

NANO-DMA/THERMAL DESORPTION PARTICLE BEAM MASS SPECTROMETRIC ANALYSIS OF NANOPARTICLES PRODUCED IN DIESEL EXHAUST

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ABSTRACT

Due to recent epidemiological studies that have found a correlation between atmospheric fine particle (diameter $< 2.5 \mu\text{m}$) mass concentrations and increased human morbidity and mortality, the chemistry of particles produced from diesel engines are of special concern. Diesel engines are known to emit high concentrations of nanoparticles (diameter $< 50 \text{ nm}$), but due to their relatively small mass, chemical analysis is difficult. Here, a nano-differential mobility analyzer (Nano-DMA) was used to size select nanoparticles produced from diesel engine exhaust for subsequent chemical analysis by thermal desorption particle beam mass spectrometry (TDPBMS). A number of organic compound classes and sulfuric acid have been identified and the approximate molecular weights and vapor pressures determined from calibrated desorption temperatures. The effect of particle size and engine operating conditions on the composition of diesel nanoparticles was also studied.

INTRODUCTION

Recent epidemiological studies have found a correlation between atmospheric fine particle (diameter $< 2.5 \mu\text{m}$) mass concentrations and increased human morbidity and mortality. The chemistry of particles produced from diesel engines are of special concern since some laboratory studies suggest a stronger link between adverse health effects and smaller particles.¹ Diesel engines are known to emit high concentrations of nanoparticles (diameter $< 50 \text{ nm}$) and analysis of total diesel aerosol has identified the presence of a number of toxic compounds.² A knowledge of nanoparticle composition is important for understanding the physical and chemical mechanisms by which they are formed in diesel exhaust. Such information can be used to establish the criteria for modifications of diesel engine design or operation, fuel, and lubricating oil that will help reduce nanoparticle formation. Due to the relatively small mass of nanoparticles, chemical analysis is difficult. In principal, an inertial impactor, such as a MOUDI, could be used to sample diesel nanoparticles for chemical analysis. However, in practice this is problematic because the diesel particle mass distribution is heavily weighted towards larger particles since nanoparticles typically compose a few percent of the total aerosol mass. Therefore, even a small amount of bounce from upstream impactor stages contributes a significant amount of contaminant mass to the lower nanoparticle stages. Other sampling artifacts that arise during collection are adsorption and volatilization of compounds. No data has been available for chemical composition of diesel nanoparticles for these reasons.

Here, we use a nano-differential mobility analyzer (Nano-DMA) to size-select nanoparticles produced from diesel engine exhaust for subsequent chemical analysis by thermal desorption particle beam mass spectrometry (TDPBMS). The Nano-DMA provides high concentrations of size-selected diesel nanoparticles without any contamination from larger particles. A number of organic compound classes and sulfuric acid have been identified and the approximate molecular weights and vapor pressures determined from calibrated desorption temperatures. The effect of particle size and engine operating conditions on the composition of diesel nanoparticles was also studied.

EXPERIMENTAL

Diesel particles were generated using a 4-cylinder, 4-cycle John Deere model 4045 TF250 diesel engine rated at 415 N-m @ 1400 rpm, but for which only 350 N-m can be achieved. All experiments were performed at a steady state at an engine speed of 1400 rpm in four modes: 15% load (50 N-m), 25% load (88 N-m), 40% load (140 N-m), and 50% load (175 N-m). The fuel used was commercial EPA on-highway DF2 with 410-ppm sulfur. The lube oil used was John Deere +50 Supreme 15W-40 motor oil. The engine exhaust particles were sampled under constant conditions that closely simulate those in the ambient environment using a two stage air injector, variable residence time, micro-dilution system (VRTDS) previously described in detail.³ A primary dilution ratio of ~16, a secondary dilution ratio of ~4, and a residence time of ~1700 ms was used for generation of high concentrations of nanoparticles with sufficient mass so that subsequent chemical analysis could be performed above the detection limits of the TDPBMS downstream of the VRTDS.

After diesel exhaust sampling through the VRTDS, three different modes of particle size selection were used before chemical analysis using a TDPBMS. In one mode, total particles were analyzed without size selection by sampling diesel exhaust directly from the VRTDS into the TDPBMS and is referred to as the total mode. In the second mode, which is referred to as the 40 nm mode, the diesel exhaust was sampled from the VRTDS into a unipolar charger for high efficiency, high throughput particle charging, followed by a Nano-DMA for size selection of charged nanoparticles with a diameter of average mass of ~40 nm. In the third mode, which is referred to as the 30 nm mode, diesel particles were sampled into a radioactive bipolar charger, followed by a Nano-DMA for size selection of charged nanoparticles with a diameter of average mass of ~30 nm.

Temperature-programmed thermal desorption (TPTD) analysis using TDPBMS⁴ was used for diesel nanoparticle chemical analysis. Particles of ~20-500 nm in diameter are sampled into a high-vacuum chamber with ~40-100% efficiency using aerodynamic focusing techniques. All focused particles impact onto the inside walls of a v-shaped molybdenum foil. The particles were either continuously vaporized for real-time analysis by resistively heating the foil at ~250°C, or cryogenically collected over time for fast-TPTD analysis by cooling the foil to -50°C. The desorbing molecules are ionized by impaction with 70 eV electrons and mass analyzed using a quadrupole mass spectrometer.

Particles sampled in all three modes were cryogenically collected onto the cold foil over times ranging from 15-70 min. After collection, the components of the sample were quickly desorbed according to their vapor pressures and therefore separated to some degree in time. During desorption, the foil is resistively heated from approximately -50 to +300°C over ~6 min. The non-linear temperature ramp rate is about 150, 100, and 50°C/min in the first, second, and third minutes of the desorption. A portion of the evaporating molecules is sampled into the mass spectrometer for mass analysis over the desorption period. Particles generated at each of the four engine conditions (15%, 25%, 40%, 50% load) were chemically analyzed from all three sampling modes (total, 40 nm, 30 nm) using the fast-TPTD procedure. Mass spectral analysis was conducted either by scanning over an appropriate mass range or single-ion monitoring (SIM) of five mass-to-charge ratios (m/z) during the fast-TPTD process.

At certain conditions where considerably less nanoparticle mass was available (e.g. the 30 nm mode, 50% load), full mass spectral analysis was not possible with 60 min sample collections. Increasing collection times to enhance S/N wasn't feasible, therefore SIM of five m/z signals was used instead to provide sufficient S/N to distinguish low nanoparticle signal from the background. With this enhanced S/N, vapor pressure measurements from well defined desorption profiles (m/z signal versus temperature) were also possible. The five masses used in the SIM method were chosen to represent the major organic compound classes identified from the full mass spectra (m/z 69, 85, 95), and sulfuric acid (m/z 81, 98). Diesel particles were collected for 60 min for all fast-TPTD analyses performed using the SIM method. Measurements of signal due to background gases were performed by sampling diesel under the same conditions as the 30 nm Mode and 40 nm

Mode, except that the Nano-DMA was set at 0 volts to allow only diesel exhaust gases to pass through the classifier.

The TDPBMS was calibrated with known standards so that the approximate molecular weights and vapor pressures of the diesel particle components could be estimated. Solutions of pure organic compound, diesel fuel, or lubricating oil in hexane or sulfuric acid in water was atomized using clean air, then dried and sent through a bipolar charger and DMA. The aerosol standard was cryogenically collected on the foil in the TDPBMS high-vacuum chamber and then analyzed using fast-TPTD in the same manner as for the diesel exhaust particles.

RESULTS AND DISCUSSION

Full mass spectra were obtained at the signal peak during desorption for all the 40 nm and 30 nm particle modes at the 15% engine load condition and for total mode particles at the 50% engine load condition. The mass spectra are very similar to each other and by themselves show no major difference in chemical composition as particle size and engine load change; however, desorption profiles using the five mass method reveal compositional differences and will be discussed below. Mass spectra for standards of the fuel and lubricating oil were also obtained using the same fast-TPTD analysis and are very similar to the diesel particle spectra. The fragmentation patterns within the mass spectra of the diesel particles analyzed in this work verify the presence of at least a few of the major organic compound classes found in other studies of diesel exhaust particles that involved filter collection of particles, solvent extraction, and GC-MS analysis.⁵ Our results indicate branched alkanes and cycloalkanes are probably the greatest contribution to the diesel particles. It was not possible to ascertain the presence or absence of PAH in the diesel nanoparticles.

Figures 1 and 2 show a few of the desorption profiles or mass thermograms (m/z signal versus vaporizer temperature) of m/z 69 and 98, respectively, from the matrix of fast-TPTD experiments performed using the five mass method. These plots provide information on the relative volatilities of the particle components, since compounds with lower volatility desorb at higher vaporizer temperatures. For example, analysis of total mode particles at 15% engine load reveals a peak in the m/z 69 signal at $\sim 37^\circ\text{C}$ (Figure 1A), while total mode particles at 50% engine load peak out at $\sim 107^\circ\text{C}$ (Figure 1B). This desorption peak generally shifts to higher temperatures as engine load is increased in all particle modes, indicating a decrease in average compound volatility with increasing engine load. Analysis of m/z 85 and 95 reveal the same trend as for m/z 69. When engine load is held constant, the m/z 69, 85, and 95 desorption peaks also shift to higher temperatures for smaller particle sizes. This temperature difference is indicative of large increases in average compound volatility with increasing particle size. This observation is consistent with particle growth theory, where a compound adds to a particle depending on the difference between rates of compound condensation and evaporation, which in turn depends on the difference between the partial pressure and equilibrium vapor pressure of the compound. Because of the Kelvin effect, the equilibrium vapor pressure of a compound increases with decreasing particle size. Therefore, it is expected that diesel nanoparticles will initially grow by addition of lower volatility compounds, with growth by condensation of higher volatility components increasing with particle size.

For all particle modes at 15% engine load, the desorption profiles of m/z 81 and 98 contain single peaks at the same temperatures as in the profiles of m/z 69, 85, and 95 indicating an organic contribution to these m/z 's. However, for the 40 nm mode at 40% and 50% engine loads (Figure 2A and 2B), in which m/z 69, 81, 85, 95, and 98 all peak at temperatures higher than 150°C , a second peak appears in the desorption profiles of m/z 81 and 98 at $22\text{--}43^\circ\text{C}$, which was determined to be due to sulfuric acid. These results suggest that the nanoparticles form by nucleation of sulfuric acid and water, and that organics subsequently condense onto these nuclei to form the bulk of the particulate mass. At lower loads, more of the higher volatility organics are present in the exhaust and add to the mass of the particles.

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