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Analytica Chimica Acta 543 (2005) 1–8
ANALYTICA CHIMICA ACTA
www.elsevier.com/locate/aca

Ordered mesoporous silica coated capillary for in-tube solid phase microextraction coupled to high performance liquid chromatography

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Received 7 March 2005; received in revised form 1 April 2005; accepted 7 April 2005

Abstract

Ordered mesoporous silica coating modified with octadecyl groups was introduced into the capillary for in-tube solid phase microextraction coupled to high performance liquid chromatography (in-tube SPME–HPLC). Improved extraction efficiency was demonstrated for the capillary when comparing with those of non-mesoporous structural coatings. The coatings produced by using different structure directing agents were compared and the highest sample capacity was achieved with the most ordered mesostructural coating.

The capillary with the octadecyl modified ordered mesoporous silica coating was used to perform in-tube SPME–HPLC analysis of bisphenol A in water samples. Tap water and Donghu lake (Wuhan, China) water samples spiked with bisphenol A were tested under optimized conditions with the linearity ranged from 0.01 to 1 μg/mL and the detection limits were found to be 2.8 and 2.9 ng/mL, respectively. The precision of the method was satisfactory with the R.S.D. values smaller than 2.7%.

Keywords: Ordered mesoporous silica; Capillary coating; In-tube solid phase microextraction; Bisphenol A

1. Introduction

There has been widespread interest in developing the solventless sample preparation technique—solid phase microextraction (SPME), since it was introduced by Author and Pawliszyn [1]. As the automated form of SPME combined to liquid chromatography, in-tube SPME–HPLC was put forward at 1997 [2]. It was able to provide shorter analysis time, better precision, more convenient operation than the off-line mode and thus has obtained extensive acceptance in many area such as biological, biomedical, environmental researches and so on [2–4].

As to the in-tube SPME–HPLC method, further development of the coating for the extraction capillary is of great importance. Since the samples with analytes existing at low concentration or in complicated matrix are commonly encountered in sample management these days, the materials that provide great sorption capacity or distinct selectivity towards certain analytes could be applied as robust and capacious extraction coatings. For in-tube SPME, increasing the extraction efficiency can be achieved by enhancing the stationary phase loadings. A direct method is to increase the coating thickness, as it is recognized that the extracted amount doubles when the film thickness is doubled [5]. However, the equilibrium time will increase four times meanwhile because the extraction becomes a dynamic diffusion-controlled process. Another solution is to apply thinner coatings with large available surface area, which will provide enhanced extraction efficiency and help faster mass transfer during extraction as well as analyte desorption processes [6]. Therefore, porous coatings are employed in

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doi:10.1016/j.aca.2005.04.024

SPME, such as poly(divinylbenzene) porous coating transplanted from gas chromatography [7,8], and the polypyrrole coating introduced by Pawliszyn and coworkers [9,10]. As to the porous coatings based on inorganic matrix, they are expected to facilitate conveniently chemical modification with desired functional groups and thus create variety of novel extraction media. Furthermore, they could provide higher thermal stability and endurance against organic solvent. Therefore, this is likely to become an important orientation of the future advancement in SPME.

The ordered mesostructure silica materials were introduced by Mobil researchers in 1992 [11], and the intense interests in this research area are generated thereafter. These kinds of materials possess large surface area, highly ordered pore structure, very tight pore size distributions and thus have been regarded as attractive candidates for a wide range of applications in catalysis, sensors and separations technologies. Because of the existing of high concentration of surface silanol groups, the modification of these materials by grafting functional groups or incorporation of ligands, such as amino and thiol [12–14], cyclodextrin [15,16] and alkyl groups [17] into the mesoporous structure has been identified as an convenient method to obtain highly effective adsorbents, most of which have been taken for environmental cleanup applications. Besides small molecules, the mesoporous materials have been also exploited as protein adsorption supporters [18,19]. Another important research area for expanding the application of ordered mesoporous silica is liquid chromatography [20–24], in which crucial parameters are high surface area and well-defined pore sizes. Recently, a stain steel fiber with the mesoporous silica particles modified was also applied to SPME [25].

Ordered mesoporous film is another morphology of ordered mesoporous material that holds great promise for use as separation media. Many researches concentrated on the formation of the mesoporous metal oxides films with periodic pore structures using poly(ethylene oxide)–block–poly(propylene oxide)–block–poly(ethylene oxide) triblock copolymer non-ionic surfactants as the structure directing agents in conjunction with dip-coating [26–28]. They also exhibit highly ordered and oriented mesostructures with variable pore size and porosity just like that of bulk mesoporous materials and can be used as separation media and chemical sensors [29–31]. It is worthy of doing further exploitation of this unique material as separation media, especially for microseparation technologies.

As an attempt, an ordered mesoporous silica coating modified with octadecyl groups was introduced into the in-tube SPME–HPLC system [32,33] as the capillary coating in the present work. High extraction efficiency was expected in view of the introduction of the large surface area and the uninhibited access of the analytes resulted from the well-defined nanometer-scale open pore structure. And a strong estrogenic endocrine-disrupting agent, bisphenol A, was extracted from the water samples with the in-tube SPME system combined with the capillary.

2. Experimental

2.1. Chemicals and materials

Tetraethylorthosilicate (TEOS, 95%) was obtained from Chemical Plant of Wuhan University (Wuhan, China); Pluronic P123 ($EO_{20}PO_{70}EO_{20}$) and F127 ($EO_{106}PO_{70}EO_{106}$) were kindly offered by BASF. Octadecyltrimethoxysilane (95%) was purchased from Fluorochem Ltd. (Derbyshire, England).

Bisphenol A and biphenyl were obtained from Shanghai Chemical Reagent Co. Ltd. (Shanghai, China), and of analytical grade. The stock solutions of these two compounds were prepared in methanol at 1 mg/mL, with which the sample solution was diluted to a certain concentration. The water used in the experiment was double distilled water.

2.2. Instrumentation and analytical conditions

The configuration of the in-tube SPME–HPLC used for the study is shown in Fig. 1. The whole system consisted of a pre-extraction segment, which included a Shimadzu LC-4A six-port valve (valve 1), a Shimadzu LC-6A pump (pump A) (Shimadzu, Tokyo, Japan) and a PEEK loop (0.03 in. i.d., 575 μL total volume), and an analytical segment, which included a Shimadzu LC-10AT pump (pump B) (Shimadzu), Rheodyne 7125 six-port valve (valve 2) with a 20 μL loop (Cotati, CA, USA) and a Shimadzu SPD-10A UV detector (Shimadzu) or a FD-100 Filter Fluorescence Detector (Groton Tech., MA, USA). Valves 1 and 2 were connected with a stainless steel tube.

The analytical column was 150 mm × 4.6 mm, i.d., packed with Kromasil ODS (5 μm), which was purchased from Eka Chemicals (Bohus, Sweden). The optimized mobile phase was 75% methanol and 25% 0.025 mol/L KH_2PO_4 buffer solution (pH adjusted to 4.5 with H_3PO_4), and the flow rate was kept at 1 mL/mim. The detection for biphenyl was performed at 254 nm with the UV detector. And the detection of bisphenol A was performed with UV detector at 220 nm or with the fluorescence detector at 280 and 330 nm for excitation and emission, respectively.

The pore structure of the JEOL-2010 FEF Transmission Electron Microscopy (TEM) (Tokyo, Japan).

2.3. Preparation of octadecyl grafted ordered mesoporous silica film coated capillary

The inner surface of the capillary was first coated with the ordered mesoporous silica film by sol–gel method and then chemically modified with octadecyltrimethoxysilane.

The fused silica capillary (60 cm × 0.25 mm, i.d.), obtained from Yongnian Fiber Plant (Hebei, China), was first activated by 1 mol/L NaOH and then 1 mol/L HCl. After rinsing with double distilled water, it was dried at 160 °C under N_2 flow for 10 h.