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Application of Phenyl Bonded Mesoporous Silica as A Novel Coating Layer of Solid-phase Microextraction for Determination of Benzo[a]pyrene in Water Samples

Xin Zhen DU*, Ya Rong WANG, Qian MA, Xue Feng MAO, Jin Guo HOU

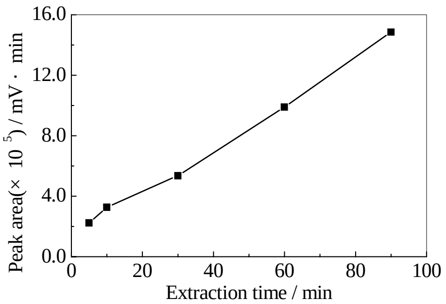
College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070

Abstract: Phenyl bonded mesoporous silica (C_6H_5-MCM-41) was applied as the fiber coating of solid-phase microextraction (SPME). The performance of the fiber coating was discussed coupling to HPLC. Applicability of mesoporous fiber coating was examined for the determination of benzo[a]pyrene (B[a]P) in water samples. The limit of detection (LOD) is $0.28\mu g\cdot L^{-1}$. Good recovery and relative standard deviation (RSD) were obtained.

Keywords: Mesoporous silica, solid-phase microextraction, HPLC, benzo[a]pyrene.

SPME can integrate sampling, extraction, concentration and sample introduction in a single step[1-4]. Up to now, many fiber coatings have been used for the determination of organic analytes in environmental samples[5-14]. In this paper, mesoporous materials were introduced as a novel coating of SPME. Mesoporous materials have a very large specific surface area and well-defined mesopores[15,16]. In this laboratory, MCM-41 typed mesoporous silica with template was used as an alternative fiber coating of SPME[17]. However, the lifetime of the fiber coating was greatly affected when the template was removed by the mobile phase. For these reasons, C_6H_5-MCM-41 was prepared consulting the literature[18], characterized by X-ray diffraction and used as fiber coating of

Figure 1 Dependence of extraction on time.



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[*] E-mail: duxz@nwnu.edu.cn

SPME for quantitative extraction of B[a]P. FT-IR and elemental analysis showed the organic loading (C_6H_5-) of 33.09 %. BET and BJH measurements demonstrate that the specific surface area and the pore size of C_6H_5-MCM-41 are 927 $m^2 \cdot g^{-1}$ and 2.1 nm, respectively. C_6H_5-MCM-41 is stable until 480℃ and highly hydrophobic in water.

The SPME device was modified from a commercial 1μL HPLC syringe. The metal needle was removed and replaced by a shorter needle and the size of the shorter needle is dependent on the fiber coating length and thickness. The stainless steel plunger (160 μm O.D.) inside the needle was cleaned with ethanol and C_6H_5-MCM-41 was fixed on the plunger with epoxy glue. The coated plunger was heated for cure at 80 ℃ for 12 hours. The fiber coating is 10 mm long and 10 μm thick. A 15 mL glass bottle sealed with a silicone septum was used as a sample container. The time of extraction was 30 min at 20℃ on a agitation platform with the magnetic stirring rate of 600 rpm. After extraction, the needle holding SPME fiber was withdrawn from the sample matrix and introduced into desorption chamber connected with six-port injection valve and statically desorpted for 5 min with methanol/water (90/10 v/v) served as mobile phase.

Figure 1 shows the influence of time on extraction of B[a]P by monitoring the chromatographic peak area counts. A period of time is needed to reach an extraction equilibrium for the extraction of B[a]P. Actually, the extraction time of 30 min was employed in the experiment in views of a compromise between a peak area and an acceptable time. In this case, accurate time-controlling is required to obtained good reproducibility. Desorption is the reverse process of adsorption. Greater content of methanol in mobile phase facilitates desorption of B[a]P. Generally, 5 min is enough to reach the equilibrium of desorption in methanol/water compared to adsorption. This procedure was easily coupled with HPLC.

Temperature of aqueous solution is an important parameter because of its potential influences on thermodynamics and kinetics of extraction equilibrium of analytes between fiber coating and water matrix. Temperature dependence shows that the amount of extracted B[a]P increases from 15℃ to 50℃. Vigorous stirring is also favorable to mass transfer of B[a]P. By increasing the stirring rate, higher sensitivity of the coated fiber was obtained. In contrast to SPME with bonded porous silica coated fibers[10], the mesoporous fiber may involve a diffusion-limited process for mass transfer of B[a]P from bulk solution into the mesopores of the particles because perfect stirring can not be achieved in the mesopores of C_6H_5-MCM-41.

In general, the addition of salt to the water solution causes decrease solubility of organic analytes in the water, leading to increase extraction efficiency[19]. **Figure 2** shows that the addition of sodium chloride is unfavorable to the extraction of B[a]P. This result may arise from the increased ionization of silanols at the surface of mesoporous coating[20]. The concentration of adsorbed sodium ions at the liquid-solid interface is higher than that in bulk solution, which changes the physical properties in local microenvironment. Consequently higher concentration of sodium chloride results in lower concentration of B[a]P at the interfacial area compared to the bulk solution. On the other hand, addition of salt can increase the viscosity of aqueous solution[3,4], especially the solution at liquid-solid interface. This may limit the diffusion of B[a]P from bulk solution to the mesoporous surface of fiber coating and contribute to lower extraction efficiency of B[a]P.

The extraction efficiency of SPME depends on the mass adsorbing onto the coating from a sample matrix, which can be expressed as follows:

$$K = \frac{c_s}{c_{aq}} = \frac{n_s V_{aq}}{n_{aq} V_s}$$

Where K is the distribution coefficient of an analyte in the sample, n_s and n_{aq} are the number of moles extracted in fiber coating and in aqueous solution at equilibrium, respectively, V_s and V_{aq} are the volume of the coating and aqueous solution , respectively. The K's value was estimated to be 1.70×10^3 for the extraction of B[a]P under the experimental conditions. The linearity was established in the range 0.25-252 μg • L^{-1}. LOD is 0.28 μg • L^{-1} (S/N=3). Trace amount of B[a]P in various water samples in local area was determined (See **Figure 3** and **Table 1**). Both recovery and RSD show that C_6H_5-MCM-41 is a novel alternative fiber coating of SPME which can stably undergo 200 times adsorption and desorption toward fast stirring. Since the presented silanols at the surface of mesoporous silica are reactive, various mesoporous silica with functional groups can be designed for the generalpurpose and the selective extraction of analytes of interest, maximizing the potential applications of this technique.

Figure 2 Dependence of extraction on ionic strength.

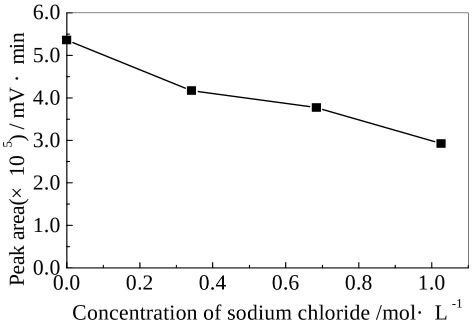
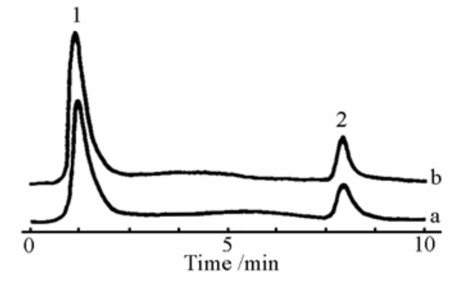


Figure 3 Chromatograms of B[a]P in river water



a: river water b: river water of standard addition. 1:air peak; 2:B[a]P peak;

Table 1 Analytical results of B[a]P in water sample (n=3) [a]

Samples	Original (μg·L^{-1})	Added (μg·L^{-1})	Found (μg·L^{-1})	Recovery (%)	RSD (%)
Purified water	n.d. [b]	20.18	20.10	99.75	2.45
Spiked water [c]	5.05	2.52	8.07	106.8	0.60
Drain water	n.d. [b]	50.54	43.64	86.50	4.77
River water	0.45 [d]	2.02	2.17	88.02	1.80

[a] stirring rate, 1200 rpm. [b] Not detected. [c] Mixture of 3.56 μg·L^{-1} anthracene and 5.05 μg·L^{-1} B[a]P.
[d] Obtained from HPLC.

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