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Silk fiber for in-tube solid-phase microextraction to detect aldehydes by chemical derivatization

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ABSTRACT

Aldehydes are the potentially damaging pollutants in the environment, but it is difficult to be determined due to the low concentration level. Therefore, to accurate analysis of aldehydes, it is important for efficient sample preparation with selective enrichment and rapid separation. Environmentally friendly silk fiber as adsorbent material was directly applied to develop in-tube solid-phase microextraction for analyzing aqueous samples combined with high performance liquid chromatography. 2,4-Dinitrophenylhydrazine as a derivative reagent was used for chemical derivatization of aldehydes before extraction. Under optimum conditions, an online analysis method was built with the limits of detection in the range of 0.005–0.01 $\mu g\,L^{-1}$ and the linearity in the range of 0.03–10 $\mu g\,L^{-1}$. Three aldehydes were determined in two real samples, and the relative recoveries were in the range of 95–102%.

1. Introduction

The volatile organic compounds (VOCs) in the air can be absorbed through the breath, digest and skin into the blood system, which have been recognized as potential biomarkers [1]. At present, more than 200 kinds of VOCs were detected from indoor air, which mainly involve aliphatic hydrocarbons, aromatic hydrocarbons, aldehydes, ketones and chlorinated hydrocarbons. And because of the photochemical oxidation of hydrocarbons, combustion of fossil fuels by motor vehicles and industrial activities, aldehydes are acknowledged to be harmful organic pollutants that exist naturally in the atmosphere [2,3]. Therefore, determination of aldehydes may provide indicators for early clinical diagnosis. It is very important to develop an efficient method to detect aldehydes sensitively.

Many sample preparation methods were frequently applied in the analysis of some trace targets, such as solid-phase extraction [4], stir bar sorptive extraction [5], liquid–liquid microextraction [6] and liquid-phase microextraction [7]. However, these sample preparation techniques have abundant shortcomings including time-consuming, power-consuming, pollution-carrying and off-line analysis. Solid-phase microextraction (SPME) was a powerful sample preparation method, that introduced by Pawliszyn in the early 1990s as its time-efficient, operation convenience and organic solvent-free [8]. Then it has been extended to in-tube SPME by Pawliszyn and Eisert in 1997 [9]. Combined with high performance liquid chromatography (HPLC) or gas chromatography (GC), it has been successfully applied in various fields, such as food [10], clinical [11], environmental [12–14] and biological analysis [15–17]. Furthermore, HPLC [2,18] and GC [19,20] with various detectors including ultraviolet (UV) [21,22], fluorescence (FLU) [23] and mass spectrometry (MS) [24] have been widely applied for the aldehydes analysis.

Since aldehydes can not present a signal in the diode array detector (DAD), chemical derivation is a good way for detecting aldehydes. Taking the volatility and reactivity of aldehydes into account, the reaction of aldehydes with amino groups is widely applied for their detection and quantification in biological and environmental samples [25]. 2,4-Dinitrophenylhydrazine (DNPH) is the most popular derivative reagent for carbonyls. Sheikh et al. used the C_{18} column to analyze the derivative product of formaldehyde, achieving a lower detection limit [26]. Chen et al. used DNPH to derive and determine formaldehyde in textiles, the relative standard deviation (RSD) obtained by the on-line method was 3.2% [27]. To evaluate the degree of oxidation of lipid peroxides in tissues and plasma, the derivatization method with DNPH was also

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applied to detect aldehydes [28]. A variety of sample preparation methods have been developed on the basis of aldehyde-DNPH derivatization reaction including in situ or continuous derivatization [2], pre-column derivatization [3], post-column derivatization [18]. Post-column derivatization required additional equipment and only had limited reaction yield. In situ or continuous derivatization need another pump to the delivery of DNPH solution, and may obtain not complete derivatization due to short contact time between DNPH and aldehydes Therefore, pre-column derivation was used in this work because it can select the reaction conditions relatively freely, as well as complex instrumentation or another delivery pump are not necessary.

The extraction material is the most important for in-tube SPME to detect aldehydes. Divinylbenzene-polydimethylsiloxane [29,30], polydopamine modified polystyrene/graphene electrospun nanofiber membrane [31], polystyrene/metal-organic frameworks-199 [32] and zinc oxide [33] have been reported as sorbents to detect derivatives of aldehydes, but their synthesis processes are complex, and the use of organic solvent is too much. Thereby, it is most important to develop a green, cheap and easily available sorbent. Recently, silk fibers as natural and environmentally friendly material have attracted more and more attentions. It is widely used as biomaterials due to its superior mechanical performance, excellent flexibility and stable biocompatibility [34–37]. Nilghaz et al. exploited the differing surface morphologies of silk and cotton fibers for the separation of red blood cells by elution chromatography, the result showed that the smooth surface of silk fibers provided a much more efficient separation than cotton fibers for differentiating free red blood cells [38]. Silk fiber was used as 3D functional scaffolds for cell culture by Mandal [39]. Cabot et al. developed a novel and effective fiber-based microfluidic methodology to move and isolate charged solutes, biomolecules, and intact bacterial cells [40]. As the silk fibers contain hydroxyl, carboxyl, amino and other hydrophilic groups, as well as a lot of pores inside, thereby it has a strong adsorption capacity. However, as far as we know, it has not been applied to SPME, its surface properties and large specific surface area indicates that it has a good extraction potentiality for environmental pollutants.

In this work, silk fibers were used as the extraction material, an online in-tube SPME-HPLC system was built. After chemical derivatization with DNPH, the online analysis system was used to detect aldehydes with optimum extraction and desorption conditions. The method has also been applied to the actual analysis of environmental samples.

2. Experimental

2.1. Materials and reagents

All chemicals and solvents were analytical-reagent. Silk fibers were obtained from Feihong silk industry Co. (Binzhou, China). PEEK tube (750 μm i.d., 0.16 cm o.d.) was purchased from Haohai Chemical Co. (Wuhan, China). Three aldehydes including propanal, butanal and pentanal were obtained from Shanghai Macklin Biochemical Co. (Shanghai, China). DNPH was provided by Sinopharm Chemical Reagent Co. (Shanghai, China). Acetonitrile and methanol were HPLC grade and purchased from Tedia Chemical Reagent Co. (USA). All the water samples were filtered through 0.45 μm membrane and stored at 4 °C to analysis.

2.2. Apparatus

A P102 HPLC pump was applied to move sample solution through extraction tube and bought from Dalian Elite analytical instruments Co., Ltd. (Dalian, China). All chromatographic tests were performed on an Agilent 1260 HPLC system (USA) equipped with a 20 μL sample loop, a Zorbax C_{18} column (250 × 4.6 mm i.d., 5 μm) and DAD. Surface property of silk fibers was characterized by a field-emission scanning electron microscope (SEM, SUPRATM55, Carl Zeiss, AG, Germany).

2.3. Chemical derivatization of aldehydes

To be closer to the actual sample, working solutions of aldehydes were prepared daily at a concentration of 0.5 μg L^{-1}, 400 μL of DNPH (72 mmol L^{-1}) was added into 1 L of working solution. Then the working solution was placed in a water bath at 60 °C for 2 h to obtain the propanal-DNPH, butanal-DNPH and pentanal-DNPH.

2.4. SPME-HPLC online procedure

In order to increase extraction capacity, as many as possible silk fibers were placed into a PEEK tube (30 cm length) for extraction. In this work, 0.10 g of silk fibers are packed into a PEEK tube. The PEEK tube was connected into the HPLC six-port valve. Online SPME-HPLC analysis consisted of two steps, i.e., extraction and desorption. When the six-port valve was in the “load” position, the sample solution was introduced into the tube by a syringe pump at a rate of 1.50 mL min^{-1} to achieve extraction process. After extraction, the six-port valve was switched from “load” to “inject” position, the mobile phase would pass through the tube at a rate of 1.0 mL min^{-1} to desorb analytes into the analytical column for separation and further detection by DAD. The cycle of online SPME-HPLC could greatly shorten analysis time, when the desorption procedure lasted 1.5 min, six-port valve could be switched to the “load” position for next sample extraction process, and the separation on C_{18} column and detection still continued at the same time.

All chromatographic tests used methanol-acetonitrile-water (50:40:10, v/v) as the mobile phase at 25 °C and 1 mL min^{-1}. The DNPH derivatives of aldehydes were detected at 360 nm.

2.5. Sample preparation

Stock solution of aldehydes was prepared at a concentration of 5 mg L^{-1} in methanol solvent and stored at 4 °C for use. Working solutions were prepared daily by appropriate dilution of the stock solution with ultrapure water to 0.5 μg L^{-1} for the optimization of extraction conditions. The real water samples filtered with 0.45 μm membrane were used to prove the application of SPME-HPLC method in environmental analysis. Tap water was obtained from the laboratory. 1 L of water was put into the newly renovated house (20 m^2) for three days to get the water sample of indoor air.

3. Results and discussion

3.1. Characterization of silk fibers

SEM was employed to characterize the surface of the silk fibers. Fig. 1a shows that size of silk fibers is uniform and the surface is relatively smooth. Under a relatively low magnification (Fig. 1b), we can see that there are many small bulges on the surface, which can increase the adsorption site of silk fibers, thereby improving the extraction efficiency. Fig. 1c and d are the comparison before and after 110 extractions, and the surface of silk fiber still has a lot of gully lines. There was no significant change before and after extractions.