Journal of Chromatography A, 1406 (2015) 27–33

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Development of a full automation solid phase microextraction method for investigating the partition coefficient of organic pollutant in complex sample

Ruifen Jiang, Wei Lin, Sijia Wen, Fang Zhu, Tiangang Luan, Gangfeng Ouyang*

MOE Key Laboratory of Aquatic Product Safety/KLGHEI of Environment and Energy Chemistry, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, China

ARTICLE INFO

Article history:
Received 16 May 2015
Received in revised form 9 June 2015
Accepted 10 June 2015
Available online 17 June 2015

Keywords:
Solid phase microextraction
Depletion method
Partition coefficient
Complex matrix
Automation

ABSTRACT

A fully automated solid phase microextraction (SPME) depletion method was developed to study the partition coefficient of organic compound between complex matrix and water sample. The SPME depletion process was conducted by pre-loading the fiber with a specific amount of organic compounds from a proposed standard gas generation vial, and then desorbing the fiber into the targeted samples. Based on the proposed method, the partition coefficients (K_{matrix}) of 4 polyaromatic hydrocarbons (PAHs) between humic acid (HA)/hydroxypropyl-β-cyclodextrin (β-HPCD) and aqueous sample were determined. The results showed that the logK_{matrix} of 4 PAHs with HA and β-HPCD ranged from 3.19 to 4.08, and 2.45 to 3.15, respectively. In addition, the logK_{matrix} values decreased about 0.12–0.27 log units for different PAHs for every 10 °C increase in temperature. The effect of temperature on the partition coefficient followed van't Hoff plot, and the partition coefficient at any temperature can be predicted based on the plot. Furthermore, the proposed method was applied for the real biological fluid analysis. The partition coefficients of 6 PAHs between the complex matrices in the fetal bovine serum and water were determined, and compared to ones obtained from SPME extraction method. The result demonstrated that the proposed method can be applied to determine the sorption coefficients of hydrophobic compounds between complex matrix and water in a variety of samples.

1. Introduction

The presence of complex matrices such as dissolved organic matter (DOM) in environmental water, protein and lipid in biological fluid can significantly affect the partitioning behavior of hydrophobic organic compounds (HOCs), thus determine the fate of many pollutants present in these samples [1–3]. Generally, this process takes place when a portion of the HOCs bind to the matrices, decreasing the concentration of freely dissolved compounds, which is considered as effective concentration that controls several diffusive mass transfer processes such as evaporation and sorption to macro- and microorganisms. Commonly, the relationship between the free dissolved and matrix-bound concentration of HOCs is described by partition coefficient (K_{matrix}), which indicates the sorption capacity of the matrix. In literature, the partition coefficient was only available for a limited number of chemicals due to the degree of difficulty in determining the freely dissolved concentrations of HOCs in the complex samples [4,5]. Among the techniques used, solid phase microextraction (SPME) seemed to be the most promising technique since it was simpler, faster and more sensitive than other techniques [6–9]. In addition, SPME appeared to have smaller biases because it caused the least disruption in the sample, and was capable of determining freely dissolved compounds in complex matrices without additional phase separation steps in the workflow [4,5].

There were two direct immersion SPME methods, extraction and depletion, have been reported for the determination of freely dissolved HOCs in the complex sample. For the SPME extraction process [4,10–20], a sample spiked with selected target compounds should be first prepared for the sampling. Then, the freely dissolved concentration of organic compound was quantified by proper calibration methods based on the fiber extracted amount. One major issue of the SPME extraction method was the application for more hydrophobic compounds, which usually associated with higher partition coefficients and low aqueous solubility, making the spiking procedures complicated. In addition, spiking process normally

* Corresponding author. Tel.: +86 20 84110953; fax: +86 20 84110953.
E-mail address: cesoygf@mail.sysu.edu.cn (G. Ouyang).

http://dx.doi.org/10.1016/j.chroma.2015.06.018
0021-9673/

introduced organic solvent into the samples, and may influence the partition of organic pollutant in a given aqueous system. Furthermore, with SPME extraction method, either negligible depletion sampling [10,11] or equilibrium sampling [16] process should be fulfilled to minimize the disruption of partition equilibrium in the sample.

Contrastingly, the fiber depletion method (also called solid phase dosing or passive dosing method) can be employed [21–24]. In this method, the SPME fiber was first loaded with targeted compounds. Then, the analyte loaded fiber was inserted in the solutions that contained different amount of complex matrix. Ter Laak et al. [21] first introduced the manually SPME extraction method to determine the partition coefficients of six polyacromatic hydrocarbons (PAHs) with humic acid in aqueous sample. Later, Mayer and co-workers [25] replaced the disposable SPME fiber with a PDMS coated vial. The main challenge associated with the depletion method pertaining to the fiber dosing process is that it should be reproducible and the dosing amount should be easily quantified. In the reported research, directly exposing the fibers or PDMS coated vials in solution spiked with high concentration of targeted compounds was the most common way in this application. This method usually required a long exposure time, and a significant number of fibers or PDMS-coated vials were needed at the same time. Additionally, the experimental procedure for the reported depletion method was labor intensive, and full automation was difficult to achieve with the currently available autosampler.

In addition to a lack of partition coefficient data in literature, very little has been reported on the extrapolation possibilities of lab-derived partition coefficient to field situations. Partition coefficient is a thermodynamic parameter affected by the physicochemical properties of the binding matrix and the environmental conditions such as pH, salinity and temperature [2]. Among these factors, temperature was considered as the most significant and relevant parameter for nonionic HOCs, which were unaffected or only slightly affected by pH and salinity [26,27]. Since in environmental aquatic system, temperatures vary through time and within space, it is necessary to investigate the effect of temperature on the partition coefficient.

As such, in the current study, a full automation SPME depletion method was first developed to determine the partition coefficients of four selected PAHs on two model matrices, humic acid (HA) and hydroxypropyl-β-cyclodextrin (β-HPCD) in aqueous solutions. Then, the effect of temperature on the partition coefficient was investigated at three temperatures. Last, the proposed method was applied for the determination of the partition coefficient of six PAHs between the complex matrix and water in fetal bovine serum, and the result was compared to the ones obtained from SPME extraction method.

2. Material and methods

2.1. Chemicals, sampler and instrument

Six solid PAHs, acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR) were purchased from Sigma–Aldrich (Shanghai, PRC). Two types of model matrices, HA and β-HPCD, were obtained from Aladdin (Shanghai, PRC). Research grade Hyclone fetal bovine serum originated from South American was from ThermoFishier Scientific (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 1 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 literature [28].

An Agilent 7890 gas chromatography (GC) coupled with a flame ionization detector (FID) (Agilent technologies, CA, U.S.A.) was used for separation and quantification purposes. A GERSTEL Multi-Purpose System (MPS) was applied for the automation process (GERSTEL, Mülheim an der Ruhr, GE). 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.

2.2. Preparation of standard gas generation vial and model complex sample

The standard gas generation vial was prepared for loading the fiber with analytes, and should be able to constantly generate the standard gas, and compatible with the autosampler. In this work, the device was designed as follows. In a 20 mL autosampler vial, 10 mg ACE, 10 mg PHE, 50 mg FLA, 60 mg PYR and 4 g of SYLGARD 184 elastomer base were added, and the mixture was stirred with a glass rod. Then the vial was sealed and placed on an orbital agitator for at least 5 days before use. By doing this, the solid PAHs were thoroughly mixed with the elastomer base, and the concentration in the headspace could maintain constant when the environmental temperature was stable. Since the extraction amount of PAHs by each SPME sampling was relatively small compared to the total amount in the vial, the headspace concentration was not significantly change within hundreds of extractions. The reproducibility of the constructed standard gas generation vial was evaluated by 20 continuous extractions from the same vial; results have yielded a RSD% less than 5%. In addition, the reproducibility of the initial loading amount (q_0) was monitored every 5 extractions throughout the experiment.

A 2000 mg/L of HA solution was prepared in a 1 L volumetric flask, and filtered with a 0.45 μm porosity paper. The HA solution was diluted into 50 mg/L, 100 mg/L, 200 mg/L, 300 mg/L, 500 mg/L, 1000 mg/L, and 1500 mg/L in 500 mL volumetric flasks. Next, 1 g of sodium azide was added to each diluted solution to inhibit bacteria growth. Three solutions with β-HPCD concentrations of 1 g/L, 3 g/L and 4 g/L were also prepared in the similar way for the following experiment. Deionized water was used for preparation of all solutions.

2.3. Operation of the autosampler

A schematic of the experimental procedure can be found in Fig. 1. All steps were conducted using a GERSTEL MPS autosampler with MAESTRO software. An SPME sample preparation module with a pre-derivatization step was selected. The pre-derivatization step was chosen to preload the fiber with a specific amount of PAHs from the standard gas generation vial. The fiber was sampled from the headspace of the vial for a pre-determined period of time. The loading time for the fiber was optimized for different sampling temperatures: 30 min, 25 min, and 15 min were finally selected for 45 °C, 55 °C or 65 °C, respectively. The temperature was easily controlled by the autosampler with a variation of less than 0.5 °C. After being pre-loaded with PAHs, the fiber was inserted into 10 mL vial containing HA or β-HPCD solution. Desorption time profiles ranging from 0 min to 300 min were conducted for different samples at different temperatures. An agitation rate of 250 rpm was applied for both loading and desorption process. After desorption, the fiber was directly injected into the GC/FID for analyte separation and quantification. The desorption time and desorption temperature in the GC injector were 5 min and 260 °C, respectively.