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Time-weighted average sampling of airborne *n*-valeraldehyde by a solid-phase microextration device

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Abstract

A solid-phase microextraction (SPME) device was used as a time-weighted average sampler for *n*-valeraldehyde. The SPME device was first modified to improve the wearer's acceptance as a passive sampler. Then a poly(dimethylsiloxane)–divinylbenzene fiber was used and *O*-2,3,4,5,6-(pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) was loaded onto the fiber. Vapors of known concentrations around the threshold limit values time-weighted average of *n*-valeraldehyde and specific relative humidities (RHs) were generated by syringe pumps in a dynamic generation system. *n*-Valeraldehyde vapors in gas bags were also generated. An exposure chamber was designed to allow measurement of face velocities, temperatures, exposing vapor concentrations, and RHs. Gas chromatography with flame ionization detection was used for sample analysis. The appropriate adsorption time for SPME coating PFBHA was determined to be 2 min and the desorption time for oxime formed after sampling was optimized to be 2 min. The experimental sampling constant was found to be $(3.86\pm0.13)\cdot10^{-2}$ cm^3/min and face velocity was not expect to have effect on the sampler.

Keywords: Time-weighted average sampling; Solid-phase microextraction; Air analysis; Valeraldehyde; Aldehydes; Pentafluorobenzylhydroxylamine

1. Introduction

Aldehydes play an important role in aquatic and atmospheric oxidation processes. In recent years, aldehydes with low molecular masses are receiving increasing attention as disinfection and oxidation by-products formed during drinking water treatment processes [1]. In atmospheric systems, aldehydes are ubiquitous products of combustion [2–6] and are mucous membrane irritants [7]. Formaldehyde, acetaldehyde, furfural, and crotonaldehyde are animal carcinogens [8]. Formaldehyde and glutaraldehyde expose embalmers [9,10], operating theater personnel [11] and pathologists [7]. Besides the aldehydes mentioned above, exposure to low-molecular-mass aldehydes, including acrolein, butyraldehyde, glyoxal, paraformaldehyde, propiolaldehyde, propionaldehyde, and valeraldehyde were also concerned by the US National Institute of Occupational Safety and Health (NIOSH) because these aldehydes may be used as substitutes for formaldehyde [12]. On the other hand, the chemical reactivity and mutagenicity of the low-molecular-mass aldehydes are similar to those of acetaldehyde and malonaldehyde while these two aldehydes were both

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potential occupational carcinogens [12]. The number of workers potentially exposed to acetaldehyde and butyraldehyde in the USA were estimated to be 281 000 and 750 000, respectively [12]. Not only in the workplace, people will also be exposed to low-molecular-mass aldehydes in the general environment. For example, *n*-valeraldehyde emits from particleboard [13] which will cause the problem of indoor air pollution.

n-Valeraldehyde is one of the low-molecular-mass aldehydes, exposures to which, concerned the NIOSH [12]. *n*-Valeraldehyde has a molecular mass of 86.13, and it is used in flavoring compounds, in resin chemistry, and as a rubber accelerator [14]. The production of *n*-valeraldehyde exceeds $454 \cdot 10^3$ kg annually in the USA, therefore it is on the US Environmental Protection Agency's (EPA) High Production Volume Chemical List [15].

n-Valeraldehyde is an ocular and dermal irritant [16]. The threshold limit value (TLV)/time-weighted average (TWA) of 176.1 mg/m^3 is recommended by the American Conference of Governmental Industrial Hygienists (ACGIH), and also a permissible exposure limit (PEL)-TWA of 176.1 mg/m^3 was established by the US Occupational Safety and Health Administration (OSHA) to protect workers from severe eye and skin irritation [8]. For the determination of *n*-valeraldehyde in air, the 2,4-dinitrophenylhydrazine (2,4-DNPH) solid sorbent method is recommended by the EPA [17] while 2-(hydroxymethyl) piperidine on XAD-2 solid sorbent tube was recommended by the NIOSH [18]. However, there were several drawbacks with these two methods. For example, nonreactive C_3–C_5 aldehydes are not collected quantitatively by the 2-(hydroxymethyl) piperidine method [18], and volatile acids reduce loading capacity. The 2,4-DNPH method potentially allows specific quantitation of different aldehydes and ketones through high-performance liquid chromatography–ultraviolet detection (HPLC–UV) of their hydrazones but not by gas chromatography (GC) since many hydrazones decompose at high temperatures. The 2,4-DNPH method does not react quantitatively with conjugated aliphatic aldehydes, can be light sensitive, and is of variable recovery on liquid aldehyde spiking [3].

Another commonly used method for sampling aldehydes (including *n*-valeraldehyde) is based on derivatization with *O*-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA). PFBHA has been used to analyze aldehydes in water because of its fast quantitative reaction to form oximes suitable for detection at the picogram (pg) level by gas chromatography–mass spectrometry (GC–MS) and gas chromatography–electron-capture detection (GC–ECD) [19]. The PFBHA method also has been used to chemisorb aldehydes and ketones in air samples by dynamic sampling and passive sampling [20–23].

However, the methods mentioned above all involve complex procedures for sample preparations (solvent desorption, 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 and coworkers [24,25]. SPME presents many advantages over conventional analytical methods by combining sampling, preconcentration, and direct transfer of the analytes into a standard gas chromatograph [26]. The air sampling and analysis methods with SPME have been applied to both grab and TWA modes [26–28]. Furthermore, sampling and analysis method which combined PFBHA with the SPME technique for formaldehyde in air have also been reported [28,29]. This approach is superior to currently available passive 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 [29]. However, only preliminary data were presented [28] and in-depth validation studies are required [29]. The research shown here designed a new user-friendly sampling device which increased the acceptance of using SPME device as a TWA sampler. The performance of the sampler on *n*-valeraldehyde was also validated.

2. Experimental

2.1. Materials

Valeraldehyde (99%), PFBHA, *n*-hexane, and methanol were purchased from Sigma–Aldrich (Milwaukee, WI, USA). Nitrogen, hydrogen and compressed air for GC–flame ionization detection (FID)

were ultra-high-purity (UHP) grade from Sanfu (Taiwan). Harvard syringe pump (Model 11), rotameters, and Tedlar gas bags were from Fisher Scientific (Tustin, CA, USA). A Whatman Zero Air generator was from Balston (Haverhill, MA, USA) to generate the air for standard gas generation system. A M-5 Mini-Buck calibrator for air flow-rate calibrations was from Buck Scientific (East Norwalk, CT, USA). A MiniRAE PGM-76 photoionization detection (PID) system was from RAE systems (Sunnyvale, CA, USA). A calibrated hot-wire anemometer was from Kanamox (Japan). All SPME fibers, holders and molecular sieve were from Supelco (Bellefonte, PA, USA). 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, 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 m×0.32 mm I.D., 1 μm film DB-5 chemically bonded fused-silica capillary column (J&W Scientific, Folsom, CA, USA) and an FID system. The carrier gas was nitrogen at a flow-rate of 2.0±0.2 cm^3/min in the 1:1 split mode. The temperature for the injector was 250 °C. The column temperature programs was: 105 °C for 0.5 min, 105 °C to 230 °C at 10 °C/min, and hold for 0.5 min. The detector temperature was 300 °C. Detector response factors were determined by syringe injection of standard solutions.

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 [25]. Fick's first law of diffusion was 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 [27]:

$$\mathrm{SR} = D_{\mathrm{AB}}(A/Z) \quad (1)$$

where SR is the sampling rate; Z is the retracted fiber path length; A is the surface area of the needle opening; D_{AB} is the diffusion coefficient of the analyte in the gaseous phase.

The fiber was retracted 0.3 cm in this research ($Z = 0.3$ cm) while surface area of the needle opening was 0.00086 cm^2 [27]. The diffusion coefficient of *n*-valeraldehyde in air can be estimated by the following equation [30]:

$$D_{\mathrm{AB}} = \frac{0.00143T^{1.75}}{PM_{\mathrm{AB}}^{1/2}\left[(\sum_V)_{\mathrm{A}}^{1/3} + (\sum_V)_{\mathrm{B}}^{1/3}\right]^2} \quad (2)$$

where D_{AB} is the binary diffusion coefficient of analyte in air in cm^2/s at T; T is the temperature, K; M_{A} and M_{B} are the molecular masses, g/mol; $M_{\mathrm{AB}} = 2[(1/M_{\mathrm{A}}) + (1/M_{\mathrm{B}})]^{-1}$; P is the external pressure, bar; Σ_V is the summation of atomic diffusion volumes, unitless; i is all the contributing species; A is air; B is the analyte.

Therefore diffusion coefficient for *n*-valeraldehyde in air at 25 °C and 1 atm was 0.0825 cm^2/s, theoretically [21] (1 atm = 101 325 Pa). The sampling rate SR of the sampler for *n*-valeraldehyde was then estimated to be $2.37 \cdot 10^{-4}$ cm^3/s ($1.42 \cdot 10^{-3}$ cm^3/min).

2.3.2. Sensing element of the sampler

A poly(dimethylsiloxane)–divinylbenzene (PDMS–DVB) SPME fiber (65 μm) was selected because it adsorbed PFBHA with greater reproducibility [28]. For the sensing element preparation, a solution of PFBHA (17 mg/cm^3) in aldehyde-free water was placed in 4-cm^3 PTFE-capped vials with a 1-cm stir bar [28]. The solution was stirred at 1100 rpm. Then the PDMS–DVB SPME fiber (65 μm) for GC was placed in the headspace of the solution above the center of the solution. To get the adsorption profile, the SPME fibers were exposed to the vapors of the aqueous for 5, 10, 20 and 30 min, respectively. Chromatographic peak areas and calibration curves were used for adsorbed PFBHA quantification. To ensure the desorption was complete when the SPME needle was inserted into the heated GC injector, different desorption times (including 0.5, 1, and 2

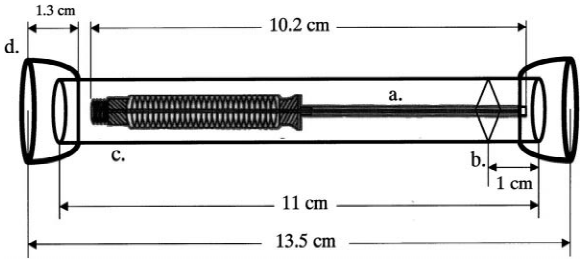

Fig. 1. Perspective view of the passive sampler: (a) SPME fiber assembly, (b) PTFE septum, (c) PTFE tubing, (d) cap/PTFE tape.

min) were tested to examine the desorption efficiencies.

2.3.3. Modified SPME device for diffusive TWA sampling

Both the commercially available SPME holder device and the SPME field sampler are too bulky and too risky (because of the needle) to be a good diffusive sampler with great user's acceptance. Therefore the SPME device should be modified for improved operation, and a new user-friendly device designs will benefit acceptance of the technology [29,30]. In this research, a modified SPME device was designed. After loading with PFBHA, the SPME fiber was retracted 3 mm into its needle housing. The SPME fiber assembly was then 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 and the tubing were capped by two caps lined with PTFE tape to avoid contamination (Fig. 1). The path length (Z) was 0.3 cm, the surface area was 0.00086 cm^2, the theoretical diffusion coefficient of *n*-valeraldehyde in air was 0.0825 cm^2/s, and the theoretical sampling rate SR for *n*-valeraldehyde was $1.42 \cdot 10^{-3}$ cm^3/min.

The cap near the needle, as shown in Fig. 1, was opened only when exposing the sampler to the exposure chamber. After sampling, the cap was closed again. The fiber assembly in the PTFE tubing was removed and assembled with the SPME holder right before the GC analysis was performed.

2.3.4. Vapor exposures

Two different vapor exposure systems were used to validate the designed diffusive TWA sampler. One was the air bag method [20] which allowed direct insertion of the SPME fiber. The other one was the dynamic vapor generation system. The vapor generator, air dilution system, and exposure chamber were shown in Fig. 2 while more details have been described elsewhere [21]. The air generator was connected to the vapor and water generation sites.

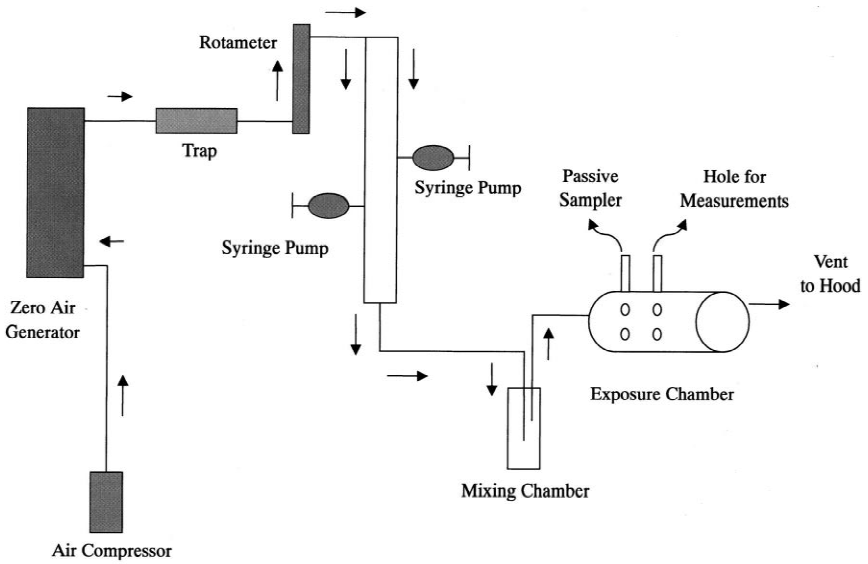

Fig. 2. Vapor generation and exposure system.

The generators were syringe pumps set at known plunger velocities to generate the desired concentration of organic vapor for dilution, or relative humidity (RH) for humidification. Heating tape wrapped around the outside of the stainless steel tubing at the needle exit from the syringe pumps ensured total volatilization of organic vapor or water. The two streams were then routed through a stainless steel T-joint adapter, and the outlet connected by PTFE tubing to a Greenburg–Smith impinger which acted as a mixing chamber. PTFE tubing then conveyed the diluted organic vapor into the exposure chamber through a hole bored on the side of the chamber, and a fan was installed next to the inlet of the chamber. The exposure chamber was made by a glass cylindrical vessel (45 cm×11 cm I.D.×12 cm O.D.) and the fan was connected to a variac which allowed different fan blade velocities and hence face velocities, as well as adequate mixing.

In the air bag method, *n*-valeraldehyde of 1409 mg/m^3 (equivalent to eight times TLV/TWA) was prepared and the sampler was inserted into the air bag for 10, 20, 30 and 60 min, respectively. During the exposures, the air bag stayed still on the laboratory bench without any movement and all the experiments were performed in triplicates. In dynamic vapor generation system, 1409 mg/m^3 of *n*-valeraldehyde was also prepared and four samplers were inserted into the chamber at the same time (as shown in Fig. 2). The diffusive samplers were exposed for 10, 20, 30, 45, 60 and 90 min, respectively. There was a closable hole nearby the samplers in the chamber wall for probe insertion to measure RH, temperature, organic vapor concentration, and face velocity. The relative humidities, temperature, and face velocities during experiments were 23±3%, 23.6±1.6 °C and 0.17±0.02 m/s, respectively. The calibrated PID system was used to monitor the chamber *n*-valeraldehyde concentrations. The total mg m^{-3} h was obtained by summing the area under the mg/m^3 versus time exposure plots.

After exposures, the fiber assembly in the diffusive sampler was removed and assembled with the SPME holder. The needle of the SPME was directly inserted into the injector of the Perkin-Elmer Autosystem XL chromatograph for analysis. Detector response factors were determined by syringe injection of standard solutions.

2.4. Synthesis of PFBHA-valeraldehyde oxime and standard solutions in hexane

The oxime formed from the reaction between PFBHA and *n*-valeraldehyde was synthesized using a modified literature method [19]. Injection of the oxime into the GC–FID system showed the purity was 99.0±0.9% (based on FID response). Standard PFBHA-valeraldehyde oxime solutions (93.9–9390 ng/mm^3) were prepared for GC–FID calibration. Method detection limits (defined as the amount of analyte giving 3 times the background response) for *n*-valeraldehyde was 27 ng.

3. Results and discussion

The condition for thermal desorption of the SPME fiber was first optimized before the determination of the adsorption time needed for sensing element preparation. The desorption efficiency was found to be 99.96% when the desorption time was 2 min. For adsorption time, as shown in Fig. 3, the capacity of the sampler was not reached even the time for headspace extraction was 30 min. However, the trend for reaching capacity was observed. The mass of PFBHA loaded on the fiber was 17.65 μg when the loading time equaled 2 min. Assuming the stoichiometry between *n*-valeraldehyde and PFBHA was 1:1 and the theoretical sampling rate SR of the designed diffusive sampling for *n*-valeraldehyde was $1.42 \cdot 10^{-3}$ cm^3/min, 17.65 μg of PFBHA can provide the reaction needed when sampling at *n*-valeraldehyde concentration of 176.1 mg/m^3 (TLV/TWA) for 380 h. It was more than sampling needed

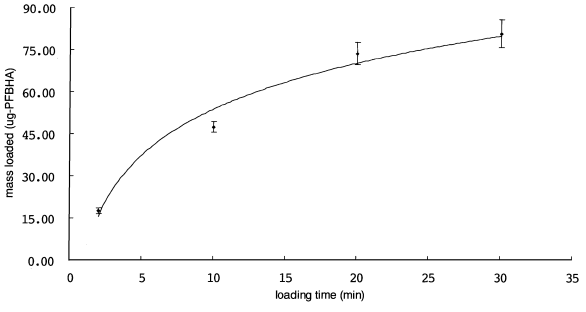

Fig. 3. PFBHA loading time versus mass loaded.

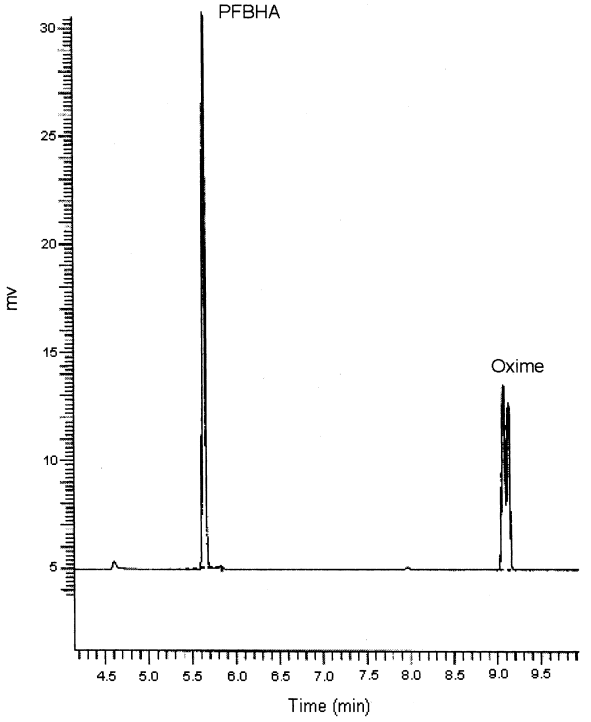

Fig. 4. Chromatogram of sample injection.

and therefore the time for headspace extraction was determined to be 2 min even the capacity was not reached.

Fig. 4 showed the typical chromatogram of vapor exposure sample from SPME direct injection. It was observed that there were syn and anti isomers of the oxime because *n*-valeraldehyde was an asymmertrical carbonyl compound. Fig. 5 shows the vapor exposure results from air bag methods while Fig. 6 shows the exposure results from the standard gas

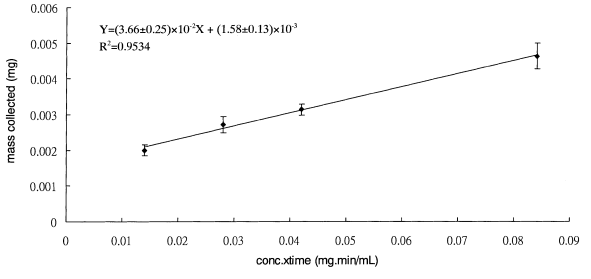

Fig. 5. Vapor exposures from gas bag.

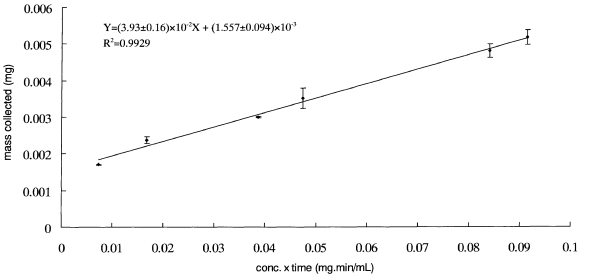

Fig. 6. Vapor exposures from standard gas generation system.

generation system. By doing simple linear regressions, the slopes of these two regression lines were $(3.66\pm0.25)\cdot10^{-2}$ and $(3.93\pm0.16)\cdot10^{-2}$ cm^3/min, respectively, which actually stand for the experimental sampling rates of the sampler. These two sampling constants showed no statistical difference ($P \cong 0.15$).

The sampler designed in this research weighed around only 8.73 g while the commercial SPME holder weighed roughly 39 g. On the other hand, the risky needle of SPME device was kept in a PTFE tubing which increased the acceptance of the technique.

Theoretically, the sampler in this study can also be applied to sample other aldehydes and/or ketones because the reactions between PFBHA and carbonyl compounds were alike. If more PFHBA are needed for the reaction, increasing loading time in sensing element preparation will add more PFBHA onto the SPME fiber.

Several diffusive sampling methods for aldehydes can be found from the literature, including the DNPH method [31] and the PFBHA method [21,22]. However, these methods all involved complex procedures for sample preparations (solvent desorption, for example) and therefore were very time-consuming. The sampler designed in this research avoided these drawbacks because it utilized the SPME device which combined the processes of sampling and preconcentration.

NIOSH protocol was usually used for the evaluation of diffusive sampler [32]. Parameters to be evaluated including face velocity, relative humidity, shelf life, and sample stability, etc. From Fig. 4 and Fig. 5, the slopes of two regression lines were $(3.66\pm0.25)\cdot10^{-2}$ and $(3.93\pm0.16)\cdot10^{-2}$ cm^3/min,

respectively, which showed no statistical difference ($P \cong 0.15$). One of the differences between air bag method and standard gas generation system was air movement. The face velocities in standard gas generation system were 0.17 ± 0.02 m/s while it was basically zero in air bag system. The results from two regression lines suggested that face velocities have no effect on the sampler because no difference in sampling rate was observed. For the effects of other parameters in NIOSH protocol, no specific evaluation was performed in the current research and more studies will be needed.

The theoretical diffusion coefficient of *n*-valeraldehyde in air was 0.0825 cm^2/s, and the current sampler's theoretical sampling rate SR for *n*-valeraldehyde was $1.42 \cdot 10^{-3}$ cm^3/min. The experimental sampling rate was $(3.86 \pm 0.13) \cdot 10^{-2}$ cm^3/min if both data from Fig. 4 and Fig. 5 were combined. The experimental sampling rate was more than 27 times higher than the theoretical sampling rate. The bias from the estimation of diffusion coefficient could be ruled out because the experimental diffusion coefficient of *n*-valeraldehyde was found to be 0.062 cm^2/s (25% lower than estimation) [21]. The possible explanation for this difference might be the errors from the estimation of sampler's path length and surface area. The SPME fiber can be retracted at any desired distance from the opening of the needle. This means that there must be some space between the fiber and the wall of the needle. Therefore, *n*-valeraldehyde will be able to diffuse to not only the cross-section of the fiber but also the whole surface area of the 1-cm long SPME fiber. The cross-section area of the fiber was 0.00086 cm^2 while the whole surface area of the fiber was around 0.1 cm^2. Therefore the mass collected by the sampler was far more than expected and the experimental sampling rate was higher than the theoretical sampling rate.

4. Conclusions

The research shown here designed a new user-friendly sampling device which increased the acceptance of using SPME device as a TWA sampler for *n*-valeraldehyde. TWA sampling by SPME requires no pumps and no solvents, which reduces the sampling costs and the time for sample analysis.

The diffusive sampling with the SPME device has an advantage over other methods. The SPME fiber can be retracted to different path lengths therefore the same sampling device can be used for TWA sampling over a large range of analyte concentrations. However, the theoretical estimation of the sampling rate could lead to great errors and experimental calibration is a must.

Acknowledgements

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