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Investigation of the kinetic process of solid phase microextraction in complex sample

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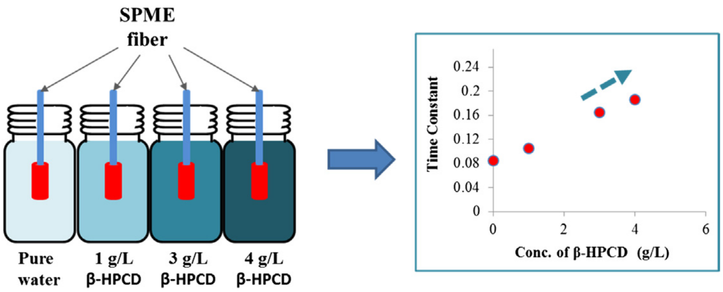
HIGHLIGHTS

- We investigate the effect of complex matrix on the kinetic process of SPME.
- Good agreement is achieved between the theoretical value and the experimental one.
- High temperature increases the sampling rate as well as the lability of the bound compounds.
- Calibration based on non-equilibrium SPME is successfully applied for the complex sample analysis.

GRAPHICAL ABSTRACT



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ABSTRACT

The presence of complex matrix in the aquatic system affects the environmental behavior of hydrophobic organic compounds (HOCs). In the current study, an automated solid-phase microextraction (SPME) desorption method was employed to study the effect of 2-hydroxypropyl-β-cyclodextrin (β-HPCD) on the kinetic process of 5 selected polyaromatic hydrocarbons (PAHs) desorbing from the fiber in aqueous sample. The results showed that the added β-HPCD facilitated the desorption rates of PAHs from SPME fiber coating, and the enhancement effect can be predicted by a proposed theoretical model. Based on this model, the kinetic parameters of organic compounds desorbing from the SPME fiber can be determined, and the calculated results showed good agreement with the experimental data. In addition, the effect of temperature on the desorption kinetic was investigated. The results found that the SPME desorption time constant increased as the sampling temperature elevated, and followed the Arrhenius equation. Also, the temperature facilitated the desorption of HOCs from the bound matrix so that increased the lability degrees of the bound compounds. Finally, a calibration method based on the proposed theoretical model was developed and applied for the analysis of unknown sample.

1. Introduction

The presence of complex matrices such as dissolved organic matters (DOMs) and suspended particulates (SPs) in environmental aquatic systems can significantly affect the partitioning behavior of hydrophobic organic compounds (HOCs), thus determine the fate of many pollutants present in the environmental [1]. Generally, the organic pollutants can interact with the complex matrices and a portion of the HOCs were bound to the complex matrices, and thus decrease the freely dissolved concentration of the HOCs in the sample. On the other hand, research also found that the bound HOCs significantly influence the uptake kinetic of freely dissolved HOCs in various environmental matrices including aquatic

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organism [2–4], sediment [5–7] as well as passive sampler [8–10]. Therefore, understanding the underlying mechanisms dictating such effects is particularly important when monitoring the environmental behavior of organic pollutants in water sample.

Because of its simplicity and ease of implementation, solid phase microextraction (SPME) become an increasingly popular technique for measuring freely dissolved concentration [11–13], binding coefficient [14–19], bioavailability [20] and the effect of complex matrices on the uptake kinetic of organic pollutants onto the aquatic organism. In the last application, SPME fiber was used to mimic the aquatic organism, and the effect of DOMs and SPs on the uptake kinetic of SPME can elucidate the transport mechanism of organic pollutants onto the aquatic organism [21–23]. In literature, both enhancement [9,10,24] and hinder effects [25] of the complex matrices on the transport of HOCs to the SPME fiber were reported. However, the enhancement effect was more commonly observed in the reported works. A theoretical model from facilitated transport theory of metal ion was proposed to elucidate the observed enhancement effect [26,27]. In the model, the SPME absorption process was considered as a flux of freely dissolved and matrix-bound analytes diffused through the unstirred water layer adjacent to the SPME fiber. The matrix-bound analytes can desorb from the matrix and contribute to the flux into the fiber. Fick's first diffusion law was applied to describe the transport mechanism. Later, this proposed diffusion model has been employed to interpret the enhancement effect in several studies [28,29] including the effect of nanoparticles [30].

In the current study, we further studied the theoretical model and proposed an improved equation to describe this enhancement effect on the environmental aqueous sampling. A fully automated SPME depletion method was employed to determine the sampling kinetic parameters of 5 PAHs in hydroxypropyl-β-cyclodextrin (β-HPCD) solution. Besides, we investigated the effect of temperature on the enhancement effect and further elucidated the kinetic parameters in the model. Lastly, an approach for calibrating the enhancement effect was proposed for real sample analysis.

2. Material and methods

2.1. Chemicals, sampler and instrument

Five solid PAHs, naphthalene (NAP), acenaphthene (ACE), phenanthrene (PHE), fluoranthene (FLA), pyrene (PYR) were purchased from Sigma Aldrich (Shanghai, PRC). A model complex matrice, β-HPCD, was obtained from Aladdin (Shanghai, PRC). A SYLGARD184 silicone elastomer kit purchased from Dow Corning (Shanghai, PRC) was used to prepare a standard gas generation vial. A home-made PDMS fiber with a length of 0.5 cm, thickness of 44 μm, and volume of 0.18 μL was used for the experiments. The detailed procedure for preparation of the PDMS fibers can be found in the literature [31].

An Agilent 7890 gas chromatography (GC) coupled with a flame ionization detector (FID) (Agilent technologies, CA, USA.) was used for separation and quantification purposes. A split/splitless injector was used, and desorption temperature was set at 260 °C. Chromatographic separation was performed with a HP-5MS (30 m × 0.25 mm I.D. × 0.25 μm thickness) fused silica column from Agilent, and with nitrogen as the carrier gas. A GERSTEL Multi-Purpose System (MPS) was applied for the automation process (GERSTEL, Mülheim an der Ruhr, GE).

2.2. Determination of the SPME kinetic parameter

The sorption kinetic of the SPME liquid coating has been proved to follow the one-phase association equation. On the other hand, the desorption process has been demonstrated to be symmetrical to the adsorption process, and also followed the one-phase dissociation equation as follows [32].

$$Q = \left(q_0 - q_{f,e}\right)\exp(-at) + q_{f,e} \tag{1}$$

where q_0 is the original loading amount of analyte on the coating; $q_{f,e}$, the amount left on the fiber when equilibrium is reached; Q is the amount left on the fiber at time t. a is the desorption time constant.

Time constant "a" is a measurement of how fast an adsorption/desorption equilibrium can be reached in the SPME process. It is determined by physical dimensional of the sample matrix and the SPME fiber, the distribution coefficient of compound between the fiber and the sample, and the diffusion coefficient of free dissolved compound and binding matrix. For a sample with constant temperature, agitated condition as well as fiber and sample properties, "a" is only influenced by the complex matrix present in the sample. Experimentally, "a" can be obtained by fitting the SPME desorption time profile with a one-phase association/dissociation curve using data process software like Graphpad Prism. In the current study, the desorption time constant of 5 PAHs in β-HPCD solutions with the concentrations of 0, 1, 3, 4 g/L at the temperatures of 35, 45, 55 and 65 °C were determined.

2.3. Theoretical consideration of the kinetic process

Research work showed that for an SPME sampling process whose mass transfer rate was limited by the mass transfer through the aqueous boundary layer, the time constant can be expressed as follows [33]:

$$a = \frac{A\left(K_{fs}V_f + V_s\right)}{K_{fs}V_sV_f} \times m_{aq} = \frac{A\left(K_{fs}V_f + V_s\right)}{K_{fs}V_sV_f} \times \frac{D_{aq}}{\delta_{aq}} \tag{2}$$

where K_{fs} is the partition coefficient of the analyte between the fiber coating and the aqueous solution; V_s and V_f are the volume of sample matrix and the fiber coating, respectively. m_{aq} is the mass transfer coefficient of analytes in the aqueous boundary layer which equals to D_{aq}/δ_{aq}. When only dissolved organic compound exists in the sample, D_{aq} and δ_{aq} refers to the diffusion coefficient and the thickness of the boundary layer of free dissolved organic compound, respectively. In the sample that contains complex matrix, the diffusion coefficient of the organic compound should consider the co-effect of free dissolved ones and the bound ones. According to the literature [27,34], the diffusion coefficient can be expressed by $\overline{D}$ as follows.

$$D_{aq} = \overline{D} = \frac{D_u + D_b{}^*\xi K_{matrix}C_{matrix}}{1 + K_{matrix}C_{matrix}} = F\%D_u + B\%\xi D_b \tag{3}$$

The above equation has been introduced by Georgi [29] and Simith [28] to interpret the enhanced mass transfer of organic pollutant through the aqueous boundary layer. D_u and D_b are the diffusion coefficients of free dissolved compound and binding matrix in the aqueous boundary layer, respectively. K_{matrix} is the partition coefficient of organic compounds between the complex matrix and water, while C_{matrix} is the concentration of the binding matrix [35]. $F\%$ and $B\%$ are the percentage of free dissolved and bound compounds in the matrix. ξ is defined as the ratio of bound compounds that contribute to the free flux during the sampling process, also called "degree of lability" [36]. The introduction of ξ in the equation indicates that not all the bound compounds can desorb from the matrix and contribute to the compound uptake