Extraction of Gaseous VOCs Using Passive Needle Trap Samplers

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ABSTRACT

Gaseous toluene, ethylbenzene and *o*-xylene (TEX) were extracted by using the divinylbenzene (DVB) particle of 60–80 mesh as a sorbent packed in series of needle trap samplers (NTS). The feasibility of using this self-designed DVB-NTS as a diffusive time-weighted average (TWA) sampler for occupational hygiene applications was evaluated by examining extended sampling periods of 4–12 hr. Additionally, the NTS was compared in terms of extraction efficiency by simultaneously using the 75 μm Carboxen/polydimethylsiloxane-solid phase microextration (Carboxen/PDMS-SPME) fiber for sampling TEX. Experimental results indicated that, regardless of static (in a bulb) or dynamic samplings (in a flowing gas stream), the packed DVB-NTS achieved higher TEX extraction rates (ng VOCs/min) than those of 75 μm Carboxen/PDMS-SPME fiber. The decreasing rates of extracting TEX for SPME fiber were 24–34% and 28–36% as NTS performed during the sampling periods of 240 and 480 min, respectively. Typically, the maximum VOC adsorption capacities per mg DVB were measured as 5.692 μg toluene, 7.669 μg ethylbenzene and 5.199 μg *o*-xylene. During the sampling period of 12 hr, the DVB-NTS extracted 1600–1800 ng of individual TEX components from a continuously flowing air stream, in which the gas flow rate equals 200 mL/min. We recommend the badgelike or penlike NTS as an alternative passive sampler to the legal active sampling method 1501, National Institute of Occupational Safety and Health (NIOSH), owing to its small size and high extraction capacity of TEX.

Keywords: Solid phase microextraction (SPME); Needle trap; Volatile organic compound (VOC); Time-weighted average (TWA) sampling; Occupational hygiene.

INTRODUCTION

Coated fiber samplers of solid phase microextraction (SPME), manufactured by Supelco, have been extensively adopted in sampling gaseous organic compounds (Lord and Pawliszyn, 2000). Composed of a defined distance from the needle opening arrangement, the commercial SPME (Fig. 1) can sample volatile organic compounds (VOCs) based on the sampling mode of passive time-weighted average (TWA) (Tuduri *et al.*, 2002; Larroque *et al.*, 2006; Cheng, 2008). This in-tube sampling device can also generate a response proportional to the integral of the analyte concentration over time (Pawliszyn, 2009).

The needle trap sampler (NTS, Fig. 1) is an extraction trap containing a sorbent inside a small needle, through which, VOCs can be introduced passively to the extracting phase by diffusion (Lord *et al.*, 2010). However, despite the similarity of the theory of TWA sampling VOCs with

that of SPME, users can select the sorbent types packed in a NTS and their packing structures depending on the adsorption characteristics of analytes. Wang *et al.* (2005) designed a NTS, packed with segmental layers of adsorbents, polydimethylsiloxane (PDMS), divinylbenzene (DVB) and Carboxen particles for extracting gaseous benzene, toluene, ethylene and *o*-xylene (BTEX); in addition, the individual detection limits ranged from 0.23 to 2.10 ng/L for BTEX. Gong *et al.* (2008) packed a NTS with the sorbent Carboxen1000 as a TWA diffusive sampler to collect BTEX under different sampling conditions, *i.e.* air flowing speeds of 1.44–32.48 cm/min and relative humidity (RH) of 17–53%. All values of relative standard deviation (RSD) of extracting BTEX mass at different sampling conditions were less than 5%, that means air flowing and RH were independent on the extraction performance of NTS.

In this work, the DVB particulate of 60–80 mesh was used as a sorbent packed in series of passive NTS. An aspirating pump was used for examining the sampling flow rates through the packing phase of all NTS. The relations of extracting VOCs mass and sampling flow rates were evaluated. Actually, the NTS has the potential to be used as a personal passive VOC sampler due to its small size for wearing by a worker for a long period, like a badgelike or

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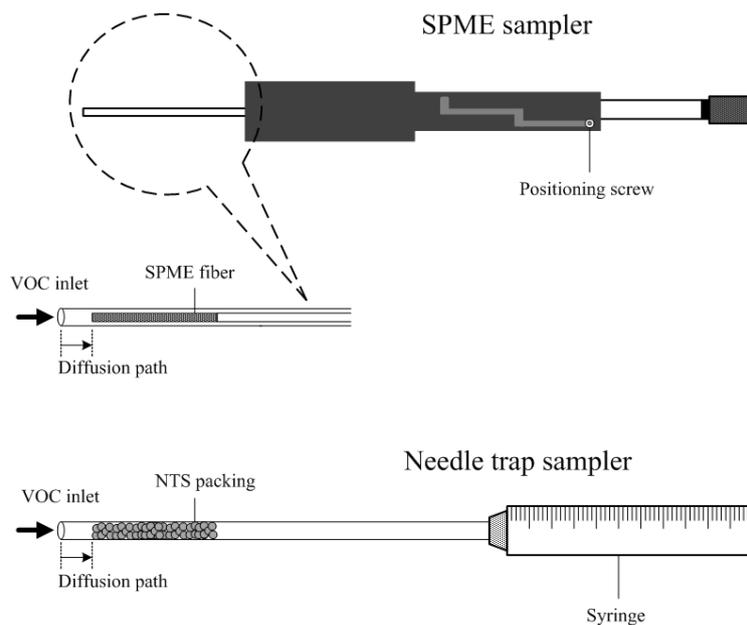
SPME sampler

Needle trap sampler

Fig. 1. Schematic SPME and needle trap samplers.

penlike sampler (Pawliszyn, 2003; Gong *et al.*, 2008). In order to assessing the feasibility of this self-designed DVB-NTS as a passive sampler for the working place, the long sampling periods of 4–12 hr was also examined. The Carboxen/PDMS coated SPME fiber has been extensively adopted to sample gaseous BTEX due to its strong affinity to BTEX (Koziel and Novak, 2002; Larroque *et al.*, 2006; Gong *et al.*, 2008). Therefore, TEX (toluene, ethylene and *o*-xylene) was also simultaneously sampled using a 75 μm Carboxen/PDMS-SPME fiber for comparing in terms of extraction efficiency of NTS.

MATERIALS AND METHODS

Fundamental Theory of Extracting Gaseous VOCs via a Needle Trap Sampler

The only mechanism of gaseous VOC transport to the extraction phase is diffusion through the diffusion path in the needle. During this process, a linear gaseous concentration profile ($c(Z)$, as shown in Fig. 2) is established along the diffusion path between the small needle opening and the position of the extracting phase, which are characterized by an opening area (A) and the diffusion path distance (Z). The amount of extracted analyte (n) during time interval (t) can be estimated by considering the Fick's first law of diffusion (Lord *et al.*, 2010):

$$dn = AD_m \frac{dc}{dz}dt = AD_m \frac{\Delta C(t)}{Z}dt \qquad (1)$$

where D_m denotes the diffusion coefficient of components sampled by the sorbent inside the needle. The amount of analyte accumulated over time can therefore be calculated as

$$n = D_m \frac{A}{Z}\int C(t)dt \qquad (2)$$

As expected, the amount of extracted analyte is proportional to the integral amount of the sample concentration over time ($C(t)$) under the constant values of D_m for given VOCs, as well as the uniform needle opening area (A) and diffusion path distance (Z). Notably, Eqs. (1) and (2) are valid only when the amount of analyte extracted onto the sorbent is a small fraction of the equilibrium amount for the lowest concentration in the sample, which can be evaluated based on the RSD of double or triple duplicates of measurements, *i.e.* typically below 5%.

Chemicals, Materials and Equipment

The 3.5″ long, 22-G stainless-steel needles (ID 0.41 mm and OD 0.71 mm) were purchased from Dyna Medical Corporation (London, ON, Canada). DVB (HayeSep Q, 60–80 mesh size particles) was packed as a sorbent in the NTS. The 75 μm Carboxen/PDMS-SPME were purchased from Supelco (Restek, Bellefonte, PA, USA). The aspirating pump for testing the sampling flow rates of NTS was purchased from Kitagawa (AP-20, Kawasaki, Japan). The 5-min syringe epoxy glue (LePage, Henkel Corporation, Mississauga, ON, Canada) was purchased locally. All gases were supplied by Praxair (Kitchener, ON, Canada) and were of ultra-high purity. Target VOCs (toluene, ethylbenzene and *o*-xylene) were purchased from Sigma-Aldrich (St. Louis, MO, USA).

VOCs were analyzed by Varian 3800 gas chromatograph (GC), equipped with a flame ionization detector (FID). VOC separations were performed using a capillary column of DB-5HS (30 m × 250 μm × 0.25 μm) (J&W Scientific, Mississauga, Ontario, Canada). A gas generator (491MB base module, Kin-Tek Laboratories, Inc., LaMarque, TX, USA) produced organic gases with constant emission rates by using permeation tubes, which were certified by Kin-Tek Laboratories, Inc.. The packed mass of DVB particle was measured by a precision scale (ME type, Sartorius,
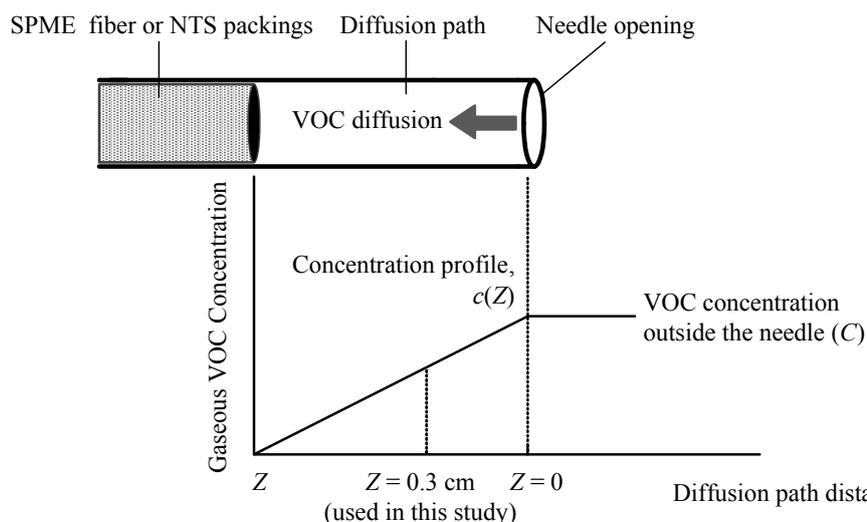
Fig. 2. Gaseous VOC concentrations linearly decrease along the diffusion path from the opening of a needle trap sampler.

Germany), which had a minimum reading value of 0.0001 mg, and reproducibility < 0.0001 mg.

Preparation of Needle Trap Sampler

The NTS consisted mainly of a stainless steel needle, packed with a 60–80 mesh DVB particle (Fig. 1). Sorbent particles inside the positioned needle must be immobilized without bleeding and with minimum flow restrictions. Therefore, a stainless-steel wire spring plug, was initially fixed in position (Z = 10 mm). DVB particles were then packed by aspirating almost grain by grain until the desired length of 7 mm was packed; *i.e.* the distance of diffusion path is 3 mm. Packing was then completed by applying a slight amount of epoxy glue at the outside end of the sorbent layer, in order to hold the sorbent particles firmly. The average packed DVB mass of all tested NTS were 0.347 mg with a standard deviation of 0.0380 mg, which were weighed by a precision scale. For practically convenient, the other long straight stainless-steel wire were used as the pole for moistening epoxy glue. To avoid complete blockage of the NTS by the epoxy-resin plug, air was also drawn continuously through the NTS packing while the epoxy resin was cured. Finally, the packed DVB inside a NTS was conditioned by heating at the injection port of GCFID under 260°C for 30 min. The prepared NTS was stored at room temperature for future use. Six pieces of NTS were prepared in this study. The packing adsorbent phases of three NTS were of higher porosities, and the others had lower porosities. We adjusted packing pressures by hand for different porosities of the packed adsorbent between NTS.

Until now, the uniformity of packing phase in a NTS has seldom been evaluated. With respect to the sampling procedures for an active NTS (Saito *et al.*, 2006; Niri *et al.*, 2009), the desired sampling flow rates (mL/min), as drawn by an aspirating pump through the packing phase of all NTS in this study, were performed. The RSD for triple duplication tests of sampling flow rates should be less than < 5%. Namely, the filled materials in the NTS should be considered to be uniformly immobilized. We also assessed the reproducibility of samplers using the RSD of adsorbed VOC mass between different NTS.

VOC Sampling and Analysis

Static VOC samples were prepared by injecting VOCs into a 1000-mL glass bulb. Dynamic VOC samples were initially flushed from the standard gas generator, followed by continuous flowing through a glass sampling tube (Fig. 3). Desired emission rates of the VOCs were achieved by adjusting both permeation oven temperature and dilution nitrogen flow rate flown into the gas generator. The samples were taken in the laboratory under the room temperature controlled by the HVAC system at 25°C. All NTS were used for taking static TEX samples in the bulb, and the NTS of the highest sampling rate was used for the follow-up dynamic sampling.

VOC calibrations were performed for each experiment by using a gas-tight syringe sampler. Also, VOC analysis of both calibrations and TWA samples used the same GC-FID. Both NTS and SPME, extracting VOCs, were injected into the injection ports of GC for desorbing VOCs and subsequent analysis. The desorbing times at the injection port of GC for NTS and SPME were 30 s. The GC oven had an initial temperature of 50°C and increased at 15 °C/min. The final temperature was 180°C and the holding time was 2 min. The time required to reach 150°C was 5 min. Next, the FID detector was heated to 300°C. The carrying gas flow rate was 1.2 mL/min for helium, and the operation mode of the split off was chosen. Notably, following the operation and analysis procedures, no carryovers were available for all samples extracted using NTS and SPME herein.

RESULTS AND DISCUSSION

Tests of the Sampling Flow Rate and VOC Extraction Rate of NTS

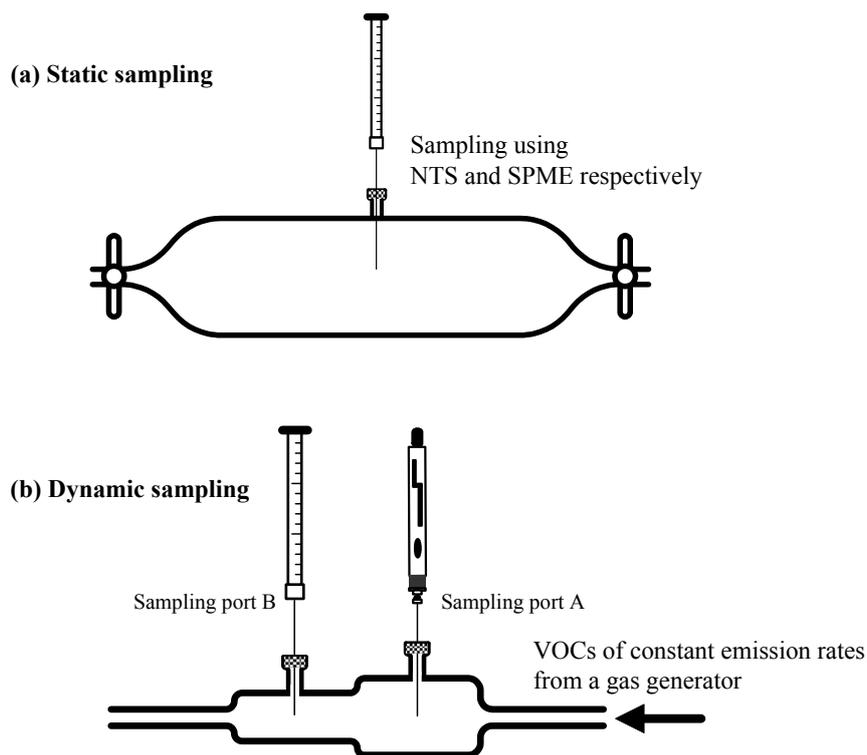Six NTS were sorted as Group#1 and Group#2, for sampling gaseous toluene of 800 mg/m³ in a bulb. According

Fig. 3. TWA sampling using NTS and SPME.

to Eq. (2), a longer sampling time (t), implies a greater amount of toluene (n) extracted by NTS under a constant concentration of toluene (C). Restated, the sampling flow rate is inversely proportional to the toluene extraction mass. Table 1 reveals that the mean sampling flow rates of NTS Group#1 and Group#2 were 66 and 15 mL/min, respectively, and the RSD values of sampling flow rates for NTS Group#1 and Group#2 were less than 5%, implying that the packed DVB phases were at uniform states. The toluene extracting rates were 2.93–2.99 and 18.51–18.66 ng/min, respectively. Comparing NTS Group#1 and Group#2, the higher flow rates through the adsorbent phase of NTS resulted in lower VOC extraction rates. The RSD of toluene extraction mass for extracting times of 20 and 40 min were less than 5%, which means NTS Group#1 and Group#2 performed satisfactorily reproducibility. Based on an enhanced performance among NTS Group#1 and Group#2, a NTS of the highest extracting rate was applied for a sampling mixture of TEX and then compared with the extraction performance of 75 μm Carboxen/PDMS-SPME sampler.

Performance of DVB-NTS and Carboxen/PDMS-SPME for the TWA Sampling of VOCs

According to the experimental data of static sampling, for the sampling times of 20–90 min for extracting gaseous TEXs of 800 mg/m^3, the adsorption fiber of 75 μm Carboxen/PDMS-SPME fiber extracted an equilibrium mass for 60–90 min. Namely, the equilibrium extraction mass was nearly 600–800 ng of individual components of TEXs (Fig. 4). However, after sampling for 90 min, the mean individual mass adsorbed by packed DVB in NTS Group#2 were 1975 ng toluene, 2661 ng ethylbenzene and 1804 ng *o*-xylene. In other words, based on the average DVB packing mass in NTS (0.347 mg), the VOC adsorption capacities per mg DVB were 5.692 μg toluene, 7.669 μg ethylbenzene and 5.199 μg *o*-xylene, respectively.

Fig. 5 displays the results of dynamic TEX samplings in the continuous air streams of 200 mL/min. The fiber of 75 μm Carboxen/PDMS-SPME extracted VOCs at the sampling port A and DVB-NTD at port B. Notably, the sampling port A was located at the portion of a higher cross area than that of port B. Restated, the air flow speed at the port

Table 1. Sampling flow rates and toluene extracting rates for needle trap samplers used in this study.

ID of sampler	Number of samplers	Sampling flow rate (mean values, mL/min)	Sampling time (a, min)	Toluene extracting mass (b, mean values, ng)	Toluene extracting rate (b/a, ng/min)
Hollow needle	6	510 (RSD = 0.5%)	–	–	–
NTS Group#1	3	66 (RSD = 0.7%)	20	59.7 (RSD = 4.5%)	2.99
			40	117.1 (RSD = 3.9%)	2.93
NTS Group#2	3	15 (RSD = 1.6%)	20	373.1 (RSD = 2.2%)	18.66
			40	740.2 (RSD = 1.5%)	18.51

(a) 75 um Carboxen/PDMS SPME
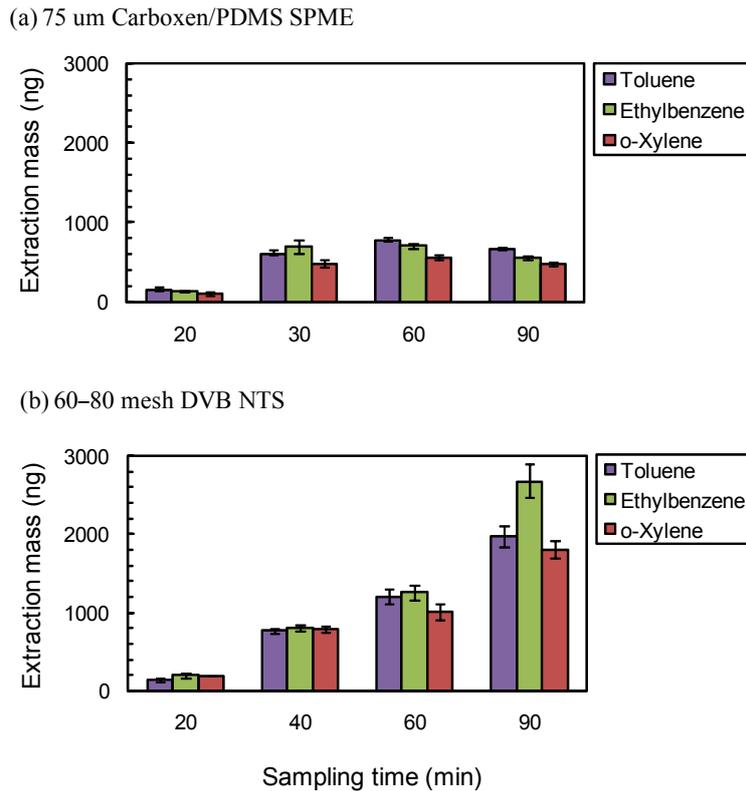

(b) 60–80 mesh DVB NTS

Fig. 4. Static sampling of BTX using SPME and NTS. The individual concentrations of VOCs were 800 mg/m^3.
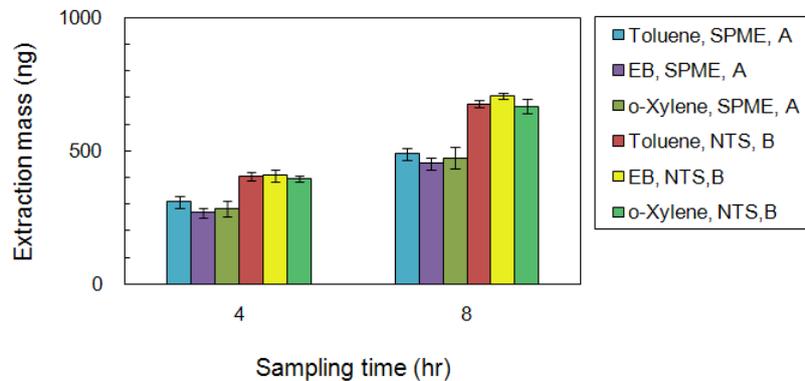

Fig. 5. Comparison of dynamic sampling of TEX for SPME and NTS.

A was lower and the VOC concentrations were higher than those at the port B. However, in contrast with NTS, even under a higher VOC concentration, SPME fiber extracted a lower amount of TEX for the sampling times of 240 and 480 min. Moreover, the decreasing rates of extracting TEX for SPME were 24–34% and 28–36% as NTS performed during the sampling periods of 240 and 480 min, respectively. The packed DVB NTS achieved higher extraction rates for TEX than those of 75 μm Carboxen/PDMS-SPME, regardless of static or dynamic samplings.

TWA Sampling by NTS for Application as VOC Exposure Sampler among Workers

Fig. 6 displays the extracted mass of TEX using NTS for an extensive sampling time. With the sampling time ranging

from 4 to 12 hr, the extraction mass of TEX increased linearly. During the sampling period of 12 hr, NTS extracted around 1600–1800 ng TEX. The workers are exposed to organic compounds for not longer than 8 hr on a working day. The NTS was satisfied with its VOC extraction performance, despite for continuous sampling for 12 hr.

The above experiments did not observe competition adsorption of mixed VOCs by DVB-NTS, even when the individual TEX concentrations are as high as 800 mg/m^3 (around 180–210 ppm). The workers are seldom exposed to gaseous VOCs of such a high concentration like these simulations under a normal operation, except an unexpected leakage of solvents. The competitive adsorption of adsorbent mixture can be disregarded during sampling of VOCs in workplaces by NTS.
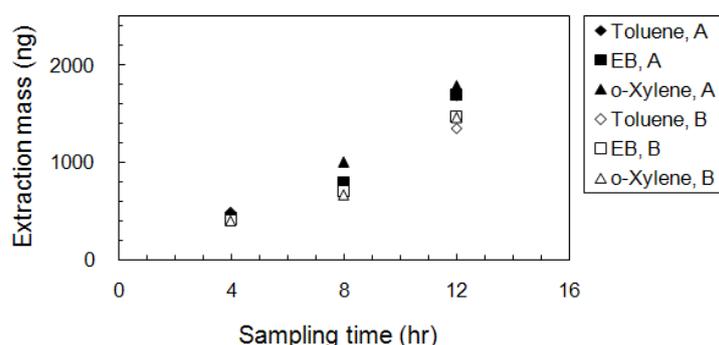
Fig. 6. Performance of TWA dynamic sampling by NTS at different sampling ports A and B.

CONCLUSIONS AND RECOMMENDATIONS

The packed DVB-NTS is a recommended passive sampler, based on its extracted mass of TEX more than that of a 75 μm Carboxen/PDMS-SPME fiber for sampling TEX during 4–12 hr. According to method 1501, National Institute of Occupational Safety and Health (NIOSH, 2003), workers must wear a charcoal sorbent tube, connected to an active personal sampling pump, for evaluating the exposure of gaseous organic compounds. Workers often express concern over inconvenience of occupying the space by large-sized facilities in order to implement this legal sampling method. This study has evaluated the feasibility of using a badgelike or penlike NTS for occupational hygiene applications.

The different porosities of packing phase inside the needle of NTS affect the amount of packed adsorbent. The packing particle of a smaller diameter has a lower porosity (*i.e.* pressed more tightly) than that of a larger-size particulate for the same packing volume inside a needle. Future, studies should use variously sized adsorbents, *e.g.*, 80–100 or 100–120 mesh DVB powder, as the packing materials for increasing the adsorption rates in order to optimize packed NTS.

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