NOVEL APPROACHES FOR MEASURING PHYSICAL AND CHEMICAL PROPERTIES OF PARTICULATE ORGANICS

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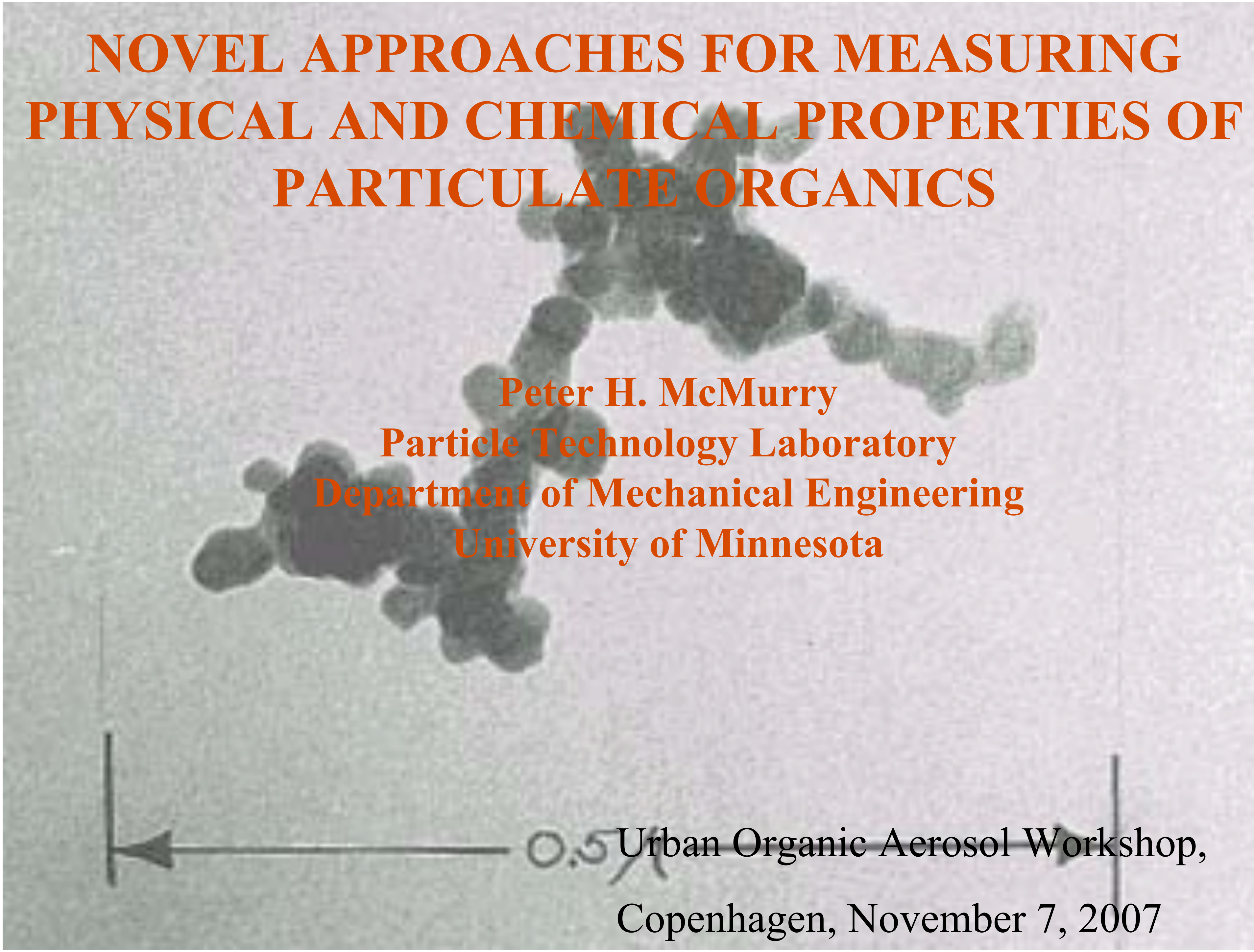

Urban Organic Aerosol Workshop,

Copenhagen, November 7, 2007

Topics To Be Discussed

- Measurement of physical/chemical properties of particulate organics
    - -hygroscopicity
    - -refractive index
    - -density
- In-situ measurements of mass concentrations of volatile organics
- Chemical composition of organics emitted from biofuel combustion

Overarching Theme: New Measurement Methods

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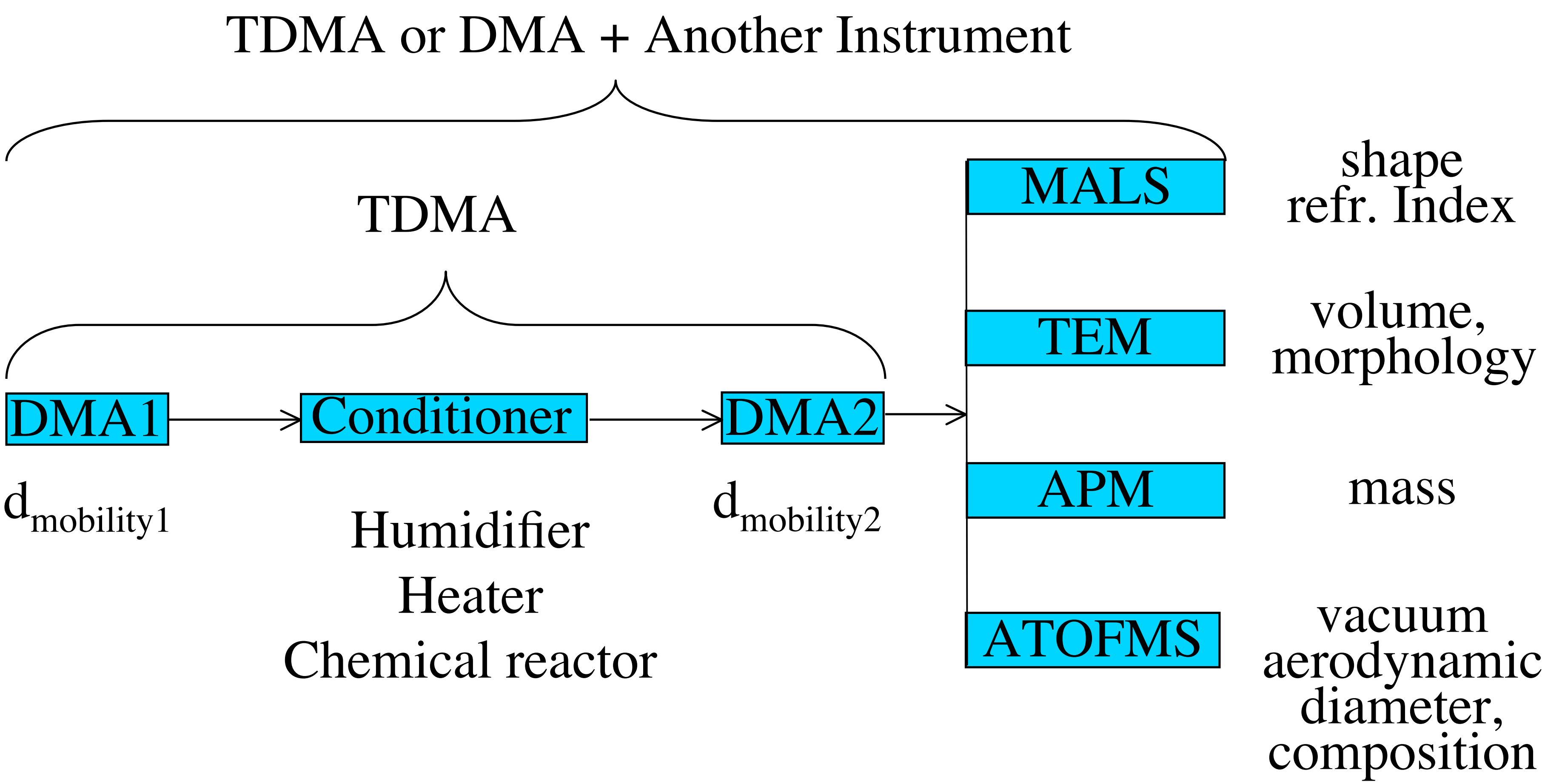
Use of Tandem Methods to measure physical/chemical properties of particulate organics

-hygroscopicity, shape, refractive index and density

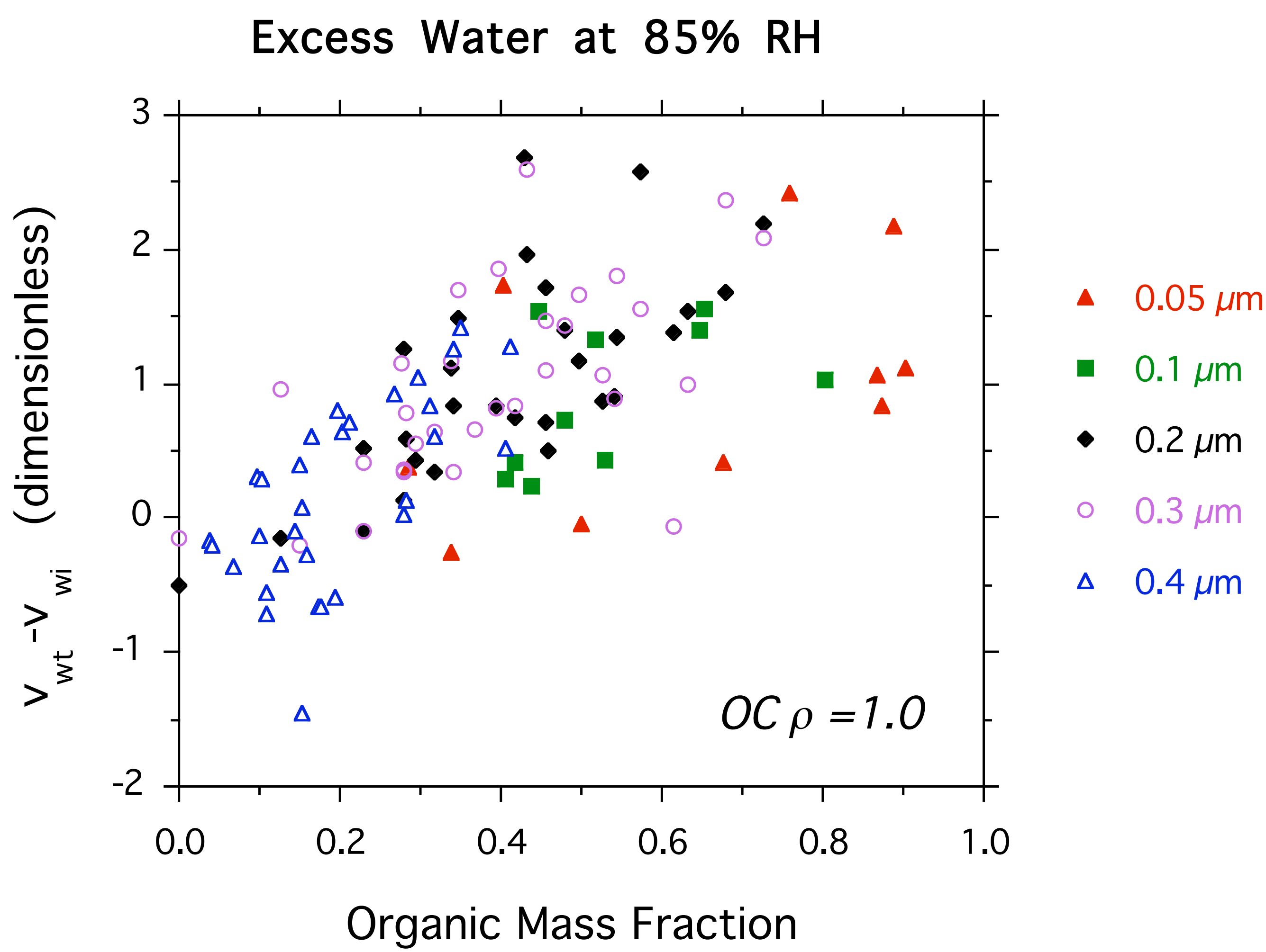
Tandem Measurement Techniques for Physical/Chemical Properties of Atmospheric POM



OC Water Uptake

TDMA + MOUDI (IC; OC/EC) + Thermodynamic Model

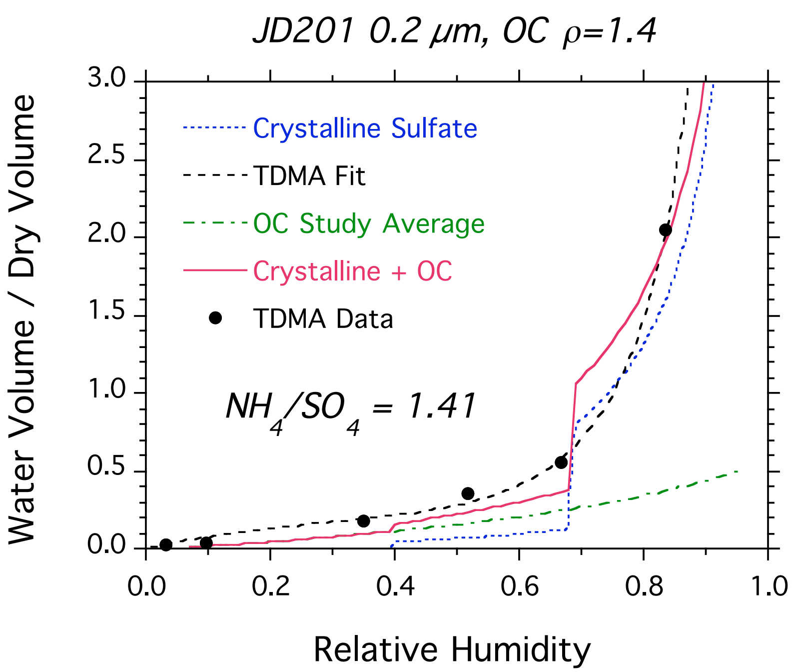
Water Uptake by Organics: TDMA Measured - Thermodyamic Model for Inorganics



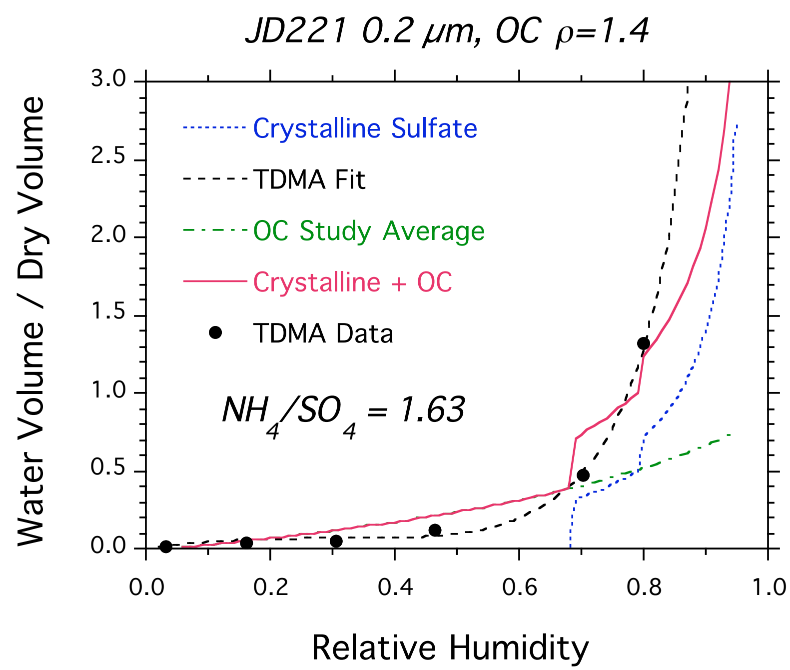
Dick et al., *JGR* **105**(D1):1471-1479, 2000.

TDMA Measurements of Water Uptake: Comparison with Thermodynamic Models

Moderate OC Fraction



High OC Fraction

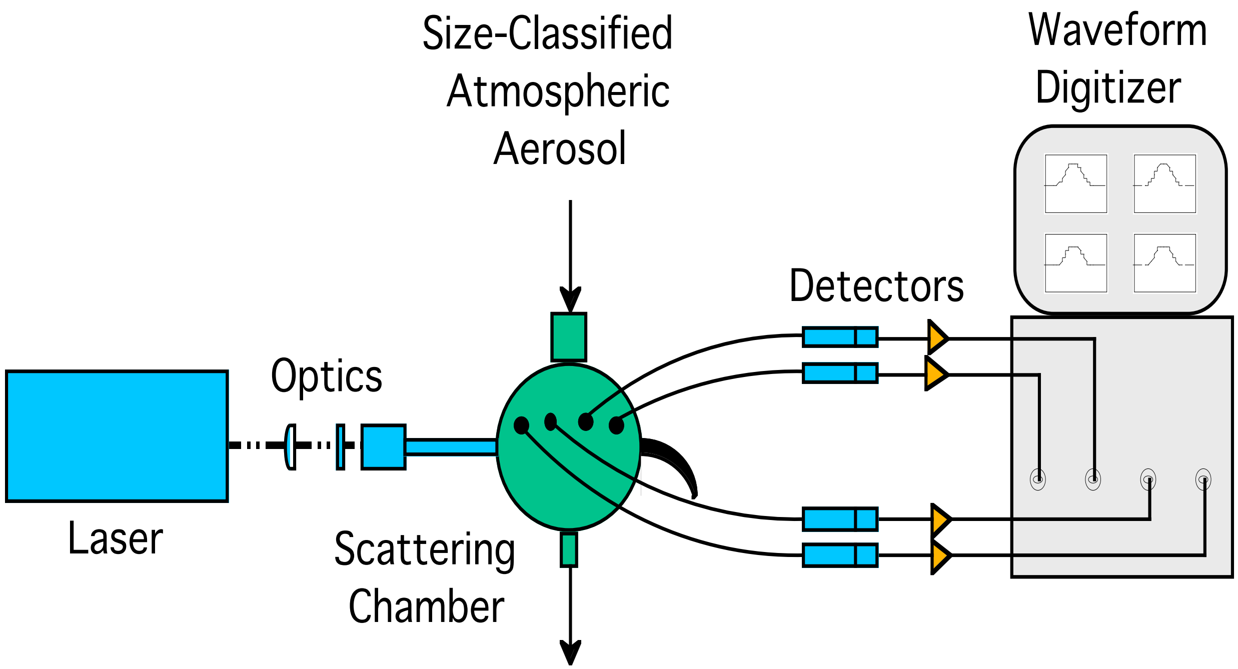


Dick et al., *JGR* **105**(D1):1471-1479, 2000.

Shape (Spherical or Nonspherical):

DMA + MALS
(MultiAngle Light Scattering)

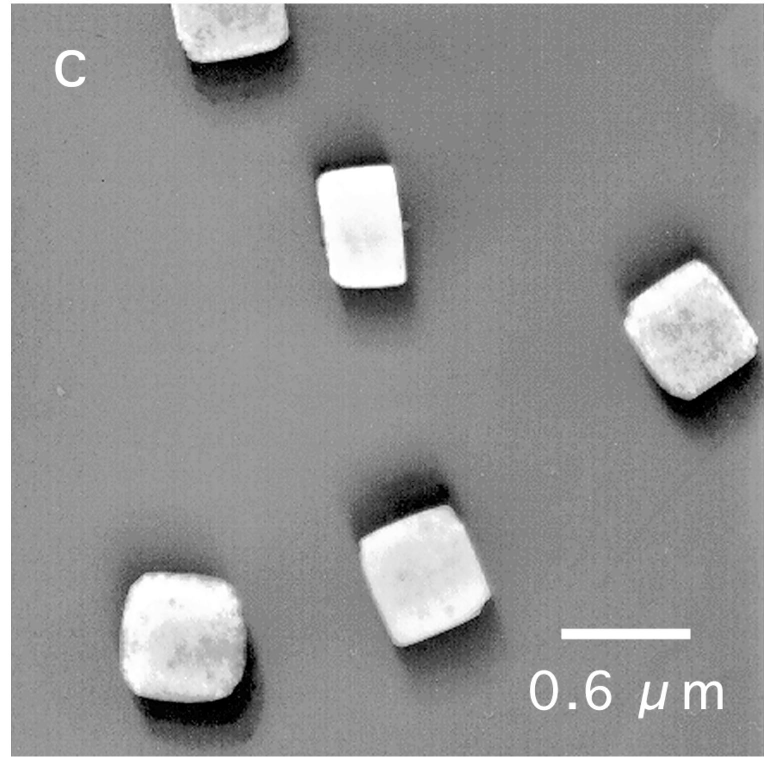
Multiangle Light Scattering (MALS) Detector



Measurement of angular-dependent light scattering by submicron particles as functions of size and relative humidity

Reference Aerosols (Shape)

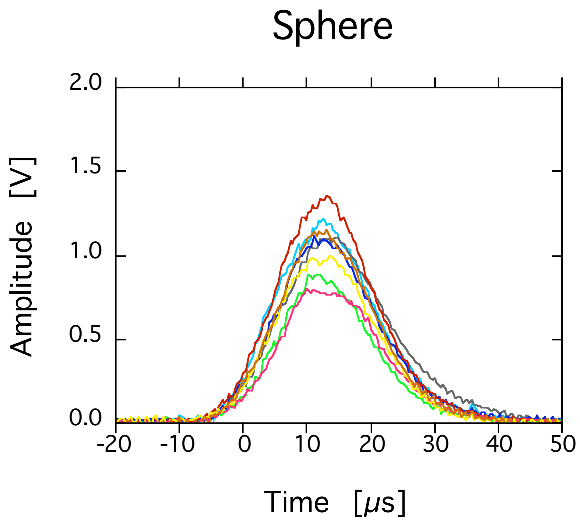
- DOS (Dioctyl Sebacate)
  - Spherical Reference
  - 0% Nonspherical, $D_p \geq 0.4$ µm
- NaCl
  - Nonspherical Reference
  - 100% Nonspherical, $D_p \geq 0.4$ µm
  - Reduced distinction for $D_p = 0.2, 0.3$ µm ; $\eta \sim 20$ %

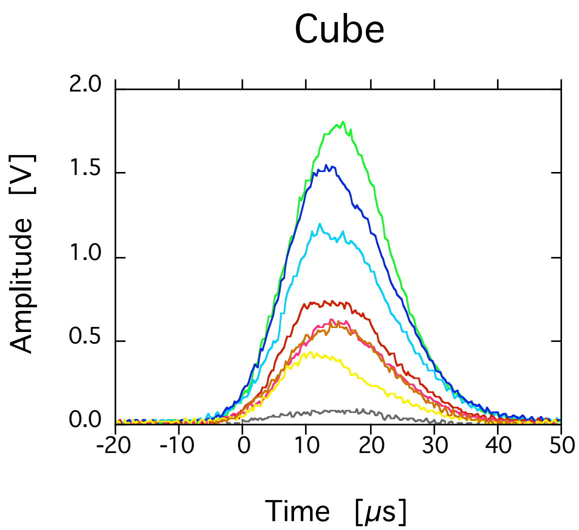


0.6 µm NaCl Cubes

Dick et al., *Measurement Sci. Technol.* **9**(2):183-196, 1998.

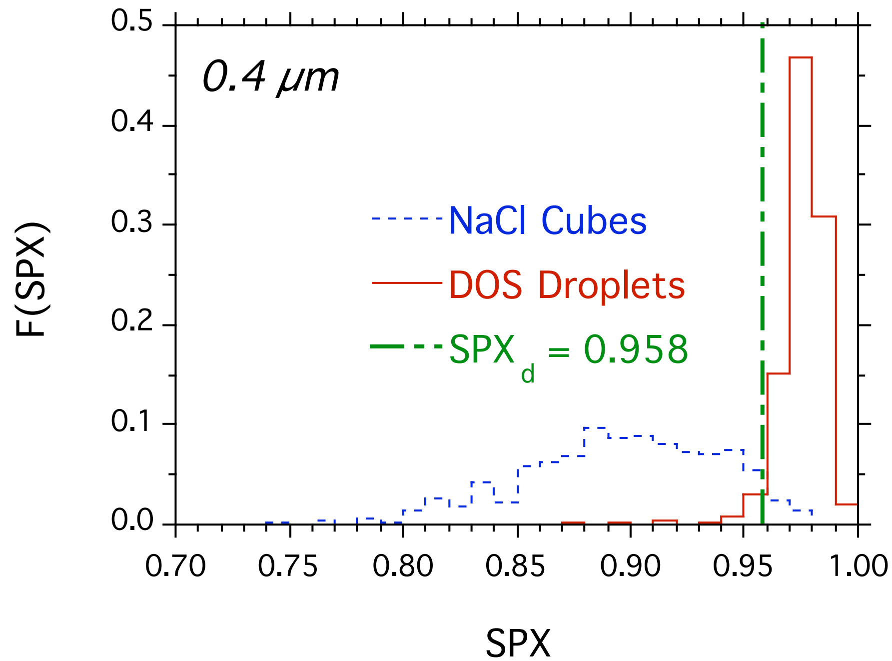
MALS 1: Distinguishing Spheres from Nonspheres (variabilities in *azimuthal* scattering)





- Sphericity Index:

$$SPX = 1 - \frac{\sqrt{\sum_{i=1}^{8} (x_i - \overline{x})^2}}{7\overline{x}}$$



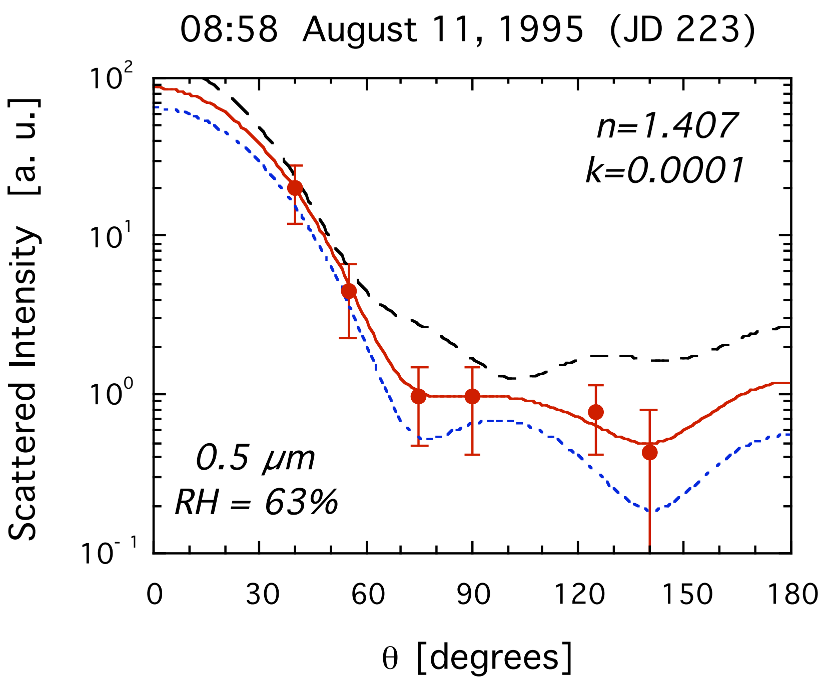
Dick et al., *Measurement Sci. Technol.* **9**(2):183-196, 1998.

OC Refractive Index

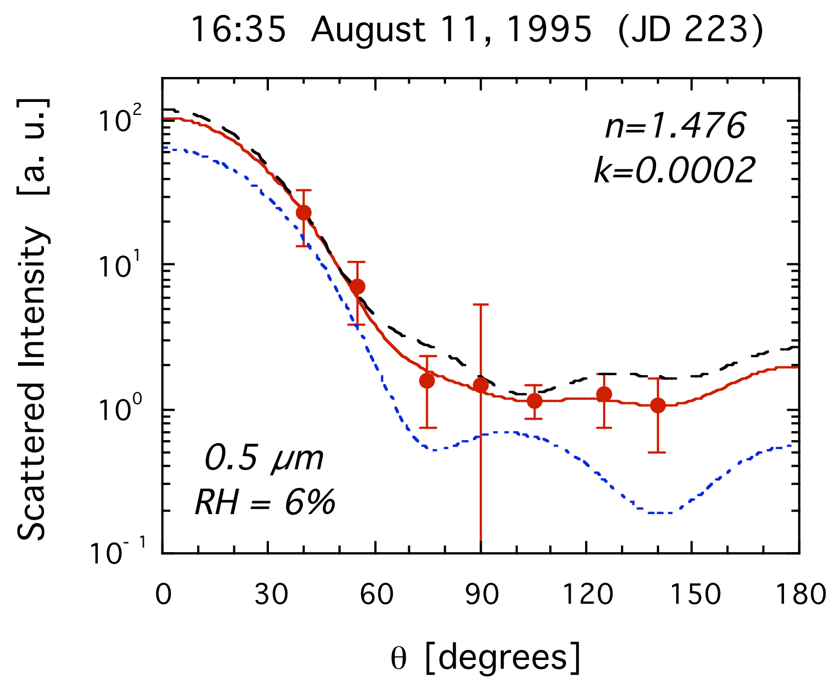
TDMA + MALS

MALS 2: Determining Refractive Index for Spheres
(*Variabilities in Polar Scattering)*

Wet 0.5 µm

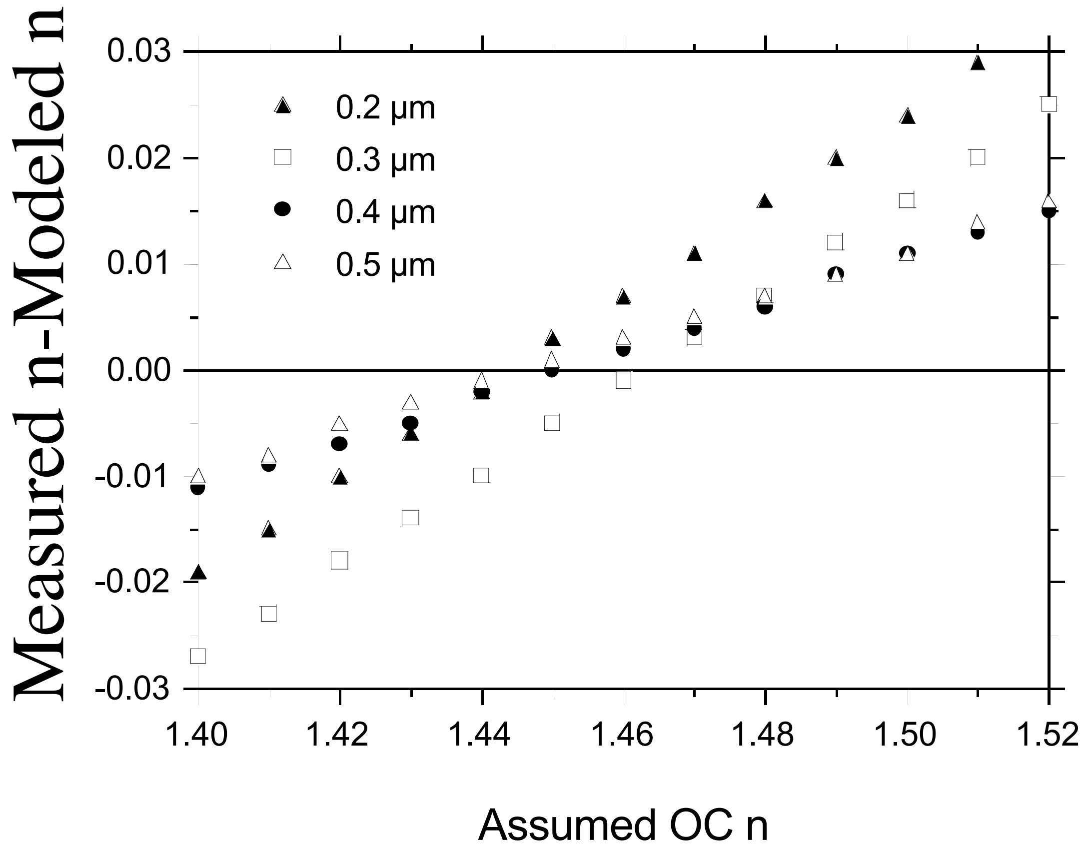


Dry 0.5 µm



Dick et al., *Aerosol Sci. Technol.* **9**(2):183-196, 1998.

MALS Measurements in the Great Smoky Mountains show that the refractive index of OC equals *n*=1.45

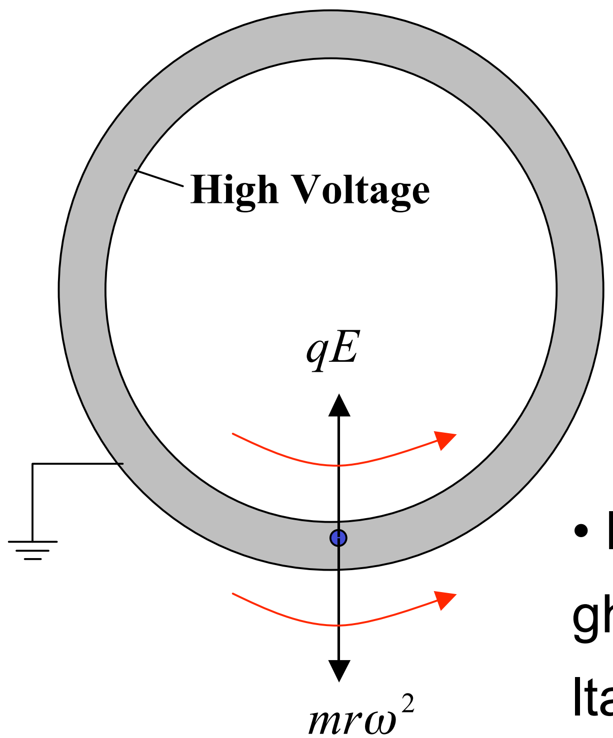


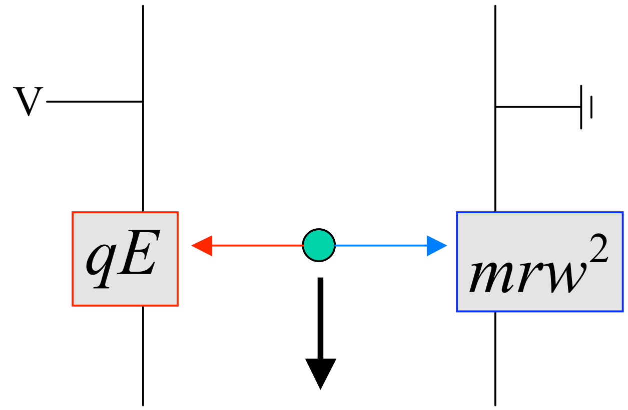
Dick et al., *AST* **41**:549-569, 2007

Carbon Soot Density:

DMA + APM + TEM

Mass Classification with the APM



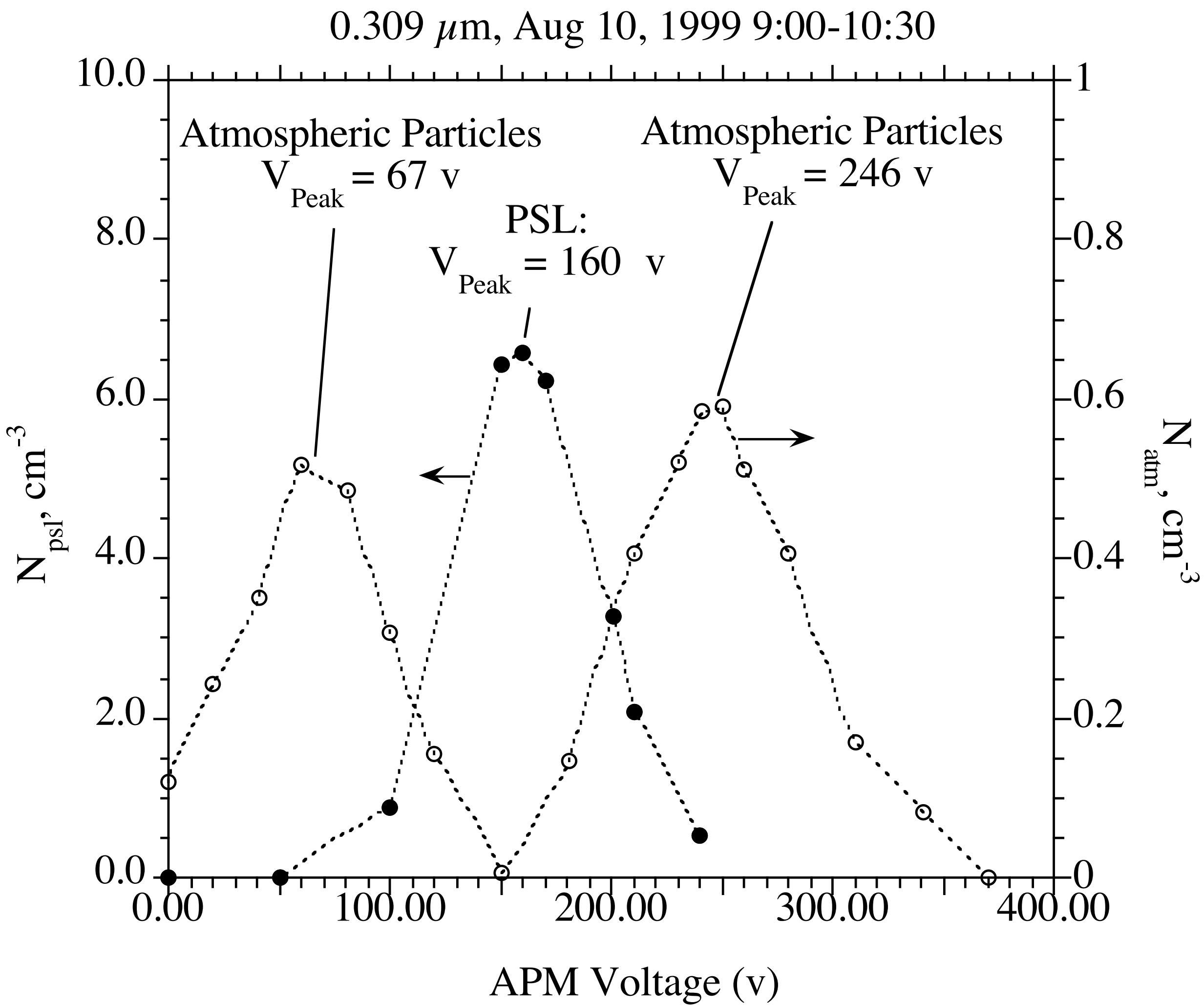


- Particles of a certain mass can penetrate throu gh the APM for the fixed rotational speed and vo ltage.
- Electrostatic force = Centrifugal force

$$mr\omega^2 = \frac{\pi d_{ve}^{\ 3}}{6}\rho_{true} r\omega^2 = neE_{APM}$$

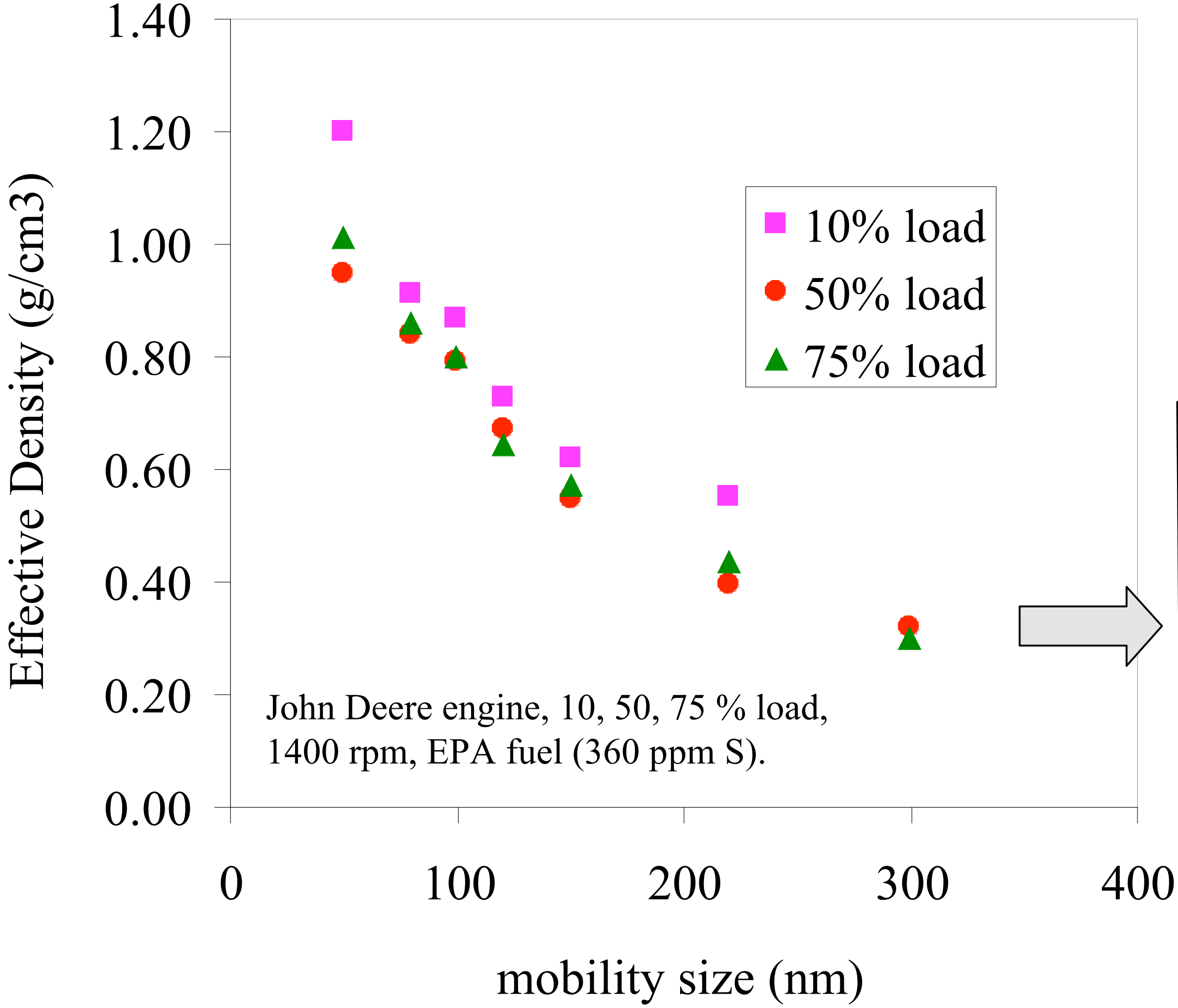
Ehara et al., *JAS* **27**:217-234, 1996

Masses of 0.309 µm Mobility Diameter Atmospheric Particles (Atlanta, GA)

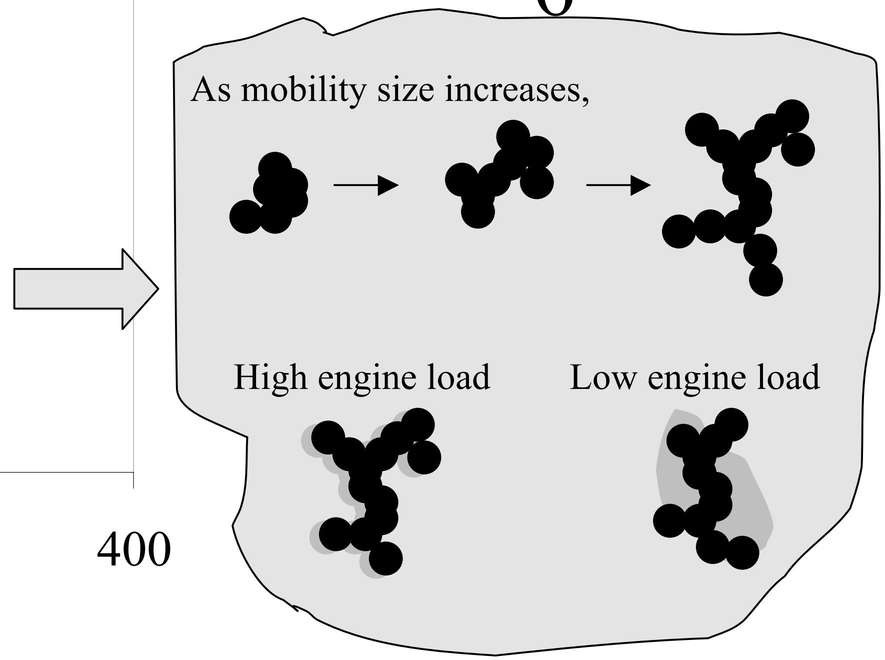


McMurry et al., *AST* **36**:227-238, 2002

Effective Density of Diesel Exhaust Particles (DEP) (DMA-APM)

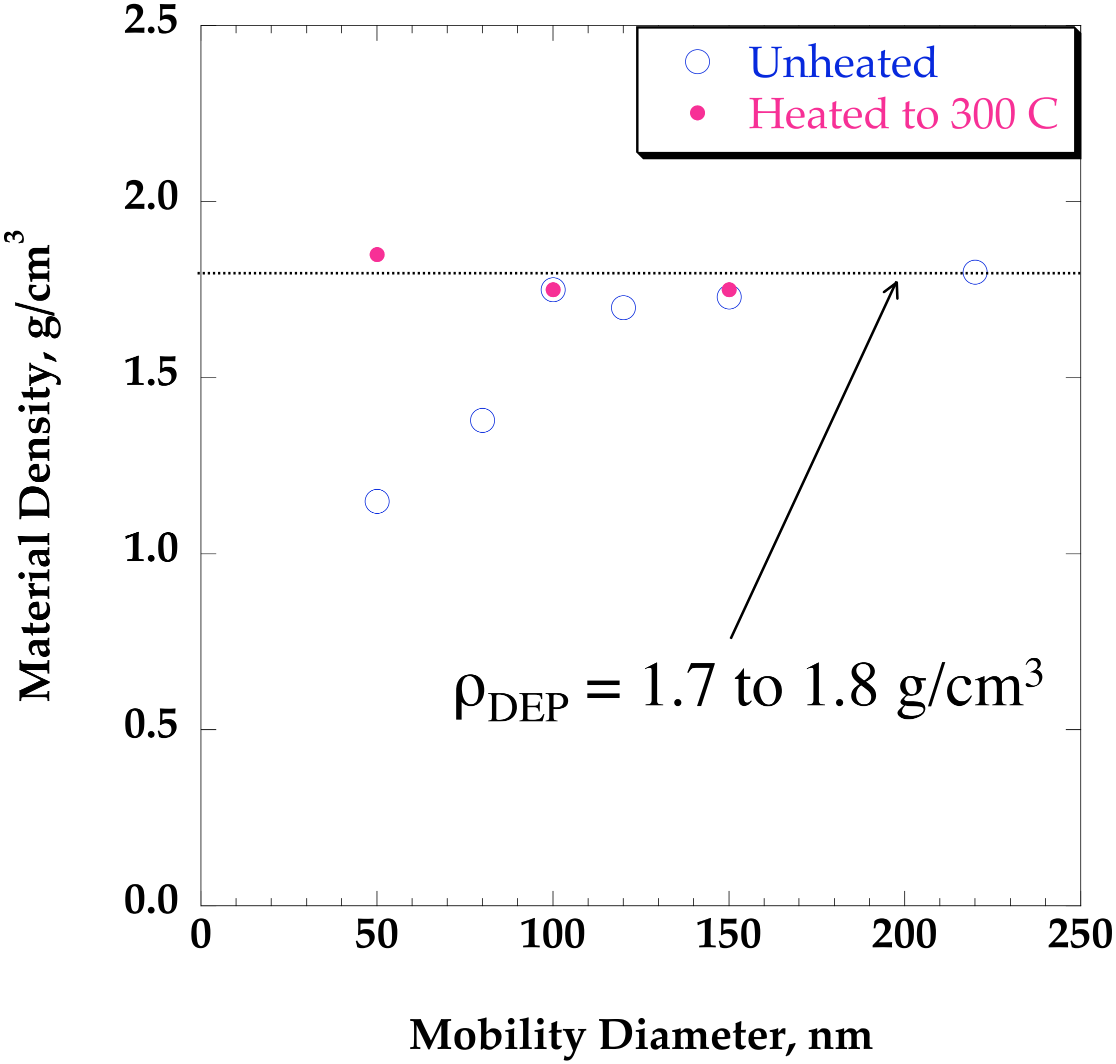


$$\rho_{effective} = \frac{mass}{\frac{\pi}{6} D^{3}_{mobility}}$$



Park et al., *ES&T* **37**:577-583, 2003

Material Density of Diesel Exhaust Particles (TDMA-APM-TEM)



$$\rho_{material} = \frac{m\ (APM)}{v\ (TEM)}$$

Park et al., *J.Nanoparticle Res.* **62(2)**:267-272, 2004

In-Situ Measurements of Mass Concentrations for Engine Emissions that contain High Concentrations of Volatile Organics

SMPS-APM
(DMA-APM)

Park et al., *Atmos. Environ.* **37**:1223-1230, 2003

Mass Concentrations of Diesel Exhaust Particles

Diluter → DMA → CPC

Number distribution

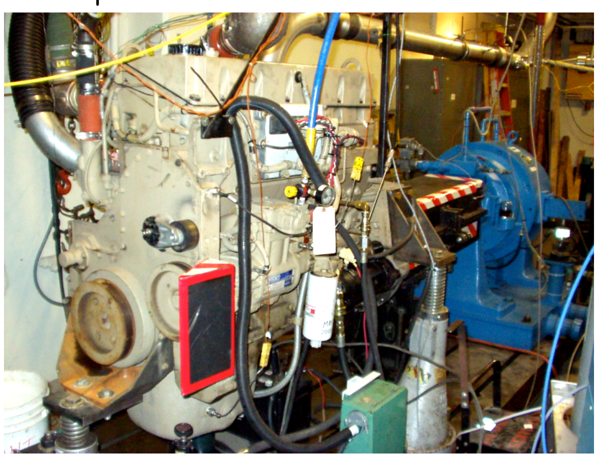
Diluter → DMA → APM → CPC

Mass per particle Vs size

} mass distribution

Diluter → Filter

} mass concentration



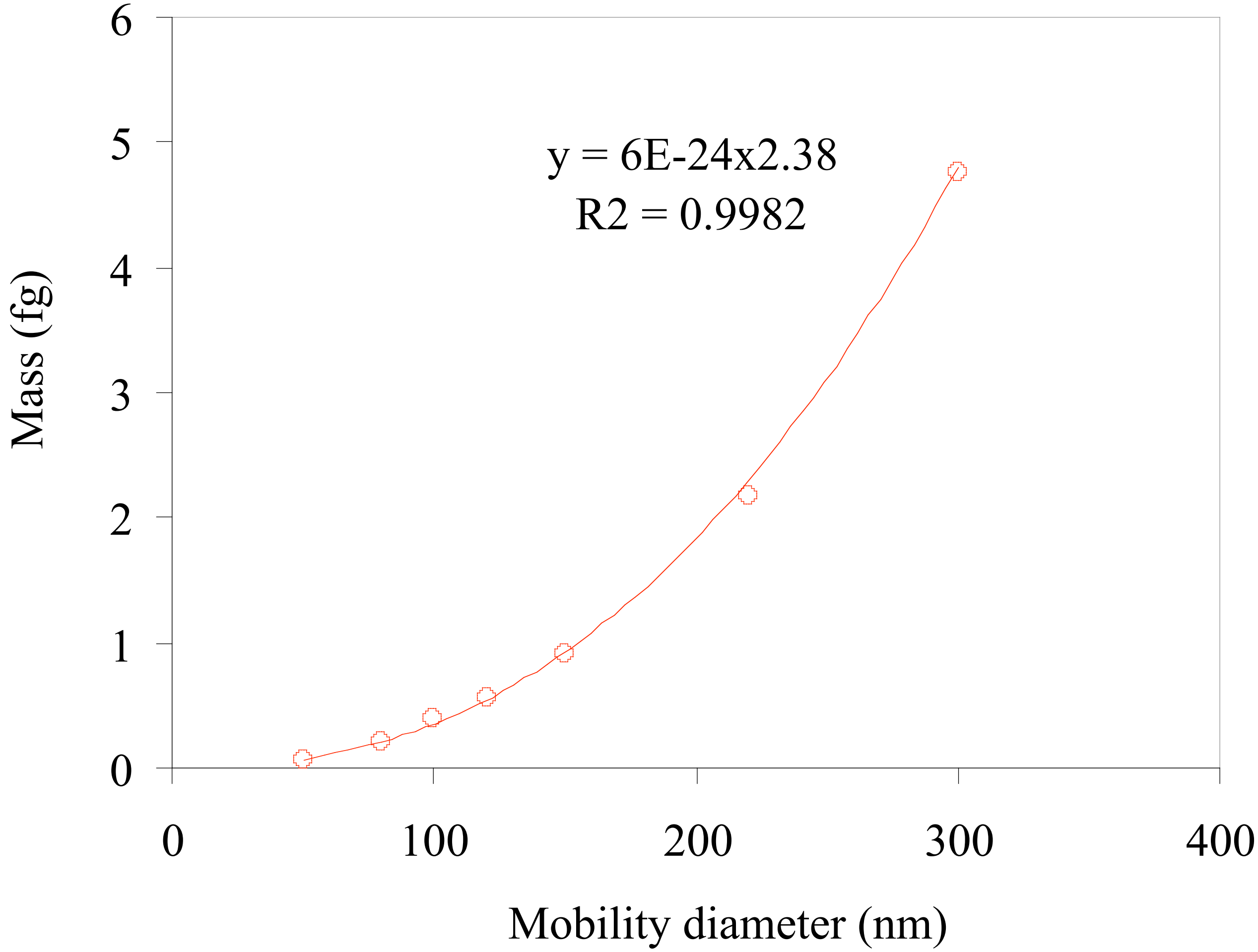
Diesel Engine

$$\frac{dc_m}{d\log D_p} = m \cdot \frac{dN}{d\log D_p}$$

APM (m) SMPS ($\frac{dN}{d\log D_p}$)

Park et al., *Atmos. Environ.* **37**:1223-1230, 2003

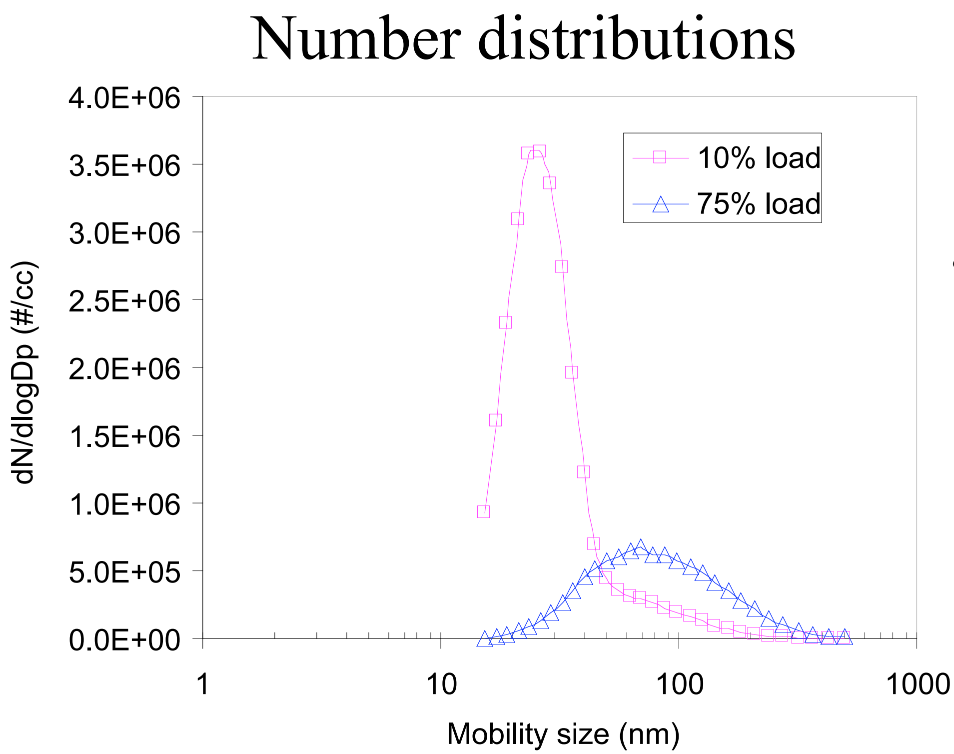
Particle Mass for Diesel Exhaust Particles
John Deere engine, 50% load, 1400 rpm, 360 ppm fuel

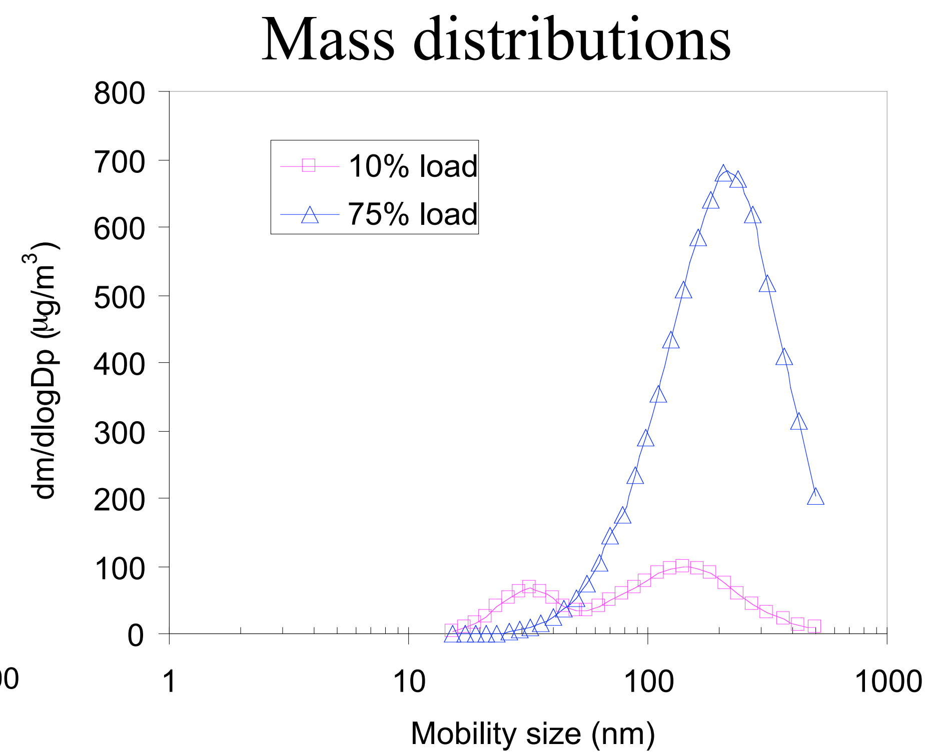


Park et al., *Atmos. Environ.* **37**:1223-1230, 2003

Number and Mass Distributions for Diesel Exhaust Aerosols.

John Deere engine, 10% & 75% loads, 1400 rpm, 360 ppm S fuel, DR~17-22



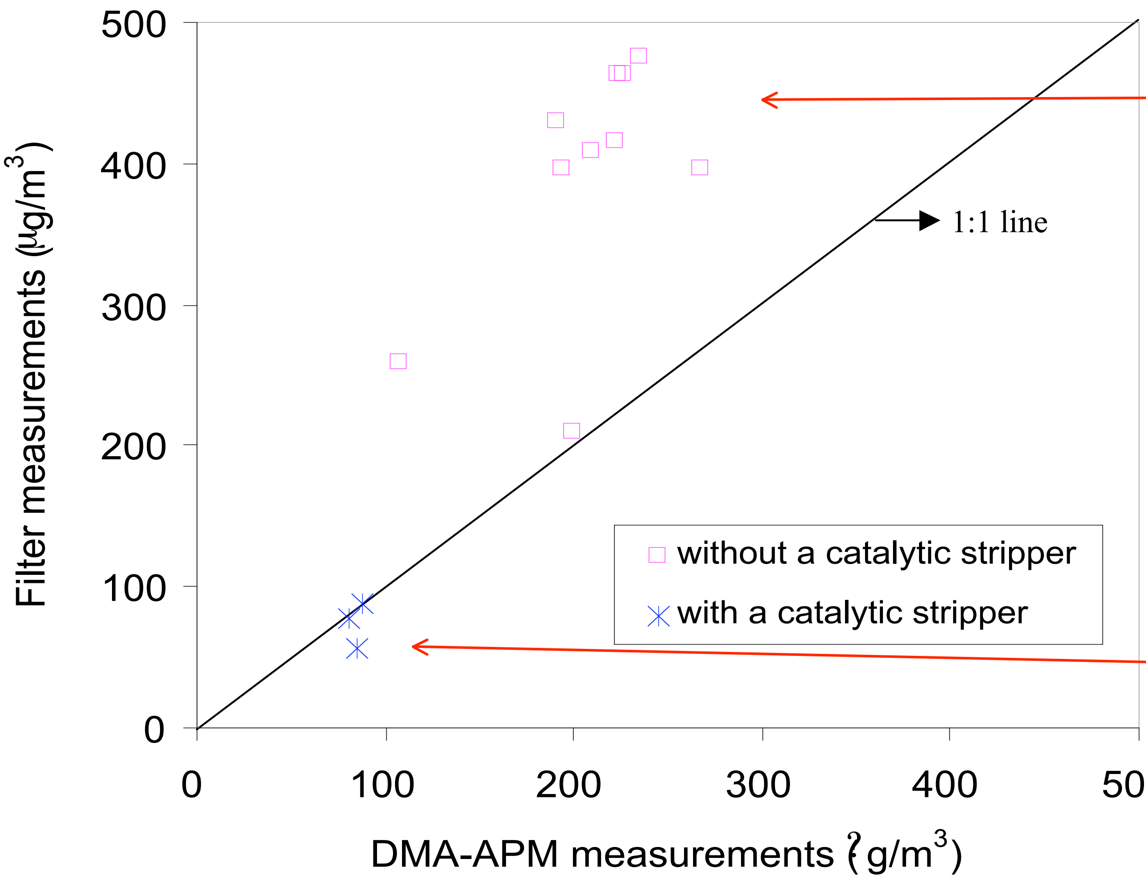


$$\frac{dc_m}{d\log D_p} = m \cdot \frac{dN}{d\log D_p}$$

Park et al., *Atmos. Environ.* **37**:1223-1230, 2003

Filter and DMA-APM Mass Concentrations: Effect of a Catalytic Stripper.

John Deere engine, 10% load, 1400 rpm, 360 ppm S fuel, DR=17



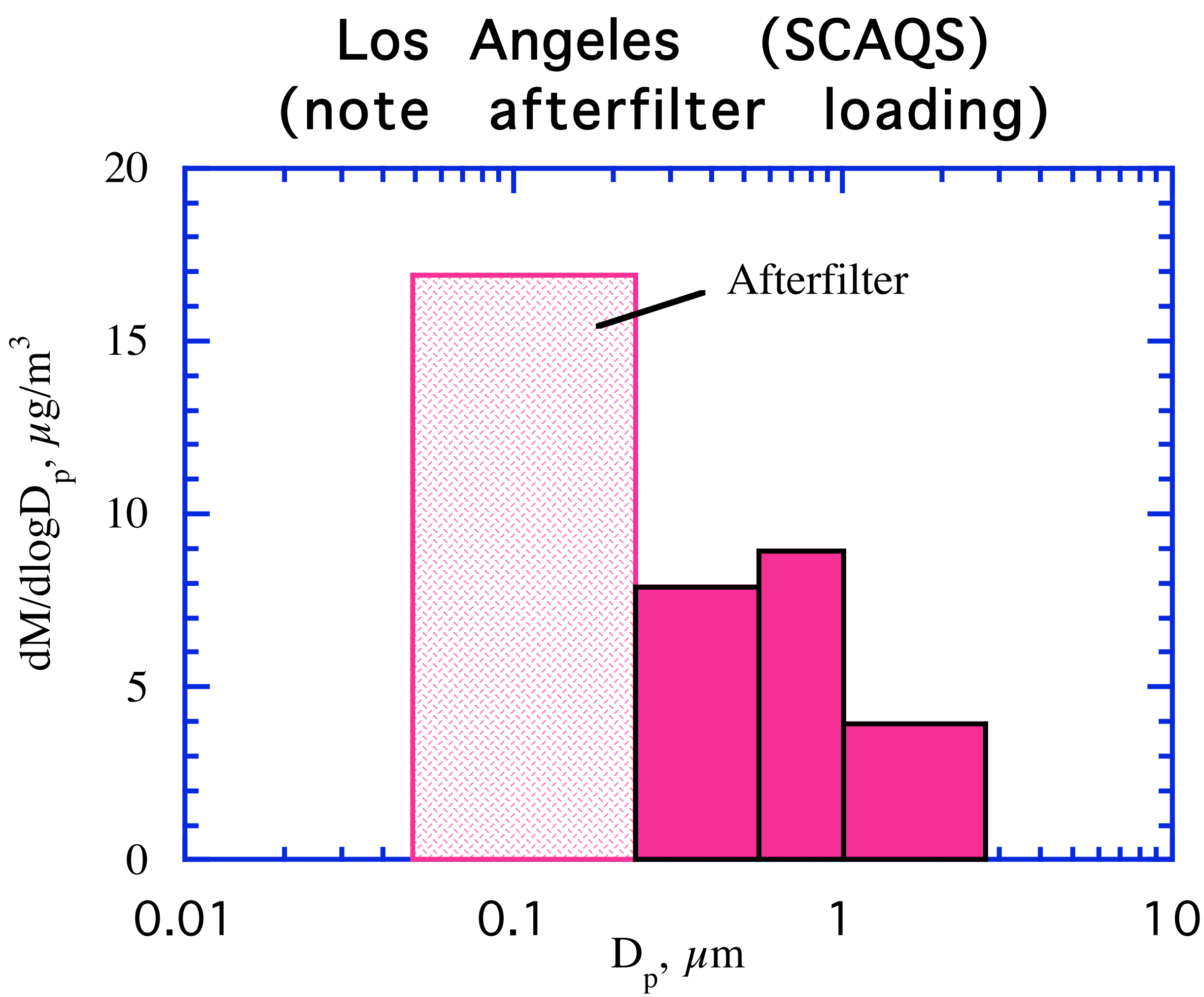
Filter > In situ measurement due to vapor adsorption (?)

Filter = In situ measurement when vapor is removed

$$c_m = \int \frac{dc_m}{d\log D_p} d\log D_p$$

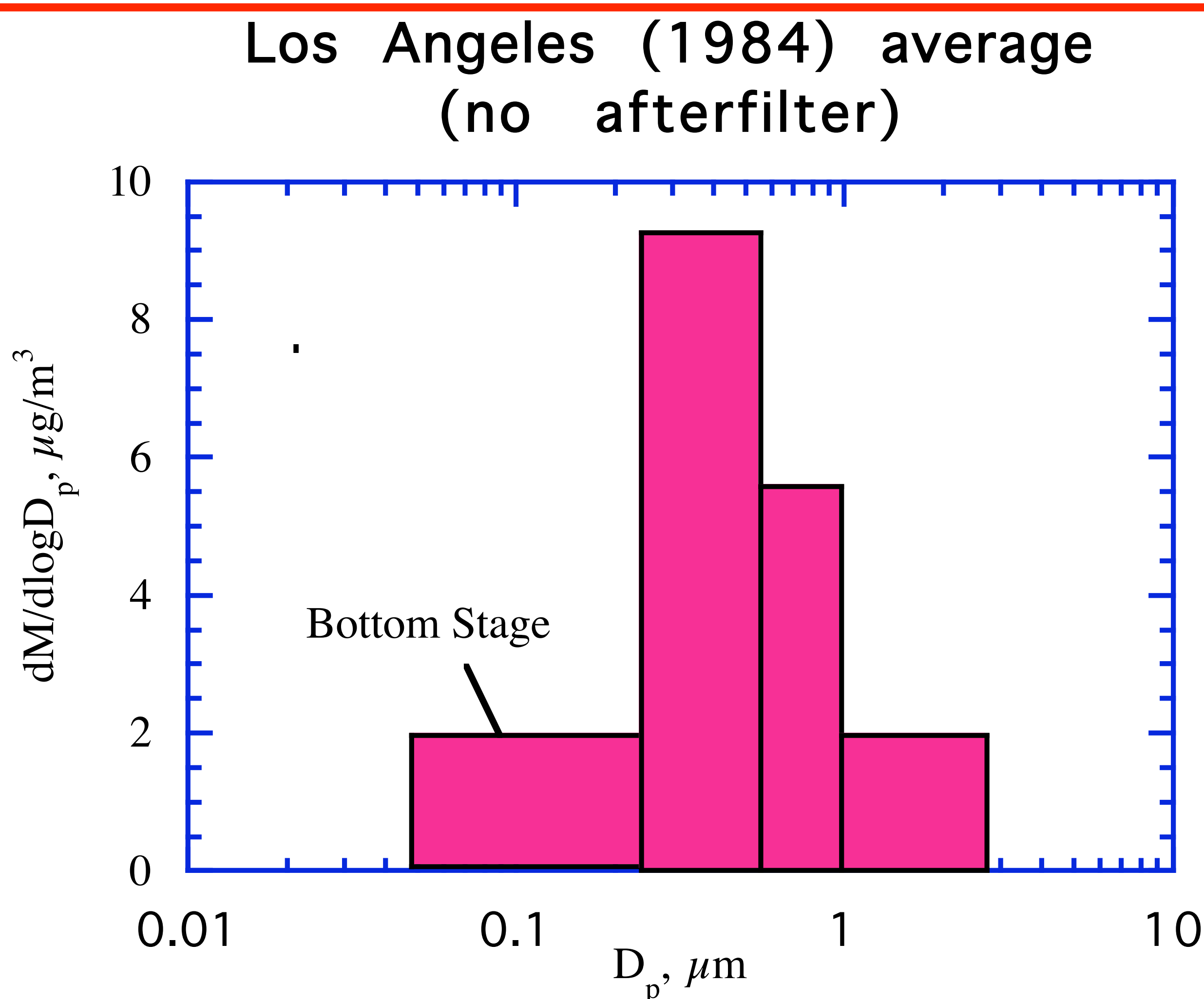
Park et al., *Atmos. Environ.* **37**:1223, 2003

Organic Carbon Sampling Errors: Quartz Filter Adsorption on MOUDI Impactor



McMurry and Zhang, *AST* **10**:430, 1989

MOUDI OC Measurements with 50 nm Stage Replacing Afterfilter



McMurry and Zhang, *AST* **10**:430, 1989

Novel Measurements of Organic Composition

-TDPBMS[1]: Ziemann et al., UC Riverside

Engine emissions

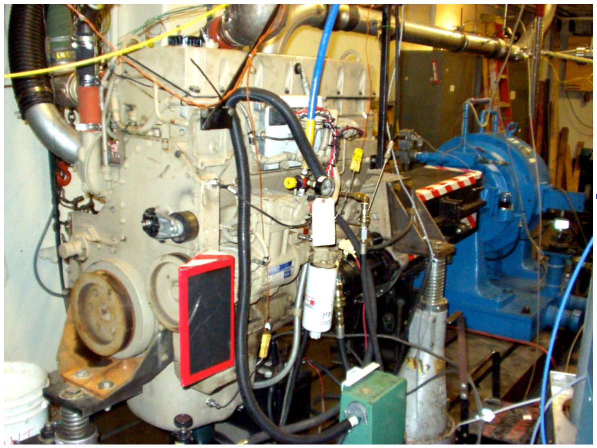
-ATOFMS[2]: Dutcher et al., UMN

Biofuel combustion

[1]Thermal Desorption Particle Beam Mass Spectrometer

[2]Aerosol Time of Flight Mass Spectrometer

Chemical and Physical Properties of Diesel Exhaust Nano Particles: Effect of CRT



CRT

No CRT

Diluters

Chemical Properties (Direct Measuremen)

- Nano MOUDI
  - Impactor
- TDPBMS
  - Mass Spectrometer

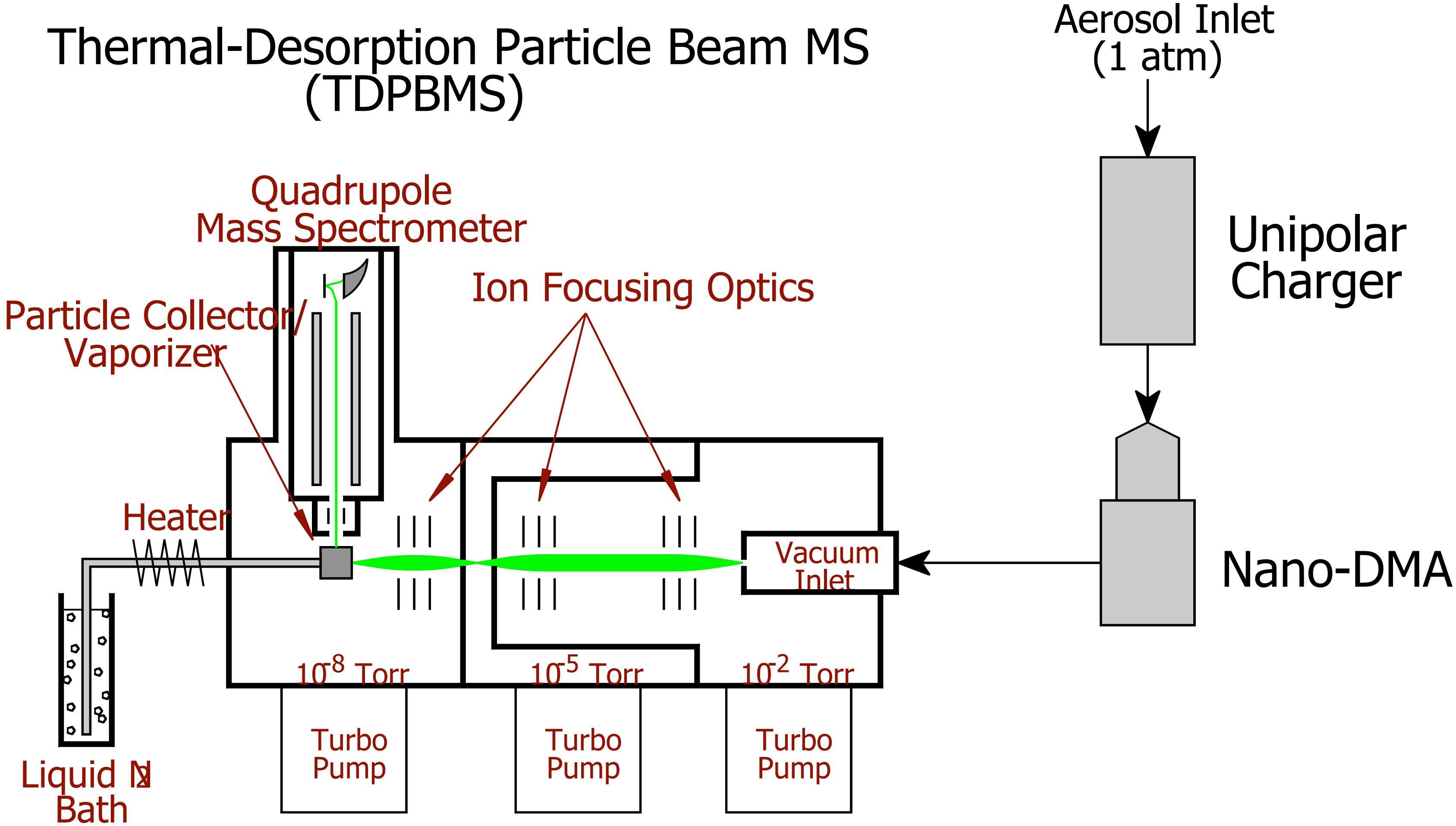
Chemical Properties (Indirect measurement)

- Nano TDMA
  - Volatility
  - Hygroscopicity

Physical Properties

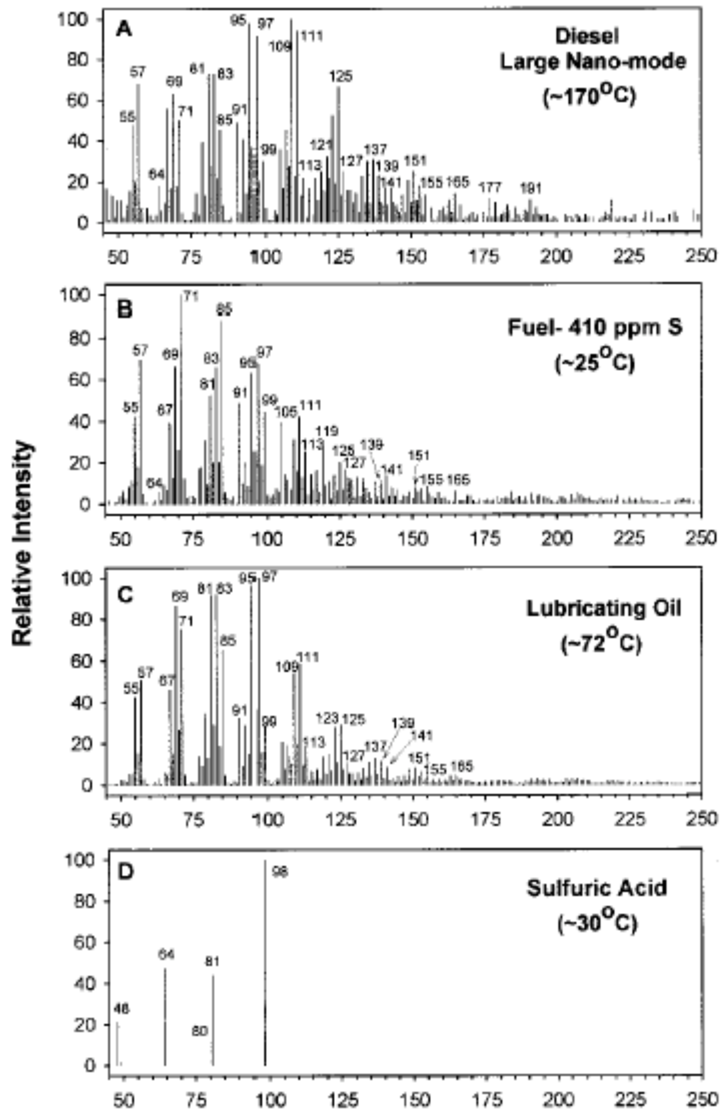
- Nano SMPS
  - Size Dist.
- APM
  - Mass

Thermal Desorption Particle Beam Mass Spectrometer (TDPBMS)



Tobais et al., *ES&T* **35**:2233, 2001; Sakurai et al, *Atmos.Environ*. **37**:1199, 2003

Thermal Desorption Particle Beam Mass Spectrometry (TDPBMS) of DEPs without CRT (with Ziemann et al.)

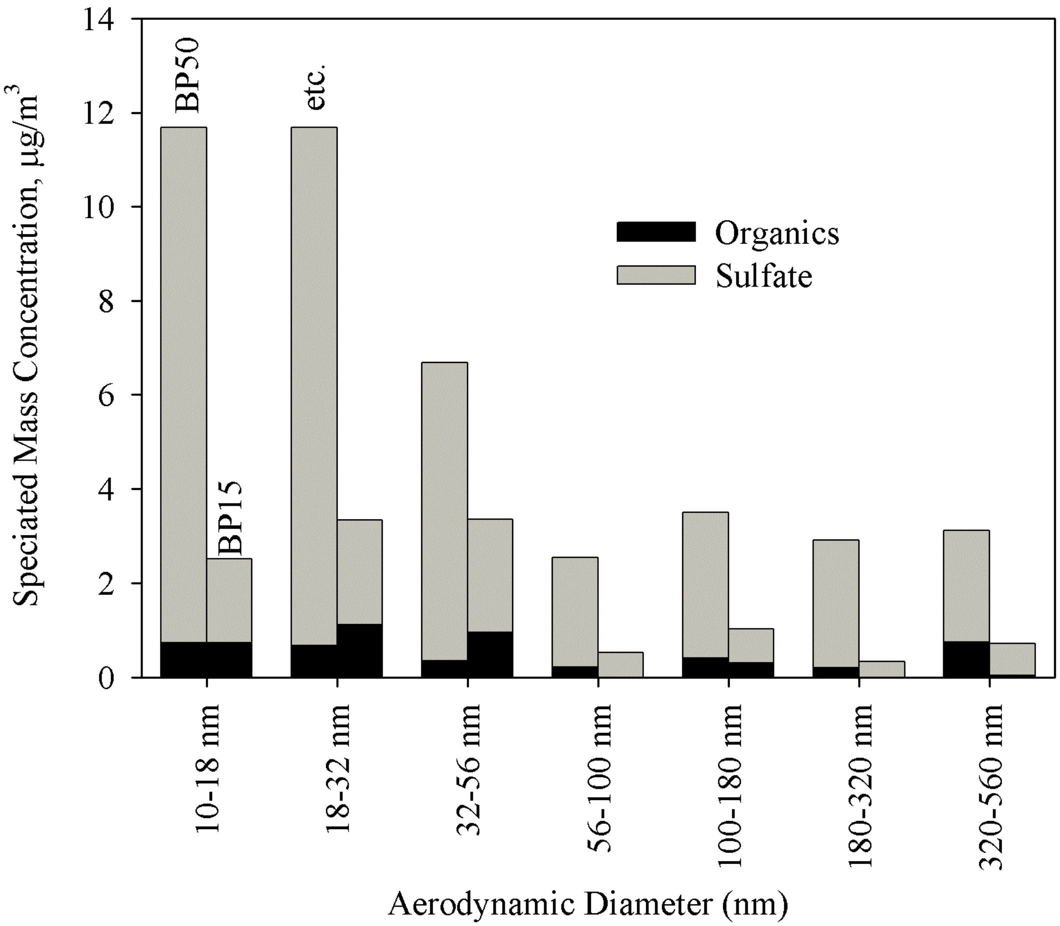


Mass spectra are dominated by alkanes and are more similar to oil than to fuel.

A small amount of sulfuric acid was detected at higher engine loads.

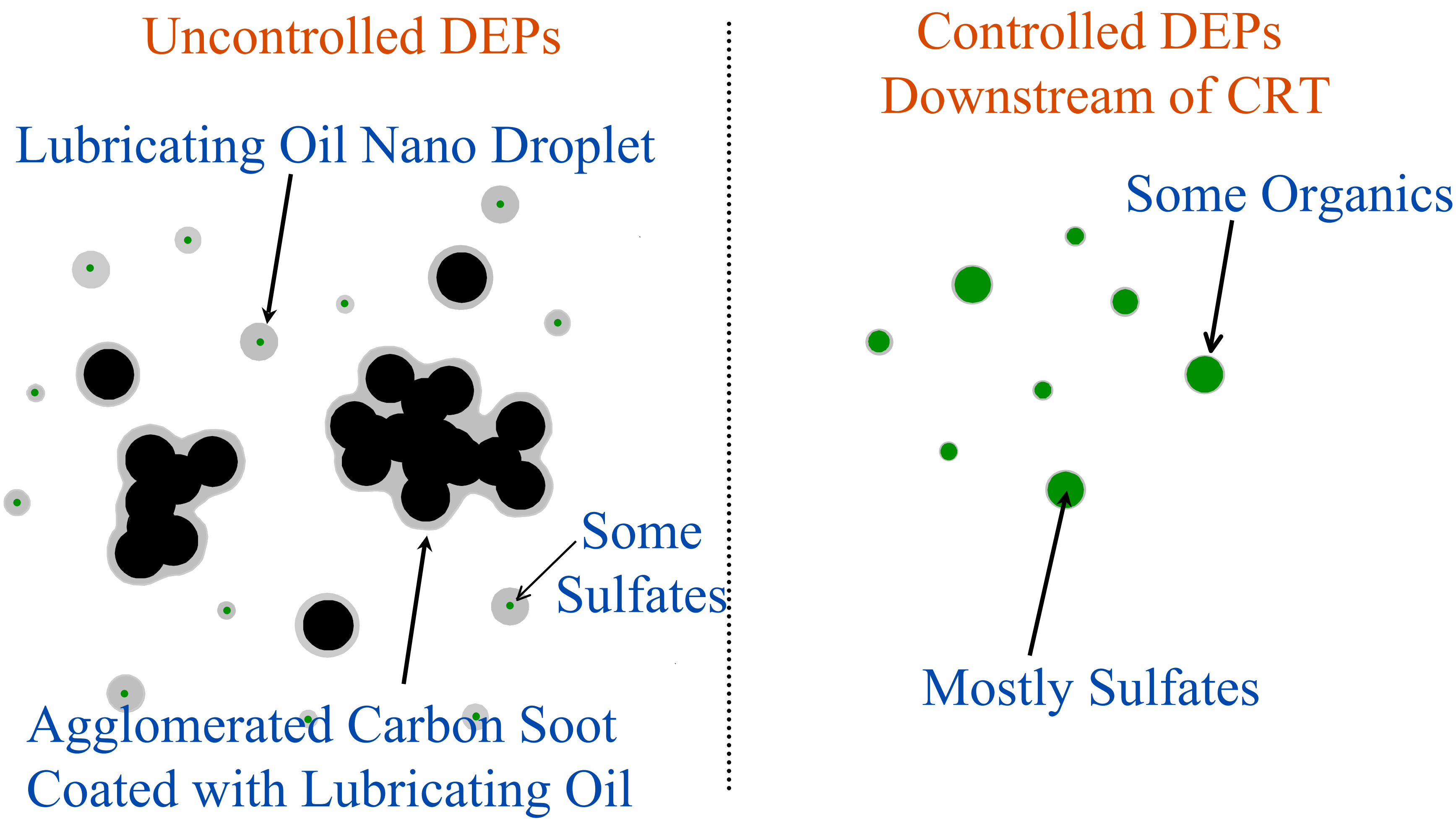
Tobais et al., *ES&T* **35**:2233, 2001; Sakurai et al, *Atmos.Environ.* **37**:1199, 2003

Nano-MOUDI Measurements of DEP Composition Downstream of CRT



Grose et al., *ES&T*, doi:10.1021/es052267, 2007

Effect of CRT on Physical & Chemical Properties of Diesel Exhaust Particles (DEPs)



Sakurai et al, *ES&T* **37**:5487, 2003; Grose et al., *ES&T*, doi:10.1021/es052267, 2007

Summary

•*Tandem measurements on particles provides rich information on physical properties, transport properties and composition.*

•*Filter measurements of organic particulate matter can be affected by vapor adsorption.*

•*Mass spectrometry is providing valuable insights on the sources and composition of organic particulate matter*

-Lubricating oil is an important primary emission from diesel engines

-Particulate emissions from biofuels differ chemically from those produced by fossil fuels

Questions?