% HNO_3 for 24 h and rinsed thoroughly by ultrapure water.

2.2. Instrumentation

Mercury speciation analysis was performed by ICP-MS with HPLC separation after the online SAX column preconcentration. Fig. 1 shows the schematic diagram of the hyphenated system. The high performance liquid chromatography system for mercury speciation consisted of a reversed-phase C_{18} column (Zorbax Eclipse Plus C_{18}, 5 μm, 4.6 mm i.d. × 50 mm long, Agilent Technology, Shanghai, China), a high pressure pump (pump 1) with a 0.01–5 mL min^{-1} flow rate range (Jasco PU-985, Jasco, Japan) and a six-port injection valve (valve 1) with a 5 μL sample loop