

Vapor-Particle Separation Using Microporous Metallic Membrane in Crossflow Filtration

Meng-Dawn Cheng

Environmental and Energy Directorate, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6036, USA
 chengmd@ornl.gov

Simultaneous separation of vapor and particles in industrial processes could be a key step toward manufacturing of high-quality goods. The separation is critical for successful measurement of volatile or semi-volatile aerosol particles, which no reliable technique exists. We have developed a technique for separation of vapor and particles simultaneously using a specialty microporous metallic membrane. The separator allows the thermally denuded particles traverse straight through the membrane tube, while the vapor molecules permeate through the membrane, separate from the particles and are removed subsequently. The separation technique virtually eliminates the possibility of contamination by vapor re-condensation. We tested the prototype of the vapor-particle separator (VPS) using aerosols prepared from sodium chloride to represent non-volatile aerosols. Chemical like dioctyl phthalate was chosen to represent volatile particles. The test aerosol particles were generated by an atomizer followed by a tandem differential mobility analyser to produce a stream of monodisperse particles in the size range of 10 to 100 nm. In real world particles, we tested the VPS using diesel engine particles that is a mixture of complex chemical composition. Number concentration of the nonvolatile particles reduced as the temperature increased, but the mode diameter of the aerosol population remained unchanged. Number concentration of the volatile particles was also reduced as the temperature increased, but their mode diameters became smaller as particles shrunk in diameter. Differences in the thermal behaviour of the particles were attributed to its transition energy barrier and evaporation rate. Mass balance analysis suggests the separation of vapor and test particles was reasonably complete. Thus, we conclude the VPS could provide an effective means for quantitative characterization of aerosol volatility and separation of vapors from particles.

1. Introduction

Membrane is an advanced technology for separating gas species (Barbieri et al. 2011). Vapor-particle partitioning, a key environmental process, controls the complicated behaviour of engine particles and environmental particles. At any given temperature, the vapor-particle partitioning process activates, and the equilibrium concentration of a species in both vapor and particle phases is established. When the temperature changes, a new equilibrium state is established. Some of the condensables will adsorb to nonvolatile soot particles by heterogeneous condensation (Ristimaki et al. 2007); others may form new particles through nucleated condensation (Ronkko et al. 2007). These processes mask the true size distribution of the nonvolatile engine particles. Due to the transient nature of the partition dynamics in the turbulent reactive plume of engine exhaust, representative sampling and accurate measurement of volatile engine particles are a major challenge. At present, there is no recommended procedure for sampling volatile particulate matter in the exhaust plume of any combustion engine. A number of devices have been developed in the past couple of decades for the study of aerosol volatility; however, most of the devices remain as research tools and have never been widely used as commercial instruments. Even the removal of volatile components is problematic for sampling and measurement of nonvolatile soot particles; inadequate removal of volatile components led to biased results (Swanson and Kittelson 2010).

To improve sampling and measurement of ultrafine (< 100 nm) and nanoscale volatile engine particles, we developed a novel instrument built around the concept of cross-flow filtration, which enables thermal

separation of desorbed vapors from nonvolatile particles without the use of an adsorbent. The prototype instrument has been shown to have high-efficiency (Cheng 2010, Cheng and Allman 2011). The objectives of this paper are to (1) report the VPS results from an engine test and (2) demonstrate successful mass transfer by the VPS to eliminate vapors and avoid the analytical bias on the size distribution due to recondensation of vapors on the tested particles.

2. Methods

2.1 Engine operating conditions and gaseous emissions analyses

The engine used for this study was a four-cylinder, 1.9 L light-duty diesel engine operated by the Oak Ridge National Laboratory (ORNL) Fuels, Engines, and Emissions Research Centre (FEERC). Data reported were collected during a conventional diesel combustion (CDC) operation. The engine was operated at 1500 RPM and 2.6 bar brake mean effective pressure with a diesel feed rate at 0.5 g/s. Conditioned air was supplied to the engine to maintain a nearly constant air temperature and humidity level. The diesel injection system, piston geometry, and compression ratio were in manufacturer production form. Figures 1 and 2 are photos taken during the CDC test. The engine is in the middle of the picture in Figure 1 and is surrounded by the emissions monitoring components. The white structure lying on the floor is the home-built PMP system. The tandem differential mobility analysis (TDMA)-VPS setup is shown in Figure 2.

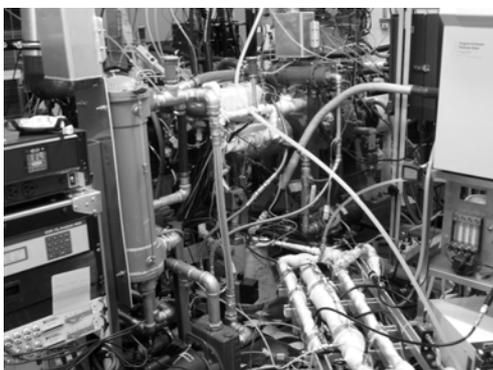


Figure 1. Photo of experimental setup showing the CDC engine

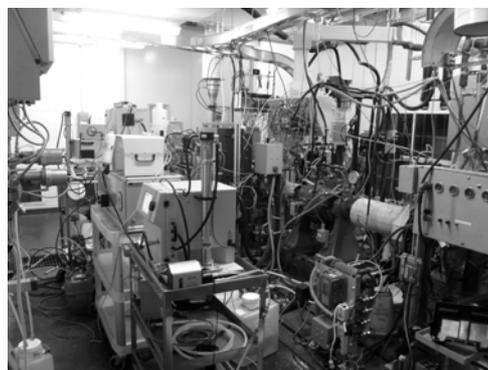


Figure 2. Experimental setup of TDMA-VPS in the engine lab

VPS design and operation

The construction of the VPS was described in detail elsewhere (Cheng 2010, Cheng and Allman 2011). We will describe briefly the instrument and its operation in the current paper. The VPS was found to have very low nonvolatile particle loss (high transmission efficiency) in previous tests (Cheng 2010, Cheng and Allman 2011).

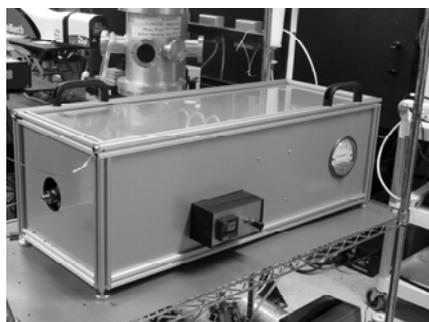


Figure 3. A photo of the VPS instrument. The aerosol inlet is on the left side of the box. The box is 88.9 cm (L) x 30.5 cm (W) x 30.5 cm (H). It weighs about 12 kg and requires a vacuum pump to operate

The transmission efficiency is greater than 95 % for particles greater than 20 nm and 99 % for 50 nm and larger. The VPS consists of two interconnected sections; the first section is a straight hollow cylinder made

of stainless steel 316, which is enclosed by a radiant heater with a ceramic casing. The second section is the vapor-particle membrane separator. The temperature of the radiant heater is proportional-integral-derivative (PID) controlled and monitored by three K-type thermocouples positioned close to the entrance, centre, and exit of the section. Figure 3 is a photo of the VPS prototype.

The VPS instrument consists of two sections in series. The first section is designed to heat the particles in a radiant heater with a residence time greater than 0.3 ms. The second section for vapor-particle separation consists of a straight microporous metallic membrane tube (MMT) enclosed by a concentric hollow cylinder. The membrane is a propriety material manufactured by ORNL. For interested readers, please refer to a previous study that used a MMT for removable of microbes in water purification (Phelps et al. 2008). The nominal pore size used in our application was ten times smaller than that in Phelps et al. (2008). Condensable materials are more sensitive to heat than soot. They can be removed or vaporized more easily than soot particles, which are converted directly into the vapor phase through sublimation at high temperature (e.g., 800 °C). Since vapor has a higher diffusivity than that of solid particles, volatilized material and condensable gases, including unburned and partially burned fuel species, permeate the membrane and are separated from the particles. At that point, the particles are noted as thermally denuded at a given temperature.

2.2 VPS evaluation using TDMA

Monodisperse particles were used to investigate the dependence of VPS transmission and vapor-particle separation efficacy on particle size. TDMA, developed in the 1980s (Rader and McMurry 1986), is a practical technique demonstrated for the production of monodisperse particles and is the technique selected in this work. In our TDMA setup, a nano-DMA (TSI model 3085) classified (i.e., size-selected) particles from the broadband size distribution. The TDMA setup requires the use of two electrical classifiers (ECs); one is used before the VPS for the generation of monodisperse particles; the other is coupled to a condensation particle counter (CPC) at the exit of the VPS to measure the size distribution. Figure 4 illustrates the adopted TDMA configuration in this work. The first EC is equipped with the nano-DMA (TSI model 3085 or DMA1 hereafter). The voltage was manually set on the classifier to the desired particle mobility diameter and was fixed throughout an experiment. The second EC equipped with a long-DMA (TSI model 3081) was connected to an ultrafine CPC (TSI model 3025A) for measurement of particle size distribution. The aerosol generator in Figure 4 can be a diesel engine during test with engine particles, but a TSI model 3076 was also used in replacement during tests when laboratory generated aerosol from pure chemicals were used.

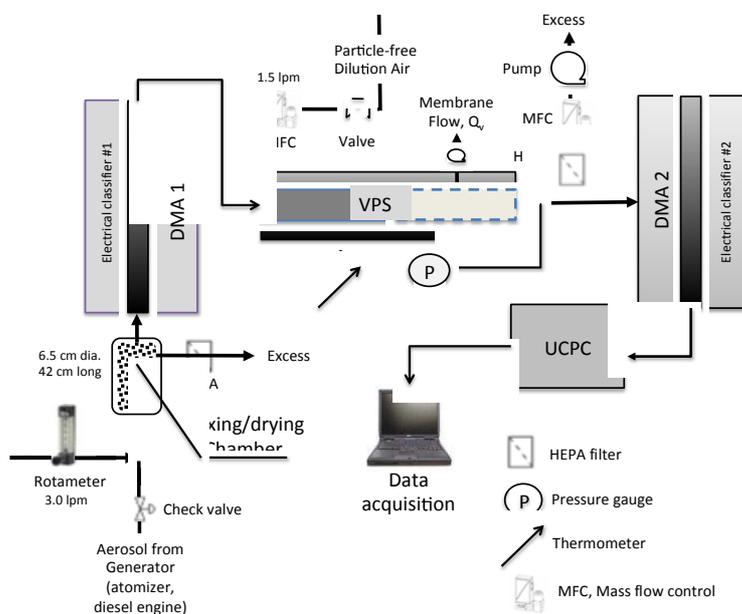


Figure 4. Experimental setup of TDMA for the VPS testing

3. Results and discussion

3.1 Thermal evolution of diesel engine particles under CDC operation

The thermal behavior of the CDC exhaust particles was investigated using monodisperse samples extracted by DMA1 [see Figure 5 (a), (b), and (c)]. Three sizes of particles, 95, 52, and 18 nm, were selected by DMA1 from a broadband engine particle size distribution that peaked at about 52 nm. The geometric standard deviations of the selected particle sizes as shown in the 40°C curves in Figure 5 were all less than 1.2. A geometric standard deviation of 1.2 or less indicates the aerosol population is practically monodisperse; i.e., one mobility size, based on the assumption that the aerosol population is log-normally distributed. The TDMA produces a stable aerosol population over several hours during the laboratory tests using the TSI 3076 as the aerosol generator. The diesel aerosol generator was stable for approximately two hours during the diesel engine test due to operational complexity in operating the diesel engine.

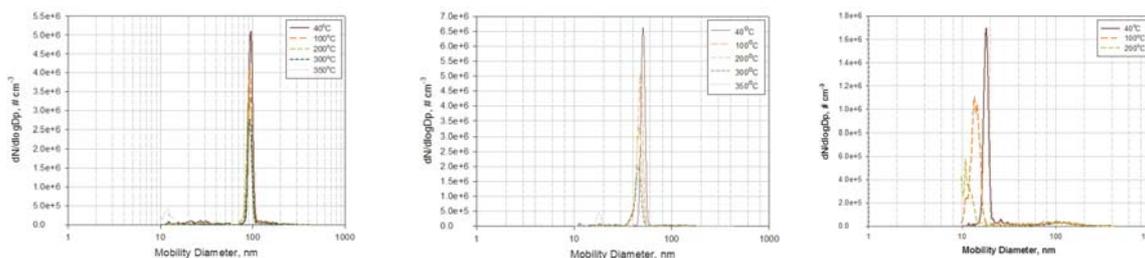


Figure 5. The mobility particle size distributions of the CDC engine particles as a function of the VPS heating temperature. Monodisperse particle size of 95nm (a - left), 52nm (b - middle), and 18nm (c - right)

The VPS was programmed to operate at five set temperatures (i.e., 40, 100, 200, 300, and 350 °C). The temperature in the aerosol stream entering DMA1 was about 40 °C corresponding to the original temperature of the aerosol stream. As shown in Figure 5a, the peak size of the 95 nm exhaust particles changed slightly from 40 to 300 °C, and the peak height (after dilution corrected) decreased as the heating temperature increased. At 350 °C, loss of particles occurred to a substantial extent, and the remaining 95 nm particle population was barely detectable. Previous VPS data from the synthetic particle tests (Cheng and Allman 2011) indicated that the peak number concentration decreased as the heating temperature increased but the peak size or location would not change significantly for nonvolatile particles.

The relatively constant peak size at 95 nm (± 2 nm) for diesel engine particles with increasing temperature shown in Figure 5(a) is consistent with our previous observations for nonvolatile particles made of a pure compound (e.g., sodium chloride) (Cheng 2010, Cheng and Allman 2011). The decrease of the dilution-corrected concentration value as the VPS temperature increased was also observed for the 52 nm [Figure 5(b)] and 18-nm [Figure 5(c)] engine exhaust particles. However, there were significant shifts in peak size toward smaller sizes as temperature increased, as shown in Figures 5(b) and particularly 6(c). This suggests that the 18 and 52 nm particles contain more volatile contents than the 95 nm particles.

As the temperature reached 350 °C, all particles were completely vaporized to less than 2 % of the baseline concentration at 40 °C. For 18 nm particles, the temperature required to reduce the concentration to 2 % of the baseline was about 200 °C lower than 350 °C, indicating that the smaller particles were vaporized much more easily than the larger ones. The results indicate that a large fraction of the small particles probably contained condensable species on a solid core. It is likely that the small particles were in the liquid droplet state (Farrell and Van Sieten 2007).

The behaviour of the CDC diesel engine particles with respect to the applied thermal energy (or heating temperature) was consistent with that for laboratory-generated particles (Cheng 2010, Cheng and Allman 2011) and reported in literature (Ristimäki et al. 2007). For nonvolatile particles or large engine particles, the particle number concentrations dramatically decreased as the heating temperature reached a critical point. The number concentration decrease for smaller or volatile particles appears to be continuous as the temperature changed. The rate of particle loss appears to be higher for smaller particles (e.g., 18 nm) than for the larger ones (52 and 95 nm), given the same material (or loosely speaking, the same engine exhaust).

3.2 Separation of Vapor and Particles

To demonstrate that the VPS was able to separate vapors (stripped off from the particles) and thermally denuded particles, we used aerosol made of a pure chemical – dioctyl phthalate (DOP). The molecular

weight of DOP (CAS # 117-81-7) is 390.56 g/mole and the formula is $C_{24}H_{38}O_4$. It is a colourless, oily liquid with low vapor pressure at the room temperature. The boiling point of DOP is 384 °C. Use a pure chemical in the demonstration eliminates the problem in identify chemical species from a complex mixture like the diesel engine exhaust that has thousands of chemical species. The aerosol generated would contain no or negligible DOP molecules in the vapor phase at the room temperature. Once it is heated, the DOP oil droplets would evaporate and the vapor should be collected at the other side of the membrane. Simple chemical analysis on the collected vapors would provide the identity of the vapor species because the aerosol input is made of only a single compound. However, the chromatogram could contain some minor species that are resulted from thermal decomposition of the DOP particles. If this demonstration were done with the diesel particles, we would have a difficult problem at hand to chemically analyse the vapor phase and identify the chemical species that could be thermally stripped from the diesel engine particles.

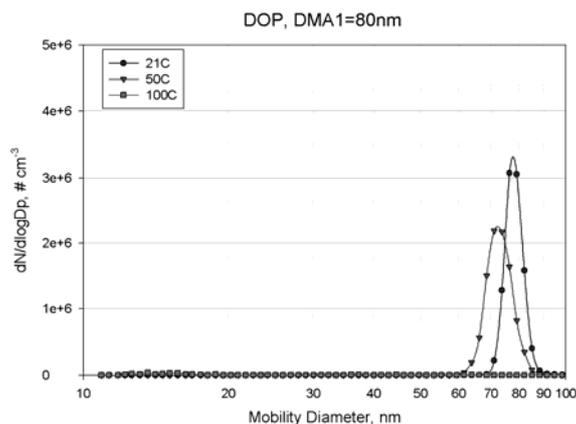


Figure 6. The DOP particle size distribution at the room temperature (21 °C) and heated temperatures (50 and 100 °C)

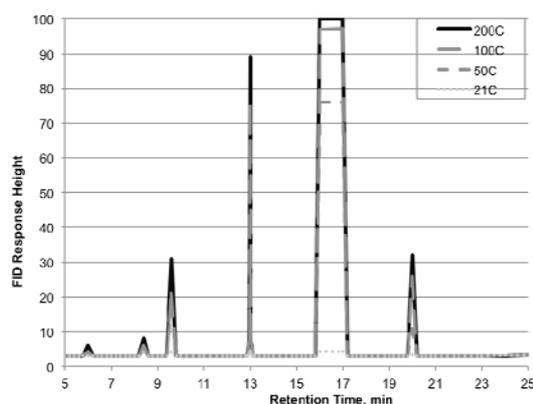


Figure 7. Chromatograms of the vapors collected and analyzed by high performance liquid chromatograph analysis

The DOP particle size distribution as a function of temperature is shown in Figure 6. The distribution at 21 °C was monodisperse and peaked exactly as the first DMA (DMA1 in Figure 4) selected as 80 nm. This 80-nm aerosol population was reduced in the peak size to 70 nm as the temperature was raised to 50 °C and the size dispersion broaden. The peak height was reduced by about 42 % indicating particle loss through mass transfer between the oil droplets and vapor phase; i.e., droplet evaporation. As the temperature was raised to 100 °C, the 80-nm aerosol population was completely eliminated and there was no size distribution curve to be measured.

Particle diffusion loss increased as the temperature increases. Thus, is it possible that the decrease in number concentration was due to the increase in the system's heating temperature? The diffusion loss is not resulting a completely loss of particles. Furthermore, if the DOP particles were attached to the membrane by the diffusional mechanism, there should not be any vapors detected on the other side of the membrane. Remember that the boiling point of DOP is greater than 390 °C. The temperature that the entire 80-nm DOP aerosol population disappears was about 100 °C, not 390 °C at the boiling point. This raises a question regarding the actual boiling point of DOP when it is in an 80-nm liquid droplet form not a bulk liquid. Research is ongoing addressing this question, but is beyond the page limit of this paper.

Figure 7 shows the chromatogram taken on the vapors collected at the 4 temperatures. The peak labeled 3 is the DOP molecule; the peak labeled 2 is octyl hydrogen phthalate resulted from thermal decomposition of DOP. Other small peaks are phthalic anhydride, benzoic acid, 1-octanol, and phthalic acid. The first peak is an injection count. The number 2-peak size increased as the temperature increased indicating more DOP vapors escape from the droplet phase into the vapor phase. Other peaks also increased as the temperature increased. This result is an indication of direct mass transfer of DOP and thermally decomposed species between the aerosol and vapor phase. Results from Figure 6 further suggest that the vaporized DOP molecules did not return to the droplets and recondensed to form secondary peak in a size distribution or to broaden the size distribution. Although it is difficult to quantify or mass balance based on the vapor measurement (in Figure 7) and particle counts (in Figure 6), the two pieces of data qualitatively suggest that vapors did penetrate the membrane and the particle size

distributions of thermally denuded particles were not biased due to recondensation. Was the evaporated DOP species removed through the membrane completely? A rough calculation assuming all evaporated particle mass was in the vapor phase measured by HPLC shows a reasonable closure ($\pm 10\%$) when the areas of all peaks (without the peak number 1) in a chromatogram were added. A mass balance was considered achieved.

4. Conclusions

Lack of a precise definition of volatile engine particles has been an impediment to engine manufacturers and regulatory agencies involved in the development of an effective control strategy. It is beyond doubt that volatile particles from combustion sources contribute to the atmospheric particulate burden, and the effect of that contribution is a critical issue in the on-going research in the areas of air quality and climate change. A new instrument, called the volatile particle separator (VPS), utilizes a propriety microporous metallic membrane to separate particles from vapors. Results presented show that the VPS was able to separate vapors from particles enabling a high-fidelity characterization of volatile particles. Mass balance analysis supports the conclusion of successful separation.

Acknowledgments

This research was supported by the Strategic Environmental Research and Development Program (SERDP) under Project #WP1627 in the Weapons Systems and Platforms Thrust Area. Oak Ridge National Laboratory is managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract number DE-AC05-00OR22725. The author acknowledges the technical support of John M. E. Storey and Scott Curran (ORNL/FEERC) during the diesel engine operation. Steve Allman (ORNL) performed assembly of the VPS and test runs. Brian Bischoff (ORNL) manufactures the MMT and characterizes the properties of the membrane filter.

Disclaimer

Mention of company name, instrument model number and products, and chemicals does not constitute endorsement of the authors nor DOE, ORNL or SERDP. The submitted manuscript has been authored by a contractor of the U.S. Government under contract DE-AC05-00OR22725. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

References

- Barbieri G., Brunetti A., Scura F., Drioli E., 2011, CO₂ Separation by Membrane Technologies: Applications and Potentialities, *Chem. Engr. Trans.*, 24, 775-780.
- Cheng M.-D., 2010, Development and Application of A Membrane-Based Thermodenuder for Measurement of Volatile Particles Emitted by A Jet Turbine Engine, *ASME GT2010-22175*.
- Cheng M.-D. and Allman S.L., 2011, Improved Measurement for Volatile Particles: VPS Design and Laboratory Tests. *Rev. Sci. Instrum.*, 82, 125106.1-125106.8.
- Farrell H.H. and Van Siclen C.D., 2007, Binding Energy, Vapor Pressure, and Melting Point of Semiconductor Nanoparticles. *J. Vacuum Sci Technol. B.*, 25, 1441-1447.
- Phelps T.J., Palumbo A.V., Bischoff B.L., Miller C.J., Fagan L.A., McNeilly M.S., and Judkins R.R., 2001, Micron-Pore-Sized Metallic Filter Tube Membrane for Filtration of Particulates and Water Purification. *J. Microbio. Methods*, 74, 10-16.
- Rader D.J. and McMurry P.H., 1986, Application of the Tandem Differential Mobility Analyzer to Studies of Droplet Growth or Evaporation. *J. Aerosol Sci.*, 17, 771-787.
- Ristimäki J., Vaaraslahti K., Lappi M. and Keskinen J., 2007, Hydrocarbon Condensation in Heavy-Duty Diesel Exhaust. *Environ. Sci. Technol.* 41, 6397-6402.
- Ronkko T., Virtanen A., Kannosto J., Keskinen J., Lappi M. and Pirjola L., 2007, Nucleation Mode Particles with a Nonvolatile Core in the Exhaust of a Heavy Duty Diesel Vehicle. *Environ. Sci. Technol.* 41, 6384-6389.
- Swanson J. and Kittelson D., 2010, Evaluation of Thermal Denuder and Catalytic Stripper Methods for Solid Particle Measurements. *J. Aerosol Sci.*, 41, 1113-1122.