

# Diffusive sampling of airborne furfural by solid-phase microextraction device with on-fiber derivatization

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## Abstract

The solid-phase microextraction (SPME) device was used as a diffusive sampler for airborne furfural. The polydimethylsiloxane/divinylbenzene (PDMS/DVB) fiber was used, and *O*-2,3,4,5,6-(pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) was first loaded onto the fiber. The SPME fiber assembly was then inserted into a PTFE tubing as a diffusive sampler. Known concentrations of furfural around the threshold limit values (TLVs)/time-weighted average and specific relative humidities (RHs) were generated by syringe pumps in a dynamic generation system. Validations of the SPME diffusive sampling with the US Occupational Safety and Health Administration (OSHA) organic method 72 were performed side-by-side in an exposure chamber at 25 °C. Gas chromatography/mass spectrometry (GC/MS) was used for sample analysis. The experimental sampling constant of the sampler was found to be  $(1.75 \pm 0.03) \times 10^{-2}$  (cm<sup>3</sup> min<sup>-1</sup>) at 25 °C, whereas face velocity (0–0.25 m s<sup>-1</sup>) as well as RHs (10–80%) were proven to have no effects on the sampler. The correlations between the results from both SPME device and OSHA organic method 72 were found to be linear ( $r=0.9849$ ) and consistent (slope =  $0.99 \pm 0.03$ ). However, the variations of diffusion coefficients at different temperatures needs to be considered, and the adjustment of sampling constant was a must when sampling at temperatures different from 25 °C.

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**Keywords:** SPME; Furfural; PFBHA; Diffusive sampling; Gas chromatography; On-fiber derivatization

## 1. Introduction

Aldehydes (R-CHO where R is alkyl, aromatic, or alicyclic) are ubiquitous products of combustion [1–3], photodegradation of dissolved natural organic matter [4], and biological oxidations [5], and are mucous membrane irritants [6]. Formaldehyde, acetaldehyde, furfural, and crotonaldehyde are animal carcinogens [7]. Among aldehydes, furfural is receiving increasing attention in recent years because there are various sources of exposures [8]. Furfural is found in numerous processed foods and beverages, including cocoa, coffee, tea, beer, wine, milk products, and bread [8]. Furfural is also a widely used industrial chemical. The US Environmental Protection Agency (EPA) estimated that the range of USA production was

$1.12 \times 10^7$ – $4.57 \times 10^7$  kg in 1994 [9]. Besides being used as fungicide and herbicide [10], furfural is often used as a selective solvent in the production of lubricating oils, as a reactive wetting agent in the production of refractory components, and for the resin blinder system in the production of abrasive wheels [8].

Furfural has been identified as a major flavor component in a range of food items, including beef, soy sauce, roasted nuts, fried bacon, nectarines, baked potatoes, clove oil, preserved mangoes, rum, roasted coffee, and blue cheese [11]. Besides ingestion, inhalation and dermal exposures of furfural are also possible. The US Occupational Safety and Health Administration (OSHA) promulgated furfural health standard with a work-shift 20 mg m<sup>-3</sup> permissible exposure limit (PEL) [12]. The OSHA PEL also bears a “Skin” notation, which indicates that the cutaneous route of exposure (including mucous membranes and eyes) contributes to overall exposure [12]. The American Conference of Governmental Industrial Hygienists (ACGIH) also

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assigns a “Skin” notation and has set up a threshold limit value (TLV) of  $7.9 \text{ mg m}^{-3}$  as a TWA to furfural for a normal 8 h workday and a 40 h workweek [7].

For the exposure assessment of furfural, methods of air sampling and analysis including OSHA method 72 and the US National Institute for Occupational Safety and Health (NIOSH) method 2529 are often performed [13,14]. However, these methods involve complex procedures for sample preparations (solvent extraction, for example) and are, therefore, very time-consuming. In recent years, a new extraction technique called solid-phase microextraction (SPME) has been developed by Pawliszyn [15,16]. SPME presents many advantages over conventional analytical methods by combining sampling, preconcentration, and direct transfer of the analytes into a standard gas chromatograph (GC) system [17].

Various derivatization techniques including direct derivatization in sample matrix, derivatization in GC injector port, and derivatization in SPME fiber coating can also be implemented combined with SPME [15]. For the determination of aldehydes, the technique of on-fiber derivatization where oximes formed after *O*-2,3,4,5,6-(pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) reacted with aldehydes has been reported elsewhere [18]. The on-fiber derivatization technique will not only increase the sample stability but also allow high efficiencies and can be used in remote field applications [15].

The air sampling and analysis methods with SPME have been applied to both grab and time-weighted average (TWA) modes [17,19,20]. This approach is superior to currently available diffusive sampling methods in overall analytical sensitivity because all of the sorbed analytes are introduced into the analytical instrument for quantitation rather than a small fraction of the extract [21]. Diffusive sampling using SPME combined with on-fiber derivatization has also been reported [22]. To increase the acceptance of using SPME device as a personal diffusive sampler, a user-friendly sampling device with which the risky needle of SPME device was kept in a PTFE tubing has then been developed [23–25]. The research shown here extended the design to the validation of furfural sampling where PFBHA was first loaded onto the fiber for the purpose of on-fiber derivatization and direct oxime analysis was performed to determine the amounts of furfural collected.

## 2. Experimental

### 2.1. Materials

Furfural, *O*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride, *n*-hexane, and methanol were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Helium for GC/MS was 99.999% pure and purchased from Sanfu, Taiwan. A Harvard syringe pump (model 11), rotameters, and Tedlar gas bags were from Fisher Scientific (Tustin, CA, USA). Petroleum charcoal sampling tubes were from Supelco (Bellefonte, PA, USA). Air sampling pumps (Model 224-PCXR4) were from SKC (Eighty four, PA, USA). A Whatman Zero Air generator was from Balston (Haverhill, MA, USA) and was used to provide the air for

a standard gas generation system. A M-5 Mini-Buck Calibrator for air flow rate calibrations was from Buck Scientific (East Norwalk, CT, USA). A calibrated hot-wire anemometer used to monitor face velocity was from Kanamox Instrument Co., Japan. All SPME fibers, holders, and molecular sieve were from Supelco. All retracted fiber-path length and surface area were measured by inserting a steel tube that had an outer diameter equal to the needle tube inner diameter, and then measuring the depth and outer diameter of the inserted tube.

### 2.2. Instrumentation

All analyses were performed on a Perkin-Elmer Autosystem XL Chromatograph equipped with a  $30 \text{ m} \times 0.25 \text{ mm}$  I.D.,  $0.25 \mu\text{m}$  film DB-WAX chemically bonded fused-silica capillary column (J&W Scientific, Folsom, CA, USA) and a Perkin-Elmer Turbo Mass, mass spectrometer. The carrier gas was helium with flow rate of  $1.0 \pm 0.1 \text{ mL min}^{-1}$  in the 1:10 split mode. The temperature for the injector was  $250^\circ\text{C}$ . The column temperature program was  $120\text{--}200^\circ\text{C}$  at  $10^\circ\text{C min}^{-1}$ , and held for 3 min. The temperature of mass spectrometer was  $250^\circ\text{C}$ .

### 2.3. Sampling

#### 2.3.1. Theory

By retracting the coated fiber into its needle housing during the sampling, the SPME device can be used as a TWA diffusive sampler and the theory has been reported elsewhere [16]. Fick’s first law of diffusion is used to model steady-state mass transport through the sampler and to determine the amount of analyte loaded on the fiber coating. The sampling rate SR of the sampler can be defined as follows [19]:

$$\text{SR} = D_{\text{AB}} \left( \frac{A}{Z} \right) \quad (1)$$

where SR = sampling rate,  $\text{mL min}^{-1}$ ; Z = retracted fiber path length, cm; A = surface area of the needle opening,  $\text{cm}^2$ ;  $D_{\text{AB}}$  = the diffusion coefficient of the analyte in the gaseous phase,  $\text{cm}^2 \text{ min}^{-1}$ .

As shown in Fig. 1, a modified SPME device was used in this research where the SPME fiber was retracted 3 mm into its needle housing [23–25]. The SPME fiber assembly was inserted into an 11 cm length PTFE tubing (0.48 cm I.D.  $\times$  0.64 cm O.D.). The needle was fixed by a PTFE septum

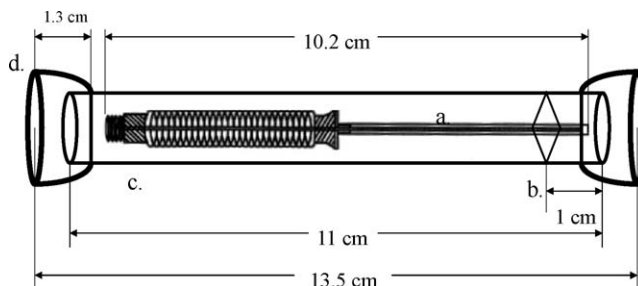


Fig. 1. Perspective view of the passive sampler: (a) SPME fiber assembly, (b) PTFE septum, (c) PTFE tubing, and (d) cap/PTFE tape.

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