Journal of Chromatography A, 1260 (2012) 16–24

Contents lists available at SciVerse ScienceDirect

Journal of Chromatography A

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

Stir bar sorptive extraction approaches with a home-made portable electric stirrer for the analysis of polycyclic aromatic hydrocarbon compounds in environmental water

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ARTICLE INFO

Article history:
Received 18 April 2012
Received in revised form 16 August 2012
Accepted 20 August 2012
Available online 27 August 2012

Keywords:
Off/on-site stir bar sorptive extraction
Polycyclic aromatic hydrocarbon compounds (PAHs)
High performance liquid chromatography (HPLC)
Environmental water

ABSTRACT

In this study, novel off/on-site stir bar sorptive extraction (SBSE) approaches with a home-made portable electric stirrer have been developed for the analysis of polycyclic aromatic hydrocarbon compounds (PAHs). In these approaches, a miniature battery-operated electric stirrer was employed to provide agitation of sample solutions instead of the commonly used large size magnetic stirrer powered by alternating current in conventional SBSE process, which could extend the SBSE technique from the conventional off-site analysis to the on-site sampling. The applicability of the designed off/on-site SBSE sampling approaches was evaluated by polydimethylsiloxane (PDMS) coating SBSE-high performance liquid chromatography-fluorescence detection (HPLC-FLD) analysis of six target PAHs in environmental water. The home-made portable electric stirrer is simple, easy-to-operate, user friendly, low cost, easy-to-be-commercialized, and can be processed in direct immersion SBSE, headspace sorptive extraction (HSSE) and continuous flow (CF)-SBSE modes. Since the stir bar was fixed onto the portable device by magnetic force, it is very convenient to install, remove and replace the stir bar, and the coating friction loss which occurred frequently in conventional SBSE process could be avoided. The parameters affecting the extraction of six target PAHs by the home-made portable SBSE sampling device with different sampling modes were studied. Under the optimum extraction conditions, good linearity was obtained by all of three SBSE extraction modes with correlation coefficient (R) higher than 0.9971. The limits of detection (LODs, $S/N = 3$) were 0.05–3.41 ng L^{-1} for direct immersion SBSE, 0.03–2.23 ng L^{-1} for HSSE and 0.09–3.75 ng L^{-1} for CF-SBSE, respectively. The proposed portable PDMS-SBSE-HPLC-FLD method was applied for the analysis of six target PAHs in East Lake water, and the analytical results obtained by on-site SBSE sampling were in good agreement with that obtained by off-site SBSE sampling. The accuracy of the developed method was evaluated by recovery test and the recoveries for the spiked sample were found to be in the range of 87.1–122.8% for off-site CF-SBSE, 88.8–114.3% for on-site sampling, and 87.7–123.6% for off-site SBSE, respectively. The developed method is one of the most sensitive methods for PAHs determination and the home-designed SBSE system is feasible for the field sampling.

1. Introduction

A whole analytical procedure involves several steps, in which sampling and sample pretreatment are the most time-consuming (approximately two-thirds of the total analytical time) and responsible for the analytical efficiency and accuracy to a great extent [1]. During sampling process, the representative samples should be collected with original chemical and physical properties of interest analytes being maintained intact, and the loss, degradation and contamination of analytes should be avoided. Additionally, in real-world sample analysis, sample pretreatment techniques are often required to preconcentrate the target analytes at extremely low concentration levels and eliminate the interference resulted from the complicated sample matrix. Therefore, appropriate sampling and sample pretreatment processes are the prerequisite to get the accurate analytical results. In traditional environmental monitoring programs, water or air samples are collected in precleaned containers and transported to the analytical laboratory for pretreatment and subsequent instrumental analysis, while contamination, loss and degradation of the target analytes might occur during the process of sample collection, storage and transportation. Field sampling could prevent the above problems to a large extent [2,3], which makes the samples to be analyzed in the field more representative. Consequently, it is of great significance to develop on-site sampling technique which combines the sampling and sample pretreatment into a single step

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http://dx.doi.org/10.1016/j.chroma.2012.08.062

and allows for a simple and fast sampling/sample preparation process.

At present, some sample pretreatment techniques based on solid phase extraction principle have been successfully employed for on-site sampling. For microcolumn field sampling (MFS) technique, water samples are collected and preconcentrated in situ by passing them with a peristaltic pump through a microcolumn packed with a highly selective adsorbent. The microcolumns immobilized with the trace analytes of interest are then brought back to the laboratory and directly inserted into a flow injection system for on-line elution and quantitative analysis. Yebra et al. [4–6] used microcolumns packed with Amberlite XAD-4 impregnated with the complexing agent 4-(2-pyridylazo) resorcinol and 1-(2-pyridylazo)-2-naphthol for in situ preconcentration of Cu and Cd in seawater. However, these methods were inconvenient because an alternator was necessary to connect the peristaltic pump for field preconcentration.

Solid phase microextraction (SPME) is a powerful tool for field investigations. Since its device is portable, SPME can be used for surface water and air sampling, even in difficult-to-reach sampling locations (such as groundwater wells and deep soil) [2]. SPME can be used for direct field analysis with the help of a portable gas chromatograph or be utilized for field sampling and then transported to the laboratory for instrumental analysis. Sigma–Aldrich/Supelco has launched a commercial SPME portable field sampler (Supelco^{TM}) with 100 μm polydimethylsiloxane (PDMS) fiber, but its cost is relatively high. There are some home-made SPME field samplers/approaches reported in literatures [2,7–10]. Pawliszyn et al. [2] designed a gas-tight valve syringe (50 μL SampleLock by Hamilton) as field sampler for volatile compounds analysis. With this device, over 80% of the initial amount of methylene chloride was retained on the 100 μm PDMS fibers after refrigeration storage (4–8 °C) for 24 h. The same group also designed a new field SPME sampler that can protect fibers during sampling, storage, and transportation, and the factors affecting the preservation of sample integrity (including sorbent efficiency, storage temperature, sealing materials) have been investigated in detail [7]. Lee et al. [8] prepared functional polymer-coated fibers and established a novel on-site sample preparation approach for the organophosphorus pesticides (OPPs) analysis with using a commercially available electric toothbrush. Pawliszyn et al. [9,10] proposed a thin-film microextraction technique for the field sampling of polycyclic aromatic hydrocarbons (PAHs) in Campus River; however, PDMS thin film was soft which could not be stirred at high stirring rate, thus a specially designed framed holder or a thin film copper mesh was needed to hold and fix PDMS film on the electric drill.

Stir bar sorptive extraction (SBSE) [11] is another microextraction technique which has the similar extraction mechanism to that of SPME. The main difference between SPME and SBSE is that about 50–250 times larger volume of extraction phase is employed in the latter, which results in higher recoveries and higher sample capacity. In recent years, SBSE has been successfully applied for organic substances analysis and elemental speciation in environmental, food and biological samples [12–20], and the extraction process has been thoroughly described in the recent reviews [21–23]. However, SBSE technique is mainly confined to laboratory analysis and no effective SBSE approach has been available for field analysis or sampling till now [20,24]. Pawliszyn et al. [9] compared thin-film microextraction and SBSE for the analysis of PAHs in aqueous samples and found that stir bar was not as convenient as thin film in field sampling. The possible reasons of SBSE inconvenience for on-site analysis were as follows: (1) the commonly used large size magnetic stirrer powered by alternating current in conventional off-site SBSE process is inconvenient to carry or use on-site; (2) commercially available and home-made stir bars are difficult to be fixed on the field sampler (such as electric drill [9]). If these two limitations were overcome, SBSE could be extended to the on-site analysis.

The purpose of this work is to design a miniature battery-operated portable electric stirrer for extension of SBSE in field sampling. The stir bar can be easily fixed onto the bottom of the designed stirrer by strong magnetic force. Employing this device to provide the agitation of sample solutions, novel off/on-site SBSE approaches were proposed. The applicability of the designed off/on-site SBSE sampling approaches was evaluated by PDMS-SBSE-high performance liquid chromatography-fluorescence detector (HPLC-FLD) analysis of six target PAHs in environmental water.

2. Experimental

2.1. Standard solution and reagents

PAHs including naphthalene (NAP, 99%), acenaphthene (ACE, 95%), phenanthrene (PHE, 95%), anthracene (ANT, 98%), fluoranthene (FLT, 95%) and pyrene (PYR, 98%) were purchased from Tianchang Chemical (Anshan, Liaoning, China). The standard stock solutions ($1\,g\,L^{-1}$) of each PAH were prepared by dissolving certain amount of respective compounds in methanol and stored at 4 °C in the dark. Polydimethylsiloxane (PDMS) sol used for coating the stir bar consisted of component A (the mixture of oligomers and catalyst) and component B (curing crosslinking) (GE RTV 615, Momentive performance materials, USA), and their mixing ratio was 10:1 (A:B). Capillary glass bars (i.d. 1 mm) were obtained from Apparatus Factory of West China University of Medical Sciences (Chengdu, Sichuan, China). All reagents used in this study were of analytical grade. High purity water obtained by a Milli-Q water purification system (18.2 MΩ cm, Millipore, Bedford, MA, USA) was used throughout the whole experiment. For SBSE conditions optimization and analytical performance evaluation, the experiments were performed with the use of Milli-Q water spiked with six target PAHs as the samples.

2.2. Instrumentation

Agilent 1100 series HPLC-FLD system (Agilent Technologies, Waldbronn, Germany) consisting of a 100-μL sample loop, a vacuum degasser, a quaternary pump and a fluorescence detector was used for identification and quantification of six target PAHs. The separation was performed on a reverse phase C_{18} HPLC column (Lichrospher ODS, 5 μm, 200 mm × 4.6 mm, Hanbon, Jiangsu, China). Methanol–water (80:20, v/v) was used as an isocratic eluent at a flow rate of $1\,mL\,min^{-1}$. The excitation wavelength (λ_{Ex}) and emission wavelength (λ_{Em}) for six target PAHs according to Ref. [25] were as follows: NAP: $\lambda_{Ex} = 220$ nm, $\lambda_{Em} = 330$ nm; ACE: $\lambda_{Ex} = 226$ nm, $\lambda_{Em} = 359$ nm; PHE: $\lambda_{Ex} = 246$ nm, $\lambda_{Em} = 370$ nm; ANT: $\lambda_{Ex} = 250$ nm, $\lambda_{Em} = 406$ nm; FLT: $\lambda_{Ex} = 234$ nm, $\lambda_{Em} = 440$ nm; PYR: $\lambda_{Ex} = 270$ nm, $\lambda_{Em} = 390$ nm.

2.3. The preparation of PDMS coated stir bar

The bare stir bar (20 mm × 1 mm) was prepared by sealing a 17 mm long steel wire in a glass bar with alcohol flame. It was cleaned by water and methylene chloride in turn, followed by soaking in $1\,mol\,L^{-1}$ NaOH and $0.1\,mol\,L^{-1}$ HCl for 3 h, respectively. After being washed by water, the bars were dried at room temperature. Then the stir bars were carefully coated with the PDMS sol solution by a mechanical pipette. The coated bars were placed into a constant temperature drier for 24 h at 60 °C. Prior to use, these PDMS coated stir bars were ultrasonicated in methanol for 30 min to get rid of the organic impurities in the coatings. The coating thickness