Contents lists available at ScienceDirect

Analytica Chimica Acta

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

Calibration of the complex matrix effects on the sampling of polycyclic aromatic hydrocarbons in milk samples using solid phase microextraction

Wei Lin [a], Songbo Wei [a], Ruifen Jiang [b, **], Fang Zhu [a], Gangfeng Ouyang [a, *]

[a] 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, PR China
[b] School of Environment, Guangzhou Key Laboratory of Environmental Exposure and Health, and Guangdong Key Laboratory of Environmental Pollution and Health, Jinan University, Guangzhou 510632, PR China

HIGHLIGHTS

- We investigated the complex matrix effects of milk on the SPME sampling process.
- The complex matrix effects on the sampling kinetics were calibrated by a previously developed theory.
- The sampling conditions of SPME for PAHs in milk samples were optimized.
- The proposed PE-SPME method was demonstrated to be fast and accurate for complex matrix sampling.

GRAPHICAL ABSTRACT
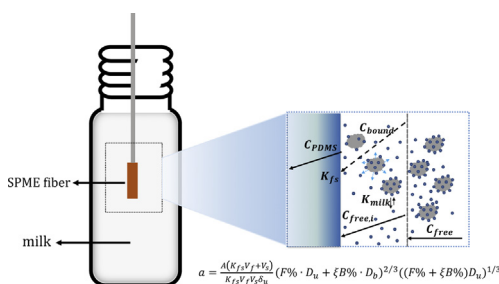
ABSTRACT

Solid phase microextraction (SPME), a simple, fast and promising sampling technique, has been widely used for complex sample analysis. However, complex matrices could modify the absorption property of coatings as well as the uptake kinetics of analytes, eventually biasing the quantification results. In the current study, we demonstrated the feasibility of a developed calibration method for the analysis of polycyclic aromatic hydrocarbons (PAHs) in complex milk samples. Effects of the complex matrices on the SPME sampling process and the sampling conditions were investigated. Results showed that short exposure time (pre-equilibrium SPME, PE-SPME) could increase the lifetime of coatings, and the complex matrices in milk samples could significantly influence the sampling kinetics of SPME. In addition, the optimized sampling time, temperature and dilution factor for PAHs were 10 min, 85 °C and 20, respectively. The obtained LODs and LOQs of all the PAHs were 0.1–0.8 ng/mL and 1.4–4.7 ng/mL, respectively. Furthermore, the accuracy of the proposed PE-SPME method for milk sampling was validated by the recoveries of the studied compounds in two concentration levels, which ranged from 75% to 110% for all the compounds. Finally, the proposed method was applied to the screening of PAHs in milk samples.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Recently, there have been growing efforts toward the development and improvement of sample preparation methods for fast and

simple analysis of complex samples [1]. Solid phase micro-extraction (SPME) that integrates sampling, preconcentration and quantitation into a single step has been nominated as one of these techniques characterized as simple, fast and sensitive [2–5]. It has been reported for an extensive range of applications in sampling different classes of organic compound residues in food such as honey, red wine, grapes and milk [6–11]. Meanwhile, a series of reviews about the applications of the SPME technique have been published for the analysis of different complex matrices including environmental samples [12], biological samples [13] as well as food samples [14]. As discussed in these reviews, despite the advantages offered by the technique, some critical limitations hindered its application to food matrix analysis. For example, sampling from complex food matrices may cause fouling by irreversible adsorption of macromolecules on the coating surface, which could not only shorten the life of a fiber, but also modify its coating properties [6,15]. In addition, recent research found that complex matrices also influenced the uptake kinetics of freely dissolved organic compounds onto the SPME coating, which in turn affected the accurate quantification of pre-equilibrium SPME [16,17].

To address the issue of coating fouling, Pawliszyn's research group proposed that polydimethylsiloxane (PDMS), as a nonporous liquid coating, suffered less from the irreversible fouling effect caused by matrix components, so it could indeed offer improved repeatability and robustness in complex matrices [15]. However, the group also pointed out that for direct immersion SPME, complex food matrices would eventually modify the chemical properties of the coatings and the absorption capacity as exposure time increased. Therefore, pre-equilibrium SPME (PE-SPME) was preferable when we considered the lifetime of fibers. In addition to resolving the lifetime concern of the fiber coatings, the pre-equilibrium method also provided a fast analysis possibility when sensitivity requirements could be met.

On the other hand, when using PE-SPME, the effects of complex matrices on the sampling kinetics should be considered and calibrated. Several papers have reported on this research topic and tried to elucidate the mechanism of the complex matrix effects on the sampling kinetics [18–20]. Recently, our group has reported on the effects of dissolved organic matters (DOMs) on the sampling of organic pollutants in water samples using SPME [16]. Results showed that the presence of DOMs in water samples facilitated the uptake rate of compounds. A mass transfer model was proposed to elucidate the enhancement effect, and an equation that considered the effects of complex matrices was derived to calibrate the kinetic parameters.

Although the mechanism of the complex matrix effects in water samples has been elucidated and theoretically the effects can be calibrated by the proposed equation, no research has applied the developed theory to real sample analysis such as milk samples, which contain a large amount of water, and other nutrition components such as lactose, fat, proteins and minerals [21]. These components may act like the complex matrices present in water samples and influence sampling kinetics when using the SPME method.

Thus, in the present study, we go further to apply the developed theory to the interpretation of complex matrix effects when using SPME for the sampling of polycyclic aromatic hydrocarbons (PAHs) in milk samples. As known, with significant toxicity and potential carcinogenic properties [22], PAHs existing in food such as milk are considered as the main source of human exposure to contaminants [23]. Therefore, it is very important to develop simple, fast sample preparation methods for monitoring PAHs in milk samples. Sampling conditions including sampling time, temperature, dilution factor, and especially, the effects of complex matrices on sampling kinetics were studied. Finally, the proposed method was applied to

the screening of PAHs in several milk samples purchased from a local supermarket.

2. Materials and methods

2.1. Chemicals and instrument

Six solid PAHs, acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR) were purchased from Sigma-Aldrich (Shanghai, PRC). All the milk samples including milk blanks which were labeled as organic milk were purchased from a local supermarket. The milk blanks were tested by the proposed method to ensure zero background signal before use. A SYLGARD 184 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. Detailed procedures for the preparation of the PDMS fibers can be found according to J. Xu et al. [24].

An Agilent 7890 GC coupled with 5975C MS (Agilent technologies, CA, U.S.A.) was used for separation and quantification. A GERSTEL Multi-Purpose System (MPS) was applied to the automation process (GERSTEL, Mülheim an der Ruhr, GE). A split/splitless injector was used. Pulsed splitless mode and injector temperature of 260 °C were chosen after optimization. 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 helium as the carrier gas at a flow rate of 1 mL/min.

2.2. SPME sampling process

Two types of SPME sampling processes including extraction and desorption were used for different experiments. Both sampling processes were conducted using a GERSTEL MPS autosampler with a MAESTRO software.

For the SPME extraction method, a milk blank was first spiked with a PAHs standard solution to a pre-set concentration. The PAHs working standard solution was diluted from a PAHs stock solution that was prepared by dissolving 6 solid PAHs in dichloromethane to a concentration of 2000 mg/L. The stock solution was kept at −20 °C till fresh working standard solutions needed to be prepared. Then 9.0 g of the spiked milk samples were transferred into 10 mL vials and placed on autosampler trays. Finally, the extracted PAHs were quantified by GC/MS.

The SPME desorption experiment was applied to the study of the complex matrix effects of milk samples on the SPME kinetics. According to the fundamentals of SPME, the SPME extraction and desorption processes are isotropic. By studying the effects of complex matrices on desorption kinetics, the effects of complex matrices on the extraction process can be understood [16,17,25,26]. In SPME desorption processes, fibers should be first loaded with target compounds. Therefore, a standard gas generation set-up was constructed according to a published work for purpose of the compound preloading [27,28]. After being pre-loaded with PAHs, the fibers were desorbed in milk blanks in 10 mL vials for a different period of time. Finally, the PAHs left on the fibers were quantified by GC/MS. All the steps were conducted by the autosampler with an SPME sample preparation module with a pre-extraction step, which was selected to preload the fibers with specific amounts of PAHs.

2.3. Traditional sampling method

The sampling procedure followed the one reported by C.M. A. Iwegbue et al. [29]. In brief, 2 g of milk was first spiked with 1 μL of