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Rapid solid-phase microextraction of polycyclic aromatic hydrocarbons in water samples by a coated through-pore sintered titanium disk

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ABSTRACT

A novel solid-phase microextraction device based on a through-pore sintered titanium disk (ST-SPME) was prepared and evaluated for the rapid extraction of organic pollutants from aqueous samples. The through-pores embedded in a sintered titanium disk were enlarged by HCl etching, yielding more Ti–O functional groups and a rough surface that should benefit the covalent binding of extraction phase with the disk. The large inner surface area (850 mm^2) of the disk and narrow through-pores (100 μm) significantly increase the extraction capacity and mass transfer rate. In addition, the resistance to water flow of the ST-SPME disk is rather low, yielding a back pressure of only 100 kPa at a flow rate of 50 mL/min. The extracted target compounds are thermally desorbed by a thermal desorption unit and transferred to a GC or GC–MS system. Taking polydimethylsiloxane as the extraction phase and 16 types of polycyclic aromatic hydrocarbons (PAHs) as model analytes, the extraction and desorption conditions were systematically investigated. The optimized extraction time was only 2 min for 100 mL of water sample. Absolute recoveries were between 5.93% and 23.02%, which are similar to that of stir bar sorptive extraction. The LODs and RSDs were 0.06–3.20 ng/L (S/N=3) and 0.57–7.08%, respectively. The method showed good linearity in the range of 0.01–10 μg/L with a squared determination coefficient $R^2 \geq 0.9939$. As our method was suitable for the measurement of organic pollutants in the water phase, the ST-SPME/GC–MS method was assessed by analyzing three filtered real environmental samples. Some PAHs were detected at the ng/L level in river water and sea water.

1. Introduction

Sample preparation is considered to be the main bottleneck of the analytical process, especially for complex samples because it is estimated to account for two-thirds of the total analysis time and cause the primary errors [1]. Currently, many sample preparation methods have been developed, such as Soxhlet extraction for solid samples as well as liquid–liquid extraction (LLE) and solid-phase extraction (SPE) for liquid samples. However, these methods either suffer from intensive labor, a long analysis time, or the need for the disposal of toxic solvent [2,3]. To overcome these drawbacks, solid phase microextraction (SPME) was developed by Pawliszyn and co-workers [4], as it integrates sample extraction and injection into a single step. In addition, in-tube SPME was also evolved by using a fused-silica capillary with stationary phase coated on its inner surface to adapt to on-line and automated analysis [5].

With the combination of a large surface area and high mass transfer rate, the through-pore structure is a promising solution to shorten the sampling time while maintaining a high extraction capacity. We have developed an array capillary in-tube solid-phase microextraction (ACIT-SPME) cartridge for fast sample preparation [6,7]. A bundle of glass capillary tubes coated with extraction phase were inserted inside a quartz liner to extract organics from hundreds of milliliters of water sample in a few minutes. However, the assembly of the fragile glass capillaries into the liner is rather tedious and hard to move into the production stage.

Another improvement is to replace the fragile glass capillaries with flexible metal wire, including stainless steel [8,9], zinc [10], copper [11], anodized aluminum [12,13], gold [14], platinum [15] and silver [16] wire. In 2006, titanium wire was first used as a SPME fiber substrate, and it could tolerate high temperature and organic solvents [17]. The Ti-OH groups on the surface could be exploited during the sol-gel coating process of the extraction phase [18,19]. Furthermore, by using a titanium open tubular capillary as a substrate, a robust SPME device with a high extraction efficiency was constructed [20]. However, all of these methods needed an hour or more to complete the extraction process due to the small area of the extraction interface.

Through-pore foamed metal or sintered metal, filled with

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three-dimensional through-pores on the inside, has a number of interesting physical and mechanical properties, such as a high stiffness, large surface area, high permeability and low weight. Sintered metallic materials have been applied as heat exchangers [21], filters [22], catalyst supports [23] and other functional materials in many industrial sectors [24]. A bare sintered stainless steel, more specifically a HPLC solvent filter, was used to directly extract PAHs from a water sample [25]. However, the analysis time is about an hour because of the low extraction efficiency and mass transfer rate from just immersing the bare steel filter into the water samples.

In this work, we reported a highly porous solid-phase microextraction based on a coated sintered titanium disk for fast sample preparation. Our primary hypothesis was that the through-pores in the sintered titanium disk coated with extraction phase should act as hundreds of in-tube SPME columns, providing robust and fast SPME with a high capacity. The sintered titanium disk could be coated with diverse extraction materials for different target analytes via Ti–O–Si covalent bonding by sol-gel technology. Hundreds of milliliters of water samples could be pushed through the disk in a few minutes. After extraction, the disk was put in a homemade thermal desorption unit, and the analytes were desorbed and transferred into a GC system for further analysis. We demonstrated our method by using polydimethylsiloxane (PDMS) as the extraction phase and polycyclic aromatic hydrocarbons (PAHs) as model analytes.

2. Experimental

2.1. Chemicals and materials

A sintered titanium plate with an average pore diameter of 100 μm and thickness of 3 mm was purchased from the Sitai Co. Ltd. (Xi'an, China). Naphthalene, acenaphthene, phenanthrene, anthracene, fluoranthene, and pyrene (6 types of PAHs) were obtained from the Shanghai Chemical Reagent Co. (Shanghai, China). The mixed stock standard solution of these PAHs, each with a concentration of 200 mg/L, was prepared in methanol. Another standard solution containing 2 mg/mL each of 16 types of PAHs listed as priority pollutants by the US EPA in benzene/methylene dichloride (1/1, v/v) was purchased from AccuStandard Inc. (New Haven, USA). The studied compounds and their properties are listed in Table 1. All other solvents were of HPLC grade. Wahaha® purified water (Hangzhou, China) was used to prepare all of the standard solutions for analysis. All of the spiked samples were prepared daily by adding the corresponding amount of stock standard solution into water samples. Trifluoroacetic acid (TFA) and phenyltriethoxysilane (PTES) were purchased from the Alfa Aesar Tianjin Co., Ltd. (Tianjin, China). Hydroxyl-terminated polydimethylsiloxane (OH-PDMS) with a molecular weight of 500,000 was obtained from the Keguang New Material Co., Ltd. (Jiangsu, China).

Three types of environmental water samples were collected including tap water, Malan River water (Dalian, China), and sea water near Xinghai Square (Dalian, China). Before the spiking and extraction, all of the samples were filtered through 0.45 μm polyvinylidene fluoride (PVDF) membranes and stored at 4 °C in the dark.

2.2. Apparatus

A MX-RL-E rotary mixer (Scilogex, USA) was used for thorough mixing of various ingredients in the sol-gel solution. The morphology of the as-fabricated sintered titanium disk was examined by scanning electron microscopy (SEM) (JSM 6360, Japan). The elemental and infrared spectral analyses of the coated disk were conducted by energy dispersion spectroscopy (EDS) (Oxford X-act, England) and diffused reflectance infrared Fourier transform spectroscopy (DRIFTS) (Bruker Alpha, Germany), respectively.

A homemade thermal desorption unit previously described [26] was employed for thermal desorption of the disk and the transfer of the extracts into the GC.

2.3. Preparation of the sol–gel mixture

The preparation of the sol–gel mixture was adopted from references [18,26]. To improve the extraction efficiency, PTES was used as the precursor in the sol-gel preparation as it increased π-π interactions between PAHs and the phenyl groups in the sol-gel network.

OH-PDMS (500 mg), PTES (500 μL) and TFA (125 μL) were dissolved by methylene chloride (2000 μL) in a 5 mL PE tube. After being mixed on a rotary mixer for 20 min, the sol solution was ready for coating the titanium disk.

2.4. Preparation of the ST-SPME disk

A sintered titanium plate was cut into a round disk with a diameter of 3.8 mm and thickness of 3 mm (~0.1 g). Before coating, the titanium disk was etched by 20% (v/v) HCl at 60 °C for 2 h. After etching, it was cleaned by purified water and then immersed in 1 M NaOH at room temperature for 2 h to expose surface titanol groups, followed by subsequent rinsing with 0.1 M HCl, purified

Table 1
Physicochemical properties and GC–MS parameters of the target PAH compounds.

Compounds	Molecular weight	Structure (# of rings)	Log Ko/w	B.P (°C)	Retention time (min)	Quantify ions (*m/z*)	Qualitative ions
Naphthalene	128.2	2	3.3	218	10.48	128	127, 129
Acenaphthylene	152.2	3	3.2	280	12.13	152	151, 153
Acenaphthene	154.2	3	3.9	279	12.34	154	152,153
Fluorene	166.2	3	4.0	295	13.01	166	165, 167
Phenanthrene	178.2	3	4.4	340	14.83	178	176, 179
Anthracene	178.2	3	4.4	340	14.95	178	89, 179
Fluoranthene	202.3	4	4.9	384	18.91	202	101, 203
Pyrene	202.3	4	4.9	404	19.80	202	101, 203
Benzo[a]anthracene	228.3	4	5.5	428	25.23	228	114, 229
Chrysene	228.3	4	5.5	448	25.37	228	114, 229
Benzo[b]fluoranthene	252.3	5	6.1	481	31.03	252	126, 253
Benzo[k]fluoranthene	252.3	5	6.1	480	31.19	252	125, 253
Benzo[a]pyrene	252.3	5	6.1	496	33.14	252	126, 253
Indeno[1,2,3-cd]pyrene	276.3	6	6.7	536	43.89	276	138,227
Dibenz[a,h]anthracene	278.3	6	6.7	524	44.21	278	139, 279
Benzo[g,h,i]perylene	276.3	6	6.7	550	46.74	276	138, 277