Sulfonation of Divinylbenzene Adsorbents Packed in a Micro Sampler to Extract Airborne Organic Compounds

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ABSTRACT

In this work, sulfonated divinylbenzene (SDVB) adsorbents, with the 60–80 mesh diameter, were packed inside a 22-gauge stainless steel needle to fabricate a sulfonated needle trap sampler (SNTS), which is a micro sampler. An analysis of Fourier-transform infrared spectroscopy (FTIR) scanning data, thermal gravimetric analysis (TGA) data, and scanning electron microscope (SEM) observations, confirmed the physiochemical characteristics of sulfonated DVB adsorbent resins. A gas mixture of approximately 20 ppm of ethanol, methyl ethyl ketone (MEK), benzene, toluene, ethylbenzene and *o*-xylene (BTEX) was prepared to evaluate the sampling efficacies of the SNTS. The results reveal that, in 1–2 h, SNTS adsorbed increased 92–116% more methanol and 12–20% more MEK than NTS. The SNTS adsorbed 4–15% less BTEX than the NTS. The tested SNTS exhibited remarkable adsorption capacities of methanol, which emitted in a metal frame manufacturing plant. The SNTS is recommended as an alternative passive sampler to the active adsorbent tubes.

Keywords: Sulfonation, Divinylbenzene, Adsorption, Micro sampler, Solid phase, Microextraction

1 INTRODUCTION

Solid phase microextraction (SPME) involves the adsorption of analytes by extracting phases, and relevant technology has been developed for over 30 years. SPME was developed as a solvent-free technique for preparing samples using less than 1 μL of an extracting phase. The extracting phase can be a solid sorbent, which is packed inside a stainless needle, and is typically of high porosity to provide a high surface area for adsorption (Pawliszyn, 1999).

To adsorb organic compounds in the liquid, gaseous or solid phases, various adsorbents must be used. Polar adsorbents are effective for extracting polar analytes and nonpolar adsorbents are effective for extracting nonpolar analytes from various matrices (Pawliszyn and Mani, 1999). Divinylbenzene (DVB) is a universal semipolar particle adsorbent with a high specific surface area of $750\text{ m}^2\text{ g}^{-1}$ using to sample many gaseous organic compounds in the environment and working places (Cheng *et al.*, 2017; Cheng and Wu, 2019; Cheng *et al.*, 2020; Cheng and Yuan, 2021). DVB has higher adsorption capacities for $\text{C}_6\text{--C}_{15}$ compounds than for $\text{C}_1\text{--C}_3$ alcohols and ketones, including methanol, ethanol, propanol and methyl ethyl ketone (MEK) (Pawliszyn and Mani, 1999).

Adsorbents whose surface have been modified with specific functional groups have been proved to be the feasible for the adsorbing of mixed compounds. To increase the adsorption capacities of polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/Fs) by activated carbon, Atkinson *et al.* (2015) developed carbon-based adsorbents by adding specific functional groups, including oxygen, sulfur, bromine and nitrogen. Tests revealed that modified carbons increased the removal efficiencies of PCDD/F to over 98%. Organic compounds have been also used as functional groups to modify the surface characteristics of adsorbents. Janus *et al.* (2011) modified the mesoporous silica support, MCM-41, by introducing polyacrylonitrile (PAN) with an optimal PAN/MCM-41 mass ratios of 0.1 for

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eliminating gaseous MEK, achieving adsorption capacities of over 0.275 g MEK g⁻¹ adsorbent. Mu *et al.* (2018) used organosilanes, including phenyltriethoxysilane (PTES), aminopropyltriethoxysilane (APTES), and trimethylchlorosilane (TMCS), to modify the adsorption capacities of diatomite (DE) for methane in the flue gas. Their experimental results revealed that PTES-DE and APTES-DE have excellent methane adsorption capacities at room temperature and low operation pressures of 3–7.5 bar. Polyethyleneimine has been used for increasing the adsorption capacities of formaldehyde by carbon nanotubes (Song *et al.*, 2018). Ethylene-diamine has been used for modify diatomaceous earth to adsorb formaldehyde (Bernabe *et al.*, 2015).

Lou *et al.* (2018) coated polystyrene-divinylbenzene (PSDVB) with graphene to modify it to increase its organic adsorption capacities. They separated ten allergenic disperse dyes from industrial wastewater using SPME samplers with detection limits of 1.1–15.6 ng mL⁻¹. Sulfonated porous PSDVB has been used in the hydrophilic and chiral separation of oxalic acid, formic acid, acetic acid, acrylic acid (Cong *et al.*, 2020), and separation of aromatic matrices, including 1,4-hydroquinone, benzoic acid, phenol, benzaldehyde and toluene (Huang *et al.*, 2018). PSDVB magnetic porous microspheres have been prepared by sulfonation to adsorb 2,4-dichlorophenol and 2,4,6-trichlorophenol from aqueous solution (Yu *et al.*, 2015).

The SPME micro sampler, which is a needle trap sampler (NTS), was developed over a decade by Cheng *et al.* (2017, 2019, 2020, 2021) to collect airborne organic compounds. Notably, PDVB particles with diameters of 60–80 meshes were used as the packed adsorbent as its most proper operation among different sizes of particles for packing inside a needle. The traditional DVB-NTS exhibits excellent efficiencies of adsorption of aromatic compounds; however, C₁–C₃ alcohols and ketones, which are extensively used in industry as solvents, cannot be extracted effectively by a DVB-NTS. Sulfonation has been successfully used to modify adsorption characteristics of various adsorbents (Liu *et al.*, 2010; Azhagapillai *et al.*, 2020; Khomein *et al.*, 2021). In this work, sulfonated PDVB particles with diameters of 60–80 meshes were packed inside 22-gauge stainless steel needles to extract mixed organic compounds.

2 METHODOLOGY

2.1 Extraction of Gaseous Compounds Using Needle Trap Samplers

An NTS extracts gaseous chemical compounds through the needle by air diffusion. A linear gaseous concentration profile ($C(Z)$ in Fig. 1) is obtained along the diffusion path (Z), and the extraction of the analyte is characterized by the area (A) of opening and the length of the diffusion path in the needle. The total extracted mass (n) of analyte in a time interval (t) is estimated using Eq. (1) (Lord, *et al.*, 2010).

$$n = D_m \frac{A}{Z} \int C(t) dt \quad (1)$$

where D_m is the diffusion coefficient of the extracted analyte. Accordingly, the quantity (n) of the extracted analyte is assumed to be proportional to the weighted average (TWA) concentration ($C(t)$), given a constant D_m , a uniform needle opening (A), and a fixed diffusion path length (Z).

2.2 Preparation of Needle Trap Samplers

The NTS consists of a 22-gauge stainless steel needle that is packed with DVB adsorbent of a size consistent with 60–80 mesh. The diameter of a 22-gauge needle corresponded to the size of injection port of gas chromatograph (GC). DVB particles were packed by aspiration to the desired length of 7 mm and a diffusion path length of 3 mm (Fig. 1). A very small amount of epoxy glue was applied to the exposed portion of the adsorbent layer to immobilize the DVB particles. To prevent blockage by an NTS epoxy-resin plug, air was drawn continuously through the NTS packing phase as the epoxy cured. Finally, the DVB in the NTS was conditioned by heating at the injection port of the GC to 280°C for 30 min.

The uniformity of the packing phase in an NTS was studied by a procedure that has described in earlier works (Cheng *et al.*, 2017; Cheng and Wu, 2019; Cheng *et al.*, 2020; Cheng and Yuan, 2021). The desired air exhaustion rate through the NTS was obtained by drawing air through the

Fig. 1. Schematic needle trap sampler (NTS).

packing phase using an aspirating pump. When the relative standard deviation (RSD) of the air flow rates in triplicate tests did not exceed 5%, the packed materials inside the NTS were assumed to be uniformly immobilized. Gaseous standard samples of a mixture of benzene, toluene, ethylbenzene (EB) and o-xylene (BTEX) (around 20 ppm) were prepared in a 500 mL Pyrex glass bulb, in which the NTS was inserted for 1 h or 2 h to adsorb BTEX. When the RSD of the sampled mass in triplicate tests was less than 10%, the tested NTS was ready for use. An SNTS, which was packed with SDVB, was also prepared by the procedures that was used to prepare the NTS. Ethanol and MEK were also mixed with BTEX to assess the effectiveness of the SDVB adsorbent for extracting mixed VOCs.

2.3 Sulfonation Synthesis of Adsorbent Divinylbenzene Resins

Sulfonated DVB (SDVB) was synthesized by sulfonation using a modified version of the method that was used by Liu *et al.* (2010) and Khomein *et al.* (2021). 3 g mass of DVB resin was swollen in dichloromethane (DCM) for 24 h. The swollen DVB resin was transferred into a three-neck round bottle. A 45 mL volume of concentrated sulfonic acid was added dropwise to the bottle and reacted with the swollen DVB at 90°C for 1 h. Thereafter, 100 mL of deionized water was slowly added to dilute the concentrated sulfonic acid solution. The final product, SDVB adsorbent was dried in an oven at 50°C.

Fourier-transform infrared spectroscopy (FTIR, Thermo Nicolet iS5, USA) was used to identify the chemical structure of SDVB, and especially to verify that the sulfonation was complete. A scanning electron microscope (SEM, FEI Quanta-200, Hillsboro, OR) with a scanning range from 400 to 4,000 cm^{-1} was used to observe the morphology of the DVB resin following sulfonation. Thermal gravimetric analysis (TGA, TA Q50, New Castle, DE) was performed to determine the thermal properties of the SDVB adsorbent and to optimize the operating conditions for regeneration. TGA was conducted in the range from 40 to 800°C at a scanning rate of 20°C min^{-1} .

2.4 Chemicals, Materials and Instrumentation

Stainless steel needles (22 G, length 7 cm and ID 0.41 mm) were purchased from a local company (Herling Co. Ltd., Pingtung, Taiwan) for use in preparing the NTS. DVB resin was purchased from Supelco (Bellefonte, PA, USA). Aspirating pumps, which were used to determine the NTS sampling flow rates, were purchased from Kitagawa (AP-20, Kawasaki, Japan), and epoxy glue was purchased from Nao-Pao Applied Material Co. Ltd. (Taoyuan, Taiwan). All gases that were used in chromatographic analysis (Jing-De Gas Co., Ltd., Kaohsiung, Taiwan) were of ultra-high purity. All chemicals that were used in analysis and sulfonation synthesis were obtained from Sigma-Aldrich (Munich, Germany).

Gaseous samples were analyzed using a GC (6890N, Agilent, Wilmington, DE, USA) that was equipped with a flame ionization detector (FID). The capillary column was HP19091Z-413 HP-1 PDMS (30 m $\times$ 320 μm $\times$ 0.25 μm) (Agilent). The unknown chemical compounds were analyzed to determine the constituents using another gas chromatography-mass spectroscopy system (MS 5973, Agilent).

2.5 Sampling and Analysis

A target industrial site of Plant A, which is located in the Nanzih Export Processing Zone, Kaohsiung City, southern Taiwan, was monitored to determine workers' exposure to organic solvents. The

Fig. 2. The worker was wearing gas samplers. Left dotted circles: a charcoal tube and a sampling pump (the NIOSH sampling method); Right dotted box: Two types of NTS fixed on a plastic plate.

target plant mostly manufactures metal frames used in the semiconductor processing. Workers always used different tools for preparing machines and metal molds, therefore alcohols were used for wiping and grinding oils for repairing tools. Two types of micro samplers, an NTS and an SNTS fixed on a plastic sheet, were worn on workers' breathing zone (Fig. 2). Each worker also wore an other personal sampling device, comprising an adsorbent tube (Method 2000 for methanol and Method 1500 for alkanes (NIOSH, 2003)), which was connected to a personal air pumps for active sampling (Fig. 2). The solvent vapors in the adsorbent tubes after sampling were analyzed by a corporation that was contracted by the owners of Plant A to identify the compounds and their concentrations.

After sampling, each NTS and SNTS was taken to the laboratory and inserted into the injection ports of a GC-FID to desorb analytes for analysis. The desorption time and temperature at the injection port were 30 s and 250°C, respectively. The temperature of the GC was increased from 50°C in increments of 15°C min⁻¹ to 180°C, which was held for 2 min. The FID detector was heated to 300°C. The flow rate of the carrier gas, nitrogen, was 1.2 mL min⁻¹, and the split-off operating mode was used. The calibration analysis for analytes were implemented following the same operating procedures.

3 RESULTS AND DISCUSSIONS

3.1 Characteristics of Sulfonated Divinylbenzene Adsorbent

Fig. 3 presents the FTIR spectrum of DVB and SDVB. The OH stretching and scissoring vibration for H₂O were observed at 3,449 and 1,632 cm⁻¹, respectively. Compared with DVB, these peaks in SDVB exhibited higher intensity than in DVB indicating sulfonation of DVB would effectively improve the hydrophilicity. Vrancken *et al.* (2017) also reported that the hydrophilicity would performed higher peak intensity of water compared with hydrophobic surface. The characteristic peaks of SDVB were observed at approximately 1,323, 1,176, 1,069, 1,007 and 612 1 cm⁻¹. The

Fig. 3. FTIR spectra of divinylbenzene resin (DVB) and sulfonated DVB (SDVB).

Fig. 4. SEM image of resin: (a) DVB; (b) SDVB (scale bar: 100 μm).

peaks at $1,323\text{ cm}^{-1}$ to the asymmetric stretching vibration of S=O and the peak at $1,069$ and $1,007\text{ cm}^{-1}$ corresponded to the symmetric stretching vibration of S=O. The peak at 612 cm^{-1} corresponded to the C-S bending vibration.

Fig. 4 displays SEM images of DVB and SDVB. The resin comprised microspheres with diameters of $100\text{--}150\text{ }\mu\text{m}$. A comparison of DVB with SDVB revealed that treatment with sulfonic acid did not change the size or shape of the particles. The filling resin was regenerated at 280°C . Therefore, the thermal properties of DVB and SDVB were determined by TGA and shown in Fig. 5. DVB began decomposing at 392.82°C , and dramatically decreased at 405.4°C . The decomposition temperature was 463°C . Owing to the hydrophilicity of SDVB, moisture caused initial weight loss of SDVB at 187.01°C . The decomposition of SDVB also occurred around 468°C . TGA results also revealed that sulfonated DVB resins not only maintain their thermal properties but also exhibited hydrophilicity in the adsorption of polar hydrocarbons.

3.2 Adsorption Tests of Sulfonated Divinylbenzene Adsorbent

Fig. 6 shows the total mass (ng) of a 20-ppm mixture of gaseous BTEX, ethanol and MEK in a bulb that were adsorbed by the NTS and SNTS. Notably, the 2-h adsorption mass of organic compounds was approximately double the 1-h adsorption mass for all compounds indicating that the adsorption had not saturated at 1–2 h, and the adsorption mass was proportional to the

Fig. 5. Thermal gravimetric analysis of DVB and SDVB.

Fig. 6. Adsorption mass of organic compounds by NTS and SNTS.

sampling times. Table 1 presents the RSD values for NTS and SNTS in the extraction of BTEX, ethanol and MEK. A sampling times of either 1 h or 2 h, all RSDs of the adsorption masses in duplicate tests of the NTS and SNTS were under 10%. Accordingly, the procedures of preparing the NTS and the SNTS effectively ensured their extraction of gaseous BTEX, ethanol and MEK.

The SNTS adsorbed twice as much ethanol as did the NTS for adsorption periods of 1 h and 2 h (Fig. 6). The sulfonation of DVB improved the hydrophilicity of the adsorbent, so SDVB had a greater affinity than DVB for ethanol. However, the SNTS adsorbed 12% more MEK than did the NTS at 1 h, and 20% more at 2 h. According to the data in Fig. 6, the mass of BTEX that was adsorbed by SNTS was a little lower than adsorbed by the NTS. The SNTS adsorbed 6–14% less than the NTS at 1 h, and 4–15% less at 2 h.

3.3 Monitoring of Organic Vapor Emissions at a Working Place Using Micro Samplers

Personal sampling devices, including passive NTS and active charcoal tubes, were simultaneously worn in the breathing zones by four selected operators at the target site (Fig. 2). Table 2 shows that the concentrations of low-polarity compounds (*n*-hexane and iso-dodecane), that were measured using NTS, SNTS and adsorbent tubes, did not vary significantly from each other. The

Table 1. Deviation distribution of three duplicate tests for needle trap samplers.

Compounds	Relative standard deviation (%)			
	DVB-NTS ^a (1 h)	SDVB-NTS ^a (1 h)	DVB-NTS ^a (2 h)	SDVB-NTS ^a (2 h)
Ethanol	9.6	9.2	4.7	8.9
MEK	9.7	9.8	6.0	10.0
Benzene	9.2	8.4	9.1	10.0
Toluene	10.0	5.6	5.6	8.8
EB	6.6	2.6	9.2	9.6
<i>o</i> -Xylene	2.9	2.6	3.9	9.1

^a Four DVB-NTS and four SDVB-NTS were prepared and tested.

Table 2. Workers' organic vapor exposures in the wiring frame processing plant.

Organic compounds	Exposure concentrations from standing processing (ppm) ^a			Exposure concentrations from tooling repair (ppm) ^a		
	NTS	SNTS	Adsorbent tube	NTS	SNTS	Adsorbent tube
Methanol ^b	6.2 ± 0.6	15.2 ± 0.3	15.3	< 0.26	< 0.26	< 0.32
<i>n</i> -Hexane ^b	16.4 ± 0.7	17.7 ± 1.5	17.9	12.3 ± 0.2	12.4 ± 1.8	12.8
<i>iso</i> -Dodecane	14.9 ± 3.7	14.5 ± 3.5	N.A. ^c	6.6 ± 1.6	6.8 ± 1.3	N.A. ^c
Toluene	< 0.15	< 0.15–0.44	N.A. ^c	< 0.15	< 0.15	N.A. ^c
<i>o</i> -Xylene	< 0.14	< 0.14–0.59	N.A. ^c	< 0.14	< 0.14	N.A. ^c

^a Concentrations are displayed as the actually detected ranges.

^b Methanol was sampled and analyzed using Method 2000 and *n*-hexane using Method 1500 (NIOSH, 2003) by the contracted corporation.

^c N.A. (not available) indicates *iso*-dodecane, toluene and *o*-xylene were not analyzed by the contracted corporation.

NTS and the SNTS are alternatives to the standard method (Method 1500) for sampling low-polarity hydrocarbons. The SNTS had better adsorption capacities than the NTS for methanol which has a high polarity, owing to the effect of sulfonation of the SDVB adsorbent. Notably, the concentrations of methanol, that were obtained by sampling by the SNTS and the Method 2000, were close to each other (15.2 ± 0.3 ppm vs. 15.3 ppm). Therefore, the SNTS, which is packed with SDVB adsorbent, is a suitable sampler of hydrophilic and hydrophobic hydrocarbons for occupational health-related purposes.

The permissible exposure limits (PEL) for methanol is 200 ppm, and that for *n*-hexane is 50 ppm (NIOSH, 2007). In Plant A, the exposure concentrations of methanol and *n*-hexane were lower the respective PELs for organic solvent operators. *iso*-Dodecane is a low-hazard petroleum hydrocarbon, which is often used as a thinner. The exposure concentrations of toluene and *o*-xylene were much lower than the PELs of 100 ppm (NIOSH, 2007). Based on the exposure concentrations in Table 2, the health risks of those organic solvents to workers are low and operational management of organic solvents in Plant A is satisfactory.

4 CONCLUSIONS

In Taiwan, solvent vapors in a working environment must be monitored at least once every six months (Ministry of Labor, Taiwan, 2016). Accordingly, workers in Plant A, who used solvents that contain methanol and *n*-hexane, must wear an adsorbent tube and a sampling pump to sample organic vapors. The effectiveness of SNTS as an alternative sampler was evaluated in this work. The SNTS can be reused when the adsorbed analytes are thermally desorbed at the insert port of a chromatograph, and SNTS analysis does not require solvents for extraction during the injection sample preparations. Additionally, an SNTS is small and very light, so a worker can wear it more easily than an NIOSH sampling device.

In this work, sulfonated DVB adsorbents, which were packed into SNTS to extract airborne organic compounds, were verified to be effective for adsorbing high-polarity hydrocarbons. For testing purposes, more organic compounds should be adsorbed by SDVB in the future, with a focus on

those hazardous compounds, and those commonly used in industry, such as dimethylformamide (DMF), aniline, acetonitrile and pyridine.

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DISCLAIMER

The authors declare no conflict of interest.

SUPPLEMENTARY MATERIAL

Supplementary material for this article can be found in the online version at <https://doi.org/10.4209/aaqr.210157>

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