PHYSICAL AND CHEMICAL CHARACTERISTICS OF DIESEL EXHAUST PARTICLES

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Exhaust particles from modern diesel engines without aftertreatment are found in two distinct, but overlapping size modes: a mainly volatile nuclei mode and a mainly solid accumulation mode in roughly the 3-30 and 30-500 nm diameter ranges, respectively. These particles have been characterized through size-fractionated measurements of volatility, hygroscopicity, density, and chemical composition using a tandem differential mobility analyzer (TDMA), an aerosol particle mass analyzer (APM) and a thermal desorption particle beam mass spectrometer (TDPBMS).

Volatility measurements showed that nuclei and accumulation mode particles are externally mixed across a wide size range, with the chemical components being distributed between two particle types: “less volatile” (probably comprised of an elemental carbon core with a small organic component) and “more volatile.” The volatility experiments showed that, except for the smallest particles, heating could differentiate volatile and solid particles. The fraction of solid particles decreased as particle size decreased, and only a volatile mode was detectable for the smallest particles tested (7 nm). More than 97 percent of the volume of the volatile constituents of 12- and 30-nm particles disappeared on heating to 400°C. The volatility was found to resemble that of C24-C32 normal alkanes, which implies a significant contribution of lubricating oil to the volatile particles.

APM mass and density measurements showed fractal-like behavior with particle mass increasing with approximately the $D_p^{2.4}$ (D_p = mobility diameter) and effective density decreasing from about 1 to 0.3 g/cm^3 in the 50-300 nm diameter range.

TDMA hygroscopicity experiments and TDPBMS analysis suggest the presence of sulfuric acid in diesel nanoparticles when a 350-ppm sulfur fuel was used, but not when a 96-ppm sulfur CA fuel was used. Hygroscopic measurements found that the smallest particles were the most hygroscopic, suggesting enrichment with sulfuric acid. TDPBMS measurements showed that the organic component of total diesel particulate matter and nanoparticles appears to be comprised predominantly of unburned lubricating oil, while the fuel contribution to the total organic component appears to be negligible. The major organic compound classes (alkanes, cycloalkanes, and aromatics) appear to be distributed fairly uniformly across the volatility spectrum. Low-volatility oxidation products (e.g., organic acids) and PAH’s do not appear to be a major portion of the organic mass. The oil that forms particles appears to be derived primarily

from material evaporated from the cylinder walls, although there may also be a significant component from atomization. Nanoparticles formed using 410-ppm sulfur fuel contained small amounts of sulfuric acid, which may enhance nucleation. No sulfuric acid was detected in nanoparticles formed using 96-ppm sulfur or Fischer-Tropsch (< 1 ppm sulfur) fuel. These results are consistent with hygroscopicity measurements.