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Determination of ethylene oxide by solid-phase microextraction device with on-fiber derivatization

Shih-Wei Tsai*, Kai-Kuang Wu

Department of Occupational Safety and Health and Institute of Environmental Medicine, China Medical College 91, Hsueh-Shih Road, Taichung, Taiwan

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Abstract

The solid-phase microextraction (SPME) device was used as a time-weighted average (TWA) sampler for ethylene oxide. Carboxen/polydimethylsiloxane (CAR/PDMS) fiber was used and hydrogen bromide (HBr) was loaded onto the fiber. The SPME fiber assembly was then inserted into PTFE tubing to improve the wearer's acceptance as a diffusive sampler. Known concentrations of ethylene oxide around the threshold limit values (TLVs)/time-weighted average and specific relative humidities (RHs) were generated by syringe pumps in a dynamic generation system. Ethylene oxide 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–mass spectrometry (GC–MS) was used for sample analysis. The appropriate adsorption time for SPME coating HBr was found to be 30 s and the desorption time for 2-bromothanol formed after sampling was determined to be 5 min. The experimental sampling constant of the sampler was found to be $(2.96\pm0.09)\times 10^{-2}$ cm^3/min, while face velocity (0–0.25 m/s) as well as RHs (10–80%) were not expected to have effects on the sampler.

Keywords: Derivatization, GC; Solid-phase microextraction; Ethylene oxide

1. Introduction

Ethylene oxide (EtO; C_2H_4O; epoxyethane; oxirane) is a colorless gas at room temperature with an ether-like odor at concentrations above 895–1253 mg/m^3 [1]. The odor threshold for EtO is 442 mg/m^3 [1]. Ethylene oxide is processed in various applications, for example, in the production of ethylene glycol, or as the starting material for the manufacturing of acrylonitrile and nonionic surfactants [2]. Ethylene oxide is also used to sterilize surgical instruments, as a fumigant for foodstuffs and textiles, and as an agricultural fungicide [2]. According to the US Environmental Protection Agency (US EPA), EtO is among the top 3% of high-volume chemicals produced in the US [3]. Exposure to EtO has been reported predominantly in workers occupied in sterilization units, whereas contact with EtO during chemical syntheses is presently unlikely to occur [4]. The US National Institute for Occupational Safety and Health (NIOSH) estimated that 270 000 US workers are potentially exposed to ethylene oxide, with the largest concentration being

*Corresponding author. Fax: +886-4-2202-3481.
E-mail address: shihwei@mail.cmc.edu.tw (S.-W. Tsai).

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in the health care industry [5]. EtO irritates the eyes and skin; it may also irritate mucous membranes and cause a strange taste in the mouth [1]. EtO may cause allergies, adverse reproductive effects, and possibly asthma [1]. EtO is also a known human carcinogen, a potential reproductive hazard, an allergic sensitizer, and a potent neurotoxin [6]. The US Occupational Safety and Health Administration (OSHA) promulgated an ethylene oxide health standard with a work-shift 1.79 mg/m^3 permissible exposure limit and 0.895 mg/m^3 action level in 1984 [7] and revised in 1988 to add a 8.95 mg/m^3 short-term excursion limit [8], while the American Conference for Governmental Industrial Hygienists (ACGIH) has set up a threshold limit value (TLV) of 1.79 mg/m^3 EtO for workplace air [9].

For the determination of ethylene oxide in air, many methods have been developed. For example, a charcoal tube was used for sampling and carbon disulfide was used for desorbing EtO [10], an acid bubbler filled with ethylene glycol was used for sampling and followed by colorimetric analysis [11], and Ambersorb XE347 coated hydrobromic acid (HBr) was used to collect EtO as 2-bromoethanol [12]. Gas chromatographs equipped with photoionization detectors (PIDs) and other field instruments based on infrared (IR) absorbance or flame ionization detection (FID) were also available [13]. Besides, a hydrobromic acid-coated charcoal tube method was recommended by both OSHA and the US National Institute for Occupational Safety and Health (NIOSH) [14,15]. The reaction of EtO with HBr to produce 2-bromoethanol was frequently utilized in the sampling and analysis methods mentioned above because lower detection limits, good recoveries and sample stabilities can be obtained [12,14–16].

The major drawback from the methods of OSHA and NIOSH is the complexity of experimental procedures. Derivatizing an aliquot sample of 2-bromothanol with heptafluorobutyrylimidazole (HFBI) in isooctane to form 2-bromoethyl heptafluorobutyrate was required because acid matrix gave a non-reproducible detector response [14] and long analysis time were required to separate 2-bromoethanol from excess HBr [16]. To overcome the inconvenience, a 30 m×0.25-mm I.D., 0.25-μm film DB-225 chemically bonded fused-silica capillary column (J&W Scientific, Folsom, CA, USA) with gas chromatography–mass spectrometry (GC–MS) was used after solvent desorption [17], instead of 3-m×4-mm glass, 10% SP-100 on 80/100 Chromosorb WHP column with gas chromatography–electron capture detection (GC–ECD) used in the NIOSH method [15]. The improvements from column separation and selected ion monitoring (SIM) detection of GC–MS increase the reproducibility of direct 2-bromomethanol analysis and avoid the need for further derivatization [17].

All the methods mentioned above 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 [18,19]. SPME presents many advantages over conventional analytical methods by combining sampling, preconcentration, and direct transfer of the analytes into a standard gas chromatograph (GC) [20]. The air sampling and analysis methods with SPME have been applied to both grab and time-weighted average (TWA) modes [20–22]. 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 [23]. To increase the acceptance of using an SPME device as a time-weighted (TWA) sampler, a user-friendly sampling device has recently been reported for the analysis of *n*-valeraldehyde in air [24]. The research shown here extended the new design to the validation of EtO sampling where HBr was first loaded onto the SPME fiber and direct 2-bromoethanol analysis was performed to determine the amounts of EtO collected.

2. Experimental

2.1. Materials

Ethylene oxide, 50 000 μg/ml in methanol, was purchased from Supelco (Bellefonte, PA, USA). Methanol and 2-bromoethanol were purchased from Sigma–Aldrich (Milwaukee, WI, USA). Dichloromethane, and 1-pentanol were from Wako Pure Chemical Industries (Osaka, Japan). Hydrogen bromide,

48% (w/w) aqueous solution, was from Lancaster (Eastgate, White Lund, Morecambe, UK). Helium for GC–MS was 99.999% purity from Sanfu (Taiwan). A 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 calibrated hot-wire anemometer was from Kanamox Instrument (Japan). All solid-phase microextraction (SPME) fibers, holders and molecular sieve were from Supelco (Bellefonte). 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×0.25-mm I.D. 0.25-μm film DB-225 chemically bonded fused-silica capillary column (J&W Scientific, Folsom, CA, USA) linked with the 70 eV electron impaction source of a Perkin-Elmer Turbo Mass, mass spectrometer. The carrier gas was helium with flow-rate of 1.0±0.1 ml/min in the 1:4 split mode. The temperature for the injector was 250 °C. The column temperature programs was: 60 °C for 3 min, 60–180 °C at 25 °C/min, and hold for 1 min. The temperature of the mass spectrometer was 220 °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 [19]. 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 followed [21]:

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

where SR is the sampling rate; Z is the retracted fiber path length; A is the surface area of the needle opening; and 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 [21]. Diffusion coefficient of EtO in air can be estimated by the following equation [25]:

$$D_{\mathrm{AB}} = \frac{0.00143 \times T^{1.75}}{P M_{\mathrm{AB}}^{1/2} [(\sum_V)_{\mathrm{A}}^{1/3} + (\sum_V)_{\mathrm{B}}^{1/3}]^2}$$

where D_{AB} is the binary diffusion coefficient of analyte in air in cm^2/s at T; T is temperature, K; M_{A} and M_{B} are molecular mass, 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 EtO in air at 25 °C and 1 atm was 0.155 cm^2/s, theoretically. The sampling rate SR of the sampler for EtO was then estimated to be 4.45×10^{-4} cm^3/s (2.67×10^{-2} $\mathrm{cm}^3/\mathrm{min}$).

2.3.2. Sensing element of the sampler

Three different kinds of SPME fibers including poly(dimethylsiloxane)/divinylbenzene (PDMS/DVB), carboxen/polydimethylsiloxane (CAR/PDMS) and carbowax/divinylbenzene (CW/DVB) were examined to establish one that would provide the highest loading and stability of HBr and 2-bromoethanol retention characteristics. For the sensing element preparation, HBr aqueous solutions with different concentrations including 48% (w/w), 33, 30, 25 and 20% were placed in 4-ml PTFE-capped vials with 1-cm stir bars, respectively. The solutions were stirred at 1100 rpm. Two different time periods were tested, including 5 min and 30 s, for the SPME fibers to be placed in the headspace of the HBr solutions for extraction. After the coating of HBr, the fibers were then inserted into another 4-ml PTFE-capped vials filled with 2 ml of 0.05 mg/ml EtO

solution and stirred at 1100 rpm. To estimate the amount of HBr loaded on the fiber, the SPME fibers were exposed to the EtO vapors of the aqueous for 5, 10, 30, 60 and 120 min, respectively. Chromatographic peak areas and calibration curves were used for adsorbed 2-bromoethanol quantification. To ensure the desorption was complete when the SPME needle was inserted into the heated GC injector, different desorption times were tested to examine the desorption efficiencies.

2.3.3. Modified SPME device for diffusive TWA sampling

A new modified SPME device to increase the acceptance of using SPME device as a TWA sampler has recently been reported [24]. In this research, the modified SPME device was extended to the validation of EtO sampling. After loading with HBr, 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 EtO was 0.155 cm^2/s, and the theoretical sampling rate SR for EtO was 2.67×10^{-2} cm^3/min.

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 [26] which allowed direct inserting of the SPME fiber. The other one was the dynamic vapor generation system. The vapor generator, air dilution system, and exposure chamber are shown in Fig. 2 [24,27]. The air generator was connected to the vapor and water generation sites. The generators were syringe pumps set at known plunger velocities to generate the desired concentration of EtO for dilution, or 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 EtO solution 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 EtO 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$\times$11 cm I.D.$\times$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.

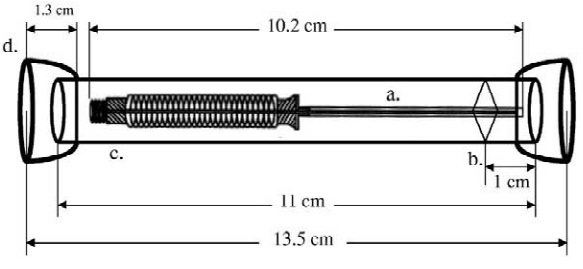

Fig. 1. Perspective view of the passive sampler: (a) SPME fiber assembly, (b) PTFE septum, (c) PTFE tubing, (d) cap/PTFE tape.

In the air bag method, EtO of 14.38 mg/m^3 (equivalent to eight times TLV-TWA) was prepared and the sampler was inserted into the air bag for 10, 30, 40, 50, 60 90, 100, and 120 min, respectively. During exposures, the relative humidities and temperatures were 10$\pm$2% and 23.6$\pm$1.6 °C, respectively, while the air bags stayed still on the lab bench without any movement and all the experiments were performed in triplicate. Another air bag method similar to the system mentioned above but with RH of 80% instead was used as well to determine the effect of relative humidity. On the other hand, 14.38 mg/m^3 of EtO was also prepared in dynamic vapor generation system and four samplers were inserted into the chamber at the same time (as shown in Fig. 2). The diffusive samplers were exposed for 10, 30, 40, 50 and 90 min, respectively. Besides the tests on 14.38 mg/m^3, EtO of 0.89, 1.79, and 3.58 mg/m^3 (equivalent to 0.5, 1, and 2 times TLV-TWA) were generated as well by the dynamic system and the diffusive sampler were exposed for 1, 2, 3, 4, 6, and 8 h, respectively. There was a closable hole nearby the samplers in the chamber wall for probe insertion to measure RH, temperature, and face velocity. The relative humidities, temperature, and face velocities during experiments were 10$\pm$2%, 23.6$\pm$1.6 °C and 0.25$\pm$0.02 m/s, respectively. The concentrations of EtO from dynamic vapor generation system were

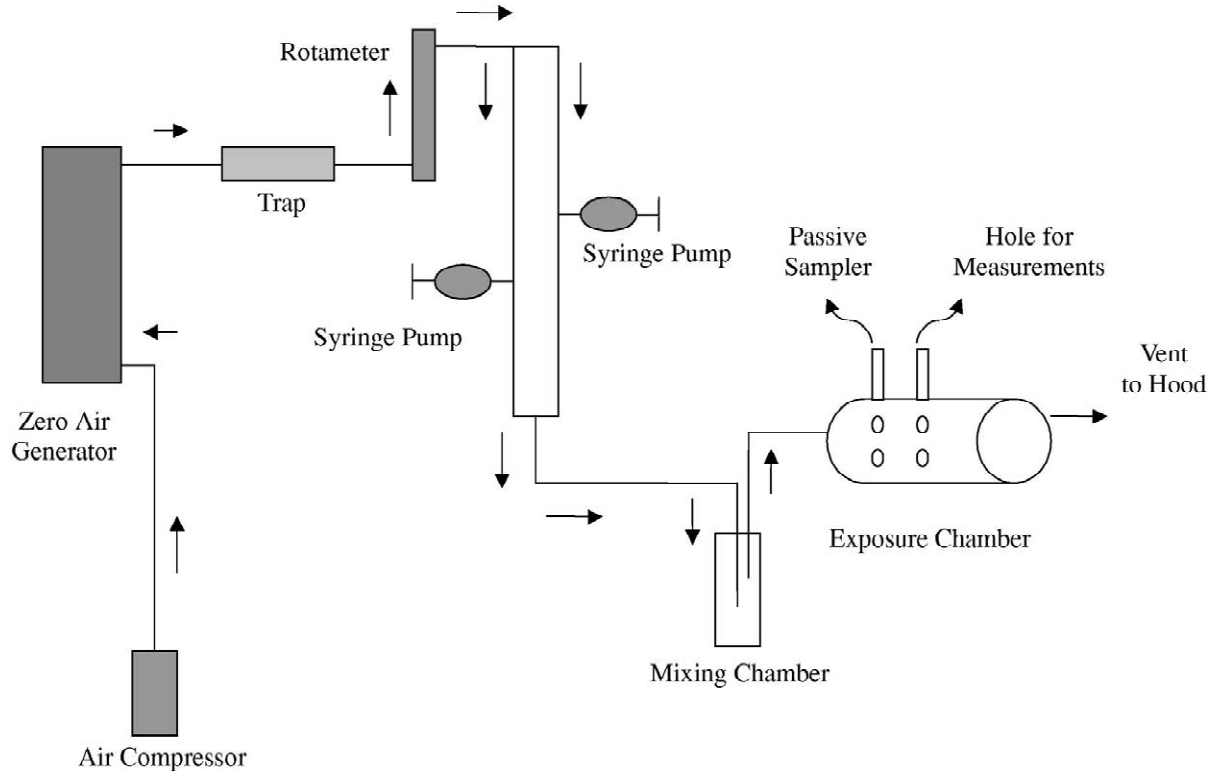

Fig. 2. Vapor generation and exposure system.

monitored periodically by collecting the vapors with gas bags and followed by the sampling procedures as mentioned in the air bag method. The total mg m^{-3} h during exposures were 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 internal standard solution (1:100, v/v) was prepared by dissolving 1-pentanol into a mixture of methanol and dichloromethane (9:1, v/v) [17]. The solution was then placed in a 4-ml PTFE-capped vial with a 1-cm stir bar and stirred at 1100 rpm. The needle of the SPME was inserted into the injector of GC–MS for analysis after 1 min headspace extraction of the internal standard solution.

2.4. Standard 2-bromoethanol solutions in a mixture of methanol and dichloromethane

Standard 2-bromoethanol solutions (3.5–175 ng/μl) were prepared for GC–MS calibration by dissolving 2-bromoethanol into a mixture of methanol and dichloromethane (9:1, v/v) [17]. Selective ion monitoring utilized *m/z* 31, 42 and 45 while total ion monitoring utilized *m/z* 20 through 200. Method detection limits (defined as the amount of analyte giving three times the background response) for 2-bromoethanol was 0.31 ng.

3. Results and discussion

For all the fibers tested in this research (including PDMS/DVB, CW/DVB and CAR/PDMS), 2-bromoethanol were detected after the fibers were first exposed to 48% HBr solution for 5 min followed by the headspace extraction of EtO solution. However, severe fiber damages after 5 min loading of 48% HBr solution were observed for both PDMS/DVB and CW/DVB, while minor damage was observed for CAR/PDMS, too. The mass of 2-bromoethanol collected on the fiber also decreased as

Table 1
Stability tests on PDMS/DVB-coated HBr fiber[a]

Intervals between HBr and EtO extraction (min)	Mass of 2-bromoethanol formed[b] (mg)	Recovery[c] (%)
0	3.67×10^{-3}	100
20	8.04×10^{-4}	21.8
30	2.31×10^{-4}	6.2

[a] PDMS/DVB fiber was first exposed to 5 min of 48% HBr solution for headspace extraction, then waited for certain period of time followed by 5 min of 0.05 mg/ml EtO solution for headspace extraction and analyzed with GC–MS.
[b] All the mass were shown as mean with $n=3$ and C.V.$<10\%$.
[c] Compared with intervals = 0 min.

the intervals between HBr and EtO exposures increased for PDMS/DVB (Table 1). It suggested that the stability of PDMS/DVB-coated HBr was unacceptable for sampling needs. To decrease the possibility of fiber damages, different concentrations of HBr solutions for 5 min headspace extraction were tested and Table 2 shows the results. Severe damages were again observed for PDMS/DVB and CW/DVB while minor damage was observed for CAR/PDMS. Besides, the mass of 2-bromoethanol collected were dramatically dropped as the concentration of HBr solution decreased (Table 2). Another attempt to avoid the damage of fibers was to decrease the time period for HBr headspace extraction. When the concentration of HBr solution was 48% and the time for its headspace extraction was changed to 30 s, no more damage was found for CAR/PDMS while minor damages were still observed for both PDMS/DVB and CW/DVB. Furthermore, the mass of 2-bromoethanol collected on the CAR/PDMS fiber remained stable even the intervals between HBr and EtO exposures increased (Table 3). Therefore CAR/PDMS with 30 s of 48% HBr headspace extraction was used for the following validation.

Table 2
Loading abilities of fibers at different HBr concentrations[a]

Fiber types	Conc. of HBr (%)	Mass of 2-bromoethanol formed[b] (mg)
CW/DVB	48	2.60×10^{-3}
	35	1.27×10^{-4}
	30	7.10×10^{-5}
	25	6.12×10^{-5}
	20	$<1.23\times10^{-5}$
CAR/PDMS	48	4.45×10^{-3}
	35	5.19×10^{-4}

[a] Fibers were first exposed to 5 min of different HBr concentrations for headspace extraction followed by 5 min of 0.05 mg/ml EtO solution for headspace extraction and analyzed with GC–MS.
[b] All the mass were shown as mean with $n=3$ and C.V.$<10\%$.

After the selection of fiber, the condition for thermal desorption was then determined. The desorption efficiency was found to be 99.3% when the desorption time was 5 min. To estimate the number of moles HBr loaded on the CAR/PDMS fiber after 30 s of exposures, headspace extraction of 0.05 mg/ml EtO solution was followed for different periods of time and the adsorption profile was obtained (Fig. 3). Assuming the stoichiometry between EtO and HBr was 1:1, it was found that 2.9×10^{-9} mol of HBr will be available for the reaction on fiber after 30 s of headspace extraction based on GC–MS calibration of standard 2-bromoethanol solution. The theoretical sampling rate SR of the designed diffusive sampling for EtO was 2.67×10^{-2} cm^3/min, 2.9×10^{-9} mol of HBr therefore can provide the reaction needed when sampling at EtO concentration of 1.79 mg/m^3 (TLV-TWA) for 45 h. It was more than sampling needed even the capacity was not reached.

Fig. 4 shows a typical chromatogram of vapor exposure sample from SPME direct injection with selective ion monitoring utilizing m/z 31, 42 and 45. Fig. 5 shows the vapor exposure results from the air bag method, Fig. 6 shows the results from the air bag

Table 3
Stability tests on CAR/PDMS-coated HBr fiber[a]

Intervals between HBr and EtO extraction	Mass of 2-bromoethanol formed[b] (mg)	Recovery[c] (%)
0	8.38×10^{-4}	100
60 min	8.33×10^{-4}	99.4
120 min	8.16×10^{-4}	97.3
48 h	8.22×10^{-4}	98.1

[a] CAR/PDMS fiber was first exposed to 30 s of 48% HBr solution for headspace extraction, then waited for certain period of time followed by 5 min of 0.05 mg/ml EtO solution for headspace extraction and analyzed with GC–MS.
[b] All the mass were shown as mean with $n=3$ and C.V.$<10\%$.
[c] Compared with intervals = 0 min.

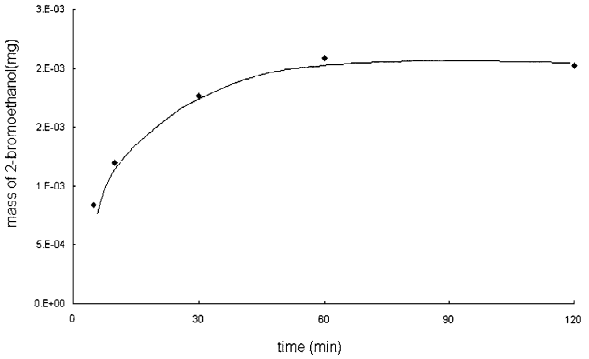

Fig. 3. Adsorption profile of EtO as CAR/PDMS fiber was first exposed to 30 s of 48% HBr solution followed by headspace extraction of 0.05 mg/ml EtO solution for different periods of time at 25 °C.

method with RH = 80%, while Fig. 7 shows the results from dynamic vapor generation system at EtO of 14.38 mg/m^3. Fig. 8 shows the combining results from the evaluation at concentrations equaled 0.89, 1.79, and 3.58 mg/m^3 (equivalent to 0.5, 1, and 2 times TLV-TWA) for 1–8 h from the dynamic vapor generation system. By doing simple linear regressions, the slopes of these regression lines were $(3.11\pm0.10)\times10^{-2}$, $(3.05\pm0.16)\times10^{-2}$, $(2.93\pm0.11)\times10^{-2}$, and $(3.12\pm0.12)\times10^{-2}$ cm^3/min, respectively, which actually stand for the experimental sampling rates of the sampler.

Several parameters including face velocity, relative humidity, shelf life, and sample stability were recommended to be evaluated in the NIOSH protocol for the validation of diffusive sampler [28]. Table 4 shows the results of shelf life and sample stability tests. The recoveries for both tests were around 100±7% after 2 days storage at room temperature and 7 days storage at 4 °C. From Figs. 5 and 7, the slopes of two regression lines were $(3.11\pm0.10)\times10^{-2}$ and $(2.93\pm0.11)\times10^{-2}$ cm^3/min, respectively, which showed no statistical difference ($P\cong0.29$). One of the differences between the air bag method and the standard gas generation system was air movement. The face velocities in the standard gas generation system were 0.25±0.02 m/s, while it was basically zero in the 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. From Figs. 5 and 6,

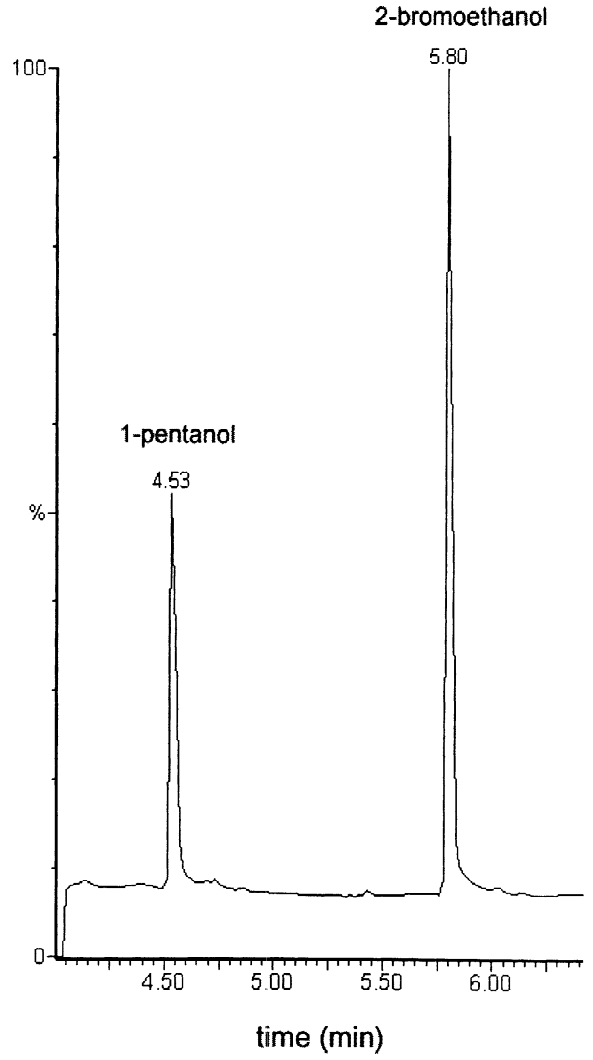

Fig. 4. Chromatogram of sample injection.

the slopes were $(3.11\pm0.10)\times10^{-2}$ and $(3.05\pm0.16)\times10^{-2}$ cm^3/min, respectively, which also showed no statistical difference ($P\cong0.8$). The only difference between these two air bag systems was relative humidity. The results suggested that RHs between 10 and 80% have no effect on the sampler because no difference in sampling rate was observed. This finding also agreed with OSHA method 50 where sampling at high humidity (70~80% RHs) and low humidity (<5% RH) using HBr-coated charcoal tubes both gave reliable results [14].

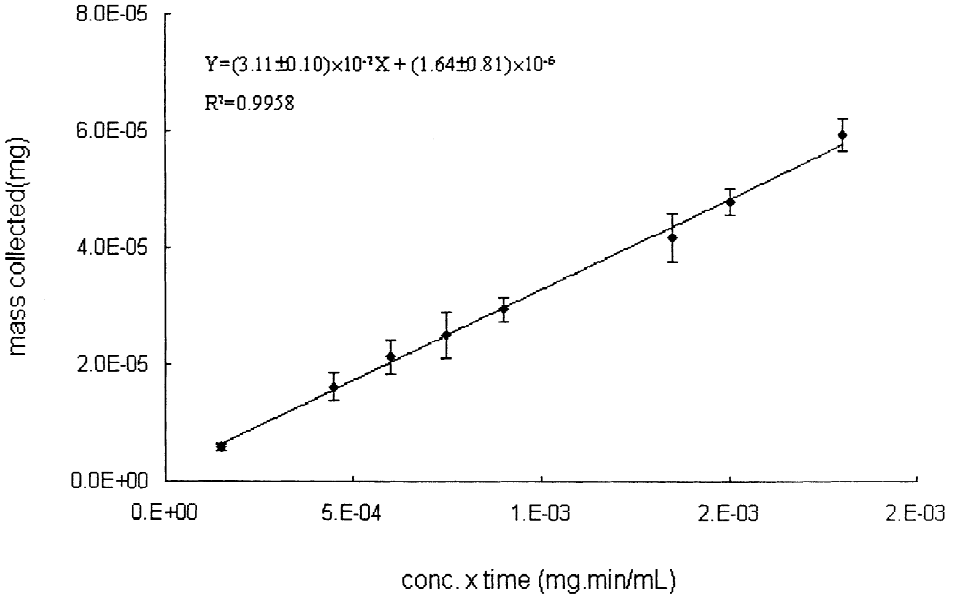

Fig. 5. Vapor exposures from gas bag with RH = 10%.

From Figs. 7 and 8, the slopes of two regression lines were $(2.93\pm0.11)\times10^{-2}$ and $(3.12\pm0.12)\times10^{-2}$ cm^3/min, respectively, which showed no statistical difference ($P\cong0.28$). The results suggested that the designed method could be applied to 1–8 h sampling at concentrations of 0.5–2 times TLV-TWA as well as only 10–90 min sampling at a concentration of 8 times TLV-TWA.

The theoretical diffusion coefficient of EtO was 0.155 cm^2/s, and the current sampler's theoretical sampling rate SR for EtO was 2.67×10^{-2} cm^3/min. The experimental sampling rate was $(2.96\pm0.09)\times$

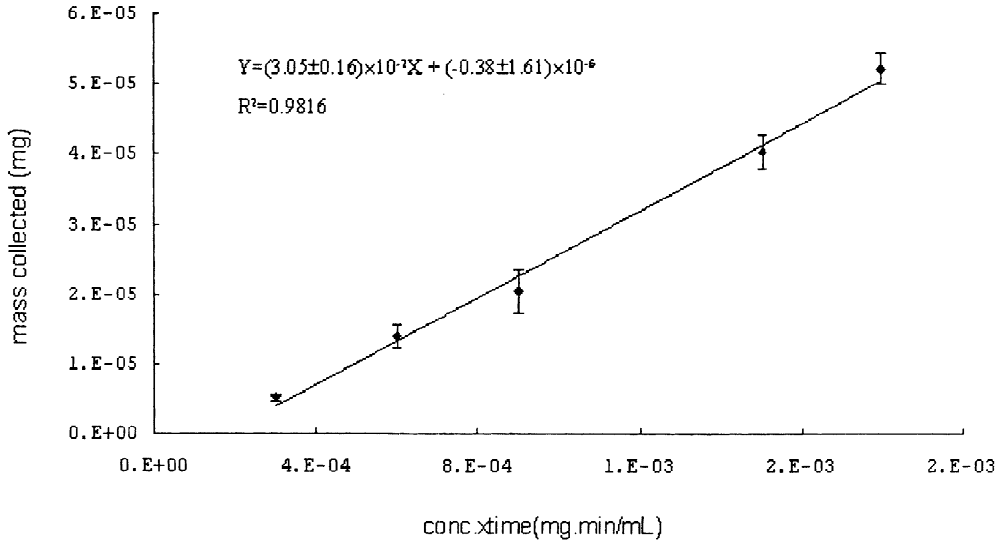

Fig. 6. Vapor exposures from gas bag with RH = 80%.

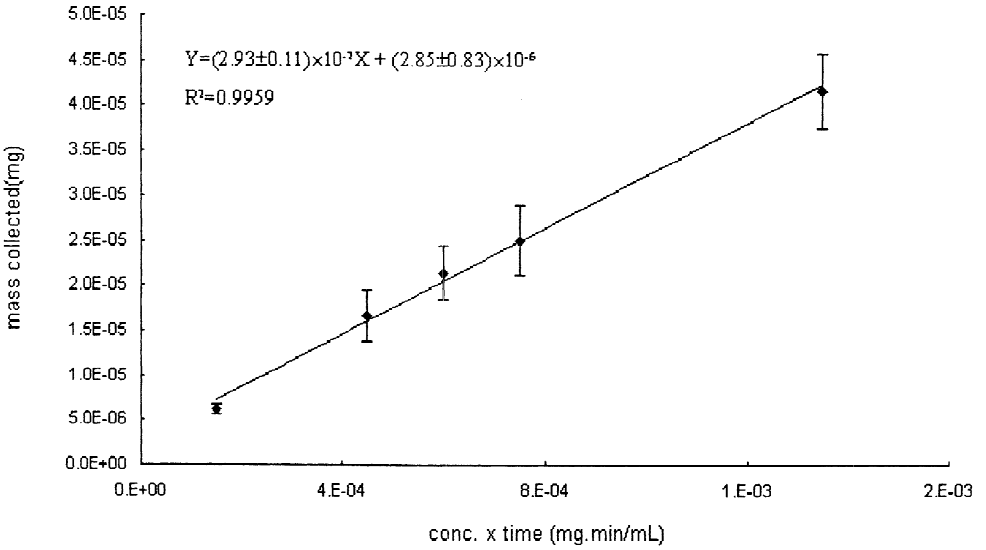

Fig. 7. Vapor exposures from standard gas generation system with conc. = 14.38 mg/m^3.

10^{-2} cm^3/min if all the data from Figs. 5–8, were combined. The experimental sampling rate was about 10% higher than the theoretical sampling rate. The possible explanation for this difference might be the bias from the estimation of diffusion coefficient as well as the errors from the estimation of sampler's path length and surface area [24].

4. Conclusions

The diffusive sampling with the SPME device has an advantage over other methods because no pumps and solvents are required which reduces the sampling costs and the time for sample analysis. The research shown here extended the newly designed user-friend-

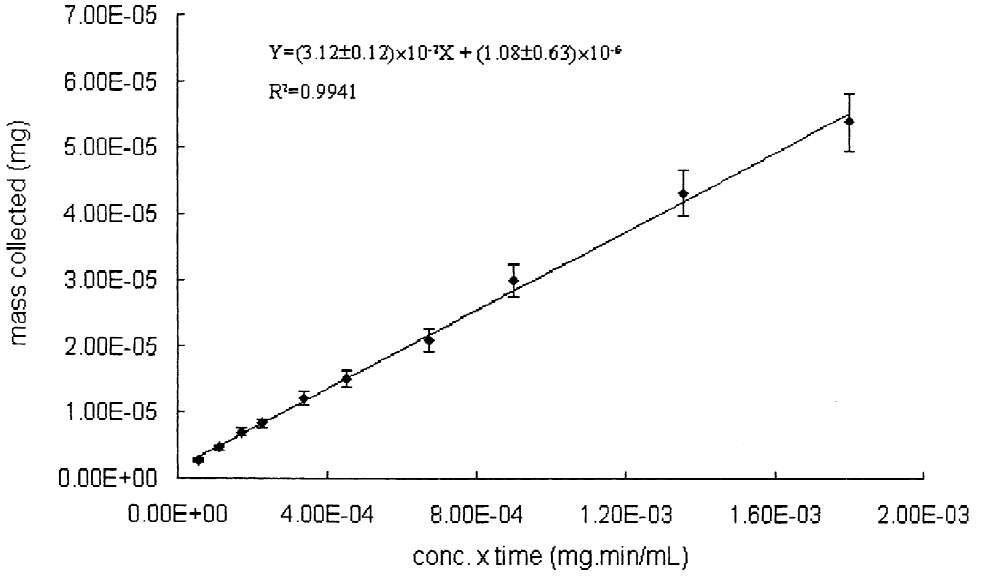

Fig. 8. Vapor exposures from standard gas generation system with conc. = 0.89, 1.79, and 3.58 mg/m^3.

Table 4
Shelf life and sample stability tests[a]

Storage condition	Mass of 2-bromoethanol collected[b] (mg)	Recovery[c] (%)
None[d]	3.71×10^{-5} ($n=8$)	100
2 days test on shelf life[e]	3.54×10^{-5} ($n=5$)	95
2 days test on sample stability[f]	3.94×10^{-5} ($n=5$)	107
7 days test on shelf life[g]	3.45×10^{-5} ($n=4$)	93
7 days test on sample stability[h]	3.59×10^{-5} ($n=3$)	97

[a] CAR/PDMS fiber was first exposed to 30 s of 48% HBr solution for headspace extraction, then the diffusive sampler was assembled.

[b] All the mass were shown as mean with C.V.$<$10%.

[c] Compared with no storage condition.

[d] Exposed to 14.38 mg/m^3 of EtO in air bag for 30 min followed by GC–MS analysis right after the sampler was assembled.

[e] The assembled sampler was stored at room temperature for 2 days, then exposed to 14.38 mg/m^3 of EtO in air bag for 30 min followed by GC–MS analysis.

[f] Exposed to 14.38 mg/m^3 of EtO in air bag for 30 min right after the sampler was assembled, then stored at room temperature for 2 days and followed by GC–MS analysis.

[g] The assembled sampler was stored at 4 °C for 7 days, then exposed to 14.38 mg/m^3 of EtO in air bag for 30 min followed by GC–MS analysis.

[h] Exposed to 14.38 mg/m^3 of EtO in air bag for 30 min right after the sampler was assembled, then stored at 4 °C for 7 days and followed by GC–MS analysis.

ly sampling device [24] to the validation of EtO sampling which will increase the wearer's acceptance.

Various derivatization techniques can be implemented combined with SPME, including direct derivatization in sample matrix, derivatization in GC injector port, and derivatization on SPME fiber coating [18]. On-fiber derivatization technique was used in this research where simultaneous derivatization and extraction were performed directly on the fiber coating.

CAR/PDMS fiber with 30 s headspace extraction of 48% HBr solution provided sufficient amounts of HBr needed for EtO sampling. On-fiber derivatization of EtO with HBr also increased the sample stability. Face velocities (0–0.25 m/s) and RHs (10–80%) were not expect to have effects on the sampler while more studies will be needed to evaluate the effect of temperatures. The current method could be applied to 1–8 h sampling at concentration equaled 0.5–2 times TLV-TWA as well as 10–90 min sampling at eight times TLV-TWA. However, the theoretical estimation of sampling rate could lead to errors and experimental calibration is a must.

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