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Synthesis of divinylbenzene polymer/Fe_3O_4 hybrid monolithic column for enrichment and online thermal desorption of methylmercury in real samples

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ABSTRACT

A novel method of divinylbenzene polymer (DVB)/Fe_3O_4 hybrid monolithic column solid phase extraction and on line thermal desorption was developed to analyze methylmercury (MeHg) in water and fish samples. The monolithic column was prepared by in situ polymerization in silica tube and its heating characteristic was studied in detail. Special accent was put on the study of parameters influencing adsorption and desorption of MeHg, such as pH, flow rate of sample solution, temperature of desorption and flow rate of carrier. Under optimum conditions, the detection limit and relative standard deviation of MeHg were 0.09 ng L^{-1} and 2.6% (10 ng L^{-1}, $N=11$), respectively. Recoveries of MeHg were never less than 96%. Standard reference material GBW10029 was analyzed for validation of the methodology. This method was successfully applied to the determination of MeHg in water and fish samples.

1. Introduction

Mercury has been recognized as an environmental pollutant for several decades and the level of mercury in land, atmosphere and ocean is rapidly increasing due to human activities. Mercury concentrations escalate along with the food chain for bioaccumulation, up to factors of 10^6 from water to predatory fish [1]. The toxicity of mercury is closely related to its chemical speciation. Methylmercury (MeHg), the most common and hazardous species, can be naturally converted by inorganic mercury in biomethylation processes. Therefore, it may be dangerous for people to consume too much marine based food supplements in daily life. To avoid the risk, the US Food and Drug Administration (FDA) has set an Action Level of 1 μg g^{-1} (wet mass) for concentration of mercury in fish and the world health organization (WHO) recommends a maximum intake of MeHg of 1.6 μg kg^{-1} per week [2–5].

Based on the facts, highly efficient analytical methodologies should be developed to quantify mercury species, especially MeHg in water and fish tissues for a more comprehensive understanding of their toxic effects and risk to biota [6]. Commonly used sensitive methods for analyzing MeHg are separation approaches, including chemical or cold vapor generation [7–9], gas chromatography (GC) [10], high performance liquid chromatography (HPLC) and capillary electrophoresis (CE) [11,12], coupled with various spectrometric detection strategies such as atomic absorption spectrometry (AAS) [13], atomic fluorescence spectrometry (AFS) or inductively coupled plasma-mass spectrometry (ICP-MS) [3]. Among those spectrometric detection methods, AFS is one of the most commonly used techniques attributing to its high selectivity, sensitivity and low cost. In addition, compared with the demand of hydride generation or alkylation which needs reagents like sodium tetrahydroborate [14], sodium tetraethylborate [8,15] and sodium tetraphenylborate [16], an AFS technique that can provide direct determination of MeHg without using organic reagents would be highly desirable.

In the last decade, solid phase extraction (SPE) methods have been widely considered as promising approaches, with less contamination and analyte loss from solvent and low limits of detection (LODs) for analysis of mercury species in water samples [17]. Commonly used sorbents of SPE were resins [13], polymers [3], activated carbons and precious metals [18–20]. However, these adsorption methods mentioned above can hardly provide separation and determination of mercury species in a single step. Acids and/or organic reagents are often used in these methods, e.g., 0.3% HCl and 0.3% HCl–0.02% thiourea were used to elute MeHg and iHg adsorbed on polyaniline [19].

The use of monoliths as sorbents, particularly for stationary phases in liquid chromatography (LC) and electrochromatography, gained popularity in the early 1990s. These sorbents have advantages of high permeability, larger specific surface area and ease of control of shape. The column also provides a potential of increased

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sample throughput, good enrichment factor and automated operation, which makes it easily integrated with FI system and some detector such as AFS.

Two types of monolith, porous polymer and silica, have been developed to date. Compared with inorganic silica-based adsorbents, polymeric materials have some intrinsic advantages. For example, their use with liquids within the entire range of pH is possible [21,22]. In this paper, a divinylbenzene polymer (DVB)/Fe_3O_4 hybrid monolithic column was prepared for the preconcentration of MeHg in sample solution, which had not been indicated in other publications. At the same time, we adopted high-frequency electromagnetic induction heating (EMIH) technology to fulfill on line thermal desorption procedure. As we know, the EMIH is characteristic of higher thermal efficiency, good temperature controllability because it is free of heat conduction and thermal convection of air. Therefore, the column can be heated up uniformaly and quickly, which reduces the degradation of analytes and increases the sensitivity of this method.

The aim of this work is to develop a sensitive method for direct preconcentration of MeHg in water and fish samples using DVB/Fe_3O_4 hybrid monolithic column and carrying out on line thermal desorption with the help of EMIH. Coupled with the column with pyrolysis–AFS systems, the present method was shown to be effective and feasible for determining trace amounts of MeHg in real samples.

2. Experimental

2.1. Instrumentation

The morphological properties of the monolith were measured by AX-650 scanning electron microscope (SEM) (Hitachi) and H-7650 transmission electron microscope (TEM) (Hitachi). The inner structure of the column was characterized by using EQUINX55 FT-IR spectrum (Bruker, Germany) and DTG-60H differential thermal-thermogravimetric simultaneous thermal analyzer (Shimadzu, Japan) were used to characterize monolithic materials.

A model AFS-230 atomic fluorescence spectrophotometer (Beijing Haiguang Instrument Co., Ltd., Beijing, China) with mercury hallow cathode lamp (General Research Institute for Nonferrous metals, Beijing, China) was used for mercury detection.

A schematic diagram of the present system for analysis of MeHg is shown in Fig. 1. Sample solution containing MeHg was pumped through to the monolith by IFIS-C peristaltic pump (Xi'an Ruimai Electronic Technology Co. Ltd., Xi'an, China). A home-made electromagnetic induction heating coil (EIHC) connected to a high-frequency induction heating power source (HFPS) was used to online desorb MeHg on the monolith. The pyrolysis column was prepared with a fused silica tube (120 mm length × 2 mm i.d. × 4 mm o.d.) packed with iron particles (200 mesh). This column was used to atomize MeHg and some parameters of it had been discussed in our previous work [23]. The sensitivity of instruments was checked every day before using.

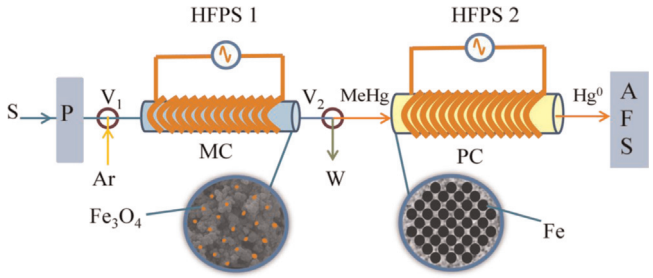

Fig. 1. The schematic diagram of the proposed system for analysis of MeHg: S, sample; P, peristaltic pump; V, valve; HFPS, high-frequency induction heating power source; W, waste; MC, monolithic column; and PC, pyrolysis column.

2.2. Chemicals and reagents

All chemicals used in this study are analytical reagent-grade or higher. Deionized water was used throughout all experiments.

Divinylbenzene (DVB) (m- and p- mixture, 80% in EVB+DEB, stabilized with TBC) was obtained from J&K Scientific Ltd. (Shanghai, China) and it was purified before using. (3-mercaptopropyl) Trimethoxysilane was obtained from Jessicachem (Hangzhou, China). Toluene, acetontrile, azodiisobutyronitrile (AIBN), dodecanol and methylmercuric chloride were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Fe_3O_4 particles coated with oleic acid were prepared as reported by Yan [24]. Stock solution (1000 mg L^{-1}) of MeHg was prepared in ethanol. Inorganic mercury (iHg) stock standard solution (1000 mg L^{-1}) was prepared from mercuric chloride, which was purchased from the National Research Center for Certified Reference Material (Beijing, China). MeHg standard reference material GBW10029 (tuna muscle tissue, 0.84 ± 0.03 μg g^{-1}) was bought from National Institute of Metrology (Beijing, China).

All the stock standard solutions were protected from light and stored at 4 °C in a refrigerator. Working solution of MeHg and iHg were obtained by stepwise dilution of stock solution, respectively. All containers were soaked in 10% HNO_3 and cleaned thoroughly with purity water prior to use.

2.3. Preparation of monolithic column

Monoliths were synthesized inside silica tubes (3 cm length × 4 mm i.d.). The surface of the tube was silanized with 20% solution of (3-mercaptopropyl)trimethoxysilane in ethanol for 2 h – a similar procedure was used by Aggarwal [25]. Subsequently, the silanized tube was rinsed with ethanol and then dried with nitrogen at room temperature.

The preparation of monolith was proceeded by pouring the well-distributed solution containing 0.8 g divinylbenzene, 0.08 g toluene, 1.12 g dodecanol, 0.008 g AIBN (1 wt% with respect to monomer) and 1.5 g magnetic Fe_3O_4 coated by oleic acid into the pretreated tube and then placing the column in an incubator at 85 °C for 10 h. Finally, pumping acetontrile through the column at a flow rate of 0.2 mL min^{-1} for 12 h to remove porogenic solvent and any remaining soluble compounds present in the monolith and then drying the column in incubator at 120 °C.

2.4. Aging of monolithic column

Before using, aging of monolithic column is need. Put the column in electromagnetic induction heating device under N_2 purge, increasing temperature from room temperature to 60 °C, holding for 3 h and up to 180 °C, holding for 4 h.

2.5. Sample preparation

Water samples were collected from Nanfei River (Heifei, China) and artificial lake in our campus, and they were filtrated through 0.45 μm pore size membrane to eliminate possible suspended material. Tap water from Hefei was also analyzed as a sample. Codfish was obtained from local markets (Hefei, China), and stocked in an ice compartment of laboratory.

A similar extraction procedure as reported by Ortiz et al. [26] was used for preparing the samples of codfish and standard reference material GBW10029. 0.5 g preconditioned fish and GBW10029 sample were transferred to 50 mL centrifuge tubes, respectively, and then 5 mL HCl (5 mol L^{-1}) was added. After sonication for 10 min, the mixture was centrifugated at 3500 rpm