CHEMICAL AND PHYSICAL CHARACTERISTICS OF DIESEL AEROSOL

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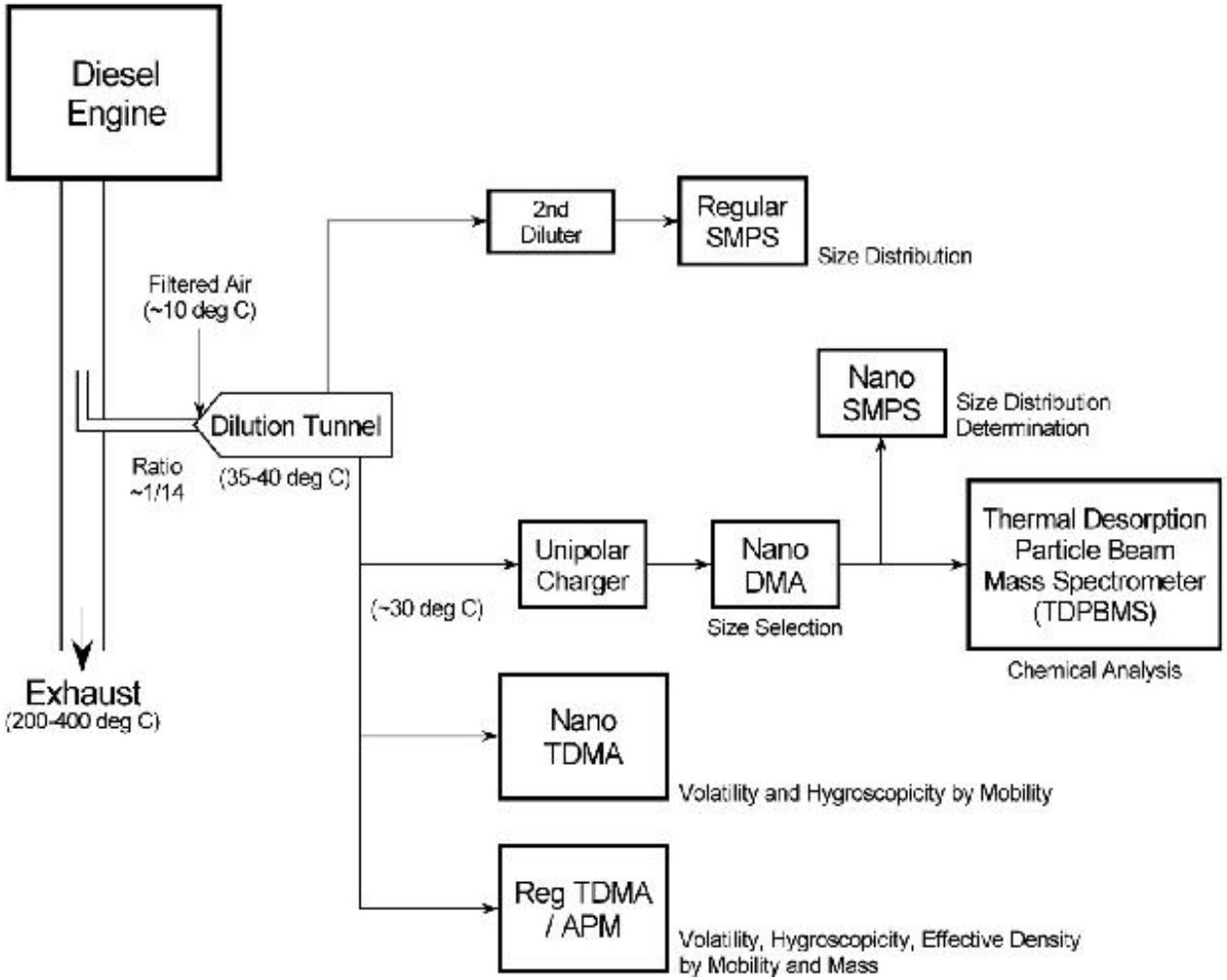
Outline

- Composition of volatile particles by thermal desorption particle beam mass spectrometer
- Equivalent organic carbon number of nuclei mode particles by volatility measurements
- Sulfuric acid content of nuclei mode particles by hygroscopicity measurements
- Effective density of accumulation mode particles by absolute particle mass measurements

Overall setup



TDPBMS measures the volatility and mass spectra of the volatile fraction of *all* the particles in selected size ranges between 15 and 300 nm - Summary Results

- Engines
  - Deere 4045T medium-duty
  - Caterpillar C12 heavy-duty
  - Cummins ISM
- Fuels
  - Federal pump fuel, 360 ppm S
  - California pump fuels, 50 and 96 ppm S
  - Fischer-Tropsch, < 1 ppm S
- Test conditions
  - Light and medium load
  - No aftertreatment

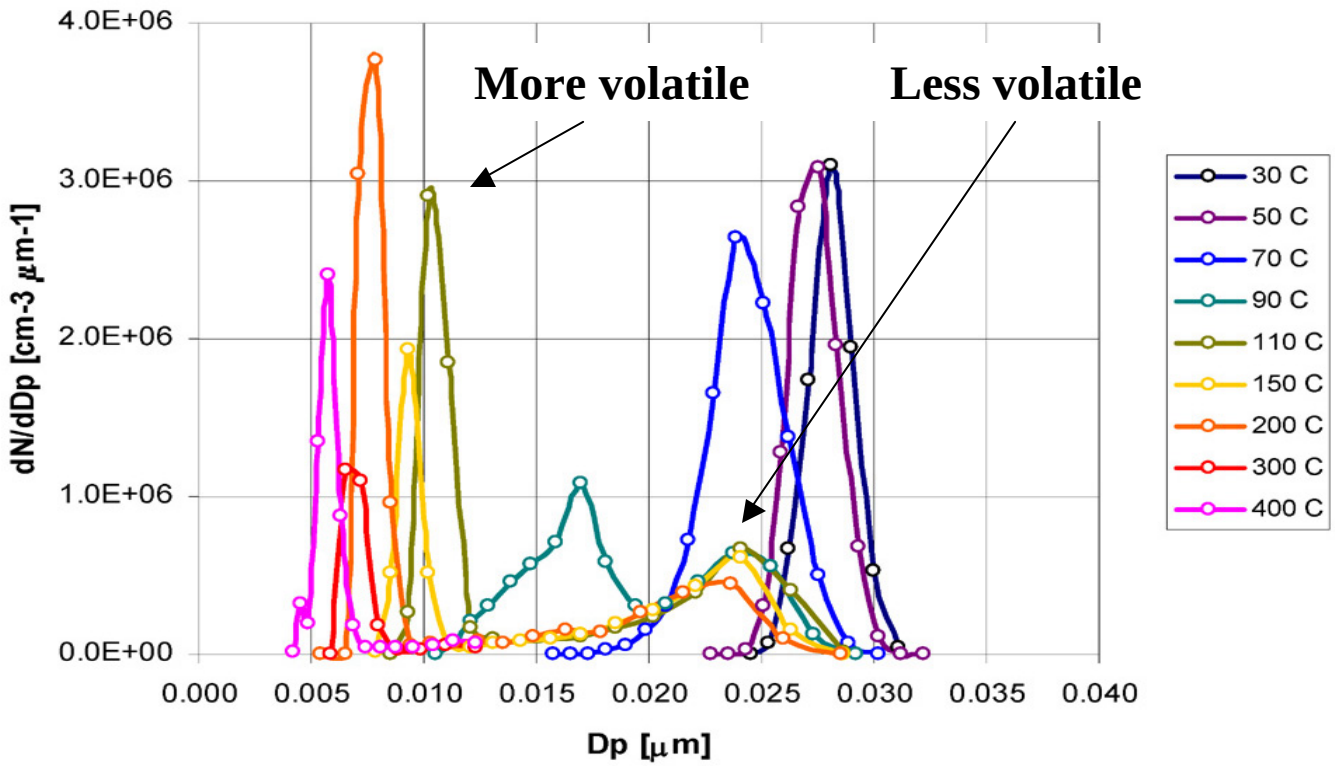
- Composition of volatile fraction
  - Organic component of total diesel particles and nanoparticles appears to be mainly associated with lubricating oil, e.g., > 80% for CA fuels, >95% for FT fuel
  - Major organic compound classes are alkanes, cycloalkanes, and aromatics
  - Low-volatility oxidation products and PAHs have been found in previous GC-MS analyses, but are only a minor component of the organic mass
  - Nanoparticles formed with higher S Federal pump fuel contain small amounts of sulfuric acid but those formed with the lower S fuels show no evidence for sulfuric acid

Physical characterization methods

- Volatility measurements
  - Select single particle size with DMA
  - Heat
  - Observe diameter change and relate to volatility
- Hygroscopicity measurements
  - Select single particle size with DMA
  - Humidify
  - Observe diameter change and relate to content of hygroscopic material
- Density measurements
  - Select single particle size with DMA
  - Measure particle mass with APM
  - Calculate effective density = mass/(DMA spherical particle volume)

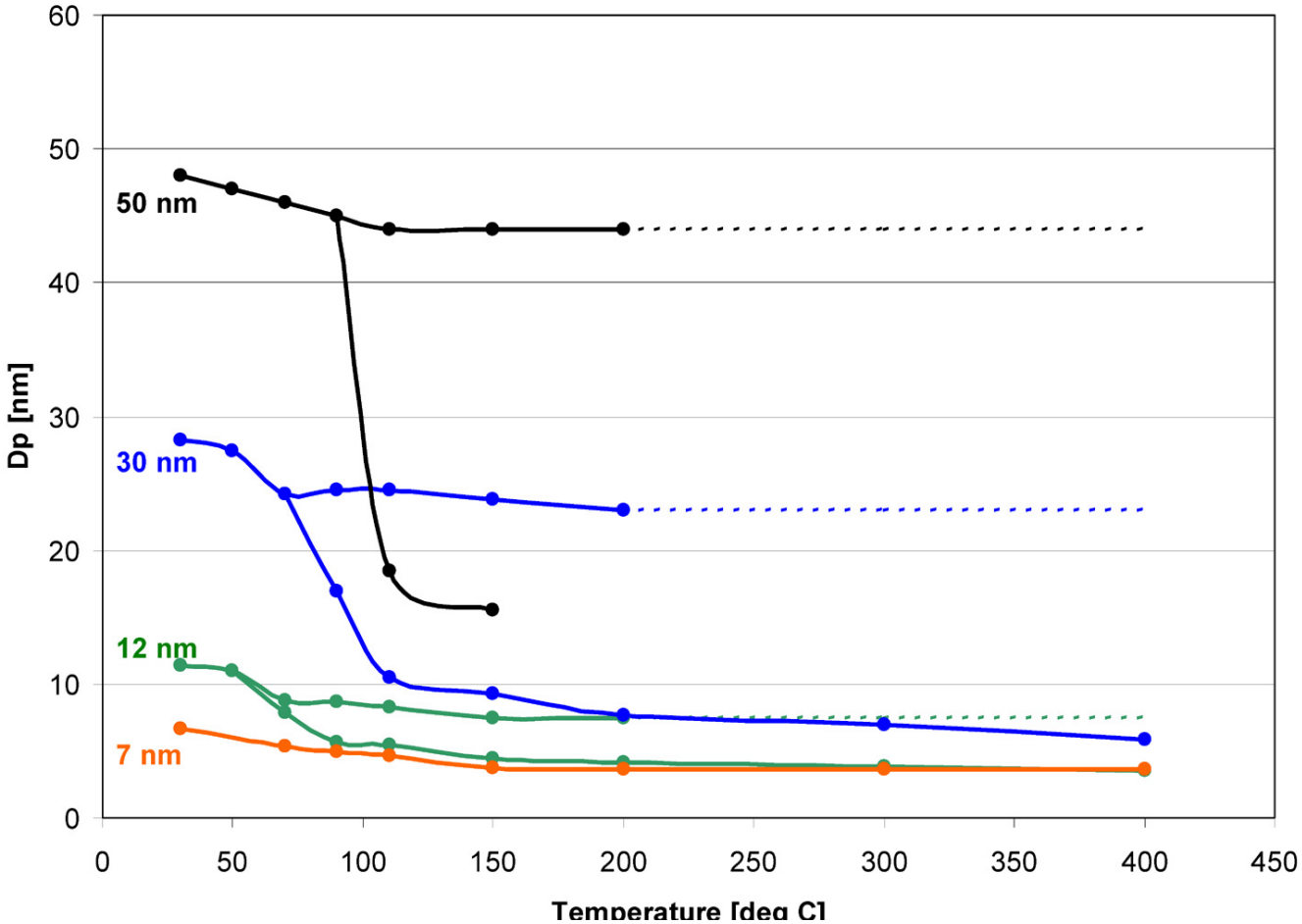
Volatility of Diesel nanoparticles – 30 nm size selected particles are heated size changes observed

Cummins ISM, pump fuel (350 ppm S), 1400 rpm , medium load

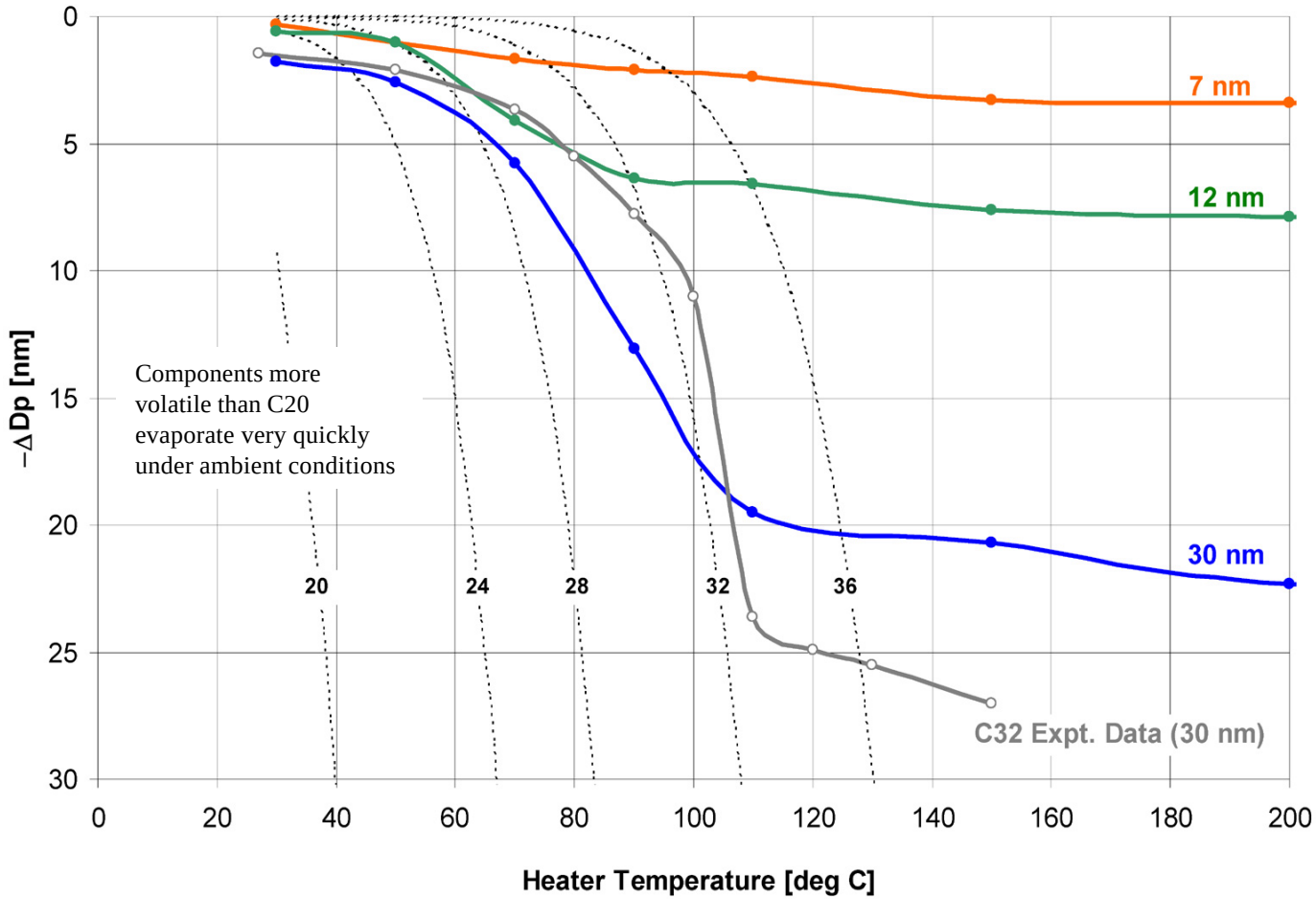


- Two particle types of different volatilities present.
- Volatile particles more abundant
- Significant shrinkage occurred when temperature was in the range of 50- 110 °C
- Method very sensitive, 6 nm peak corresponds to 0.4 ng/m^3, can go about 100 times lower

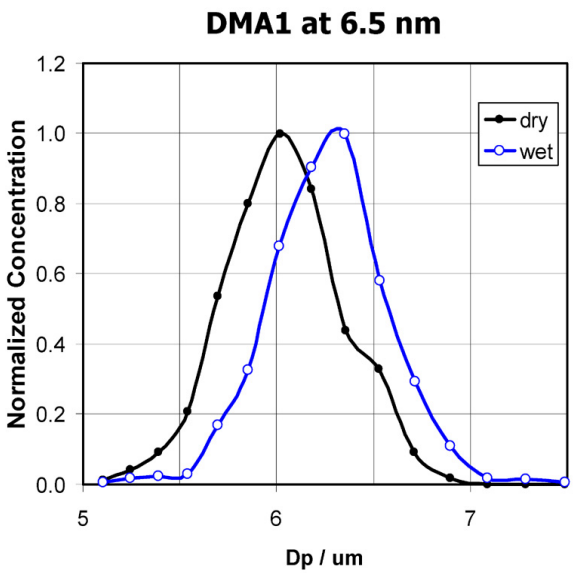
Volatility of diesel nanoparticles – plot of peak diameter shifts during heating. All but the smallest sizes consist of two particle types



Evaporative shrinkage of n-alkanes and Diesel nanoparticles. Diesel nanoparticles behave like C28-C32 – lube oil?

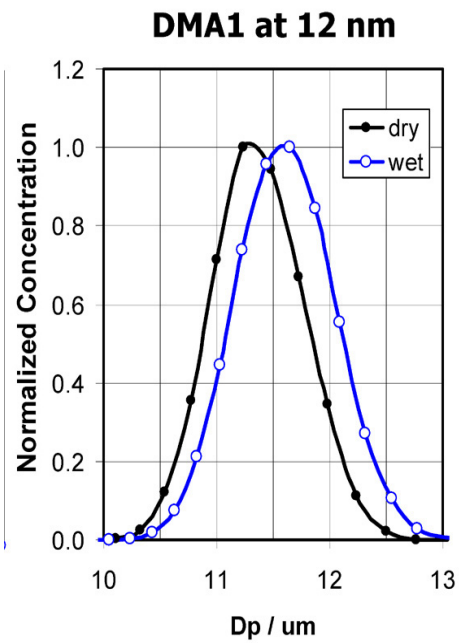


Hygroscopicity of diesel nanoparticles – ISM engine pump fuel (350 ppm S) medium load

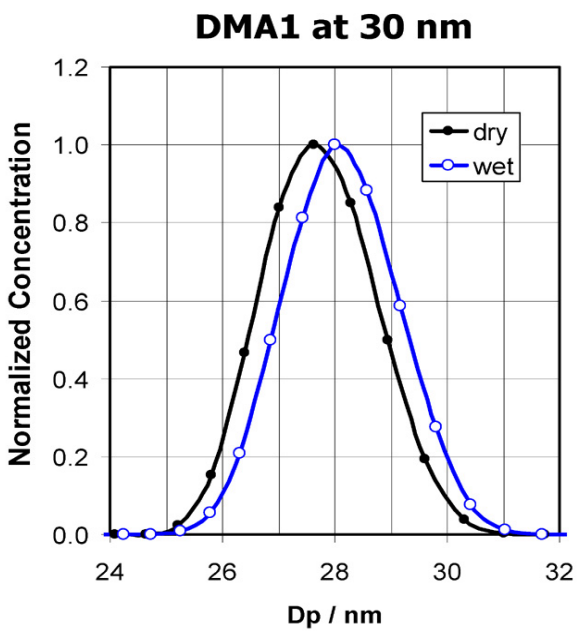


Diameter Growth Factor = 1.051

Corresponds to ~ 20% mass H_2SO_4



GF = 1.020



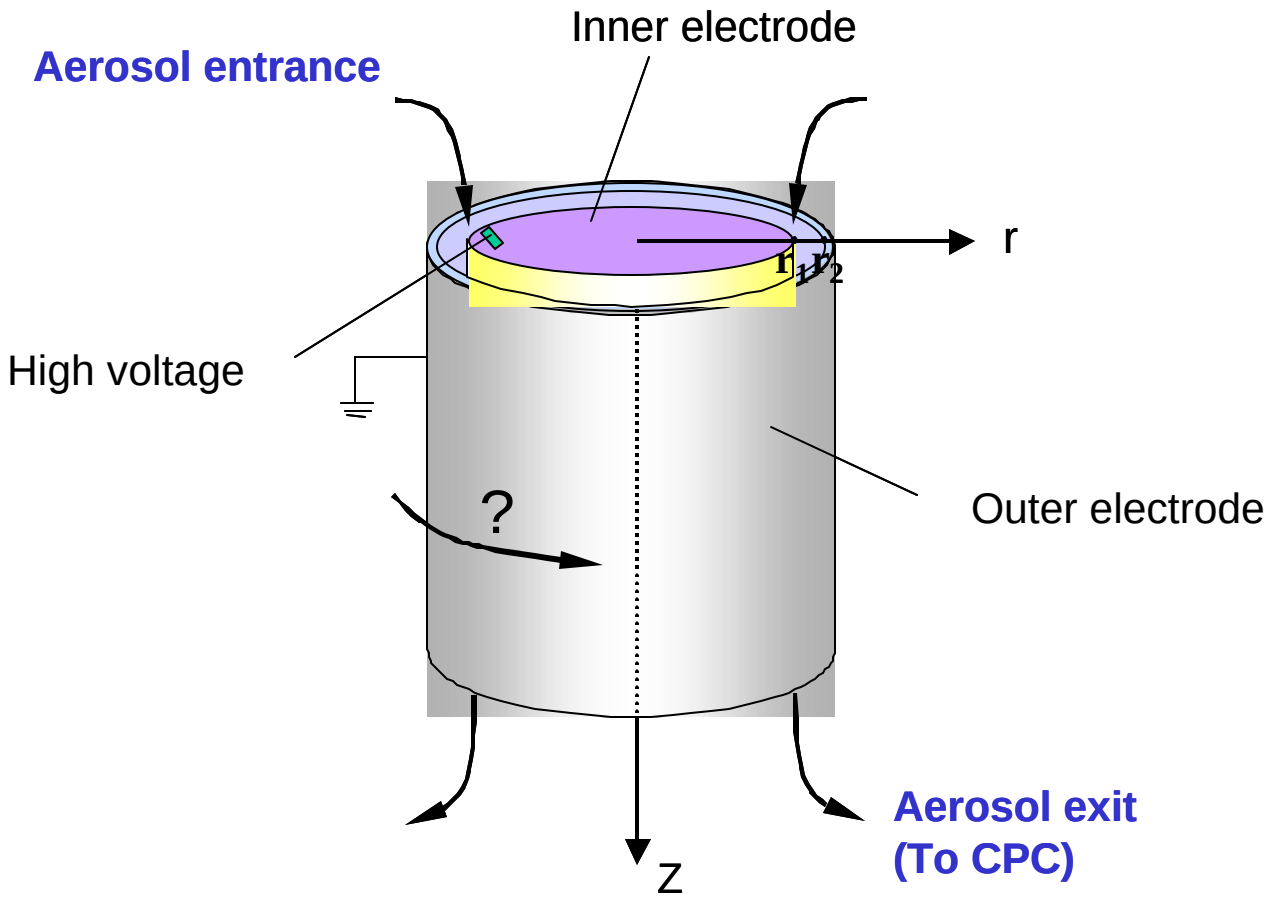
GF = 1.021

Corresponds to ~ 5% mass H_2SO_4

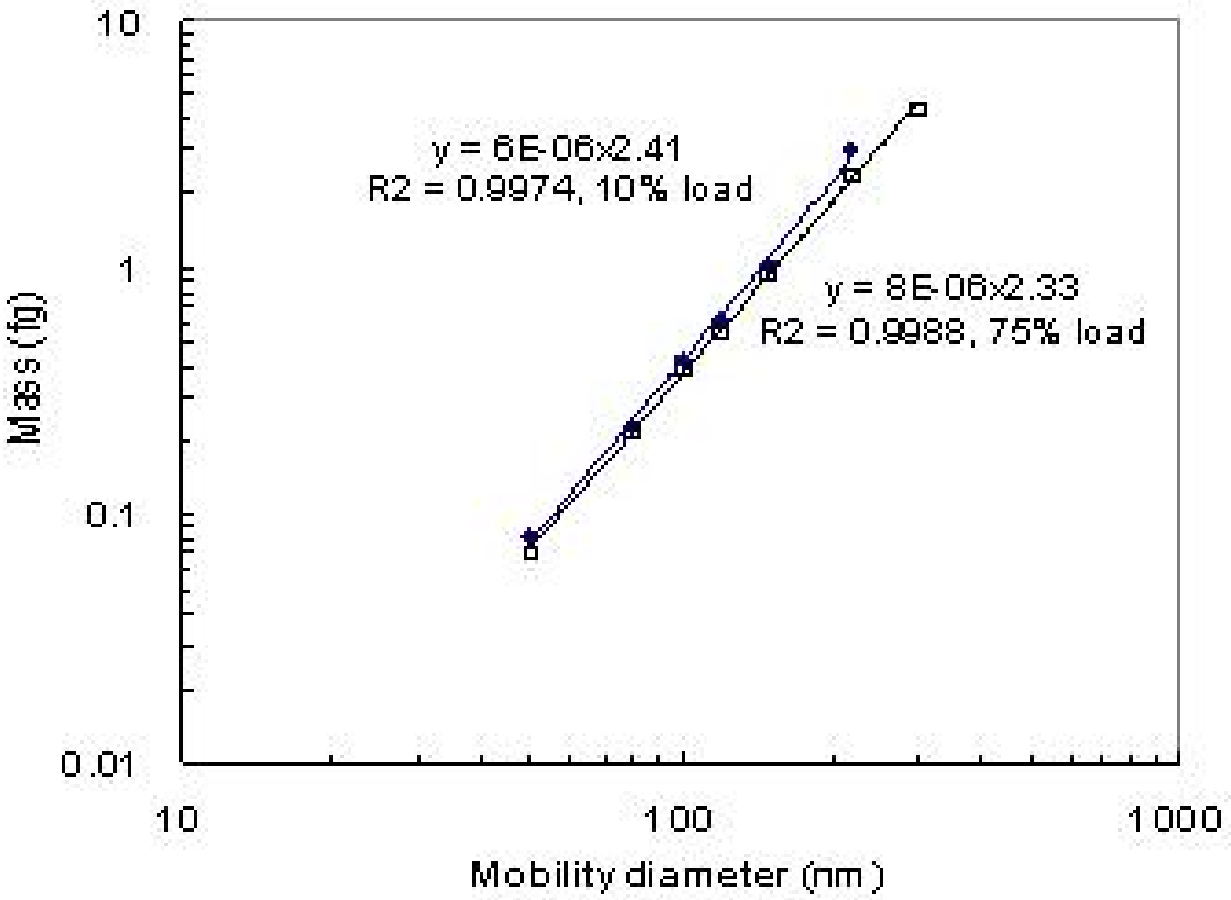
- Similar water uptake was observed light engine load with pump fuel
- With CA fuel (96 ppm S), no water uptake was observed either at medium or light engine load.

Aerosol Particle Mass Analyzer (APM)

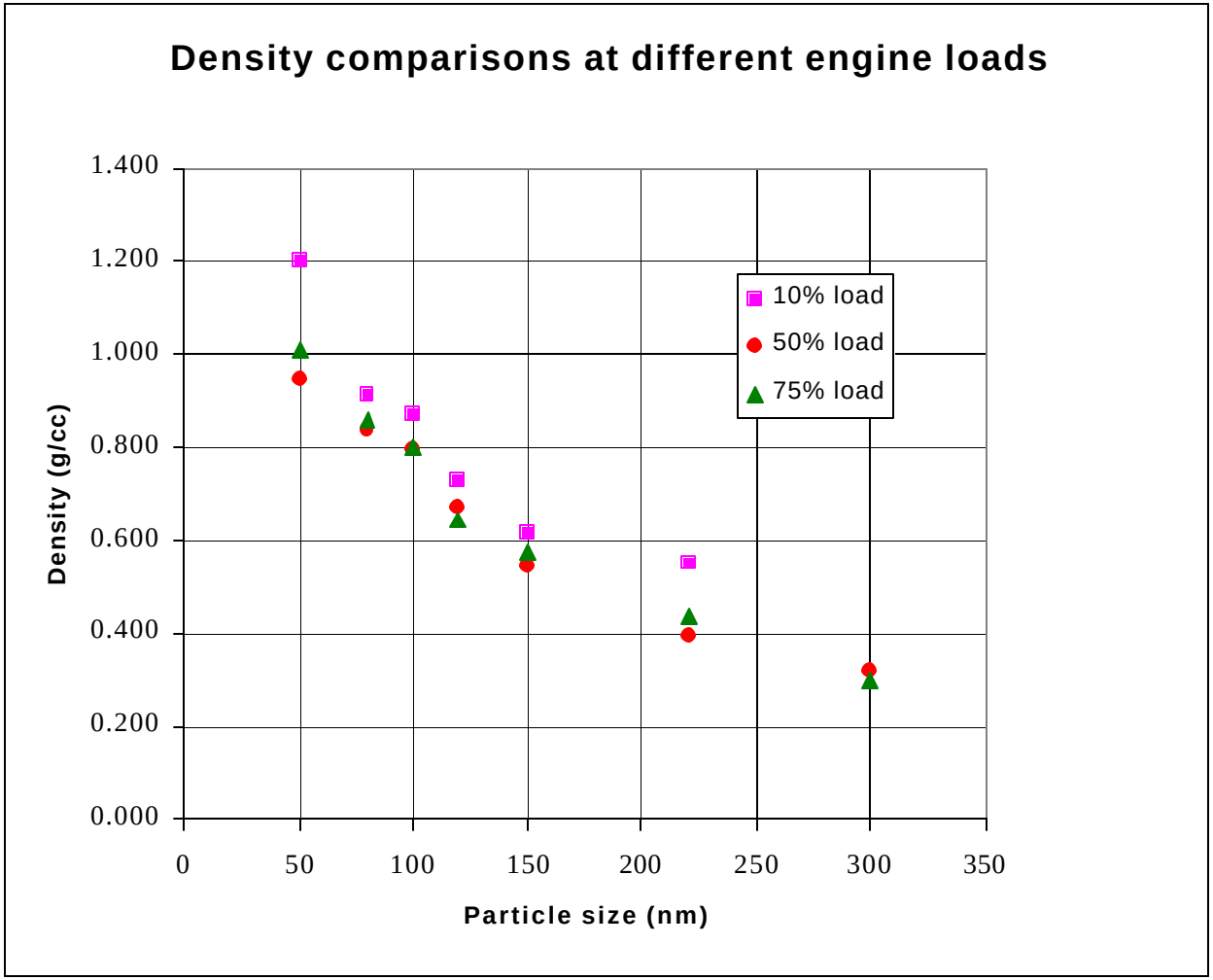
(Ehara et al., 1996)



Comparison of “fractal like” dimension at the different engine loads (10%, 75%)

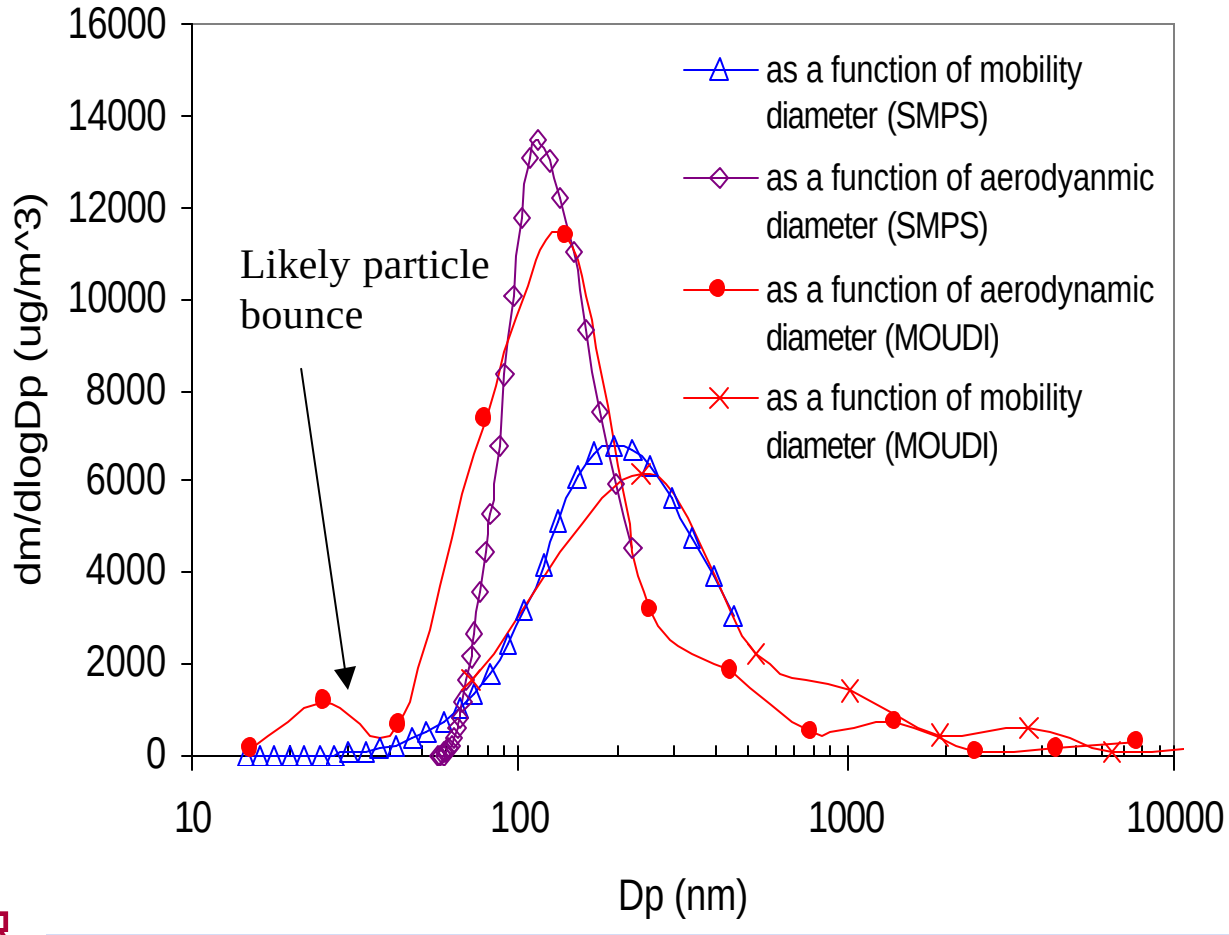


DMA / APM measurements of density of accumulation mode particles – Deere engine EPA fuel, 1000 rpm various loads

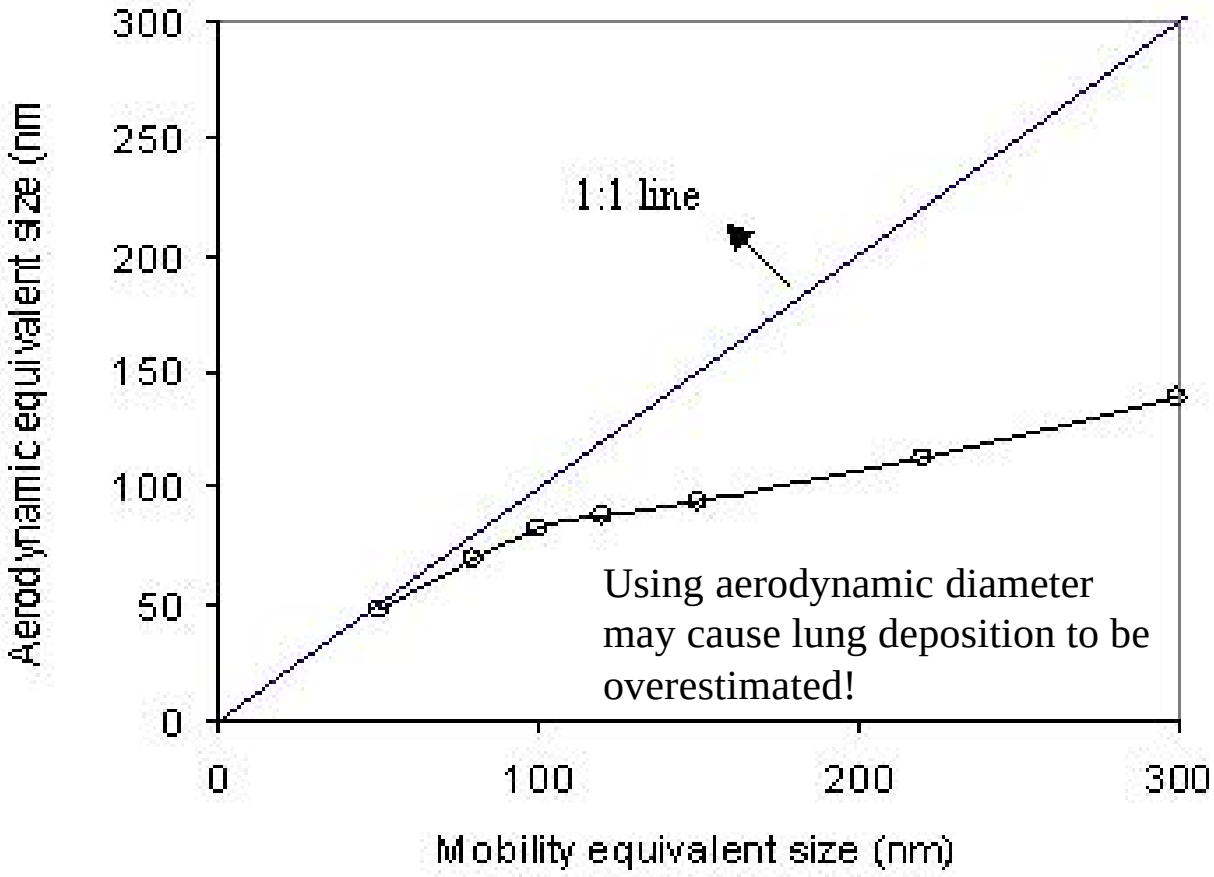


Mass size distributions obtained from SMPS and nano-MOUDI, Deere engine running at 1000 rpm and 50% load

Density measurements used to relate mobility and aerodynamic diameters



Low Effective Density Makes the Aerodynamic Diameter Smaller than Mobility Diameter



Conclusions – properties of Diesel particles

- Nuclei mode particles (~ 3 to 30 nm)
  - Primarily volatile and sometimes hygroscopic
    - » Volatile materials, mainly heavy hydrocarbons like lubricating oil, and some sulfuric acid
    - » Although volatile may be relatively insoluble, e.g., lube oil – this could influence their behavior in biological systems
  - In some cases there is a tiny solid residue in the nuclei mode range that is likely to consist of mainly of metallic ash
- Accumulation mode particles (~ 30 to 500 nm)
  - Primarily non-volatile
  - Contain most of the particle mass and elemental carbon
  - Density decreases from about 1 to 0.3 g/cm^3 as diameter increases from 50 to 300 nm
    - » Density measurements reconcile SMPS and impactor measurements
    - » Aerodynamic diameter underestimates mobility and diffusion diameters
- Wide size range of overlap of nuclei and accumulation modes consisting of an external mixture of two particle types
  - "Less volatile" particles, comprised of a significant non-volatile core (probably elemental carbon) and an organic component
  - "More volatile" particles, containing predominantly organics and sometimes small amounts of sulfuric acid, with the volatile components contributing more than 99% of the "more volatile" nanoparticle mass