Journal of Chromatography A, 1338 (2014) 17–23

Contents lists available at ScienceDirect

Journal of Chromatography A

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

Cooled membrane for high sensitivity gas sampling

Ruifen Jiang[1], Janusz Pawliszyn*

Department of Chemistry, University of Waterloo, Waterloo, ON, Canada N2L 3G1

ARTICLE INFO

Article history:
Received 30 December 2013
Received in revised form 24 February 2014
Accepted 25 February 2014
Available online 2 March 2014

Keywords:
Sample preparation
Solid phase microextraction (SPME)
Cooled extraction phase
Thin film
Gas chromatograph–mass spectrometry

ABSTRACT

A novel sample preparation method that combines the advantages of high surface area geometry and cold surface effect was proposed to achieve high sensitivity gas sampling. To accomplish this goal, a device that enables the membrane to be cooled down was developed for sampling, and a gas chromatograph–mass spectrometer was used for separation and quantification analysis. Method development included investigation of the effect of membrane temperature, membrane size, gas flow rate and humidity. Results showed that high sensitivity for equilibrium sampling, such as limonene sampling in the current study could be achieved by either cooling down the membrane and/or using a large volume extraction phase. On the other hand, for pre-equilibrium extraction, in which the extracted amount was mainly determined by membrane surface area and diffusion coefficient, high sensitivity could be obtained by using thinner membranes with a larger surface and/or a higher sampling flow rate. In addition, humidity showed no significant influence on extraction efficiency, due to the absorption property of the liquid extraction phase. Next, the limit of detection (LOD) was found, and the reproducibility of the developed cooled membrane gas sampling method was evaluated. Results showed that LODs with a membrane diameter of 19 mm at room temperature sampling were 9.2 ng/L, 0.12 ng/L, 0.10 ng/L for limonene, cinnamaldehyde and 2-pentadecanone, respectively. Intra- and inter-membrane sampling reproducibility revealed RSD% lower than 8% and 13%, respectively. Results uniformly demonstrated that the proposed cooled membrane device could serve as an alternative powerful tool for future gas sampling.

1. Introduction

Solid phase microextraction (SPME) is an attractive air sampling technique that has been reported for active sampling of volatile and semi-volatile compounds, using commercial fibers such as polydimethylsiloxane (PDMS) [1,2], PDMS/divinylbenzene (DVB) [3,4] and PDMS/Carboxen [5,6]. The results obtained by the SPME sampling were compared with the ones done by EPA (Environmental Protection Agency) [1,7] and NIOSH (National Institute for Occupational Safety and Health) standard air sampling methods [3,4,6], and demonstrated to be accurate. Compared with traditional air sampling methods such as whole-air sampling and sorbent tube sampling [8–12], SPME is a simpler, faster, and lower-cost method that combines sampling, sample pre-concentration, clean-up and injection into one step. In addition, selective sampling reduces high background results obtained due to the complexity of real air.

In spite of the aforementioned advantages, it is quite challenging to achieve high sensitivity for gas analysis with traditional SPME fibers due to the small volume of the extraction phase. In the literature, several techniques including stir bar sorptive extraction (SBSE) [13,14], needle trap (NT) [15] or microextraction packed sorbent (MEPS) [16], cold fiber SPME [17] and thin film microextraction (TFME) [18,19] have been developed to improve the sensitivity of SPME. High sampling sensitivity was achieved by either decreasing the coating temperature (cold fiber), or by using an extraction phase with a larger surface area-to-volume ratio (SBSE, TFME, NT and MEPS). Among them, cold fiber SPME and TFME have been used for aqueous [20,21] and solid sample analysis previously [17,22,23]; however, few works have been reported for gas/air sampling because of the limitations of both experimental set-ups. In cold fiber SPME, a large external device (CO_2 cylinder) restricts on-site air sampling applications. Although a potential cold fiber device with an electric coolant source was investigated, difficulties in controlling the temperature, as well as the small volume of the extraction phase, limited any further improvement on the sensitivity of the technique for gas sampling [24]. As for TFME, no sampling device has yet been developed for gas sampling. In the literature, thin film was simply placed in the gas matrix during sampling, but uncontrollable sampling flow rates resulted in

---

* Corresponding author. Tel.: +1 519 888 4641; fax: +1 519 746 0435.
E-mail addresses: jruifen@gmail.com (R. Jiang), janusz@sciborg.uwaterloo.ca, janusz@uwaterloo.ca (J. Pawliszyn).

[1] Present address: C619, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou, Guangdong 510275, China.

http://dx.doi.org/10.1016/j.chroma.2014.02.070

difficulties in calibration [25]. Another limitation of TFME comes from its lack of commercially available thin films that can be used for gas chromatography direct thermal desorption. To date, only PDMS thin films are available for this purpose; however, PDMS suffers from a lack of extraction efficiency in regards to highly volatile and polar compounds. This limitation was illustrated in a paper published by Eom et al. [25], in which thin film was used to sample air infected with *Cimex lectularius* L. Comparative results were obtained for SPME fiber, needle trap and thin-film sampling; thin film was shown to lack extraction efficiency toward highly volatile analytes when compared to CAR/DVB/PDMS fiber and needle trap SPME. Reasons for the phenomenon include the low extraction efficiency of the PDMS membrane toward volatile compounds and a potential loss of compounds during transportation due to the low extraction affinity.

In this research work, the advantages of both cold fiber SPME and TFME were combined to further improve extraction efficiency by cooling down the thin film during sampling. A homemade extraction unit was designed to accomplish the sampling process and the sampling conditions. Three fragrance compounds (limonene, cinnamaldehyde and 2-pentadecanone), representing different volatilities, were chosen as target compounds in the investigation of the developed cooled membrane device.

2. Theory

Solid phase microextraction is based on the distribution of analytes between sample matrix and extraction phase, with the ultimate goal of reaching equilibrium between phases. For direct extraction, the equilibrium extraction amount and the equilibrium time can be determined by Eqs. (1) and (2), respectively [26],

$$n = \frac{K_{es}V_eC_sV_s}{K_{es}V_e + V_s} \tag{1}$$

$$t_{95\%} = 3 \times \frac{\delta K_{es}(b-a)}{D_g} \tag{2}$$

$$\left(\frac{\mathrm{d}n}{\mathrm{d}t}\right) = \left(\frac{D_gA}{\delta}\right)C_st \tag{3}$$

where n is the equilibrium extracted amount; V_e the volume of the extraction phase; K_{es}, the distribution coefficient; V_s, the volume of the sample and C_s, the concentration of the sample matrix. In Eq. (2), $t_{95\%}$ is the equilibrium time, δ and $(b-a)$ are the thickness of the boundary layer and coating, respectively, D_g is the diffusion coefficient, A is the surface area of the extraction phase while $(\mathrm{d}n/\mathrm{d}t)$ is the initial extraction rate.

Thin film microextraction enhances sampling efficiency by using a piece of thin film to increase the volume of the extraction phase. Because of the thinness of the film (δ), a short equilibrium time ($t_{95\%}$ can be achieved. Furthermore, Eq. (3) shows that a larger surface area results in faster sampling rates. Therefore, with thin film configuration, TFME can achieve higher extraction efficiency without sacrificing sampling time.

Cold fiber SPME enhances sensitivity by improving the distribution coefficient. The high distribution coefficient is achieved by cooling down the extraction phase and heating the sampling matrix. The low coating temperature and the temperature gap between the fiber and the sample enhances the distribution coefficient, as shown in Eq. (4) [17],

$$K_T = K_0\frac{T_s}{T_e}\exp\left[\frac{C_p}{R}\left(\frac{\Delta T}{T_e} + \ln\frac{T_e}{T_s}\right)\right] \tag{4}$$

where K_T is the cold fiber distribution coefficient; K_0 is the extraction phase/sample matrix distribution coefficient of the analystes when the extraction phase and headspace temperature are both at T_e, which is extraction phase temperature. $\Delta T = T_s - T_e$; C_p and R are the constant pressure heat capacity of the analyte and the gas constant, respectively.

3. Experimental

3.1. Reagents and supplies

The compounds limonene, cinnamaldehyde, 2-pentadecanone and benzene were purchased from Sigma-Aldrich (Mississauga, ON, CA). Acetone used for preparation of the standard solution was obtained from Caledon Laboratories Ltd. (Georgetown, ON, CA). Two types of Teflon tube with wall thicknesses of 279 μm and 483 μm were purchased from Weico Wire & Cable, INC. (Edgewood, NY, USA). A sheet of PDMS membrane with a thickness of 102 μm was obtained from Specialty Silicone Product (Ballston Spa, NY, USA). Membranes were cut in a round shape with different diameters, and preconditioned in a GERSTEL® thermal conditioner under a nitrogen flow for 5 h at 200 °C, and 5 h at 250 °C prior to use. Ultra-pure helium and nitrogen were purchased from Praxair (Waterloo, ON, CA). A thermoelectric cooler was purchased from TE technology (Traverse city, Michigan, USA).

3.2. Instruments

The analytical instruments used for separation and quantification were an Agilent 6890 gas chromatograph (GC) and a 5973 quadrupole mass spectrometer (MS) (Agilent Technologies, Mississauga, ON, Canada) coupled with a GERSTEL® Multi-purpose sampler. A cooling injection system 4 (CIS 4) and twister desorption unit (TDU) were used for membrane analysis (GERSTEL, Mülheim an der Ruhr, GE.). The TDU was connected to the CIS, which served both as a cryofocusing trap, and as a temperature programmed GC inlet. After sampling, the membrane was inserted into the TDU tube by tweezers or other methods, and placed in the TDU tray. The autosampler picked up the tube from the tray and inserted it into the TDU. Then, the temperature of the TDU was elevated to desorb the analytes from the membrane, while the CIS was kept at low temperature to trap the desorbed compounds. Last step was to enhance the CIS temperature to introduce the trapped analytes into the GC column. The GC oven, CIS, and TDU conditions are shown in Table 1. For different experiments, chromatographic separation was performed with a 30 m × 0.25 mm I.D. × 0.25 μm thickness SLB™-5 fused silica column from F Supelco (Sigma-Aldrich, Mississauga, ON, CA). Helium was used as a carrier gas. The temperatures for the GC–MS transfer line, MS quadrupole analyzer and MS ionization source were set at 280 °C, 150 °C and 230 °C, respectively. The MS system was operated in electron ionization mode, and mass fragments were collected at an *m/z* 35–350 range.

3.3. Standard gas generator

Evaluation experiments were conducted in a homemade permeation-based standard gas generator. The permeation tubes were prepared by encapsulating pure analytes inside the Teflon tubing, then capped with solid Teflon plugs and Swagelok caps. Two types of Teflon tubes with different thicknesses were used for different compounds with varied volatilities. Further details on the preparation of the permeation tubes can be found elsewhere [27]. Next, the prepared permeation tubes were placed inside the permeation chamber, which was swept by a constant ultra-pure nitrogen flow. The flow rate was controlled by a Sidetrack™ mass flow controller (Sierra Instruments, Monterey, CA). The permeation chamber was held inside an oven; the temperature inside the oven was controlled by an electric heat control device designed and constructed by the Electronic Science Shop (University of Waterloo, CA).