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# Theory and Validation of Solid-Phase Microextraction and Needle Trap Devices for Aerosol Sample

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Previous aerosol studies utilizing solid-phase microextraction (SPME) predominantly focused on volatile and semivolatile compounds in the gaseous phase. Difficulties were associated with quantitative analysis of these compounds when they were associated with atmospheric particles. The present study combines SPME technology with that of carboxen packed needles (needle trap, NT) for analysis of gaseous and particle-bound compounds in atmospheric samples. The NT device is constructed as a micro trap by placing some small sorbents in a needle. Aerosol samples are collected by drawing air through the NT device with a pump. The trapped components contain both gaseous chemical compounds as well as particulate matter present in the sample. The total concentration of analytes in an aerosol sample can be obtained on the basis of the exhaustive sampling mode of the NT device. Direct SPME is simultaneously used to determine gaseous compound in the aerosol sample. As a result, the SPME and NT devices, when used together, can provide a complete solution to highly efficient and accurate aerosol studies. The theoretical considerations of SPME and NT devices for aerosol sampling are validated by sampling seasalt aerosol, barbecue, and cigarette smoke. The concentrations of PAHs in the different phases of the samples are few ng/L. Result analysis shows that SPME and the NT device demonstrate several important advantages such as simplicity, convenience, and low costs under laboratory and on-site field sampling conditions.

To date, one of the top research priorities of field and laboratory campaigns remains the measurement of atmospheric semivolatile and volatile organic compounds (SVOC and VOC) from both anthropogenic and biogenic emissions.<sup>1,2</sup> Because of their ubiquity and potential toxicity, their atmospheric concentrations are an important parameter used to monitor and manage air quality. Nevertheless, the monitoring of volatile and semivolatile compounds such as biogenic  $\alpha$ -pinene and anthropogenic PAHs is complicated by their distribution between the gas and

particulate phases.<sup>3</sup> Moreover, because the impact of SVOC or VOC on human health and their atmospheric behavior depends heavily on their atmospheric physical state, accurate methods for the simultaneous measurement of their gaseous and particle phase concentrations are required.<sup>4</sup>

Direct determination of atmospheric SVOC or VOC in different phases is an experimentally challenging problem that has not yet been fully solved. SVOC or VOC levels in ambient air are low, on the order of picograms to nanograms per cubic meter.<sup>5</sup> The relatively low concentration of SVOC or VOC is the main difficulty associated with their analysis in particle phase. Over the past decades, a variety of sampling methods including solvent extraction,<sup>6</sup> impingers,<sup>7</sup> filters,<sup>8</sup> and SPME fibers<sup>9</sup> have been employed for analysis of SVOCs associated with atmospheric particles. However, none of these methods can provide simultaneous measurements of the gaseous and particle phase concentrations of SVOC or VOC because they suffer from a lack of discrimination between these phases. Solvent extraction has the disadvantage of high detection limits due to diluted samples. Filter sampling methods are prone to both positive and negative artifacts due to the deposition and evaporation of semivolatile compounds. Among these methods, SPME is the most promising method for extracting or concentrating gaseous atmospheric volatile compounds.<sup>10,11</sup> The success of this technique is due to both its robustness and its ease of handling. Unfortunately, this sampling technique is not effective for atmospheric volatiles in the particle phase.

In response to demand for more robust miniaturized extraction systems for particulates analysis, a needle trap device (NTD) technique has recently been introduced.<sup>12</sup> Blunt type hypodermic needles, packed with a proper sorbent, are used for trapping particulate matter and aerosols from air with analysis by thermal

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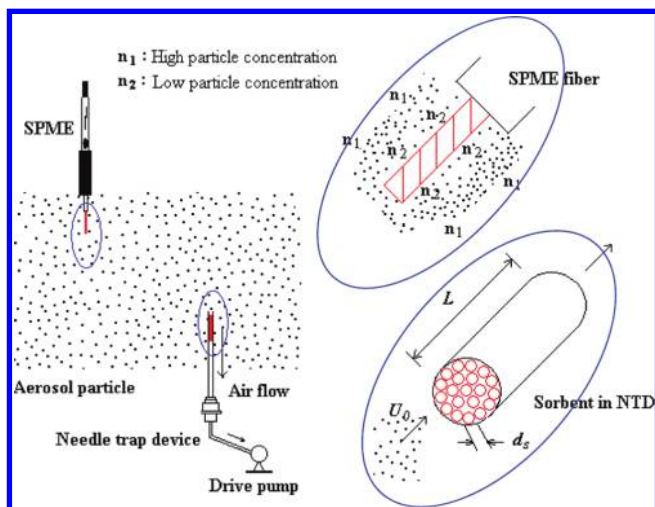
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**Figure 1.** Schematic diagram of the sampling system for the aerosol particle experiments using NTD and SPME devices.

desorption into gas chromatographic (GC) systems. The NT device combines the concept of exhaustive active sampling with the miniaturization and integration of SPME. For extraction, the sample is drawn through the sorbent, and the analytes are concentrated by the different packing materials. Desorption is performed by inserting the needle into the GC injector port. This device shares the advantages of SPME such as simplicity and convenience. Recent applications of micropacked needles have mainly been described for use in the environmental field, for example, for sampling PAHs from airborne particulate matter and aerosols, analyzing insecticides in mosquito-coil smoke, preconcentrating BTEX in air, and determining important VOCs in breath gas.<sup>13–16</sup>

The main objective of this study was to develop a simultaneous sampling method, which combines SPME with NTD for quantitative analysis of atmospheric SVOC in both gas and particle phases. The SPME fiber is only used to extract gaseous molecules based on diffusion, whereas the NTD, as an exhaustive sampling device, can collect total SVOC including gaseous and particle-bound fractions. Sampling of biogenic  $\alpha$ -pinene in seasalt aerosol and anthropogenic PAHs in barbecue and cigarette smoke was completed with the NTD and SPME fibers, followed by analysis on a conventional GC with MS or FID. Screening for  $\alpha$ -pinene and PAHs in different aerosols with these simple devices was used to investigate the concentration of the gaseous and particulate fractions. Possible extraction theories of SPME and NTDs for aerosols are also discussed.

## THERORETICAL CONSIDERATIONS

In this work, we assume that SPME measures the gaseous portion of analyte, while NT traps both particulates and the airborne portion of analyte. The schematic diagram of the

sampling system is shown in Figure 1. The theoretical considerations will be given next.<sup>17</sup>

**Calculation of the Number of Particles Deposited on the Surface of an SPME Fiber.** When a SPME fiber is exposed to an air sample matrix, particles transfer from the sample matrix and bind irreversibly to the surface of the SPME fiber coating in a rate determining step based on Brownian motion. This process follows Fick's first law of diffusion:

$$J = -D \frac{dn}{dx} \quad (1)$$

where  $J$  is the number flux of aerosol particle from the sample matrix to the SPME fiber,  $D$  is the particle diffusion coefficient, and  $dn/dx$  is the particle concentration gradient. Equation 1 for aerosol particles is the same as for gases, except that the concentration and flux are expressed in terms of the number of particles.

Aerosol particles, unlike gas molecules, can adhere by molecular interactions when they collide with a SPME fiber surface. Because particles have no inherent volatility, the adhesion is irreversible. This irreversibility means that the suspended aerosol concentration at the fiber surface is zero and that a concentration gradient is established in the region near the fiber surface. This concentration gradient causes a continuous diffusion of aerosol particles to the surface, which leads to a gradual decline in concentration.

The simplest case is a plane vertical surface in an infinitely large volume of aerosol that has a uniform initial concentration  $n_0$  (it can be used for infinite volumes, provided that the gradients established at other walls do not interfere). We assume that there is no gas velocity near the surface. The first objective is to determine the rate at which particles are removed from air sample matrix by deposition onto the surface. Here, we assume that the deposition occurs with infinitely high affinity and is not reversible. If we let  $x$  be the horizontal distance from the surface, then the particle concentration at  $x$  at any time  $t$ ,  $n(x, t)$ , must satisfy Fick's second law of diffusion:

$$\frac{dn}{dt} = D \frac{d^2n}{dx^2} \begin{cases} n(x, 0) & \text{for } x > 1 \\ n(0, t) & \text{for } t > 0 \end{cases} \quad (2)$$

The solution of this equation is:

$$n(x, t) = \frac{n_0}{(\pi Dt)^{1/2}} \int_0^x \exp\left(\frac{-p^2}{4Dt}\right) dp \quad (3)$$

where  $p$  is a dummy variable that goes from 0 to  $x$ .

The rate of particle adsorption per unit area of SPME fiber surface can be calculated by evaluating the concentration gradient at the surface and applying Fick's first law. The concentration gradient at the surface,  $dn/dx$  at  $x = 0$ , is given by eq 3 as

$$\frac{dn}{dt} = \frac{n_0}{(\pi Dt)^{1/2}} \text{ for } x = 0 \quad (4)$$

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Substituting eq 4 into eq 1 gives the deposition rate of particles onto a unit area of surface at any time  $t$ .

$$J = n_0 \left( \frac{D}{\pi t} \right)^{1/2} \quad (5)$$

By integrating eq 5, we can get the cumulative number of particles deposited per unit area of surface during a time  $t$ ,  $N(t)$ .

$$N(t) = \int_0^t n_0 \left( \frac{D}{\pi t} \right)^{1/2} dt \quad (6)$$

$$N(t) = 2n_0 \left( \frac{D}{\pi t} \right)^{1/2} \quad (7)$$

Although eq 7 applies only to an infinite volume of stagnant aerosol maintained at a concentration of  $n_0$  outside the gradient region, it is useful for predicting the upper limit of losses to the walls of a finite container.

The diffusion coefficients ( $D$ ) of different particles in air can be found in the literature or calculated with the Stokes–Einstein equation:

$$D = kTB \quad (8)$$

where  $k$  is Boltzmann's constant ( $1.38 \times 10^{-23}$ ),  $T$  is the absolute temperature, and  $B$  is the particle mobility, which is influenced by various factors such as particle size, aerosol viscosity, the mean free path, and particle collision diameter.

**Calculation of the Number of Particles Collected by Needle Trap Device (NTD).** The capture of aerosol particles by filtration is the most common method of aerosol sampling and a widely used method for air cleaning. The NTD acts like a filter, and aerosol particles can be collected on the sorbent in the needle by passing the aerosol sample through the device. A common misconception is that aerosol filters work like microscopic sieves in which only particles smaller than the holes can get through. This view may be appropriate for the liquid filtration of solid particles, but it is not how aerosol filtration works.<sup>17</sup>

When filters are used for sampling (as in NTD), their ability to collect particles is usually characterized by their efficiency of collection (the fraction of entering particles retained by the filter)  $E$ . Similar to the single fiber theory,<sup>17</sup> the NTD efficiency can be estimated by integrating the single collector efficiencies  $\eta$  for the whole sorbent length  $h$ , formed by sorbents with diameter  $d_s$ , and the result is expressed as follows:

$$E = \frac{N_{in} - N_{out}}{N_{in}} = 1 - \exp\left(\frac{-4\alpha h \eta}{\pi d_s}\right) \quad (9)$$

where  $N_{in}$  and  $N_{out}$  refer to the number of particles entering and leaving the filter, respectively, and  $\alpha$  is the volume fraction of fibers, called the packing density or solidity.

The difficulty in applying eq 9 is in determining  $\eta$ . To determine this parameter, we need to explain the deposition mechanism. There are four mechanical mechanisms by which an aerosol particle can be deposited onto a sorbent in NTD: inertial, gravitational, direct interception, and diffusional. Inertial impaction of a particle on a fiber occurs when the particle, because of its

inertia, is unable to adjust quickly enough to the abruptly changing streamlines near the fiber and crosses those streamlines to hit the fiber. The parameter that governs this mechanism is the Stokes number. Collection by interception occurs when a particle follows a gas streamline that happens to come within one particle radius of the surface of a fiber. The particle hits the fiber and is captured because of its finite size. The first two mechanisms tend to predominate in the filtration of larger particles (above  $0.5 \mu\text{m}$ , typically). The work of Lee and Liu is taken here as representative for small particle filtration.<sup>18</sup> These studies have shown that, within the submicrometer particle size range, diffusion is the dominant collection mechanism, and other mechanisms are considered to be negligible.<sup>18</sup> According to Otani's research related to granular filters, the diffusional and direct interception efficiencies,  $\eta_D$  and  $\eta_R$ , respectively, can be calculated by the following empirical eqs 10 and 11.<sup>19</sup>

$$\eta_D = 8(d_s V_0 / D)^{-2/3} \text{ for } Re \rightarrow 0 \quad (10)$$

$$\eta_R = 16R^{2-Re/(Re^{1/3}+1)^3} \approx 16R^2 \text{ for } Re \rightarrow 0 \quad (11)$$

In these equations,  $D$  is the particle diffusion coefficient,  $V_0$  is the superficial gas velocity,  $Re$  is Reynolds number, and its value should be low and below 1 in our experiment for the size of the granules packed in needle at the gas velocities.

By substituting eqs 10 and 11 into eq 9, we obtain:

$$E = 1 - \exp\left(\frac{-4\alpha h(\eta_D + \eta_R)}{\pi d_s}\right) = 1 - \exp\left(\frac{-32\alpha h}{\pi d_s^{5/3} D^{2/3} V_0^{2/3}} + \frac{-64\alpha h R^2}{\pi d_s}\right) \quad (12)$$

where  $R$  is the interception parameter, which can be written as:

$$R = d_p / d_s \quad (13)$$

where  $d_p$  is the diameter of aerosol particle.

## EXPERIMENTAL SECTION

**Chemicals and Supplies.** Methanol and other solvents (HPLC grades) used in the experiments were obtained from Fisher Scientific (Ottawa, Canada).  $\alpha$ -Pinene and polycyclic aromatic hydrocarbons (acenaphthylene, acenaphene, fluorene, anthracene, fluoranthene, and pyrene) were obtained from Sigma-Aldrich (Oakville, Canada). Other heavy PAHs were not considered because of their lower volatility. A mixed standard (0.5 mg/mL) of PAHs was prepared in methanol, stored in the refrigerator, and used as the stock solution for subsequent experiments. NaCl solutions with  $\alpha$ -pinene were prepared in the laboratory and used for seasalt aerosol. Deionized water used for dilution of stock solutions was from a Barnstead/Thermodyne NANO-pure ultra water system (Dubuque, IA). SPME fibers with commercially available coatings (PDMS 100  $\mu\text{m}$ ; PDMS/DVB 65  $\mu\text{m}$ ; and CAR/PDMS 75  $\mu\text{m}$ ) were obtained from Supelco (Bellefonte, PA). All new fibers were conditioned according to the manufacturer's

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recommendations prior to their first use, and they were kept at the temperature of desorption for an additional 30 min prior to each sample sequence. The process of SPME loading has been described in detail in the Supporting Information. Needles (22-gauge, inner diameter 0.41 mm) and sampler syringes were obtained from DynaMedical Corporation (London, Canada). Adsorbent materials (DVB and Carboxen particles, 80/100 mesh, and particle diameter 150–180  $\mu\text{m}$ ) for the needle trap package were purchased from Restek (Bellefonte, PA). A bidirectional syringe pump from Kloeohn (Las Vegas, NV) was used for sampling and the performance evaluation of NTDs.

A commercial domestic microwave oven (1000 W, model MW5490W, Samsung, Korea) and 1 L gas-sampling bulbs (Supelco, Bellefonte, PA) were used for standard gas preparation, the design and operation of which have been described previously.<sup>20</sup>

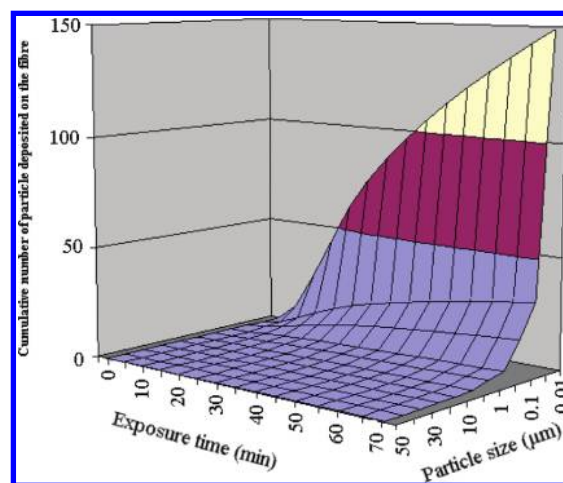
**Aerosol Generator and Sampling Devices.** Figure 1 schematically shows the test system for measuring gaseous and total PAHs in smoke aerosol using SPME and NTD devices, respectively. To determine the concentration of  $\alpha$ -pinene in different phases, a constant output atomizer (model 3076, TSI Inc., Shoreview, U.S.) was used. Aerosol generation systems were used to generate polydisperse submicrometer-sized aerosol particles with  $\alpha$ -pinene. The test material was NaCl.

**Instrument.** A Varian 3800 GC/MS system fit with a SPB-5 column (30 m, 0.25 mm i.d., 0.25  $\mu\text{m}$  film thickness) (Supelco, Mississauga, Canada) was used for SVOC and VOC analyses. The instrumental operation conditions were as follows. The injector temperature was 300  $^{\circ}\text{C}$ ; the carrier gas employed was helium (purity 99.9995%) at a constant flow rate of 1 mL/min. The oven temperature program was 1 min at 50  $^{\circ}\text{C}$ , then 1.5  $^{\circ}\text{C}/\text{min}$  up to 80  $^{\circ}\text{C}$ , and finally 5  $^{\circ}\text{C}/\text{min}$  up to 200  $^{\circ}\text{C}$ . This final temperature was maintained for 0.5 min. The injection was made in splitless mode for 2 min at a temperature of 300  $^{\circ}\text{C}$  and using a SPME inlet guide and predrilled Thermogreen LB-2 septa from Supelco (Bellefonte, PA). The MS system was operated in the electron ionization (70 eV) mode to detect the targeted compound.

**Scanning Electron Microscopy (SEM).** A LEO-1530 VP microscope (Carl Zeiss NTS GmbH, Oberkochen, Germany) was used to acquire SEM images of smoke particles using an acceleration voltage of 10 kV. Prior to analysis, fibers were placed midstream in cigarette smoke to collect particles. The sample discs were subsequently prepared by sputtering a thin layer of gold onto their outer surfaces.

## RESULTS AND DISCUSSION

**Validation of Equation 7.** SPME (100  $\mu\text{m}$  PDMS) fibers were used as passive samplers to validate the predictive ability of eq 7. Before calculating the cumulative number of particles deposited, it is necessary to determine the diffusion coefficient ( $D$ ) of particles. On the basis of Stokes–Einstein eq 8, the effect of particle size on the diffusion coefficient is shown in Table S1 (see Table S1 in the Supporting Information). Next, the cumulative number of particles deposited on the fiber (surface area for 100  $\mu\text{m}$  PDMS fiber =  $3.14 \times (300 \times 10^{-6}) \times (1 \times 10^{-2}) = 9.42 \times 10^{-6} \text{ m}^2$ ) was calculated by assuming an aerosol concentration of 1000 particle/ $\text{cm}^3$  ( $=10^9 \text{ particle}/\text{m}^3$ ). Figure 2 shows that the number of particles deposited on the SPME fiber surface is



**Figure 2.** Cumulative number of particles (0.01–50  $\mu\text{m}$ ) deposited on a 100  $\mu\text{m}$  fiber.  $n_0 = 1000 \text{ particle}/\text{cm}^3$ .

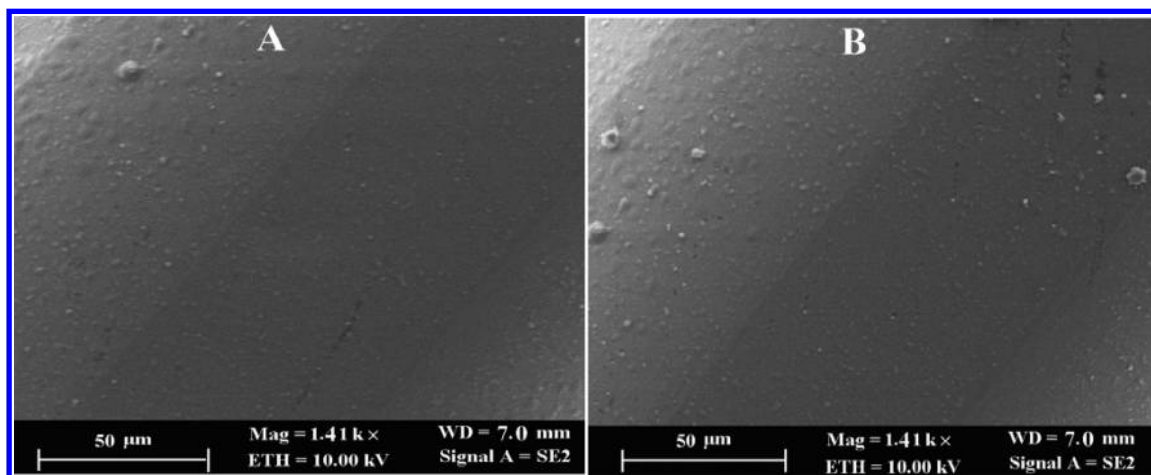
inversely proportional to the particle size. For small particles (0.01  $\mu\text{m}$ ), at a long deposition time (60 min), about 150 particles deposit on the surface of SPME fiber. By comparison, for larger particles (10  $\mu\text{m}$ ), only 1 particle is predicted to deposit on the fiber. This result indicates SPME should not effectively trap the particles.

To further confirm that SPME was not a significant particle collector, direct SEM imaging was performed. A SPME fiber (100  $\mu\text{m}$  PDMS) was exposed to cigarette smoke for 30 min and then used for SEM study. Figure 3 shows there is no significant increase in particles on the fiber after exposure to the smoke. Even for the whole fiber, only a few small particles (below 1  $\mu\text{m}$ ) can be observed on the fiber surfaces. These small particles also exist on the surface of the blank fiber. This existence means that these small particles are from earlier adsorption, and not from the smoke aerosol samples. This result proves SPME is a comparative particle-free sampling device for aerosol samples. This observed result is consistent with the well understood mass transfer processes, which are commonly described by the boundary layer model.<sup>21</sup> Analyte flux in the bulk of the sample is assumed to be controlled by convection, whereas analyte flux within the boundary layer is controlled by diffusion. In many cases, the diffusion of analytes through the boundary layer controls the extraction rate. There is a concentration gradient in the boundary layer, which causes a continuous diffusion of analyte to the surface. Diffusion coefficients for gaseous molecules in the air are about  $2.0 \times 10^{-5} \text{ m}^2/\text{s}$ , which is about a million times greater than the diffusion coefficient of a 10  $\mu\text{m}$  particle ( $2.4 \times 10^{-12} \text{ m}^2/\text{s}$ ). This difference means that the number of gaseous analyte molecules deposited on the fiber is much greater than that of particles.

To make this explanation more easily understood, we can use a simple calculation to demonstrate SPME is a particle-free sampling process. Assume that in this smoke sample matrix the studied compounds, PAHs, only exist in two states, for example, gaseous and particle-bound, and the percent of each is 50%. When the SPME fiber was exposed to this air sample matrix to collect PAHs, the cumulative number of particles or gaseous molecules

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**Figure 3.** Scanning electron micrographs of SPME fiber before (A) and after (B) collecting smoke particles from cigarette burning.

$N(t)$  deposited on fiber surface due to diffusion can be calculated with eq 7.

$$N_{(\text{PAHs, gaseous})} = 2 \times (50\%n_g) \left( \frac{D_g}{\pi t} \right)^{1/2} \quad (14)$$

$$N_{(\text{particle})} = 2n_p \left( \frac{D_p}{\pi t} \right)^{1/2} \quad (15)$$

where  $n_g$ ,  $D_g$  and  $n_p$ ,  $D_p$  are the number and diffusion coefficients of gaseous PAH molecules and smoke particles, respectively.

number of gaseous PAH molecules per each

$$\text{particle adsorbed} = \frac{50\%n_g}{n_p} \quad (16)$$

PAH molecules collected by the fiber from particle-bound sources can be calculated as below:

$$\begin{aligned} N_{(\text{PAHs, particle-bound})} &= \frac{50\%n_g}{n_p} \times N_{(\text{particle})} = \\ \frac{50\%n_g}{n_p} \times 2n_p \left( \frac{D_p}{\pi t} \right)^{1/2} &= \\ 2 \times (50\%n_g) \left( \frac{D_p}{\pi t} \right)^{1/2} \end{aligned} \quad (17)$$

The gaseous collection percent for SPME can be estimated as follows:

$$N_{(\text{PAHs, gaseous})} \% = \frac{N_{(\text{PAHs, gaseous})}}{N_{(\text{PAHs, gaseous})} + N_{(\text{PAHs, particle-bound})}} \times 100\% \quad (18)$$

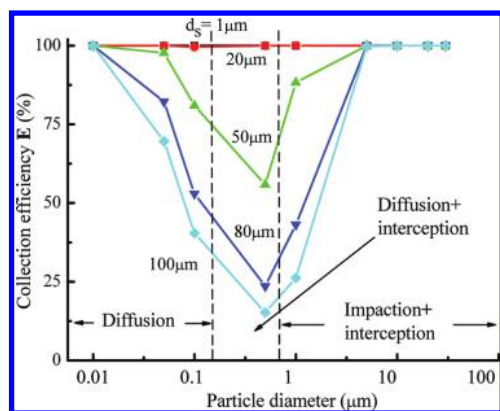
By substituting eqs 14 and 17 into eq 18, we have

$$N_{(\text{PAHs, gaseous})} \% = \frac{D_g^{1/2}}{D_g^{1/2} + D_p^{1/2}} \times 100\% \quad (19)$$

For smoke sampling with 100  $\mu\text{m}$  PDMS fiber, we can assume diffusion coefficients ( $D_g$ ) of gaseous PAHs are approximately  $2.0 \times 10^{-5} \text{ m}^2/\text{s}$ , the same as that of common gaseous molecules (see Table 1S in the Supporting Information).<sup>17</sup> By the combination of diffusion coefficients of particles with different sizes (see Table 1S in the Supporting Information), the gaseous collection percent can be calculated; for 0.01  $\mu\text{m}$  particles ( $5.4 \times 10^{-8} \text{ m}^2/\text{s}$ ), the gaseous PAHs collection percent ( $N_{(\text{PAHs, gaseous})} \%$ ) is above 95%, similarly, for 0.1  $\mu\text{m}$  particle,  $N_{(\text{PAHs, gaseous})} \% > 99\%$ . As particle size increases,  $N_{(\text{PAHs, gaseous})} \%$  becomes progressively closer to 100%. Thus, the SPME technique can be thought as a particle-free technique, which only samples gaseous chemicals.

**Calibration Curve for SPME.** A bulb was used to prepare standard gaseous mixtures of PAHs at different concentrations. The samples were subsequently analyzed using SPME under the same extraction conditions to establish the relationship between the extracted amount and the target standard concentrations. Next, the concentration of the target analyte can be calculated from the equation of the calibration curve (see Figure S1 in the Supporting Information). This calibration method does not require extensive sample preparation, but the sampling time must remain constant at 40 min for equilibrium extraction (see Figure S2 in the Supporting Information). Because the maximal gaseous concentration of each PAH compound varies with its vapor pressure, the obtained linear range of each PAH is also different (see Figure S3 in the Supporting Information). Low molecular weight PAH compounds, such as acenaphthylene, acenaphene, and fluorene, have wide linear ranges because they possess high vapor pressure. Similarly, high molecular weight anthracene, fluoranthene, and pyrene have narrower linear ranges. Although the linear range is different for each compound, it is enough to quantify their gaseous concentrations in air.

**Validation of Equation 12.** A series of needle trap devices packed with carboxen 1000 sorbent are used to extract the total PAHs of smoke aerosol in this work. All the packed lengths  $h$  are controlled at 10 mm. A solidity  $\alpha$  of 0.3 is calculated by employing the ratio of sorbent volume and total volume. This solidity value ( $\alpha = 0.3$ ) is used throughout the investigation, although a small error may result for different sorbent sizes. When the packed length  $h$  and solidity  $\alpha$  are held constant, all of NTD filters have the same pressure drop. On the basis of eq 12, a deductive Figure



**Figure 4.** NTD collection efficiency  $E$  versus aerosol particle size for different granular carboxen sorbent filters ( $d_s$ ),  $h = 10$  mm,  $\alpha = 0.3$ , face velocity 10 cm/s. (Note: They are not entirely overlapped at the 100% level between  $d_s = 1$   $\mu\text{m}$  and  $d_s = 20$   $\mu\text{m}$ .)

4 is constructed, which illustrates the effect of sorbent particle size on collection efficiency. Diffusion is the only important mechanism for sample particles smaller than  $0.2$   $\mu\text{m}$ . Interception contributes significantly to the collection of sample particles larger than  $0.2$   $\mu\text{m}$  over a wide region. Impaction is important for large particles and face velocities greater than  $1$  cm/s. This is because the NTD collection of particles is governed by mechanisms that depend on the particle's aerodynamic diameter and sorbent physical diameter. This behavior is in common with that of fibrous filtration or porous membrane filters.<sup>17</sup> Figure 4 shows that the sample particle size range that is trapped with minimum efficiency is about  $0.2$ – $0.8$   $\mu\text{m}$ . This size is in between one that is too small for diffusion to be effective and too large for impaction or interception to be effective. This result provides evidence that in general small sorbent particle sizes collect more aerosol particles and produce better collection efficiency.

The effect of face velocity on NTD efficiency as a function of aerosol particle size was also studied (see Figure S3 in the Supporting Information). The cumulative collection efficiencies are inversely proportional to the gas velocity; however, it is noted that the face velocities used for testing the NTD filters are relatively low ( $\leq 20$  cm/s). Figure S3 shows that the NTD filters that perform with high collection efficiencies are carboxen of  $150$ – $180$   $\mu\text{m}$  when operating at low velocities ( $< 5$  cm/s). Collection efficiencies obtained by using different NTD sorbent particles below  $150$   $\mu\text{m}$  show a significant improvement due to their porosity and the irregular surface of the sample particle nanoagglomerates. Similarly, when operating at a given face velocity (e.g.,  $10$  cm/s), one can identify a sample particle size that is trapped with minimum efficiency, usually in the particle range  $0.2$ – $0.8$   $\mu\text{m}$ . When the sizes of airborne particles collected are below or above this size, NTD collection efficiency will decrease or increase as particle size increases, respectively. These theoretical calculations show that by optimizing some NTD experimental parameters such as sorbent particles size, packed sorbent length, quality of packing, and sampling flow rate, it can be possible to target a certain range of particle sizes to trap on the sorbent.<sup>12,22</sup>

To test the validity of the theoretical conclusion that NTD can trap particles, two NT devices were used to investigate total

**Table 1.** PAH Concentration in Smoke Aerosol Samples Measured by Solid-Phase Microextraction (SPME) and Needle Trap Device (NTD) (ng/L)

	cigarette burning			barbecue cooking		
	$C_{\text{gaseous}}$	$C_{\text{total}}$	$C_{\text{particle-bound}}$	$C_{\text{gaseous}}$	$C_{\text{total}}$	$C_{\text{particle-bound}}$
acenaphthylene	8.9	13.9	5.0	38	69	31
acenaphenex	7.4	13.0	5.2	18	95	77
acenephene	10.1	11.2	1.2	29	78	49
anthracene	6.6	9.8	3.2	38	91	53
fluoranthene	6.0	13.5	7.5	27	58	31
pyrene	7.5	12.9	5.4	30	70	40

(gaseous plus particle-bound) PAHs in smoke aerosol. An important advantage of the NT method is that it can be used in an exhaustive extraction mode. Exhaustive extraction means that analytes can be completely extracted by the sorbent inside the needle before breakthrough occurs. If a sampling volume is smaller than the breakthrough volume, the total concentration of analyte  $C_{\text{total}}$  can be calculated with eq 19:

$$C_{\text{total}} = \frac{n_{\text{total}}}{V} \quad (19)$$

where  $n_{\text{total}}$  is the mass extracted, and  $V$  is volume of the sample. For the breakthrough volume study, two NT devices packed with DVB sorbents were connected in series with a universal GC column connector. The hub of the front NT device was cut so that it could be coupled to the back NT device. To test for breakthrough, the two-section NT devices were connected to the sampling pump, and the front NT device was exposed to the standard PAHs gas sample. The sample was drawn through the two NT devices at a recommended sampling flow rate of  $1.9$  mL/min for different total sample volumes as described below.<sup>22</sup> The enriched PAHs on the sorbent were thermally desorbed and separated in the GC. The sampling volume was increased until the analytes extracted by the back NT device could be detected by GC. The experimental result showed that the breakthrough volume of this NT device was  $80$  mL for acenaphthylene, acenephene, and fluorene and  $100$  mL for anthracene, fluoranthene, and pyrene. The lower breakthrough volume of acenaphthylene, acenephene, and fluorene was likely due to their weaker affinity to the sorbent.

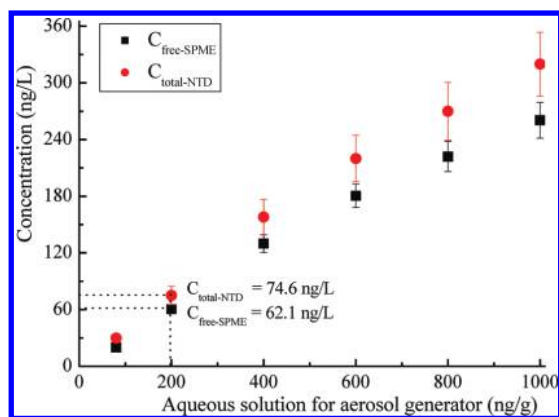
**Barbecue and Cigarette Smoke.** The feasibility of conducting SPME and NTD in parallel to evaluate gaseous versus total analyte was validated by sampling real smoke aerosols. The experiments were performed in headspace of cigarette burning and barbecue cooking. The SPME sampling time was  $40$  min, and the NTD sampling volume was  $50$  mL. After sampling, the SPME fibers and NTD were plugged and transported to the laboratory for analysis. Gaseous concentration ( $C_{\text{gaseous}}$ ) was simultaneously derived using calibration curve. Table 1 shows that concentration distributions of PAH between the gaseous and particulate phases compounds. These distributions generally gave agreement similar to those reported in the literature.<sup>23,24</sup> However, our samplers were calibrated in an indoor environment with limited samples and a

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**Figure 5.** Variation of gaseous and total concentrations with standard solution for aerosol generator.

relatively narrow range of exposure concentrations at relatively calm conditions. Some  $C_{\text{gaseous}}$  were lower than their  $C_{\text{particle-bound}}$ , which means there is a strong association of PAH with the particle phase. Because of the difference in molecular structure, each PAH congener behaved differently in particle-gas distribution. In addition, it is worthwhile to note here that barbecue smoke has a higher particle-bound proportion than does cigarette smoke. As is known, the main source of PAHs in atmosphere is from the incomplete combustion of organic matter or exhaust emission of automobiles, and large amounts of soot and PAHs can be produced during the barbecue cooking. Initially, the newly generated PAHs do not have sufficient time to volatilize into the gaseous phase and adsorb on the surface of soot particles. This made barbecue smoke have a higher particle-bound proportion for PAHs.

**Sampling  $\alpha$ -Pinene from in NaCl Aerosol.** The above smoke aerosol mainly contains solid particles with large diameter range (200–1000 nm),<sup>25</sup> while NaCl aerosol in this section consists of fine particles. A typical particle diameter of NaCl aerosol atomized from 100 mg/L solution is about 100 nm.<sup>26</sup> We chose  $\alpha$ -pinene as the studied analyte for NaCl aerosol to investigate its concentration distribution in different phases.  $\alpha$ -Pinene is one of the most

important biogenic VOCs in the atmosphere, and its oxidation products are known to significantly contribute to the aerosol mass loading.<sup>27</sup> More knowledge of biogenic  $\alpha$ -pinene is crucial in improving our understanding of their associated with climate change and health.<sup>28</sup> In this study, we explored the application of SPME and NTD for the determination of gaseous and total  $\alpha$ -pinene in NaCl aerosol. An aerosol generator was used to simulate to NaCl aerosol with  $\alpha$ -pinene. Figure 5 shows variation of gaseous and total  $\alpha$ -pinene concentrations from standard solutions for the aerosol generator. Preliminary results indicate that SPME and NT device can be used for fine particle matrix characterization. Further improvement may make it better for fine particles by the optimization of needle packing, air velocities inside the needle, and on-site monitoring.

## CONCLUSION

Quantitative analysis of VOC or SVOC associated with airborne particles is an important concern for atmospheric studies. This issue was addressed in both theoretical and experimental levels in this study by the use of SPME and NT devices. Both devices performed very well when applied to sampling NaCl aerosol, barbecue, and cigarette smoke. The simultaneous determination of  $C_{\text{gaseous}}$  and  $C_{\text{total}}$  provides information for better relating chemical concentrations to potential environmental effects. Both devices were simple and reusable and, in the case of NTDs, easy to assemble. Further research may be needed including mass transfer process involving airborne particles, on-site environmental monitoring, exhaust sampling, and characterization of sorbent material in needle packing.

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## SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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