



Exploration of metal-organic framework MOF-177 coated fibers for headspace solid-phase microextraction of polychlorinated biphenyls and polycyclic aromatic hydrocarbons



Guanhua Wang^{a,*}, Yongqian Lei^a, Huacan Song^{a,b}

^a Guangdong Provincial Key Laboratory of Emergency Test for Dangerous Chemicals, Guangdong Provincial Public Laboratory of Analysis and Testing Technology, Guangdong Institute of Analysis, Guangzhou 510070, PR China

^b School of Chemistry and Chemical Engineering, Sun Yat-sen University, 135 Xin Gang West Road, Guangzhou 510275, PR China

ARTICLE INFO

Article history:

Received 29 April 2015

Received in revised form

12 June 2015

Accepted 20 June 2015

Available online 23 June 2015

Keywords:

Metal-organic frameworks

MOF-177

Headspace solid-phase microextraction

Polychlorinated biphenyls

Polycyclic aromatic hydrocarbons

ABSTRACT

Metal-organic frameworks (MOFs) have received much attention in analytical science for their large langmuir surface and high thermostability. Herein MOF-177-coated solid-phase micro-extraction (SPME) fibers were fabricated on etched stainless steel by an adhesive method, and applied to the enrichment of polychlorinated biphenyls (PCB01, PCB05, PCB29, PCB47, PCB98, PCB154, PCB171, PCB201) and polycyclic aromatic hydrocarbons (ANY, ANA, FLU, PHE, ANT, FLT, PYR) from environmental water samples. Several parameters affecting the extraction efficiency were optimized prior to the gas chromatography-mass spectrometry analysis, including extraction temperature and time, desorption time, stirring rate and salt addition. The results indicated that the coated fiber gave low detection limits ($0.69\text{--}4.42\text{ ng L}^{-1}$) and good repeatability with the RSD ranging from 1.47% to 8.67% for PCBs and PAHs. The recoveries were between 81.8% and 113% with the spiked level of 10 ng L^{-1} for the real water samples. Besides, the MOF-177 coated fiber was stable enough over 100 extraction cycles and the RSD for fiber-to-fiber reproducibility was less than 9.82% during the experiment.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) are ubiquitous and persistent environmental contaminants [1]. Due to their high toxicity and resistance to metabolic degradation, they may cause negative effects on human health and environment [2,3]. However, both PCBs and PAHs are hydrophobic and exist in low concentration in the environmental water. Therefore, the concentration and enrichment is an important step in the research of prevention and control of PCBs and PAHs.

Solid-phase microextraction (SPME), a relatively new sample preparation technique introduced by Arthur and Pawliszyn, has attracted increasing attention due to its advantages of solvent less nature, analyte/matrix separation, and high preconcentration [4–6]. The coating material of the SPME fiber is the key factor affecting the sensitivity and selectivity of the analytes. However, the kinds of commercial fibers are very limited and expensive. The silica-based fibers also show many drawbacks, such as breakage of

the fibers, thermal instability (usually $240\text{--}280\text{ }^{\circ}\text{C}$), and so on [7]. Increasing research work has been focused on the development of the coating material, including silicalite [8], grapheme-based material [9], nanomaterials [10], ionic liquids [11], metal wires and metal oxides [12,13], bamboo charcoal [14], hyperbranched polymers [15], and so on.

Metal-organic frameworks (MOFs) have drawn much attention in analytical field due to the large surfaces, accessible cages, modifiable pores and high thermal stability [16,17]. MOFs have been successfully explored as sorbents for solid-phase extraction (SPE) [18–24], solid-phase microextraction [25–27], and as stationary phases of chromatography column [28–33]. Recently, MOFs-based SPME researches have received an increasing interest in analytical science. MIL-101(Cr) [34,35], MOF-199 [27], ZIF-8 [25], MIL-53(Al) [36], MAF-X8 [37], ZIF-90 [38], and MIL-88B [7] have been all reported as SPME fibers.

Among the porous MOFs, MOF-177, reported by Yaghi's group in 2004, possessing high surface area ($4500\text{ m}^2\text{ g}^{-1}$, langmuir) and large pore cages (the narrowest edge is 10.8 \AA) was rarely investigated in chromatography science [39]. The 4,4',4''-benzene-1,3,5-triyl-tri-benzoic acid ligand adopted in MOF-177 has four phenyl rings, which can afford abundant $\pi\text{--}\pi$ interactions with the

* Corresponding author. Fax: +86 02087686511.
E-mail address: ghwangvip@163.com (G. Wang).

phenyl-based analytes. The single cage in the MOF-177 molecule is enough to accommodate a phantom atom with the diameter of 11.8 Å. However, the synthesis and yield restrict the application of MOF-177. Based on this reason, we modified the synthesis route and yield in the previous work [40]. To immobilized MOF-177 to the SPME fiber, an adhesive method was adopted using diluted silicone sealant to an etched stainless fiber.

In this work, PCBs and PAHs, two types of persistent organic pollutants (POPs) with different polarity (the $\lg k_{ow}$ ranges from 3.49 to 8.18) and molecular sizes (from 6.5×7.1 to 7.5×12.8 Å), were investigated as analytes in the environmental water. The HS-SPME method was employed before the GC/MS analysis, and three kinds of real water (river water, lake water and waster water) were also determined.

2. Experimental

2.1. Reagents and materials

The chemical reagents employed were commercially available. Methanol of HPLC grade were purchased from Burdick & Jackson (Muskegon, MI, USA). N-hexane and hydrofluoric acid of analytical grade were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). Other reagents were all purchased from Aladin (Shanghai, China). 1-(4-methylphenyl)-ethanone, Silicon tetrachloride (SiCl_4), N,N-diethylformamide (DEF) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were used to prepare MOF-177. Neutral multi-functional silicone sealant was purchased from Guangzhou HeXin Industry Co., Ltd. (Guangzhou, China). The environmental water samples were filtered with membrane (0.45 μm) before the extraction experiment.

The standard of eight PCBs, PCB01 (2-chlorobiphenyl), PCB05 (2,3-dichloro biphenyl), PCB29 (2,4,5-trichlorobiphenyl), PCB47 (2,2',4,4'-tetrachlorobiphenyl), PCB98 (2,2',3,4',6'-pentachlorobiphenyl), PCB154 (2,2',4,4',5,6'-hexachlorobiphenyl), PCB171 (2,2',3,3',4,4', 6-heptachloro-biphenyl), PCB201 (2,2',3,3', 4,5',6,6'-octa-chlorobiphenyl) were purchased from Sigma-Aldrich (Saint Louis, USA). Seven PAH standards, acenaphthylene (ANY), acenaphthene (ANA), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR) were purchased from Dr. Ehrenstorfer GmbH (Germany). The stock solution of the mixed standard were prepared as 10 mg L^{-1} in methanol, and stored at 4 °C in darkness. The different calibration solutions were prepared daily, by dilution of the stock solution with methanol.

2.2. Instruments

X-ray powder diffraction (XRPD) patterns were recorded on a Rigaku-D/max 2500 V X-ray diffractometer equipped with a source of $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54178$ Å). The scanning electron micrographs (SEM) were obtained from a model S-3700 scanning electron microscope (Hitachi, Kyoto, Japan). The langmuir surface area was measured on V-Sorb 2800 P analyzer (Gold APP Instruments Corporation, Beijing, China). The 5 μL GC micro-syringes were purchased from Shanghai Gaoge Industrial and Trade Co., Ltd. (Shanghai, China) as the SPME holders. A commercial SPME manual holder with the fiber coated with 100 μm of PDMS, 65 μm of PDMS/DVB and 85 μm of PA (Supelco, Bellefonte, PA) was used for comparison. The fiber was conditioned in the GC inject port according to the manufacturer.

An Agilent (Santa Clara, USA) system consisting of a 5975c mass spectrometer coupled to a GC-7890A gas chromatograph were used for the identification and quantification of PCBs and PAHs. A fused-silica HP-5 column (95% polydimethyl-siloxane; $30 \text{ m} \times 0.25 \text{ mm id}$, $0.25 \mu\text{m}$), supplied by J&W Scientific was

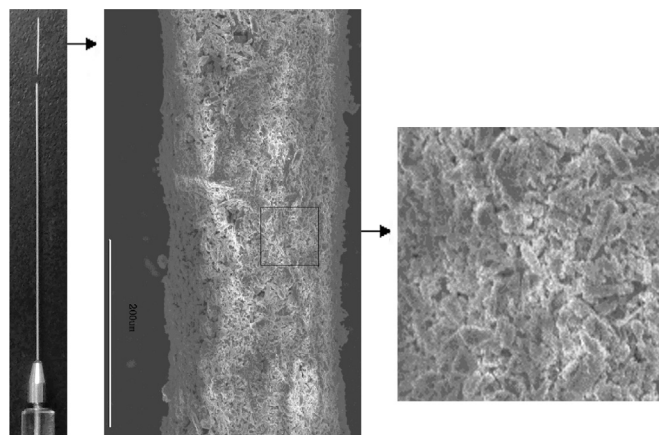


Fig. 1. A scheme of 5 μL GC micro-syringe coated with MOF-177, and the SEM of MOF-177 coated fiber (the reference scale is 200 μm).

employed with helium (purity 99.999%) as carrier gas at a flow rate of 1.0 mL min^{-1} . The column temperature was programmed as follows: 90 °C for 2 min, then heated to 200 °C at $5 \text{ }^\circ\text{C min}^{-1}$, and finally to 280 °C at $25 \text{ }^\circ\text{C min}^{-1}$, with a hold time of 6 min. The injector port was maintained at 280 °C and the extracted sample was injected in splitless mode. After sampling for 2 min, the split ratio was set at 50:1. The data were acquired and processed using Agilent GC Solution software. The interface and ionization source temperature were 280 and 230 °C, respectively. The analysis was performed in SIM mode, and the molecular ion (m/z 152, m/z 154, m/z 188, m/z 166, m/z 222, m/z 178, m/z 202, m/z 324, m/z 258, m/z 290, m/z 392, m/z 426) was used as the target ion for detection (ionization mode: electron ionization with 70 eV energy).

2.3. Fabrication of the MOF-177 coated SPME fiber

The MOF-177 powder was synthesized according to our previous work [40]. The product was fully grinded and dried in the vacuum oven at 150 °C for 30 min before use. A 5 μL GC micro-syringe was used to make the homemade SPME device. First, the outer tube of the syringe needle was cut 2 cm off, then the uncovering stainless steel wire of the micro-syringe was etched with hydrofluoric acid (38%, w/w) for 12 h to make the diameter as thin as 150 μm . The wire was washed with ethanol and distilled water, and air-dried. The silicone sealant was diluted with n-hexane (w/v: 300 mg/1 mL) in a centrifuge tube before use. The etched wire was inserted into the silicone sealant and pulled out quickly, then vertically inserted into a centrifuge tube filled with the prepared

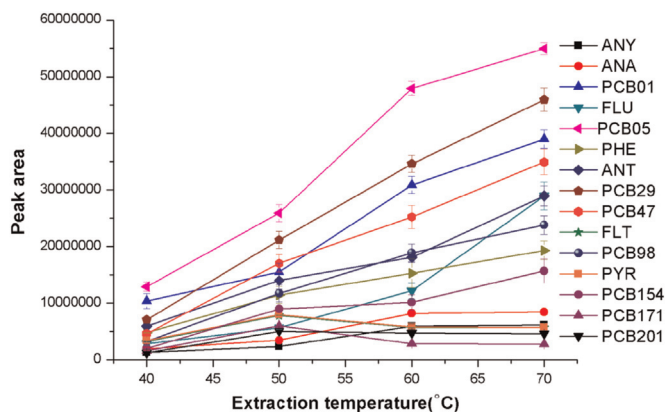


Fig. 2. The effect of extraction temperature on extraction efficiency. Other conditions: concentration, $10 \mu\text{g L}^{-1}$; extraction time, 40 min; desorption time, 8 min; stirring rate, 700 rpm; ionic strength, no salt addition.

Download English Version:

<https://daneshyari.com/en/article/7678591>

Download Persian Version:

<https://daneshyari.com/article/7678591>

[Daneshyari.com](https://daneshyari.com)