



# From porous aromatic frameworks to nanoporous carbons: A novel solid-phase microextraction coating



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## ABSTRACT

A novel nanoporous carbon (NPC) was constructed by utilizing the porous aromatic framework-6 (PAF-6) as both the template and carbon source along with KOH as a chemical activator. The newly-synthesized PAF-6 derived nanoporous carbon (PAF-6-NPC) was then employed as a solid-phase microextraction (SPME) fiber coating. Coupled with gas chromatography-flame ionization detection, the PAF-6-NPC fiber-based SPME method exhibited large enhancement factors, low limits of detection, good linearity and acceptable repeatability for the determination of some *n*-alkanes in various water and soil samples. The method recoveries for the *n*-alkanes were in the range of 89.5–102.9% for water and 86.0–104.5% for soil samples, respectively. The PAF-6-NPC coated fiber showed no obvious decrease of the extraction efficiency for the analytes after 100 replicate extractions. The PAF-6-NPC fiber-based SPME method was successfully applied for the determination of *n*-alkanes in water and soil samples.

## 1. Introduction

Long-chain *n*-alkanes, as a class of organic contaminants widespread in the environment [1], mainly originate from the exploitation of natural gas and the utilization of petroleum energy [2]. Because of their volatility, *n*-alkanes can be emitted into the environment through various channels and also can pollute soil, groundwater, river and oceans [3]. High contents of *n*-alkanes residues pose a serious threat to human health through the food chains by the direct or indirect harmful effects [4]. Therefore, to develop an effective analytical method for the determination of *n*-alkanes in the environmental specimens is of great significance.

The pioneering work on solid-phase microextraction (SPME) was reported by the Pawliszyn group in the early 1990s [5]. Due to its advantages of being solvent-free, simple to operate, easy automation and coupling with detection apparatus, SPME has been extensively developed in the analysis of forensic, environmental, cosmetic, biological, and pharmaceutical samples [6]. In SPME, the properties of the SPME fiber coating count a great deal for the extraction. Although some SPME fibers are commercially available, such as polydimethylsiloxane (PDMS) [7], PDMS/divinylbenzene (PDMS/DVB) [8] and polyacrylate (PA) [9] fibers, the variety of the current SPME coatings is still limited relative to the large number of the analytes of interest. Therefore, the advancement of SPME adsorbents is necessary to further enlarge its

applications. To date, diverse SPME coating adsorbents have been developed, including porous carbon materials [10], graphene [11], metal-organic framework (MOFs) [12] and carbon nanotubes [13].

Nanoporous carbons (NPCs) have received much attention owing to their special features such as high surface area, good chemical and thermal stability [14]. Their applications have been reported in the fields of electrochemistry [15], gas storage and separation [16,17], catalysis [18] and drug delivery [19]. NPCs can be prepared by various methods, such as template synthetic procedures [20], carbonization of polymer aerogels [21], and activation (physical or chemical) method [22,23]. Among them, template synthetic strategy was superb to prepare the NPCs with controllable and tunable pore architectures. Some traditional inorganic nanoporous templates, including nanoporous silica and zeolites, have been successfully employed to fabricate NPCs [20,24]. Recently, porous organic frameworks (POFs), which were formed by the strong covalent linkages of the light elements (C, B, O, N, and S), have been investigated as innovative templates to prepare NPCs [23,25,26]. Unfortunately, the direct carbonization of the POFs templates at high temperatures generally results in a significant shrinkage with low surface areas due to their mass loss and high surface energy [23,25].

Inspired by the fact that NPCs can get an increased surface area after chemical activation [27], we intend to use the chemical activation assisted template synthetic method to prepare POFs-derived NPCs.

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Considering that porous aromatic frameworks (PAFs) are an important subclass of POFs with permanent porosity and good heat endurance, PAF-6, synthesized by the condensation between piperazine and cyanuric chloride monomers, was selected to serve as both the precursor and template with KOH as the chemical activator for the preparation of an innovative NPC. The obtained PAF-6 derived nanoporous carbon (PAF-6-NPC) was then utilized as a fiber coating material for SPME and the extraction capability of the PAF-6-NPC coating was evaluated by the SPME of some *n*-alkanes. Moreover, a PAF-6-NPC fiber-based SPME method was successfully established for the effective extraction of some *n*-alkanes from environmental water and soil samples before gas chromatography-flame ionization detection (GC-FID).

## 2. Materials and methods

### 2.1. Reagents and materials

The eight *n*-alkanes standards including *n*-undecane ( $\geq 99.5\%$ ), *n*-dodecane ( $\geq 99.5\%$ ), *n*-tridecane ( $> 99\%$ ), *n*-tetradecane ( $> 99\%$ ), *n*-pentadecane ( $\geq 99.5\%$ ), *n*-hexadecane (99%), *n*-octadecane ( $\geq 99.5\%$ ) and *n*-eicosane ( $> 99\%$ ) were purchased from Macllin Inc. (Shanghai, China). Anhydrous piperazine (99%), cyanuric chloride (99%), anhydrous potassium carbonate ( $\text{K}_2\text{CO}_3$ , 99%), 1,4-dioxane ( $\geq 99.0\%$ ), dichloromethane ( $\geq 99.5\%$ ), ethanol (95%), KOH (90%) and NaCl (99.5%) were bought from Aladdin Chemistry (Shanghai, China). Neutral silicone sealant was obtained from Baiyun Chemical Industry (Guangzhou, China). Double-distilled water was prepared via an SZ-93 automatic double-distiller from Shanghai Yarong Biochemistry Instrumental Factory (Shanghai, China). The stainless steel wire (type, 304) used for SPME substrate was bought from Shanghai Gaoge industry and Trading Co., Ltd. (Shanghai, China).

The mixture standard stock solution at  $1.0 \text{ mg mL}^{-1}$  each of the *n*-alkanes was prepared in acetone and stored in a refrigerator at  $4^\circ\text{C}$ . A series of working standard mixture solutions of various concentrations were prepared by the appropriate dilutions of the mixture standard stock solution with double-distilled water just before use.

The tap and pond water samples were collected from our laboratory tap and the campus pond in Hebei Agricultural University (Baoding, China), respectively. The soil samples (soils 1 and 2) were taken from the farmland near a local petrochemical plant (Baoding, China) and the farmland in Zhoujiazhuang village (Shijiazhuang, China), respectively.

### 2.2. Synthesis of PAF-6 and PAF-6-NPC

A nucleophilic substitution reaction was used for the preparation of PAF-6 according to the previous report [28] with some modifications. Typically, anhydrous piperazine (6 mmol, 0.517 g) was ultrasonically dissolved in 50 mL of 1,4-dioxane followed by the addition of anhydrous  $\text{K}_2\text{CO}_3$  (12 mmol, 1.659 g). Subsequently, the solution of cyanuric chloride (4 mmol, 0.738 g) in 20 mL of 1,4-dioxane was dropwisely added to the above mixture at  $15^\circ\text{C}$  and the solution was then slowly heated to  $90^\circ\text{C}$  and maintained for 24 h. The white product was cooled down to room temperature and washed with dichloromethane, ethanol and water each for three times, respectively. The obtained PAF-6 powder was dried under vacuum at  $80^\circ\text{C}$  overnight.

The mixtures of KOH and the synthesized PAF-6 with different mass ratios (1:1, 2:1, 3:1, and 4:1) were ground uniformly and soaked in an ethanol/water solution (95: 5, v/v). These mixtures were ultrasonically dissolved for 0.5 h and stirred overnight. After being dried at  $80^\circ\text{C}$  for 12 h, the solid was collected in a ceramic boat and transferred into a tubular furnace under nitrogen atmosphere, which was heated at a rate of  $5^\circ\text{C min}^{-1}$  from the ambient temperature to 400, 500, 600, and  $700^\circ\text{C}$ , respectively and kept at the corresponding temperatures for 3 h. After being cooled down to room temperature, the black product was washed with  $1.0 \text{ mol L}^{-1}$  HCl solution, ethanol and double-distilled water for several times and dried under vacuum at  $80^\circ\text{C}$  for 12 h to

obtain the final desired carbon material PAF-6-NPC.

### 2.3. Preparation of the SPME fiber

The PAF-6-NPC coated SPME fiber was prepared in accordance with our previously reported physical coating method [29]: the pre-functionalized stainless steel wire was immersed into a silicone sealant solution (500 mg silicone sealant was dispersed in 1 mL toluene) and pulled out quickly. Then, the silicone sealant modified fiber was dipped into the PAF-6-NPC powder, rotated for a few cycles and taken out carefully. Subsequently, the PAF-6-NPC coated fiber was conditioned at  $150^\circ\text{C}$  for 30 min. The expected PAF-6-NPC coating thickness (approximately  $25 \mu\text{m}$ ) was obtained by repeating the above process for another two times. The PAF-6-NPC coated fiber was assembled into a  $5 \mu\text{L}$  microsyringe and inserted into the GC injector port at  $270^\circ\text{C}$  under a  $\text{N}_2$  flow until a stable GC baseline was gained.

### 2.4. Instruments

All chromatographic measurements were performed using Agilent 7820 A gas chromatography (Agilent, CA, USA) equipped with a flame ionization detector (FID). An HP-5 column ( $30 \text{ m} \times 0.32 \text{ mm i.d.} \times 0.25 \mu\text{m}$  film thickness, Agilent J&W Scientific, USA) was used for the chromatographic separations of the *n*-alkanes. The GC-FID conditions were set as follows: injection port temperature,  $270^\circ\text{C}$ ; FID temperature,  $280^\circ\text{C}$ ; nitrogen flow,  $1.2 \text{ mL min}^{-1}$ ; splitless mode. The separation of the analytes was carried out in the following temperature program: start at  $60^\circ\text{C}$  for 1 min, then heating at the rate of  $25^\circ\text{C min}^{-1}$  to  $220^\circ\text{C}$ , and at  $15^\circ\text{C min}^{-1}$  to  $270^\circ\text{C}$ , and finally maintaining at  $270^\circ\text{C}$  for 1 min. The Fourier transform infrared (FTIR) spectra were observed on a Bruker Alpha spectrometer (Ettlingen, Germany). The PXRD measurements were performed on a Tongda TD-3500X X-ray diffractometer (Dandong, China) with  $\text{Cu K}\alpha$  radiation. A V-Sorb 2800P automatic surface area and porosity analyzer (Gold APP Instruments Corporation, Beijing, China) was used to measure the surface area and pore size of the PAF-6-NPC. The scanning electron microscopy (SEM) was recorded via a Hitachi S4800 field emission electron microscope (Tokyo, Japan). The transmission electron microscopy (TEM) was carried out on a FEI Tecnai G2 20 (Hillsboro, USA). The thermal stability of the PAF-6-NPC coating was investigated by a Henvon HCT-2 thermogravimetric analyzer (Beijing, China) from room temperature to  $600^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$  under  $\text{N}_2$  atmosphere.

### 2.5. Sample pretreatment and SPME procedures

The water samples were filtered through a  $0.45 \mu\text{m}$  filter membrane before SPME. The soil samples were air-dried and ground to fine powders, which was sieved to a particle size of  $350 \mu\text{m}$ . One gram of the soil sample was extracted with 1.5 mL of acetone for 5 min and then centrifuged at 5000 rpm for 5 min. The supernatant was filtered and diluted to 20.0 mL with water for the subsequent SPME.

For the SPME, 20 mL of water sample was placed in a 25 mL extraction vial with 1 g NaCl (5%, w/v). Then, the needle of the homemade SPME device was penetrated through the cap of extraction vial and the PAF-6-NPC coated fiber was directly exposed to the sample solution for extraction. After the SPME at  $30^\circ\text{C}$  for 40 min under the magnetic stirring at 1000 rpm, the PAF-6-NPC coated fiber was retracted and introduced into GC inlet for thermal desorption at  $270^\circ\text{C}$  for 3 min. For the soil samples, 20.0 mL of the obtained soil extraction solution was transferred into a 25 mL glass vial with 1.0 g NaCl (5%, w/v) and the extraction conditions were the same as described above for the water samples.

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