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Sampling and Analysis of Airborne Particulate Matter and Aerosols Using In-Needle Trap and SPME Fiber Devices

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A needle trap device (NTD) and commercial poly(dimethylsiloxane) (PDMS) 7- μ m film thickness solid-phase microextraction (SPME) fibers were used for the sampling and analysis of aerosols and airborne particulate matter (PM) from an inhaler-administered drug, spray insect repellent, and tailpipe diesel exhaust. The NTD consisted of a 0.53-mm o.d. stainless steel needle having 5 mm of quartz wool packing section near the needle tip. Samples were collected by drawing air across the NTD with a Luer-tip syringe or via direct exposure of the SPME fiber. The mass loading of PM was varied by adjusting the volume of air pulled through the NTD or by varying the sampling time for the SPME fiber. The air volumes ranged from 0.1 to 50 mL, and sampling times varied from 10 s to 16 min. Particulates were either trapped on the needle packing or sorbed onto the SPME fiber. The devices were introduced to a chromatograph/mass spectrometer (GC/MS) injector for 5 min desorption. In the case of the NTD, 10 μ L of clean air was delivered by a gas-tight syringe to aid the introduction of desorbed analytes. The compounds sorbed onto particles extracted by the SPME fiber or trapped in the needle device were desorbed in the injector and no carry-over was observed. Both devices performed well in extracting airborne polycyclic aromatic hydrocarbons (PAHs) in diesel exhaust, triamcinolone acetonide in a dose of asthma drug and DEET in a dose of insect repellent spray. Results suggest that the NTDs and PDMS 7- μ m fibers can be used for airborne particulate sampling and analysis, providing a simple, fast, reusable, and cost-effective screening tool. The advantage of the SPME fiber is the open-bed geometry allowing spectroscopic investigations of particulates; for example, with Raman microspectroscopy.

The environmental impact, chemical composition, concentration trends, and health effects of airborne particulate matter have been extensively studied and described in the literature.^{1–3} Current sampling methods involve the use of gravimetric filters or impactor

devices and a wide variety of light and laser scattering devices. Many of the analytical methods for the determination of chemical composition of airborne particulate matter require sophisticated equipment and/or the use of strict sample preparation techniques. The tasks of sampling and analysis of airborne particulate matter are often complicated by the complexity of particle size, particle interactions, chemical partitioning between gaseous and particulate phase, and interactions with the sampling medium. The health effects of inhaled particulate matter are associated with both the size and shape of the particulate as well as its chemical toxicity. One of the groups of analytes from the latter category is polycyclic aromatic hydrocarbons (PAHs).

Polycyclic aromatic hydrocarbons have received increased attention in recent years due to their suspected carcinogenic and/or mutagenic nature.⁴ Polycyclic aromatic hydrocarbons originate from incomplete combustion. They are commonly found in gasoline and diesel motor exhaust, as byproducts of open fires, industrial smoke, cigarette and cigar tobacco smoke, and in charcoal-broiled foods. Other sources include coal tar, coal tar pitch, wood preserving agents and coatings, mineral oils, and asphalt.

Current sampling methods for PAHs involve the use of high-volume pumps, filters, and sorbent cartridges; for example, NIOSH 5506, NIOSH 5515, and EPA TO-13A.^{4,5} These methods require extraction from a filter (or sorbent) using an appropriate solvent, followed by subsequent analysis by HPLC, fluorescence, UV detection, or GC/MS. Many of these methods require considerable sampling expertise and sophisticated sampling equipment, long sample collection and sample preparation time, and strict extraction procedures. Thus, there is a need for faster, simpler, and cost-effective sampling for analytical methods for airborne PAHs without compromising the low detection limits achievable with some of the conventional methods. In addition, these new techniques should be applicable to on-site, fast screening.

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The great majority of the analytical methods used for the determination of steroids that are present in inhaler-administered drugs for treatment of asthma use radioimmunoassay protocols, high-performance liquid chromatography (HPLC), and gas chromatography (GC) combined with mass spectrometry (MS).⁶⁻⁸ The latter methods require derivatization prior to injection.⁹ Similarly, the sampling and analysis of consumer sprays and aerosols is usually conducted using a sophisticated sampler, or a method is specific to a particular analyte. To date, there is no simple and fast method for the screening of a wide variety of many consumer products that are delivered in the form of an aerosol.

Solid-phase microextraction (SPME) presents an attractive alternative over traditional analytical methods by combining sampling, preconcentration, and direct (and complete) transfer of the extracted analytes into a standard gas chromatograph.¹⁰ To date, SPME has been successfully applied in numerous environmental applications, including air sampling and analysis methods for total volatile organic compounds (TVOCs) and formaldehyde.¹¹⁻¹⁴ Several researchers have demonstrated that SPME may also be applied to the analysis of PAHs in water.^{10,11,16,17} However, only a few researchers indicated that SPME may be applied to air sampling for PAHs.^{18,19} Chai and Pawliszyn (1995) found naphthalene, phenanthrene, anthracene, and fluoranthene by direct exposure of the SPME device to diesel exhaust.

The main objective of this study was to show the feasibility of sampling for airborne particulate matter and aerosols with a new needle trap device (NTD) and SPME fibers from concentrated sources. Sampling of diesel exhaust, an inhaler-administered drug, and spray insect repellent was completed with the NTD and with the commercial PDMS 7- μ m fibers, followed by analysis on a conventional GC/MS. Screening for PAHs in diesel exhaust with these simple devices was used to investigate the contribution of gaseous and particulate fraction. Porous filters providing a size cutoff of 0.45 μ m were also used to determine the feasibility of fast screening of analytes within a certain particle size range. Possible developments of NTDs are also discussed. In addition, preliminary experiments to determine feasibility of single particle investigations with SPME and Raman microspectroscopy are described.

EXPERIMENTAL SECTION

Chemicals and Supplies. All SPME fibers and devices, syringes, vials, and 16 PAH standards were purchased from

Supelco (Oakville, Ont). Quartz wool was from Chrompack (Walnut Creek, CA). Filters were purchased from VWR (Mississauga, Ont). Ultrahigh purity helium was from Praxair (Waterloo, Ont). All needles were from Chromatographic Specialties (Brockville, Ont). The Azmacort inhaler (Rhone-Poulenc Rorer, Fort Washington, PA), Aerochamber (Trudell Medical, London, Ont), and the Muskol insect repellent (Schering-Plough, Mississauga, Ont) were purchased at a local drug store.

Sampling Devices. Each NTD consisted of a 40-mm long, 23-gauge stainless steel needle with a straight, point style no. 3 opening with quartz wool packing. The quartz wool was packed inside the needle by the repeated pushing of the needle opening through a wad of quartz wool that was placed on a clean and flat surface. The position of the packing was determined by placing a stainless steel wire inside the needle at an exact distance from the needle mounting tip. The packing was then completed by impacting the wool inside with a second wire to the desired depth from the needle opening. For all needles, the 5 mm long packing was positioned 4 mm from the opening.

For the SPME sampling, the PDMS 7- μ m fibers were used. These fibers are commonly used for analytes with greater partition coefficients, such as all PAHs. In addition, a portable Dusttrak model 8520 aerosol monitor (TSI Inc., St. Paul, MN) served as an aerosol sampler. This monitor uses a light-scattering laser-photometer device and was used to record particulate matter concentrations of aerodynamic size of 10 μ m or lower (PM-10) simultaneously with NTD and SPME sampling. The Dusttrak monitor was factory-calibrated for the respirable fraction of standard ISO 12103-1, A1 test dust, known also as the Arizona Test Dust. Although this standard may not be applicable to every type of airborne particulate matter, it may be used as a surrogate measure for common particulates.

Sample Collection. All diesel exhaust samples were collected from a 1998 International 4900 series DT466E truck at the Plant Operations courtyard at the University of Waterloo. Samples were taken when the vehicle was idling (at approximately 750 rpm) using a special sampling train. Whenever possible, all diesel samples were collected simultaneously with NTDs, SPME fibers, and the portable aerosol monitor. Diesel exhaust was delivered to and from a 910-mm long stainless steel pipe (102 mm o.d.) by two 2.4 m sections of corrugated, flexible aluminum tubing. One section of this tubing was placed directly at the tailpipe and all the exhaust was directed to the main sampling tube. Several sampling ports were situated 300 mm from the opening of the tube. Ports were plugged with half-hole Thermogreen septa (Supelco, Oakville, Ont) to allow insertion of the sampling devices directly into the diesel stream. The septa were wrapped with Teflon tape to minimize the sorption. In addition, surface areas of the needle trap and SPME needle that were exposed to the exhaust were minimized by using only shallow (1 mm) insertion from the septa. This was done to prevent excessive sorption of analytes to nonactive parts of samplers; for example, the outside surface of the needles. The alternative technique can be used when no special sampling trains are available. In this case, an SPME fiber (without the holder) is placed inside a modified, 100-mL vial capped with a hole cap and Teflon-coated septum. As a result, only the SPME fiber coating is exposed to an air/exhaust sample and all metal parts of the SPME assembly are inside the

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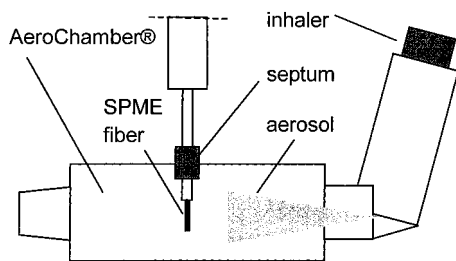


Figure 1. Schematic representation of aerosol sampling with SPME (or NTD).

vial. Such a vial can also serve as a convenient SPME container for field studies. Sampling was also completed upstream and downstream from a porous 47-mm, 0.45- μm filter (VWR, Mississauga, Ont) that was placed between two Teflon rings and flanges inside a 38-mm (1.5-in.) tube. This tube was connected to the main tube and the air sample drawn through the membrane filter using the personal I.H. pump (A. P. Buck, Orlando, FL) at 1.5 L/min.

The exhaust temperature near the SPME fibers and NTDs was measured using an Omega K-type thermocouple and an Omega microprocessor thermometer (model HH22) (Omega, Stamford, CT). Sampling was conducted after an initial stabilization period to ensure that during the sampling the temperature of the exhaust was constant. The steady-state temperature at sampling ports varied from 57 to 62 °C for the main tube and was generally a couple of degrees lower for the membrane area sampling. Exposure times varied from 1 to 16 min for a single PDMS 7- μm fiber. Air volumes pulled through NTDs were also ranged from 1 to 50 mL to vary the mass load. After sample collection, SPME fibers were pulled approximately 30 mm inside the needle, capped and kept at room temperature before analysis on a Varian Saturn-IV GC/MS. Similarly, the NTDs were separated from the sampling syringe, capped, and kept at room temperature before analysis. Both devices used narrow-bore Teflon plugs for sealing the needle opening and sample preservation.²⁰

The aerosol from inhaler-administered Azmacort was sampled inside an aerosol-holding AeroChamber (Figure 1). Additional sampling ports were made in the middle of the chamber length and plugged with half-hole septa wrapped in Teflon tape. The AeroChamber remained horizontal and at room temperature during all of the experiments. The amount of aerosol was varied by administering 1–3 metered doses (puffs). The sampling time for SPME fibers was 10 s. The air volumes varied from 1 to 10 mL for the NTD. The samples were analyzed for triamcinolone acetonide, the medicinal ingredient used in asthma treatment.

The insect repellent aerosol sampling was conducted with both devices inside a 4-L beaker that was used to contain the air during sampling at room temperature. For all experiments, only one short puff of the Muskol insect repellent was used. Sampling time for the SPME fibers was 10 s, and the volume of air drawn through the NTDs varied from 0.1 to 5 mL. Aerosol samples were also analyzed on the Varian Saturn-IV GC/MS.

Sample Analysis. All samples were analyzed within 12 h following the sample collection. Before and after sample desorption in the GC injector, fibers were visually inspected under a microscope, to evaluate particulate matter deposition and the

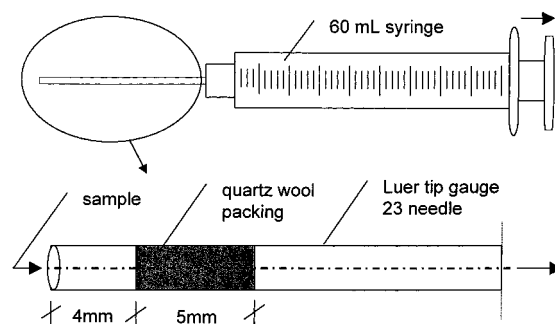


Figure 2. Schematic representation of needle trap device.

effectiveness of particulate removal following 5 min of desorption in the GC injector. The conventional injector glass insert (Supelco, Oakville, Ont.) was packed with quartz wool to prevent column loading with unwanted carbonaceous material. In the case of the needle trap injections, each needle was first attached to a clean Gastight syringe with a plunger positioned at 10 μL and was transferred to the GC injector. The analytes were then desorbed from the needle packing and introduced to the carrier gas by a 10- μL air injection.

Analytes were separated on a HP1-MS (60 m \times 0.25 mm \times 0.25 μm film) column. The column was held at 50 °C for 0.5 min, ramped at 10 °C/min to 300 °C, then held at 300 °C for 14.5 min. Injector and transfer line temperatures were set to 300 °C, and 240 °C. For liquid injections of the PAH standard, the injector temperature was set to 50 °C, followed by ramping with the nominal rate of 300 °C/min to 300 °C, where it was held for the rest of the run. Ultrahigh purity helium was used as the carrier gas at 25 psi. The mass range scanned was 45–285 amu for diesel exhaust, 40–440 amu for aerosol, and 40–200 amu for the spray analysis, respectively. Sixteen EPA 610 standards (Supelco, Oakville, Ont) were used for the calibration of PAH, the spectra library, and the estimation of column retention times.

Single particle investigations with SPME fibers was completed on a Raman microspectroscopy system. Raman spectroscopy has been used in the structural characterization of carbonaceous materials including graphite, carbon fiber, and films.^{21–24} In this research, the confocal Raman spectroscopy was used to reduce undesirable fluorescence. Raman spectra were collected using a Renishaw 1000 microscope system equipped with a 30 mW He–Ne (632.8 nm) laser, a CCD detector, and a precision optical table. This optical system allowed for targeting, collecting images, and analysis of single particles having approximately 1 μm and larger size range. Air samples were collected from diesel exhaust using the same sampling train and diesel exhaust source that was described previously. Sample collection was followed by mounting each SPME fiber on an optical table and analysis was in confocal mode. Raman analysis was completed within approximately 40 min for each SPME sample. Raman results were analyzed on the basis of available literature data and compared to spectra for fused silica fiber and PDMS coating.

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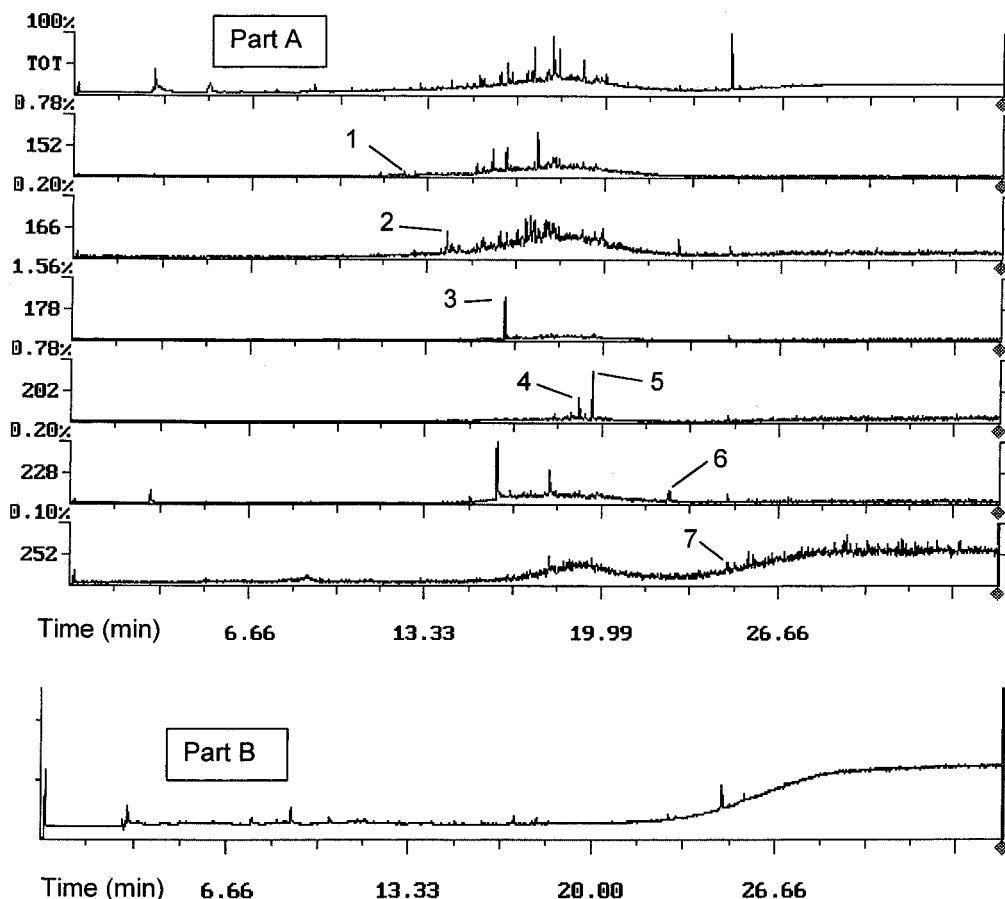


Figure 3. A: comparison of typical GC/MS chromatograms for the total and several single ions of diesel exhaust that were collected using needle devices. 1, acenaphthylene; 2, fluorene; 3, phenanthrene; 4, fluoranthene; 5, pyrene; 6, chrysene; 7, benzo[a]pyrene. B: typical carry-over after 5 min desorption at GC/MS injector at 300 °C (note A and B have the same time scale). Note: the vertical scale in B is 8 times greater than A.

RESULTS AND DISCUSSION

Needle Trap Device. A schematic representation of the needle trap device (NTD) is presented in Figure 2. The NTD combines the idea of active sampling and solid-phase microextraction. The air is drawn through a packing (or filter) and the analytes are trapped. However, unlike the conventional methods in which some sample preparation step is required to extract the analytes, the device is introduced into a conventional GC injector for analyte desorption, in a manner similar to conventional SPME. An additional 10 μ L of clean air is delivered immediately after the needle insertion by a gas-tight syringe to aid the introduction of desorption products. The advantages of such a system are many. The NTD does not require pumps, there are no solvents involved, and the total sampling and analysis time is relatively short and significantly reduced when compared to many existing methods. As such, it can serve as a screening tool wherever fast analysis is needed. In addition, such a device can also serve as a time-weighted average sampler when either continuous sampling over long sampling time or a sequence of short sampling events within a required sampling period is used.

The concept of packed needles is not new, since Tenax-filled needles for sampling and analysis of airborne VOCs were introduced in the late 1970s.²⁵ However, desorption of these

needles required a dedicated carrier-gas purge line. Sorbent-filled needles are not widely used for quantification of VOCs. This is likely because of the possibility of flow rate variations when an air sample is pulled through the needle and also because of the need to pull significant volumes of air to ensure sorption of detectable VOC mass.

Diesel Exhaust. Figure 3 (part A) shows typical GC/MS chromatograms of a diesel exhaust sampled by the NTD from the main sampling tube situated downstream from the truck tailpipe. Sampling volume was 20 mL, with a sampling time of approximately 2 min. The measured concentration of particulate matter with an aerodynamic size of 10 μ m or lower (PM-10) was 4.6 mg/m³. Several PAHs, that is, acenaphthylene, fluorene, phenanthrene, fluoranthene, pyrene, chrysene and benzo[a]pyrene were identified using single ion analysis. A fraction of the detected PAHs, particularly the analytes with lower molecular weight, were likely to be found in the gas phase for the sampling temperature of 60 °C.^{26,27} However, PAHs with higher molecular weights such as chrysene and benzo[a]pyrene were likely to be in the solid phase. This suggests that the analytes with low molecular weight present in the gas phase were likely to be adsorbed onto the packing and surface of the needle. Solid-phase particles were likely to be mechanically trapped on the packing.

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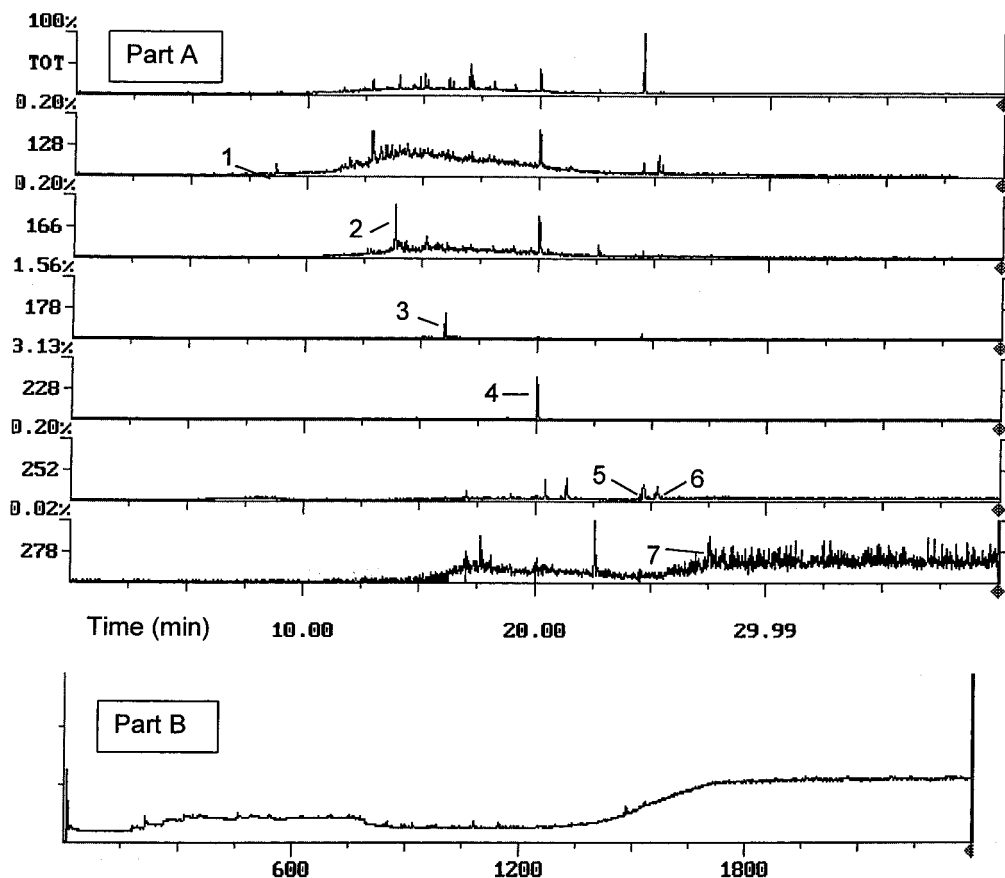


Figure 4. A: comparison of typical GC/MS chromatograms of the total and several single ions for diesel exhaust collected using 7- μ m PDMS. Sampling time, 2 min; PM-10, 4.6 mg/m³; 1, naphthalene; 2, fluorene; 3, phenanthrene; 4, chrysene; 5, benzo[k]fluoranthene; 6, benzo[a]pyrene; 7, indenopyrene. B: typical carry-over after 5 min desorption at GC/MS injector at 300 °C (note A and B have the same time scale).

The results presented in Figure 3 suggest that the NTD could be used as a fast screening tool for analysis of airborne particulates in exhaust samples. The total sampling time was reduced to a few minutes, as compared to several hours of high-volume sampling with sorbent tubes. For NTDs, even a relatively low-volume sample resulted in significant response on the GC/MS. NTDs eliminated the need for additional sample preparation. Trapped analytes were introduced to the GC/MS via temperature desorption and gentle purge from the trap by 10 μ L of clean air. Each needle was analyzed without any solvent extraction. This improvement is significant because all sorbent tubes and filter-based methods require solvent extraction and analysis of a small aliquot of liquid extract.

Reusability. Carry-over from the needle device after 5 min desorption is shown in Figure 3 (part B) at 8 times magnification, as compared to the total ion chromatogram in part A. There was no significant carry-over observed, that is, all PAHs were completely desorbed, which suggests that NTDs can be routinely reused. No significant deterioration was observed for at least 10 samples. This finding is significant, considering the aggressive sampling environment. If needed, the sorbent can be mechanically removed and replaced with fresh packing without the requirement of replacing the needle. This should further reduce the overall low cost of the NTD.

A typical GC/MS chromatogram of a diesel exhaust sampled by a PDMS 7- μ m fiber for 2 min is presented in Figure 4 (part A). The sampling conditions were nearly identical to those

presented in Figure 3 (part A). Both of the sampling devices had similar qualitative results with respect to major classes of detected analytes (including PAHs). Several PAHs, that is, naphthalene, fluorene, phenanthrene, chrysene, benzo[k]fluoranthene, benzo[a]pyrene, and indenopyrene were identified using single-ion analysis. Similar to NTD sampling results, a fraction of the detected PAHs, particularly the analytes with lower molecular weights, were likely to be in the gas phase.^{26,27} However, PAHs with higher molecular weights such as chrysene, benzo[a]pyrene, and indenopyrene were likely to be in the solid phase. This suggests that the analytes with low molecular weights present in the gas phase were likely to be absorbed on the PDMS coating and solid phase particles were likely to be "glued" onto the PDMS. No significant carry-over was observed after a 5-min desorption (Figure 4, part B). Visual inspection using a microscope revealed that particle deposition on the fiber surface was increasing with sampling time. An increase in extracted mass with the sampling time was also observed for several PAHs. Some residual carbonaceous material remained on the fiber coating when sampling time was very long and when sampling was performed on a cold idling engine. This residue did not appear to have any negative effect on the fiber blank and the reusability of the fiber. The reproducibility of sampling with SPME was generally slightly better than with the NTDs and averaged 25% for PAHs targeted in this study. These uncertainties were likely caused by sampling errors; for example, relatively short sampling times, small sampling volumes, and turbulence of diesel exhaust inside the sampling train.

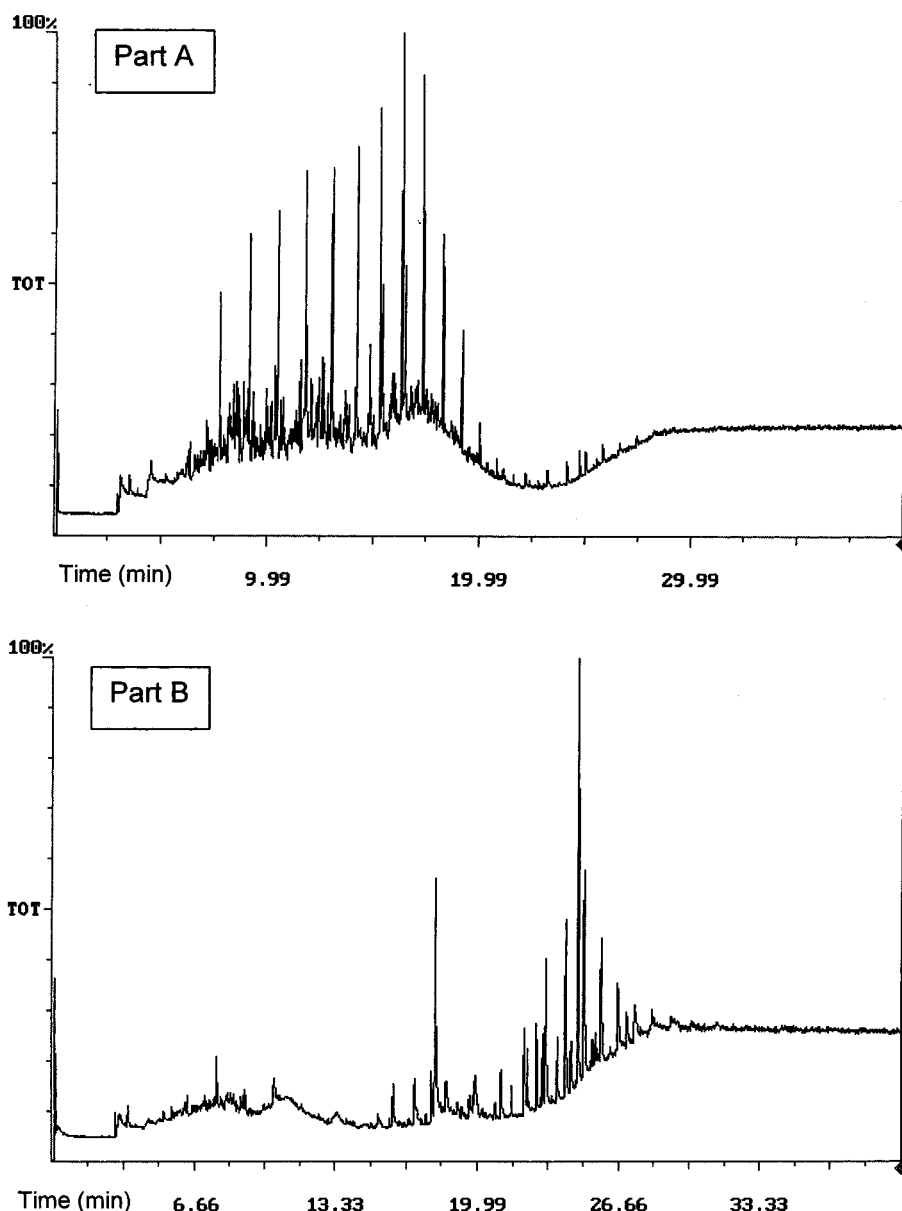


Figure 5. Comparison of CG/MS chromatograms of diesel samples collected using NTDs from the unfiltered (A) and filtered (B) exhaust. Samples were collected upstream and downstream from the 0.45- μm cutoff Teflon filter.

Effects of Particle Size. Figure 5 compares chromatograms of samples collected using NTDs from the unfiltered exhaust (part A) and filtered exhaust (part B). These samples were collected upstream and downstream from the 0.45 μm cutoff Teflon filter. Measured concentrations of PM-10 were 4.6 mg/m^3 and 0.3 mg/m^3 in the unfiltered and filtered exhaust. The sampling time was 2 min, and the temperature of the exhaust was 59 $^\circ\text{C}$. A total of seven PAHs were detected in unfiltered exhaust and only three in the filtered exhaust. Naphthalene and anthracene were detected in both samples. The ratio of unfiltered to filtered mass was approximately 5 and 40 for naphthalene and anthracene, respectively. These findings show that NTDs can also be used for fast screening of airborne particle matter by direct extraction downstream and upstream from separation membranes, impactors or cyclones. This approach could speed up speciation of particulate matter within a certain size range with only small modifications to existing sampling devices. Due to its small size, the SPME fiber

should have no significant obstructing effect on air flow rates and air flow patterns in high-volume samplers. Currently, such a sampling and analysis is very labor-intensive and requires specialized equipment.^{28,29}

Cold vs Warm Engine Exhaust. Figure 6 compares masses of several PAHs detected in diesel exhaust by a PDMS 7- μm fiber with 1 min sampling of a cold and a warm engine. The cold engine exhaust was collected immediately after the startup and the warm engine exhaust was collected after approximately 5 min of high idling. The total of 12 and 5 PAHs were found in the cold and warm engine exhausts, respectively. The abundance ratio of 5 PAHs found in both cold to warm engine exhausts ranged from 2 to approximately 10. As many as 7 other PAHs were found in cold engine exhaust. Many of these PAHs have molecular weights greater than chrysene and are likely to be in the solid phase. This

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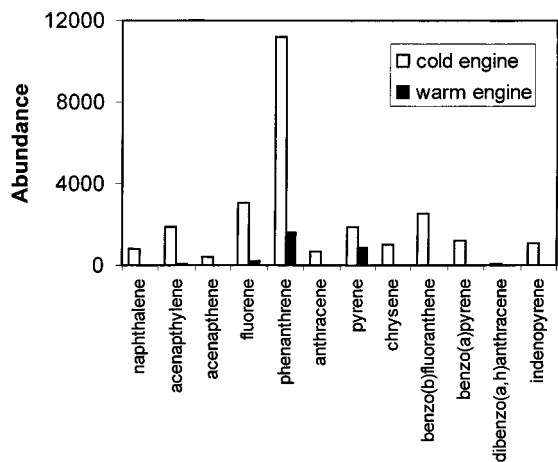


Figure 6. Comparison of PAH masses found in cold and warm diesel exhaust using 1 min sampling with 7- μ m PDMS.

result is consistent with the fact that cold engine exhaust contains more products of incomplete combustion. The use of SPME for fast screening of diesel exhaust could help to address the issue of reduction of air pollution from diesel engines. This issue has recently brought about significant regulatory attention that will likely result in promulgation of emission standards.

Aerosol Sampling. Figure 7 presents a comparison of chromatograms that were obtained from the spray of the insect repellent using the PDMS 7- μ m fiber (part A) and the NTD (part B). DEET (*N,N*-diethyl-meta-toluamide) was identified using the GC/MS NIST library. Both devices were very efficient in extracting significant amounts of DEET, with a short sampling time for

SPME (10 s) and an air volume of less than 1 mL for the NTDs. The insert in Figure 7 shows a linear increase of the DEET dose with increasing sample volume. This was also generally the case with the sampling time and SPME fibers.

A typical chromatogram of asthma drug aerosol containing Azmacort collected using 7- μ m PDMS fiber is presented in Figure 8. Triamcinolone acetonide and other peaks were identified using the GC/MS NIST library. SPME was very efficient in extracting significant amounts of the steroid, considering that a very short sampling time of 10 s was used. The insert in Figure 8 presents the linear increase of the steroid dose with each additional puff and 10-s sampling. The results presented in Figure 8 indicate that SPME can be used for the fast screening of medicinal aerosols. Such a screening is difficult if not impossible using conventional sampling methods and gas chromatography/mass spectrometry.

Development of New Devices. Considering the simplicity the NTD and SPME fibers provide for the sampling of airborne particulate matter, it is possible to envision needle sorbent traps, that is, needles with sorbent packing or coating. Furthermore, combinations of NTDs based on the existing design may be developed in the future. Possible developments may include simultaneous, side-by-side (or parallel) sampling with two needles, sampling with two needles connected in series, or sampling with a single needle containing two-section packing in series. Both devices can also be easily coupled to existing methods for particulate sampling. Needles traps filled with sorbent may serve as a possible alternative to denuders. Possible uses can include determination of partitioning between sorbed and gaseous fractions of PAHs and other analytes in airborne particulate matter.

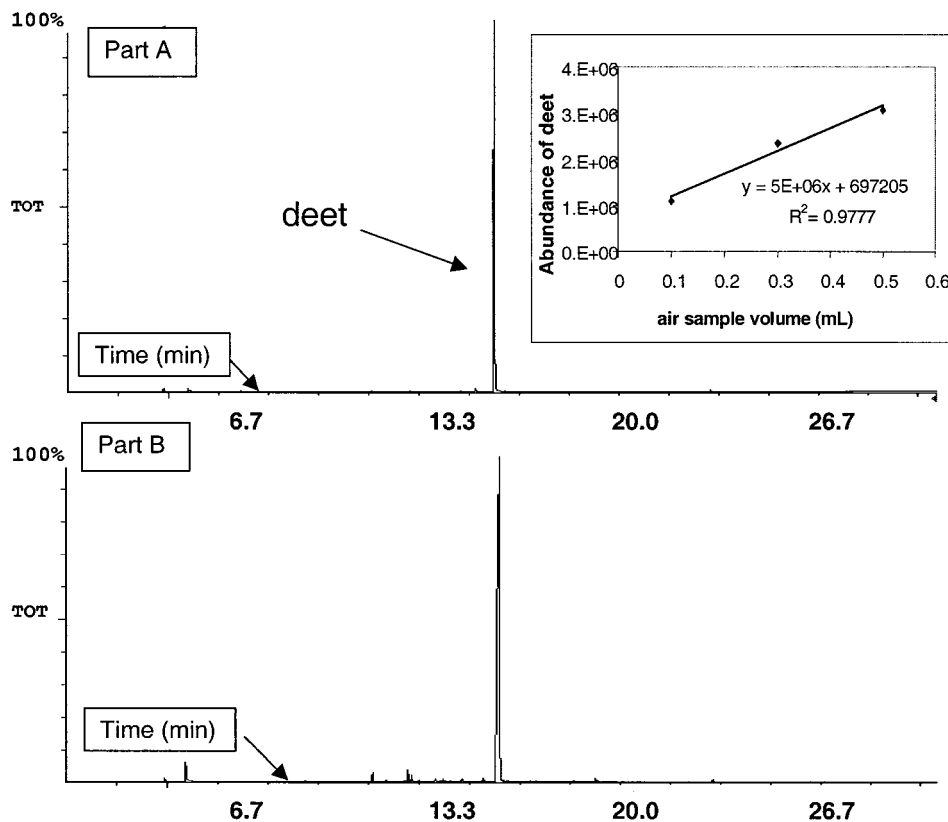


Figure 7. Comparison of typical GC/MS chromatograms of insect repellent containing DEET collected using (A) 7- μ m PDMS, 10-s sampling, and (B) the NTD and air sample volume of 1 mL. The insert plot in A indicates proportional increase of extracted DEET mass with increased sample volume drawn by the NTD. Average PM-10, 106 mg/m³; air temperature, 21 °C.

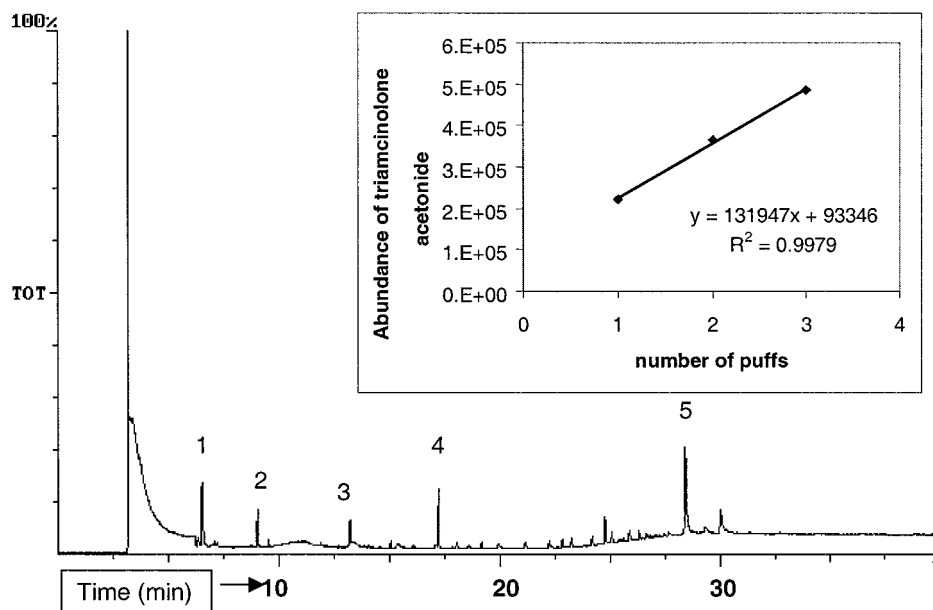


Figure 8. Comparison of typical GC/MS chromatograms of inhaler aerosol containing triamcinolone acetonide collected using 7- μ m PDMS, 10-s sampling, and the NTD and air sample volume of 3 mL inside AeroChamber. Note: 3 puffs were used for each sample; average PM-10, 50 mg/m³; air temperature, 21 °C; 1, 3-heptane, 2,2,4,6,6-pentamethyl; 2, methyl salicylate; 3, butylated hydroxytoluene; 4, morpholine ethanamine; 5, triamcinolone acetonide. Propellants not shown. The insert plot indicates proportional increase of measured mass of triamcinolone acetonide with increased sample dose.

These devices can be incorporated into conventional, active sampling and upstream and downstream sampling from size separation devices such as cyclones, nozzles, impactors and porous membranes.

Single Particle Characterization. In addition to the determination of organic molecules by mass spectrometry, preliminary experiments were completed to determine the feasibility of single particle matrix investigations with SPME. These experiments were completed using 7- μ m PDMS fiber and Raman microspectroscopy measurements.³⁰ Characteristic bands of Si–O–Si and methyl groups originating from the PDMS coating were detected and reproducible. These bands did not interfere with bands for carbon and hydrocarbon groups that originated from analyzed particles. A detailed description of this part of the research will be presented in the forthcoming article.³⁰ Preliminary results suggest that Raman microspectroscopy combined with SPME can serve as an alternative technique for fast analysis of airborne particulate matter. Another innovative approach for single particle analysis can incorporate pairing of SPME and inductively coupled plasma (ICP) detection. A polymer acting as a “glue” trap for particles (as PDMS in this research) could be coated on a carbon fiber and used for ICP determination of the particle matrix.

CONCLUSIONS

The needle trap device (NTD) and SPME fibers were used for sampling and analysis of airborne particulate matter and

aerosol. Both devices performed very well when applied to sampling of diesel exhaust, medicinal aerosol, and a spray consumer product. Both devices proved to be very versatile for handling significantly different samples. These devices allowed for simple and inexpensive screening that is very difficult, if not impossible, with conventional methods. Both devices were easy to use and robust in field sampling. Both devices were reusable, and in the case of NTDs, easy to assemble. In addition, preliminary results indicate that SPME coupled with Raman microspectroscopy can be used for single particle matrix characterization. Further research may be needed to study the effects of aging on needle packing, air velocities inside the needle, effects of air volume, and the effects of the carbonaceous residue on SPME coatings when fibers are exposed to excessive concentrations of particles.

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