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Sorptive extraction using polydimethylsiloxane/metal–organic framework coated stir bars coupled with high performance liquid chromatography-fluorescence detection for the determination of polycyclic aromatic hydrocarbons in environmental water samples

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ABSTRACT

In this work, metal–organic frameworks (MOFs, Al-MIL-53-NH_2) were synthesized via the hydrothermal method, and novel polydimethylsiloxane/metal–organic framework (PDMS/MOFs, PDMS/Al-MIL-53-NH_2)-coated stir bars were prepared by the sol–gel technique. The preparation reproducibility of the PDMS/MOFs-coated stir bar was good, with relative standard deviations (RSDs) ranging from 4.8% to 14.9% ($n = 7$) within one batch and from 6.2% to 16.9% ($n = 6$) among different batches. Based on this fact, a new method of PDMS/MOFs-coated stir bar sorptive extraction (SBSE) and ultrasonic-assisted liquid desorption (UALD) coupled with high performance liquid chromatography-fluorescence detection (HPLC-FLD) was developed for the determination of polycyclic aromatic hydrocarbons (PAHs) in environmental water samples. To obtain the best extraction performance for PAHs, several parameters affecting SBSE, such as extraction time, stirring rate, and extraction temperature, were investigated. Under optimal experimental conditions, wide linear ranges and good RSDs ($n = 7$) were obtained. With enrichment factors (EFs) of 16.1- to 88.9-fold (theoretical EF, 142-fold), the limits of detection (LODs, $S/N = 3$) of the developed method for the target PAHs were found to be in the range of 0.05–2.94 ng/L. The developed method was successfully applied to the analysis of PAHs in Yangtze River and East Lake water samples.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) contain two or more fused benzene rings in linear, angular, or cluster arrangements and are derived from the incomplete combustion of organic materials by natural and anthropogenic processes, such as oil, gas, garbage, and coal [1,2]. PAHs are ubiquitous in the environment; these substances are usually found in the air, water, and soil. Humans are exposed to PAHs mostly through food intake, although exposure through the air and drinking water has also been observed. PAHs comprise a group of chemical compounds that are known to be cancer-causing agents, and some PAHs have been demonstrated to be carcinogenic and mutagenic [1]. Once PAHs enters the human body, most of PAHs will be metabolized by the mixed function oxidase to generate a variety of intermediates and final products. Some metabolites could covalently bind with DNA to form PAH-DNA adducts, which could cause DNA damage and even induce the formation of tumor [3]. Because of their high toxicity to the human body, both the European Union (EU) and the United States Environmental Protection Agency (USEPA) have their own list of 16 PAHs as “priority organic pollutants” [4].

Conventional methods for the determination of PAHs are based on chromatographic techniques, such as gas chromatography (GC) and high-performance liquid chromatography (HPLC). GC, which is rapid and sensitive, has been coupled with mass spectrometry (MS) for PAHs determination [5]. At present, HPLC combined with fluorescence (FLD), ultraviolet (UV), and MS has been widely used for PAHs determination [4].

However, direct determination of PAHs in actual samples through HPLC is difficult because of the complexity of many sample matrices and general low levels of PAHs. Therefore, suitable sample pretreatment techniques must be employed for accurate detection. Classical sample pretreatment techniques, such as liquid–liquid extraction (LLE), consume large volumes of toxic organic solvents

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and are time consuming. Thus, several environment-friendly sample pretreatment techniques, including liquid phase microextraction (LPME) [6–8], solid phase extraction (SPE) [9,10], solid phase microextraction (SPME) [11–13], and stir bar sorptive extraction (SBSE) [14–18], have been employed for the analysis of PAHs in environmental samples.

SBSE, which was developed by Baltussen et al. [19], possesses numerous merits, such as high sensitivity, good reproducibility, high recovery, and low consumption of organic solvent. SBSE has been successfully applied in the trace analysis of environmental, food, and biomedical samples. The extraction of PAHs is mainly based on commercial PDMS-coated stir bars; however, the extraction kinetics of PDMS coating for PAHs extraction is very slow. Therefore, preparation of novel coated stir bars with high recoveries and quick extraction kinetics for PAHs extraction is necessary. Huang et al. [14] prepared co-(octyl methacrylate-ethylene dimethacrylate) monolithic-coated stir bars for PAHs determination in seawater samples. Yu et al. [16] prepared PDMS/β-CD/DVB-coated stir bars for PAHs determination in environmental water samples. These two types of coated stir bars have faster extraction kinetics and shortened the time to reach extraction equilibrium for PAHs analysis.

Metal–organic frameworks (MOFs) have recently received extensive attention because of their structures and wide range of potential applications. MOFs, as a new class of porous solid materials with exotic topologies, have been widely applied in hydrogen storage, gas separation, catalysis, sensors, and imaging field [20]. The structure and pore size diversity, high surface area, good adsorption affinity, and selective penetration of MOFs demonstrate their usability as sorbents for the analysis of different compounds, such as *n*-alkanes [21], pesticide [22,23], gaseous benzene homologs [24], chemical warfare agents [25], PAHs [10,11] and estrogens [26].

In the current work, MOFs of Al-MIL-53-NH$_2$ were synthesized via the hydrothermal method, and novel PDMS/Al-MIL-53-NH$_2$-coated stir bars were prepared through the sol–gel technique. The purpose of this work is to develop a new method of PDMS/MOFs-SBSE-ultrasonic-assisted liquid desorption (UALD)-HPLC-FLD for determination of PAHs in environmental samples. Parameters affecting PAHs extraction by PDMS/MOFs-SBSE, including extraction time, stirring rate and salt concentration, were investigated. The analytical performance of the developed method was validated, and the method was applied to the analysis of PAHs in East Lake and Yangtze River water samples to demonstrate its applicability.

2. Material and methods

2.1. Reagents and standards

Hydroxyl-terminated polydimethylsiloxane (OH-PDMS) was purchased from Sigma-Aldrich (Milwaukee, WI, USA). Methyltrimethoxysilane (MTMS) and poly(methylhydrosiloxane) (PMHS) were purchased from the chemical plant of Wuhan University (Wuhan, China). Sodium chloride (NaCl), dichloromethane (CH_2Cl_2), methanol, ethanol, hydrochloric acid (HCl), sodium hydroxide (NaOH), *N*,*N*-dimethylformamide (DMF), aluminum chloride hexahydrate ($AlCl_3\cdot 6H_2O$), and trifluoroacetic acid (TFA) were purchased from China Medicine (Group) Chemical Reagent Corporation (Shanghai, China). Acetonitrile was purchased from Tedia Company Inc. (Fairfield, USA). 2-Amino terephthalic acid was purchased from Alfa Aesar (Tianjing, China). All solid reagents and solvents used in this study were of analytical grade. High-purity water obtained from a Milli-Q water purification system (18.25 MΩ cm, Millipore, Molsheim, France) was used throughout the entire experiment.

Table 1
Programme of excitation and emission wavelengths.

FLD detector			
Time (min)	PAHs	Excitation (nm)	Emission (nm)
0–6.40	NAP	220	330
6.41–8.60	ANA, FLU	226	359
8.61–11.50	PHE	270	323
11.51–14.50	ANT	250	370
14.51–18.50	FLT	250	406
18.51–22.40	PYR	280	460
22.41–29.10	BaA, CHR	270	390
29.11–35.70	Bbk, BkF, BaP, DBA, Bghip	290	410
35.71–37.00	IPY	290	470

Standard mixtures of 16 PAHs at 0.2 mg/mL concentration in CH_2Cl_2/methanol (1/1, v/v) were purchased from AccuStandard (New Haven, CT, USA) and stored at 4 °C in a refrigerator. These solutions include naphthalene (NAP), acenaphthene (ANA), acenaphthylene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benz[*a*]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), dibenz[*a*,*h*]anthracene (DBA), benzo[ghi]perylene (BghiP), and indeno[1,2,3-cd]pyrene (IPY). The mixed working standard solutions of 16 PAHs were prepared daily by diluting the stock standard solution with high-purity water to the required concentrations. Twenty-millimeter-long commercial stir bars (Twister^{TM}) coated with 0.5 mm-thick PDMS were purchased from Gerstel GmbH (Mülheim van der Ruhr, Germany).

2.2. Instrumentation

An Agilent 1100 series HPLC-UV system (Agilent Technologies, USA) with a fluorescence detector (FLD) and a 50 μL sample loop was used for PAHs separation and detection. Separation was performed on an Eclipse PAH column (4.6 mm × 200 mm, 5 μm, Agilent). The elution was performed with acetonitile (solvent A) and water (solvent B), and the elution program was as follows: 0.00–25.00 min, 57% solvent A; 25.01–36.00 min, 100% solvent A. The excitation and emission wavelengths of the PAHs are shown in Table 1. The flow rate and injection volume were 1 mL/min and 40 μL, respectively. No fluorescence signal was detected for ACE; thus, only 15 PAHs were detected in this work.

An X-650 scanning electron microscope (SEM) (HITACHI, Japan) with 30 kV acceleration voltage was used for characterization of the morphology and thickness of the PDMS/Al-MIL-53-NH$_2$-coated stir bar. An energy dispersive X-ray analyzer (HITACHI, Japan) was used for elemental analysis of Al-MIL-53-NH$_2$ particles and the PDMS/Al-MIL-53-NH$_2$ coating. A 170SX Fourier transform infrared spectrometer (FT-IR) (NICOLET, USA) was used for characterization of the structure of the PDMS/Al-MIL-53-NH$_2$ coating. An X'Pert PRO X-ray diffractometer (PANalytcial, Netherlands) was used for Al-MIL-53-NH$_2$ particle characterization.

2.3. Stir bar sorptive extraction procedure

Stirring extraction and ultrasonic-assisted liquid desorption (UALD) were employed in this work. Ten-milliliter aqueous samples containing 16 target PAHs were placed in a 25 mL glass vial. The PDMS/Al-MIL-53-NH$_2$-coated stir bar was immersed in the sample solution at 700 rpm for 20 min. After extraction, the stir bar was placed in a glass desorption tube containing 70 μL of desorption solvent to desorb the target PAHs in an ultrasonic bath for 10 min. About 40 μL of desorption solution was injected into the HPLC instrument for subsequent analysis. The stir bar was

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