Pacific Northwest
NATIONAL LABORATORY

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Real-Time Characterization of Exhaust Particulate Matter on the Individual Particle Level

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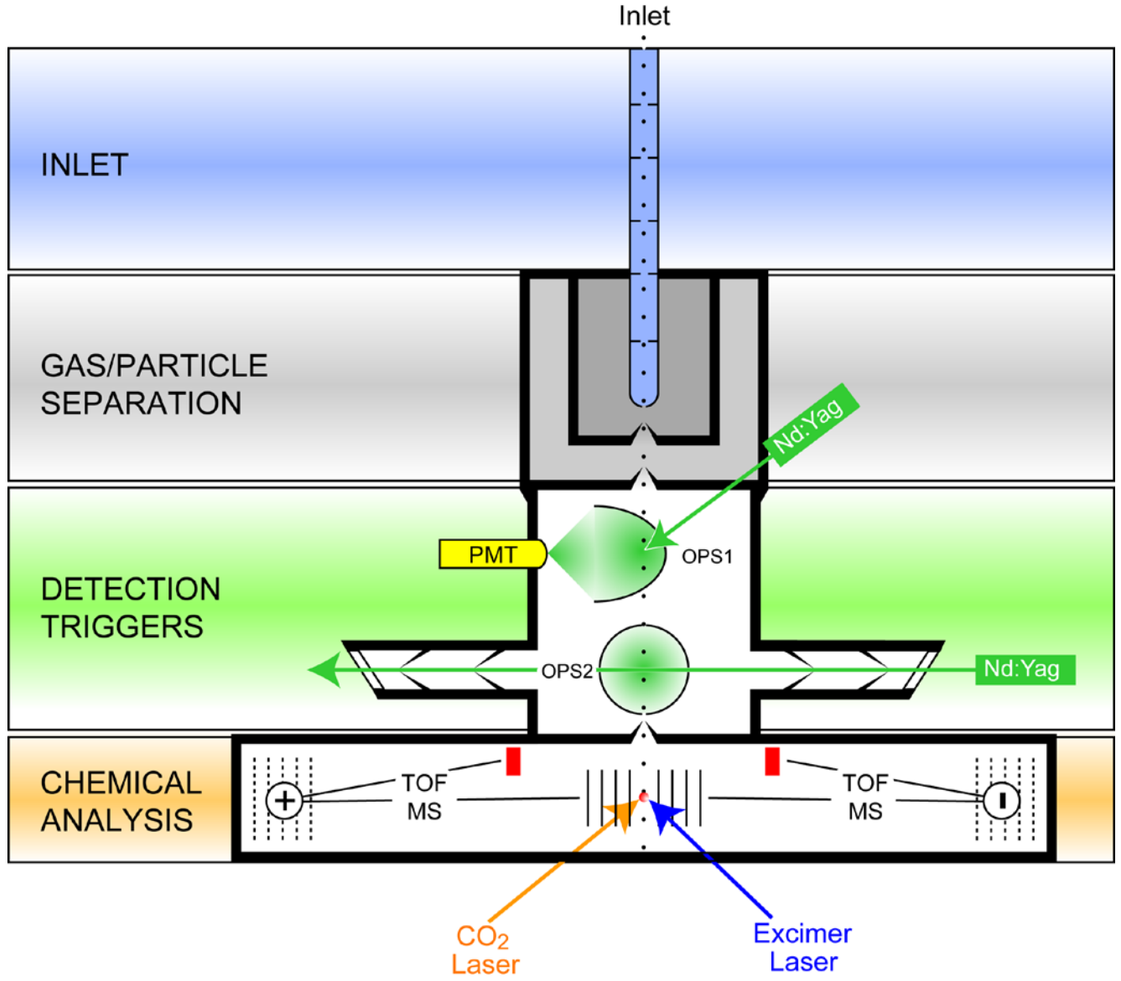
Single Particle Mass Spectrometer: miniSPLAT

- miniSPLAT is a single particle mass spectrometer that characterizes *in-situ* and in real-time *individual* aerosol particles with ultra-high sensitivity and temporal resolution

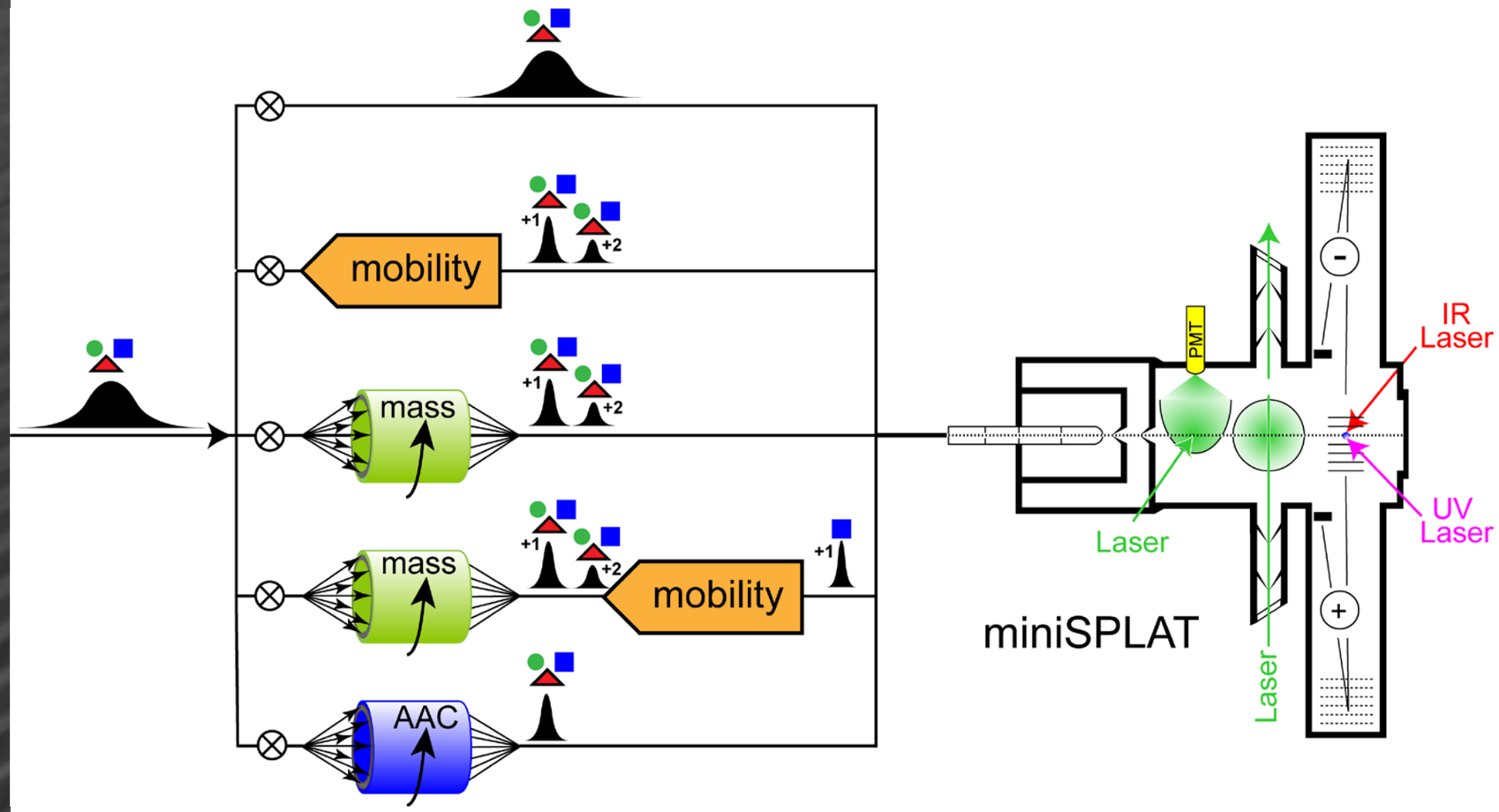
miniSPLAT

- ✓ characterizes particles with sizes from 50 nm to 3 µm (50% cut-off at 80 nm)
- ✓ sizes up to 5,000 p/sec with 0.5% precision and accuracy
- ✓ characterizes composition of 20-100 individual particles/sec
- ✓ simultaneously detects positive and negative ions
- ✓ characterizes volatile and non-volatile fractions
- ✓ detects 1 p/sec, when the concentrations of particles (>100 nm) are as low as 1 p/cm^3



Multidimensional Single Particle Characterization

- miniSPLAT measures the vacuum aerodynamic diameter (d_{va}) and composition (*MS*) of all individual particles *and* particles with narrow distributions of properties (mobility diameter, mass, mass & shape, and aerodynamic diameter)
- This approach provides information on many relevant particle properties as function of particle size

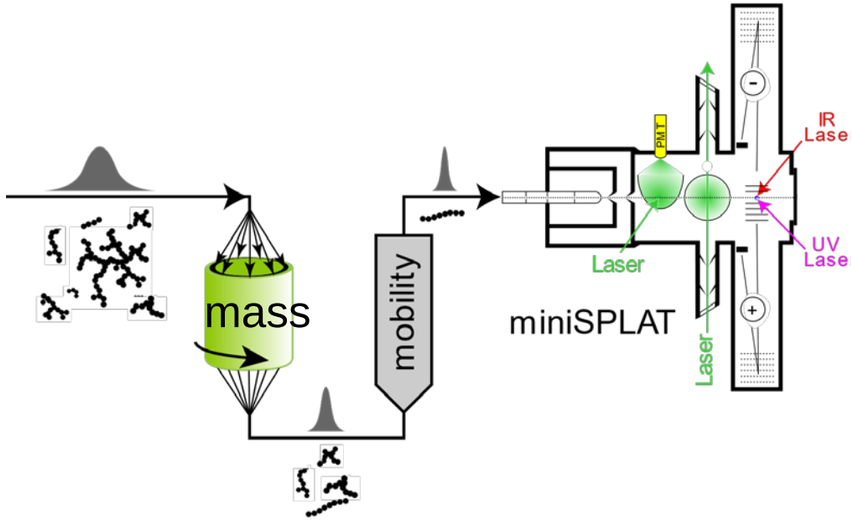


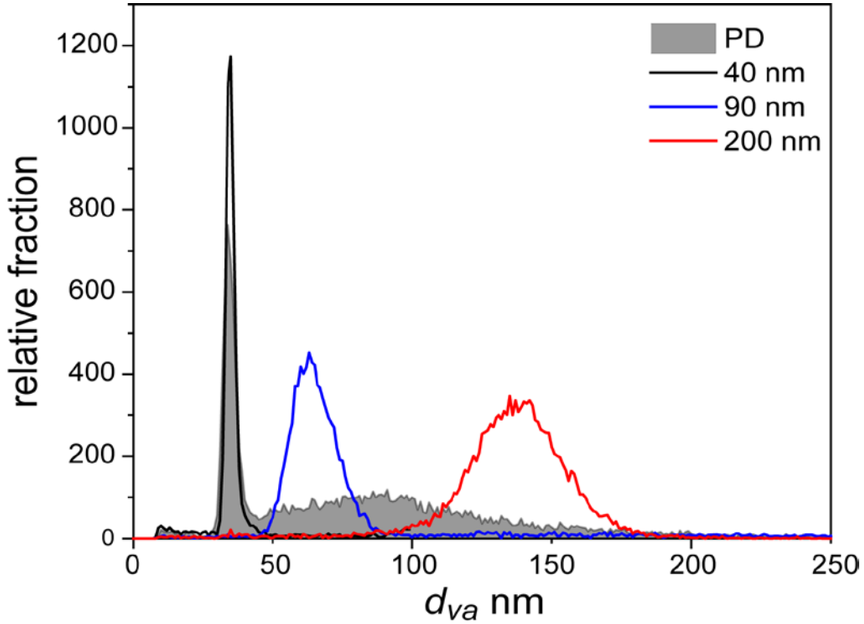
- ✓ d_m size distributions
- ✓ d_{va} size distributions
- ✓ d_a size distributions
- ✓ single particle composition
- ✓ particle mass, m_p
- ✓ effective density, ρ_{eff}
- ✓ fractal dimension, D_{fa}, D_{fm}, D_{pr}
- ✓ primary spherule diameter, d_p
- ✓ number of spherules, N_p
- ✓ void fraction, Φ
- ✓ shape (χ_t , χ_v)

Zelenyuk et al. **(2014)** Combustion and Flame, doi:10.1016/j.combustflame.2014.01.011.

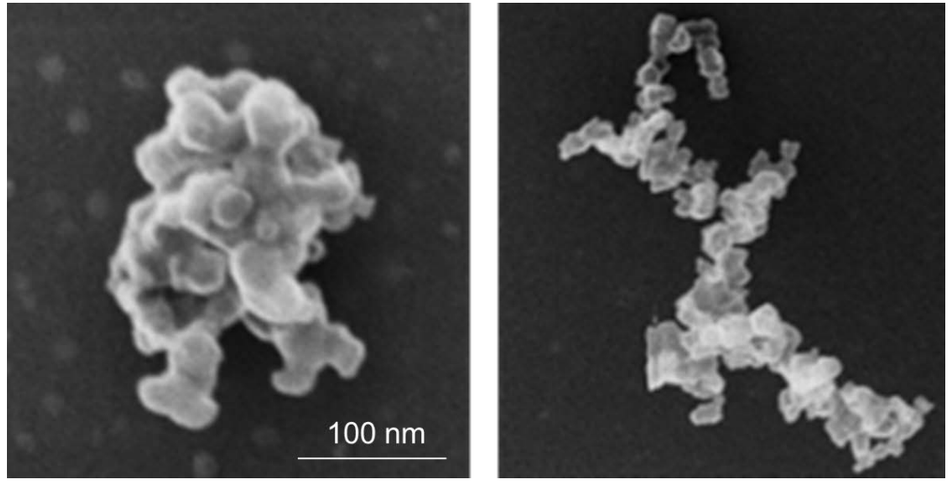
Real-time Particle Shape Separation and Characterization

- Developed approaches to ***separate*** *in situ* and in real-time particles with narrow distribution of shapes to study their size- and shape-dependent properties and behavior

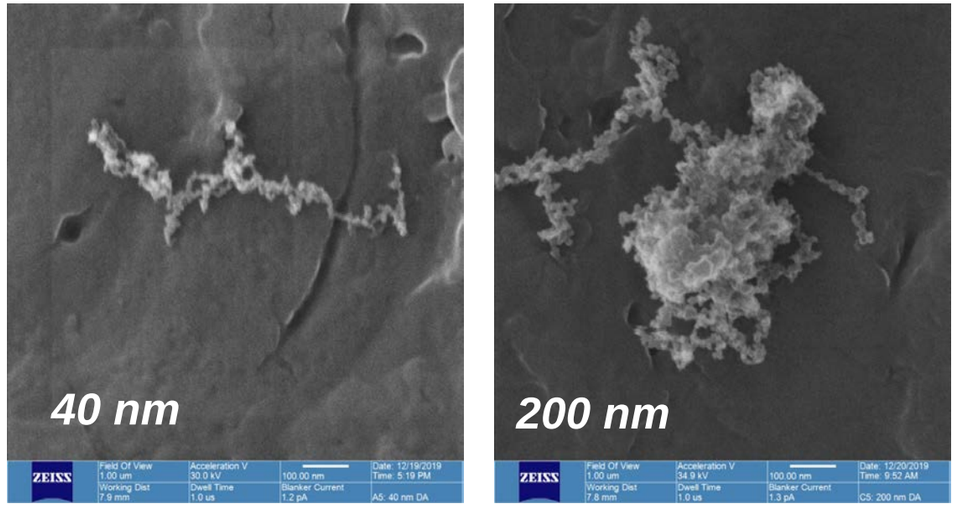




Shape-separated 1.97 fg miniCAST soot particles

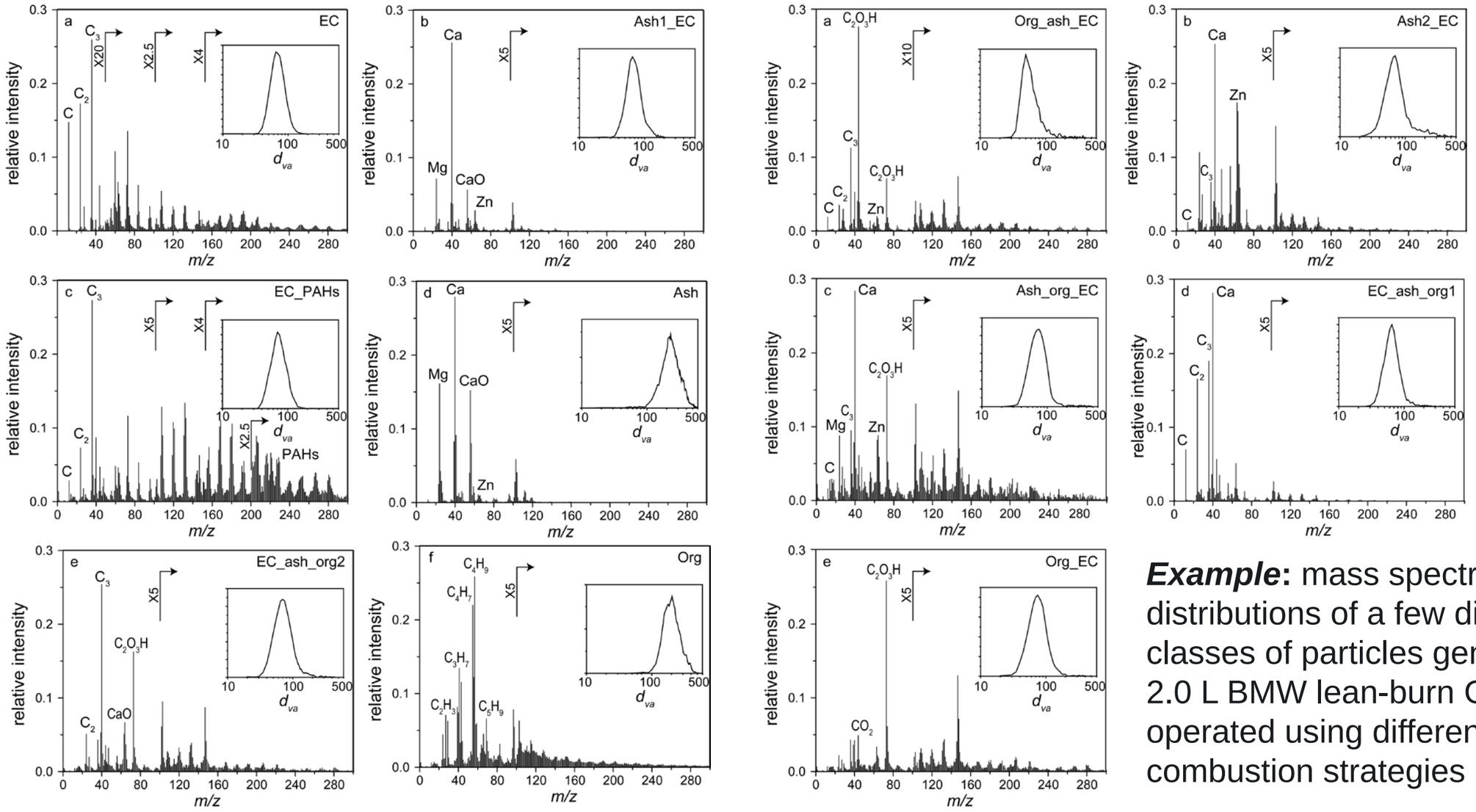


Shape-separated PALAS soot particles



Size and Composition of Individual Exhaust Particles

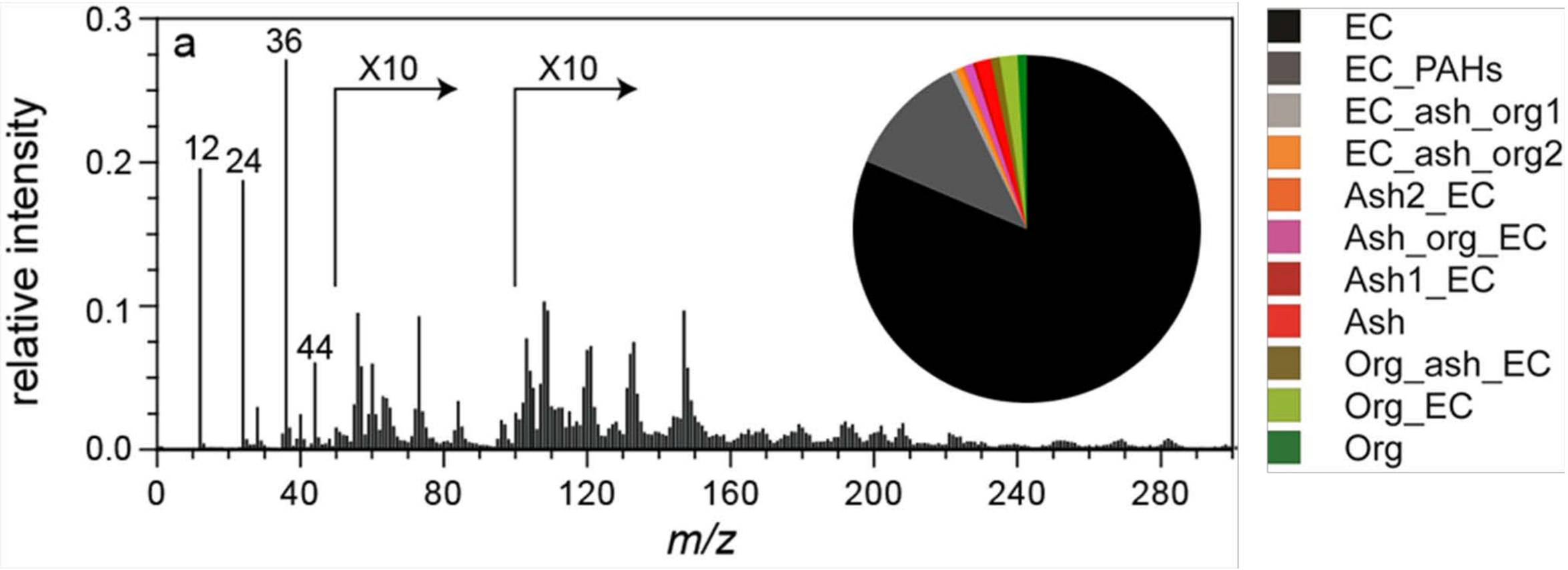
- The resultant data analyzed to identify and quantify different types (classes) of particles, *e.g.* elemental carbon, ash, organic particles, corrosion products, *etc.* Particles with different compositions have different shapes, morphologies, densities



Example: mass spectra and size distributions of a few different classes of particles generated by 2.0 L BMW lean-burn GDI engine operated using different combustion strategies

Size and Composition of Individual Exhaust Particles

Lean stratified, 2000 rpm, 2 bar, Engine out



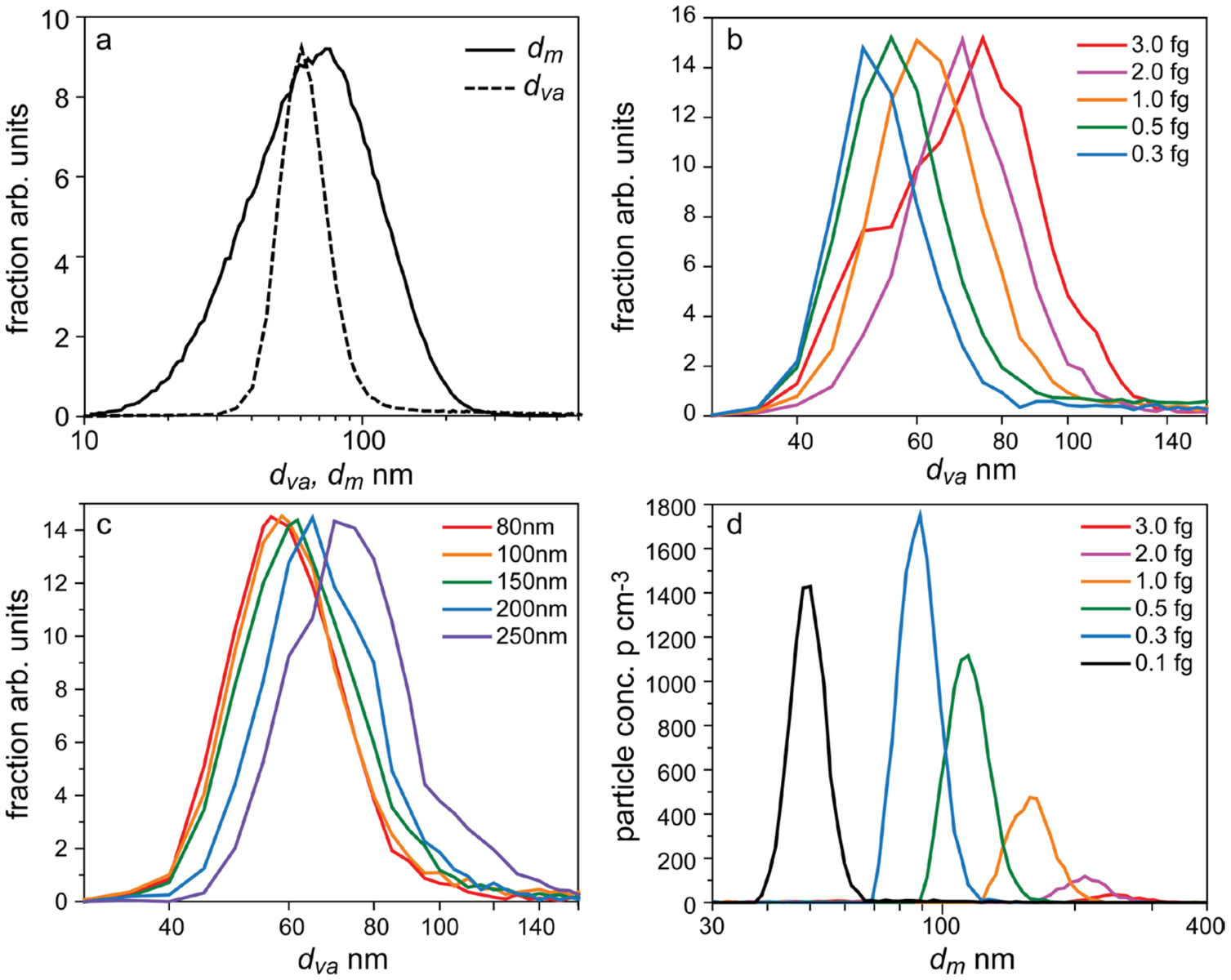
- Particles are composed of elemental carbon (>80%), small amount of organics (very little HC, mostly carboxylic acids, little PAHs), and some ash (Ca from lube detergent additives)
- All exhaust particles are internally mixed, but there are clear classes

Zelenyuk et al. *Int J Engine Res* **(2017)**.

Size and Composition of Individual Exhaust Particles

- d_{va} size distribution is significantly narrower than d_m size distribution, indicating that the majority of the particles are fractal
- When particle d_m increase from 80 nm to 250 nm (312%), their d_{va} increase from 59 nm to only 75 nm (27%)
- When particles masses increase from 0.3 fg to 3 fg, their d_{va} increase from 53 nm to only 74 nm
- Measured relationship between particle mass and d_m to yield another measure of fractal dimension and particle effective density

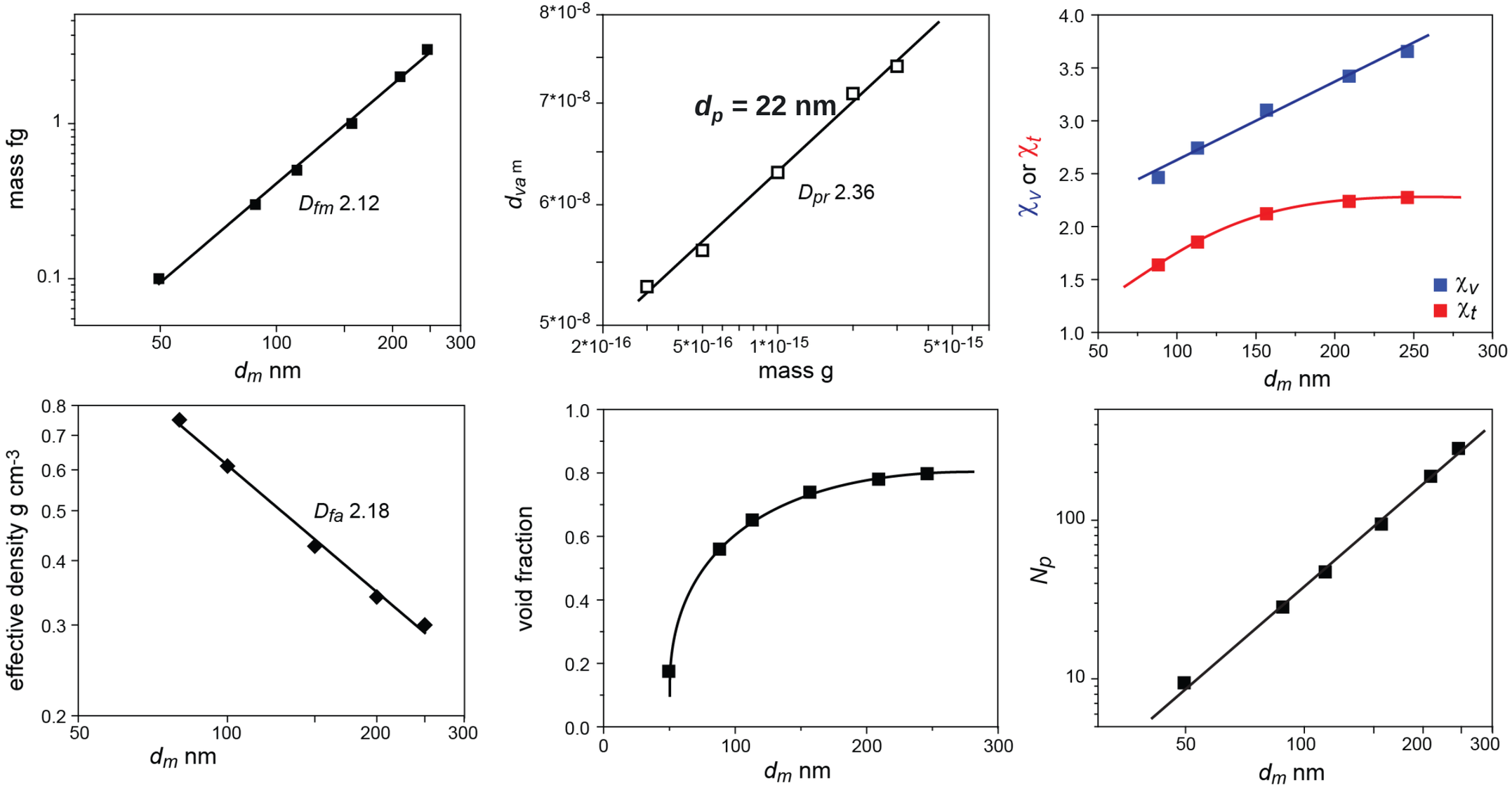
Lean stratified, 2000 rpm, 2 bar, Engine out



Zelenyuk et al. *Int J Engine Res* **(2017)**.

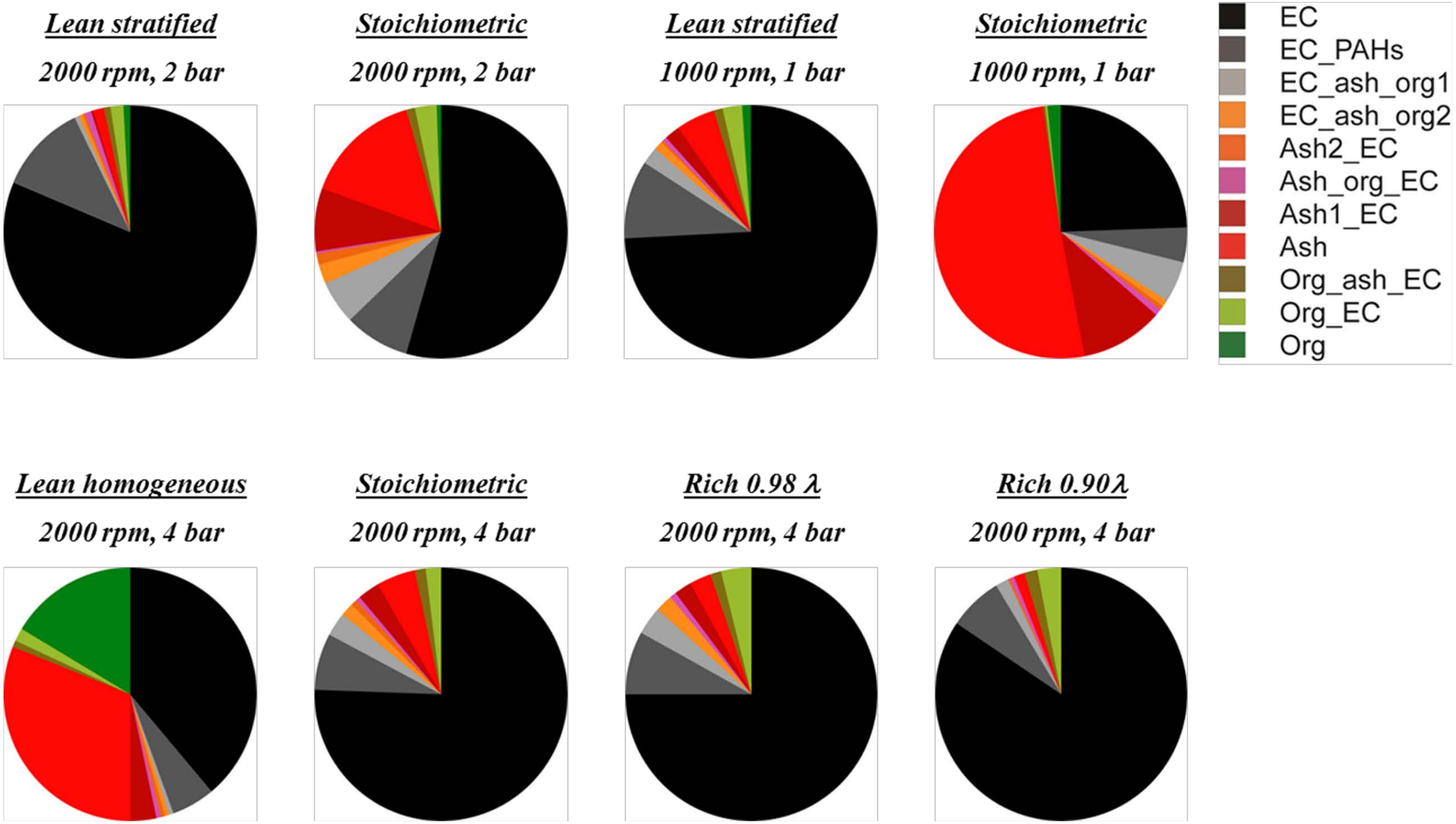
Multidimensional Single Particle Characterization

- Measurements of m_p, d_{va}, d_m, and composition are used to determine a large number of particle properties as a function of particle size or mass.



Composition of Exhaust Particles

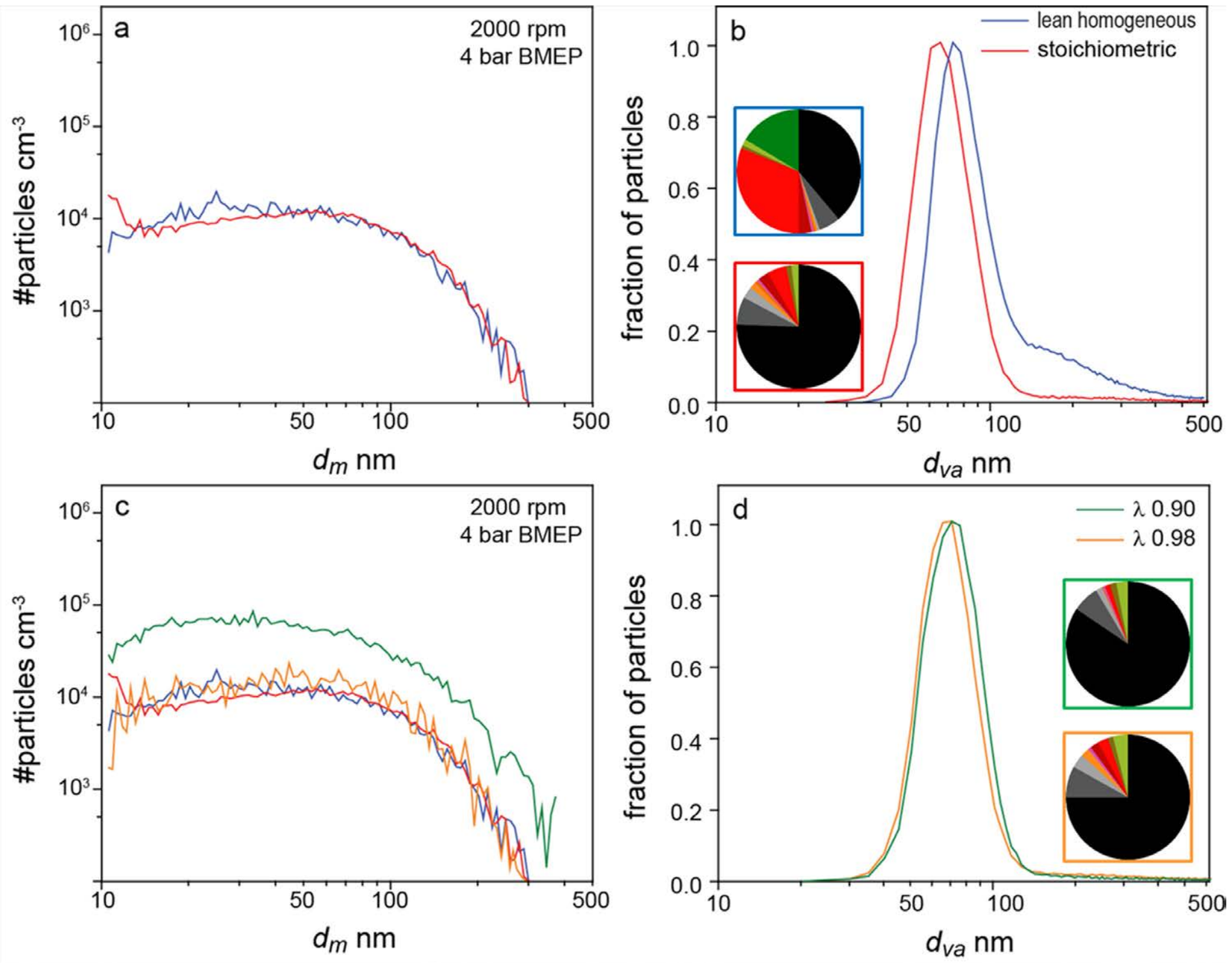
- Particles properties strongly depend on engine operating conditions



Composition of Exhaust Particles

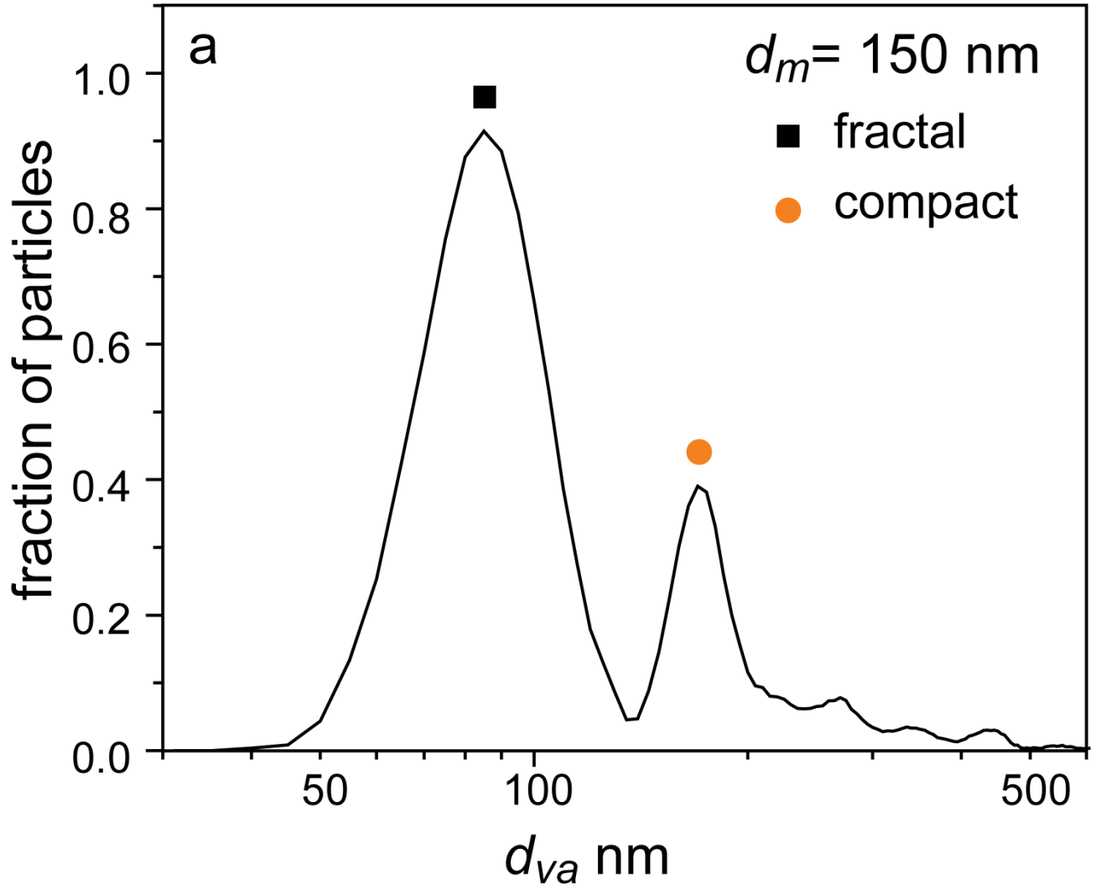
- Particles properties depend on engine operating conditions
- At 2000 rpm, 4 bar richer conditions lead to significantly higher number concentrations
- d_{va} distributions are nearly independent of λ
- At *0.9* λ the fraction of EC particles is slightly higher
- Lean homogeneous PM contains higher fraction of larger Ca-dominated particles and of organic particles

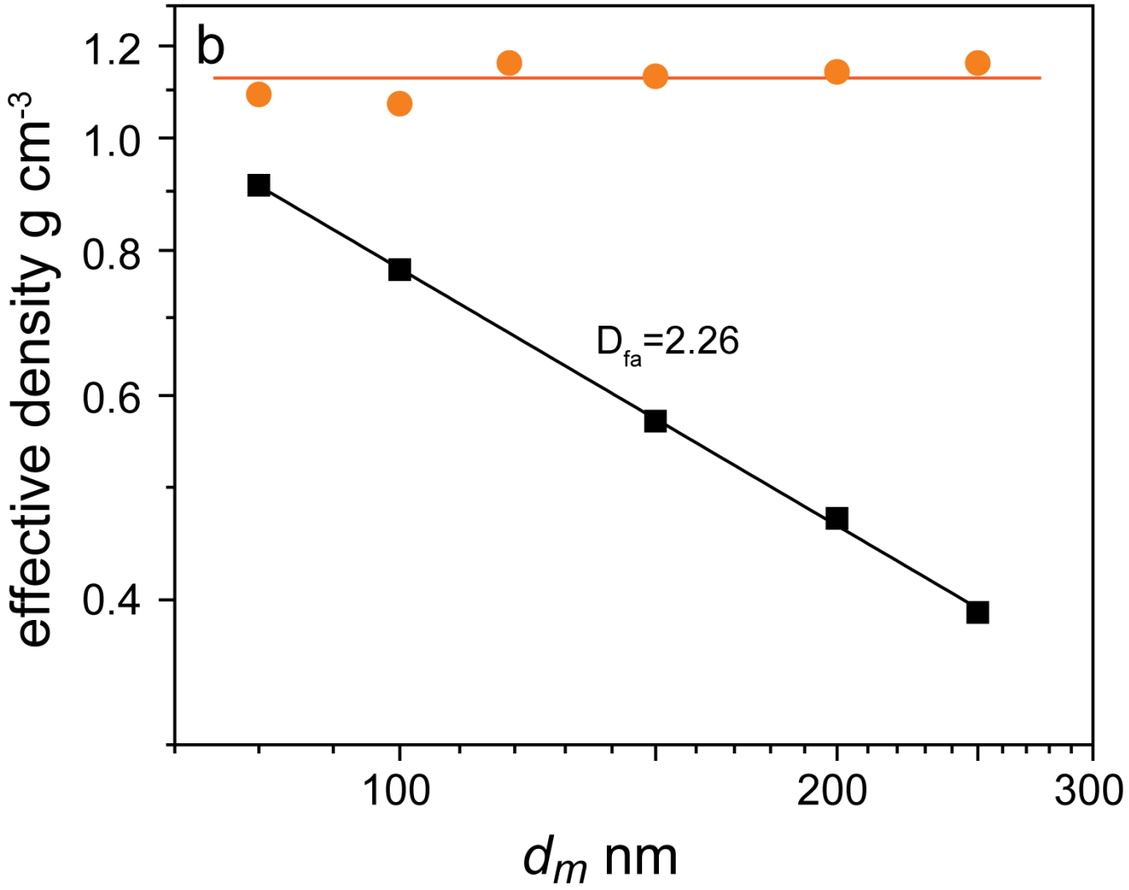
2000 rpm, 4 bar, Engine out



Multidimensional Single Particle Characterization

- Particles with different compositions have different shapes, morphologies, densities



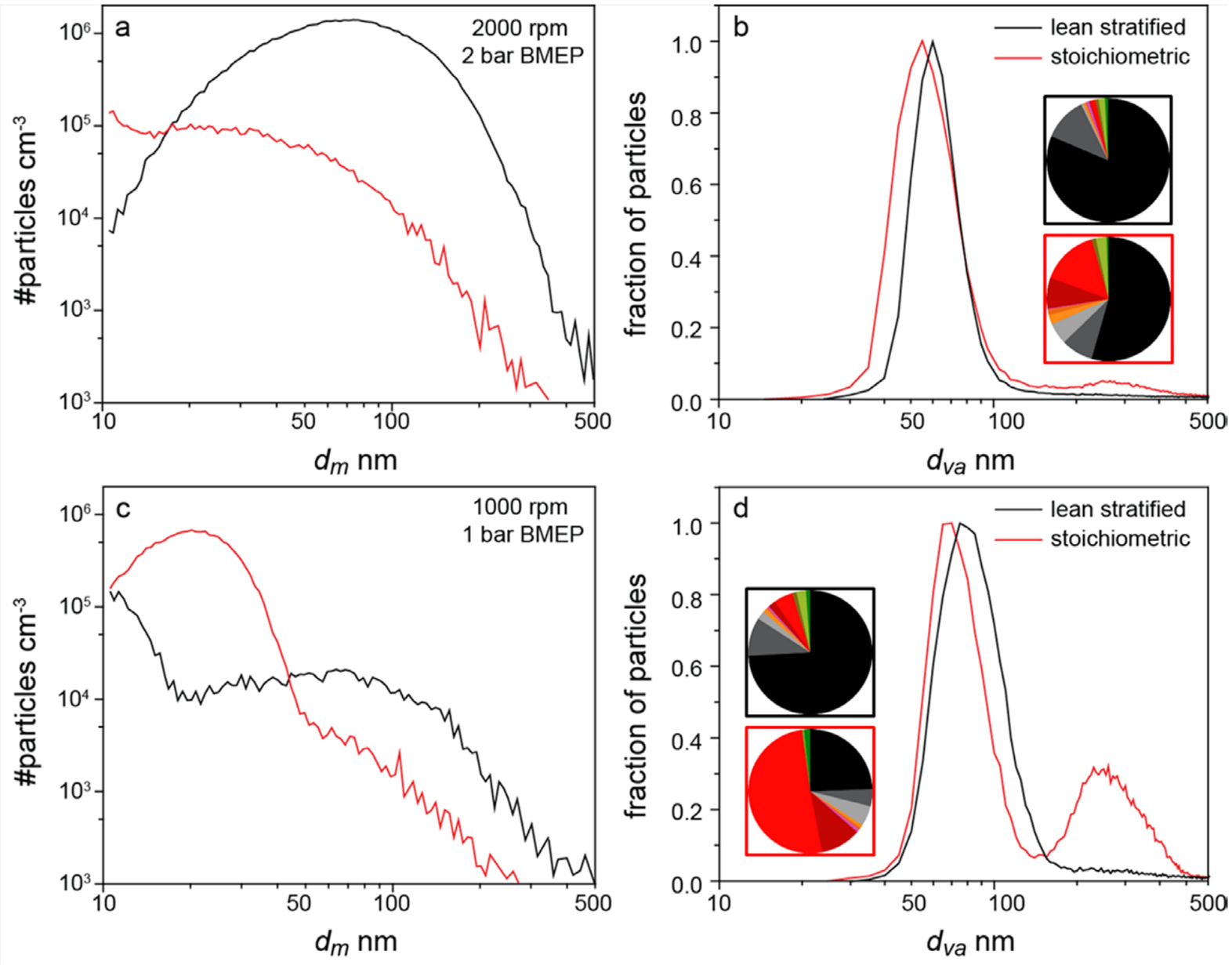


- d_m-selected 150 nm particles produced under lean homogeneous combustion, at 2000 rpm and 4 bar, exhibit two distinct modes: fractal soot particles and compact organic particles
- The calculated particles effective densities plotted as a function of d_m, show that while the effective density of fractal particles decreases with particle size, it remains nearly constant for compact organic particles.

Composition of Exhaust Particles

- Particles properties strongly depend on engine operating conditions

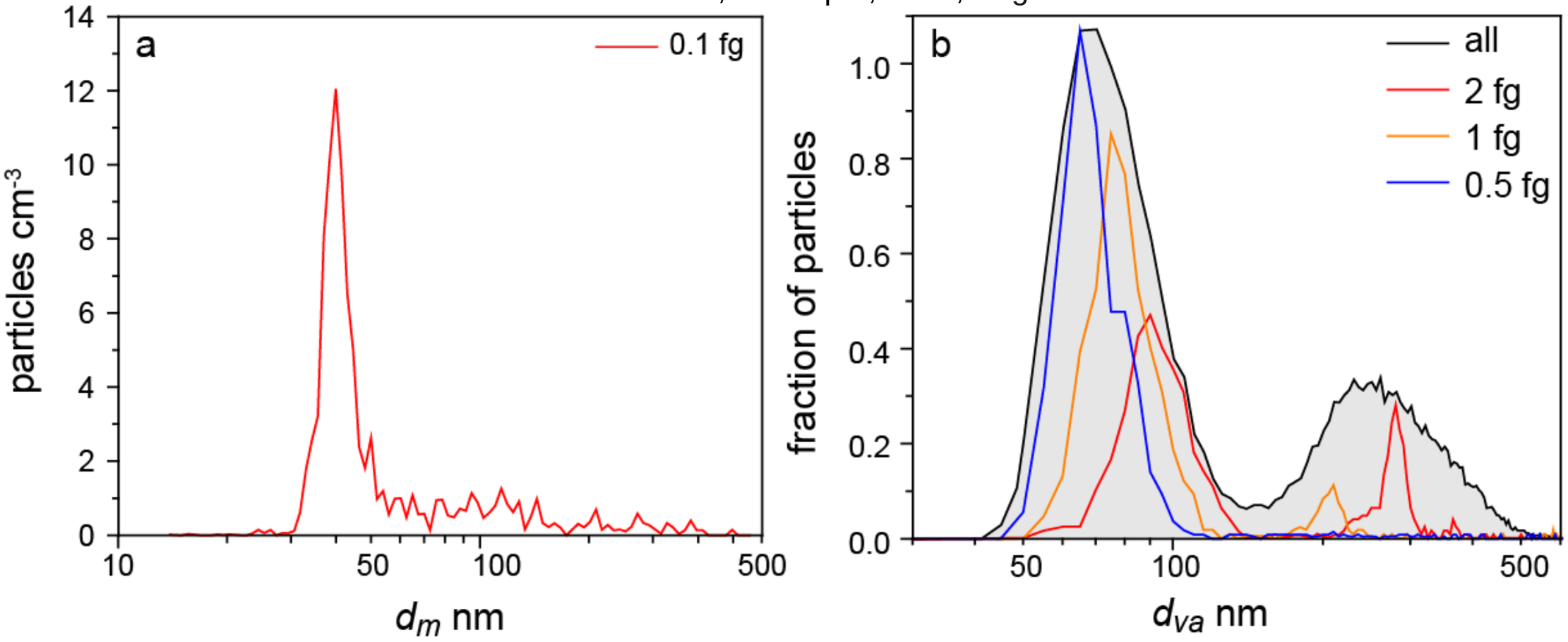
- At low load, stoichiometric PM contains high fraction of larger Ca-dominated, ash particles
- Ash particles significantly contribute to PM mass
- Ash particles were recently suggested to serve as a catalyst in soot oxidation
- It was recently suggested that toxicity of ash particles can be larger than that of diesel exhaust emissions



Multidimensional Single Particle Characterization

- Particles with different compositions have different shapes, morphologies, densities

Stoichiometric, 1000 rpm, 1 bar, Engine out

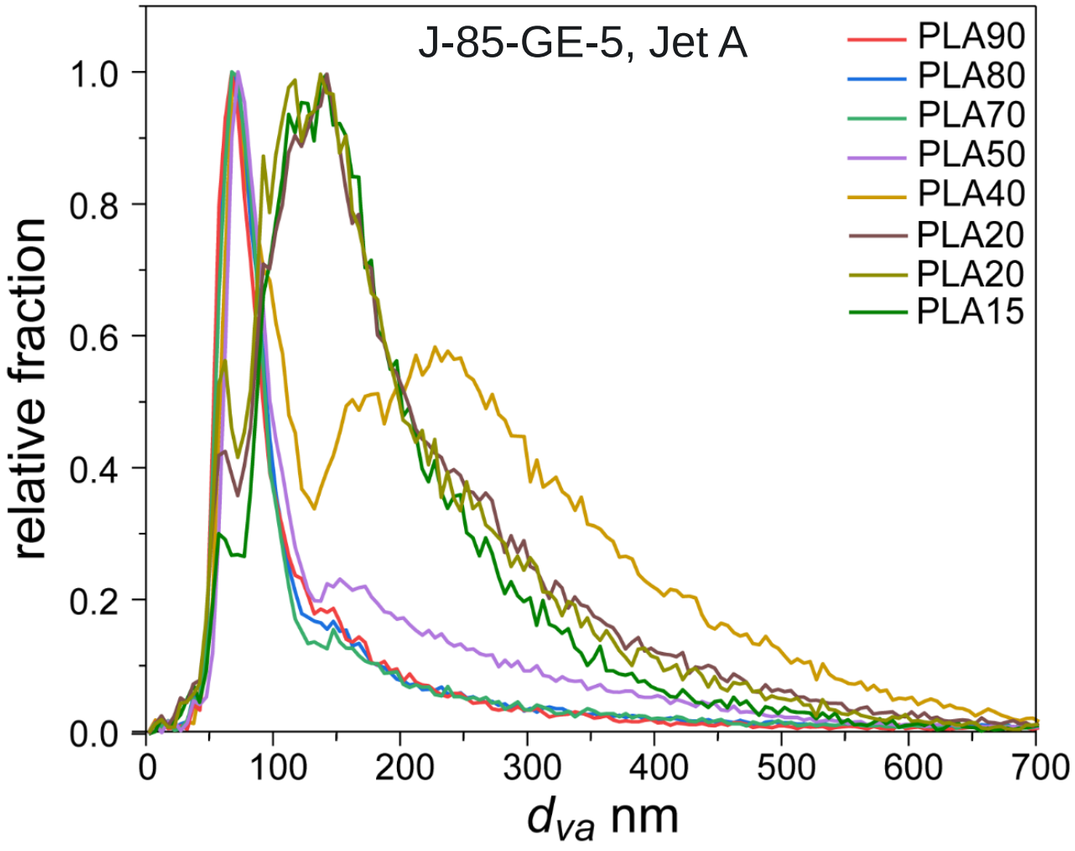


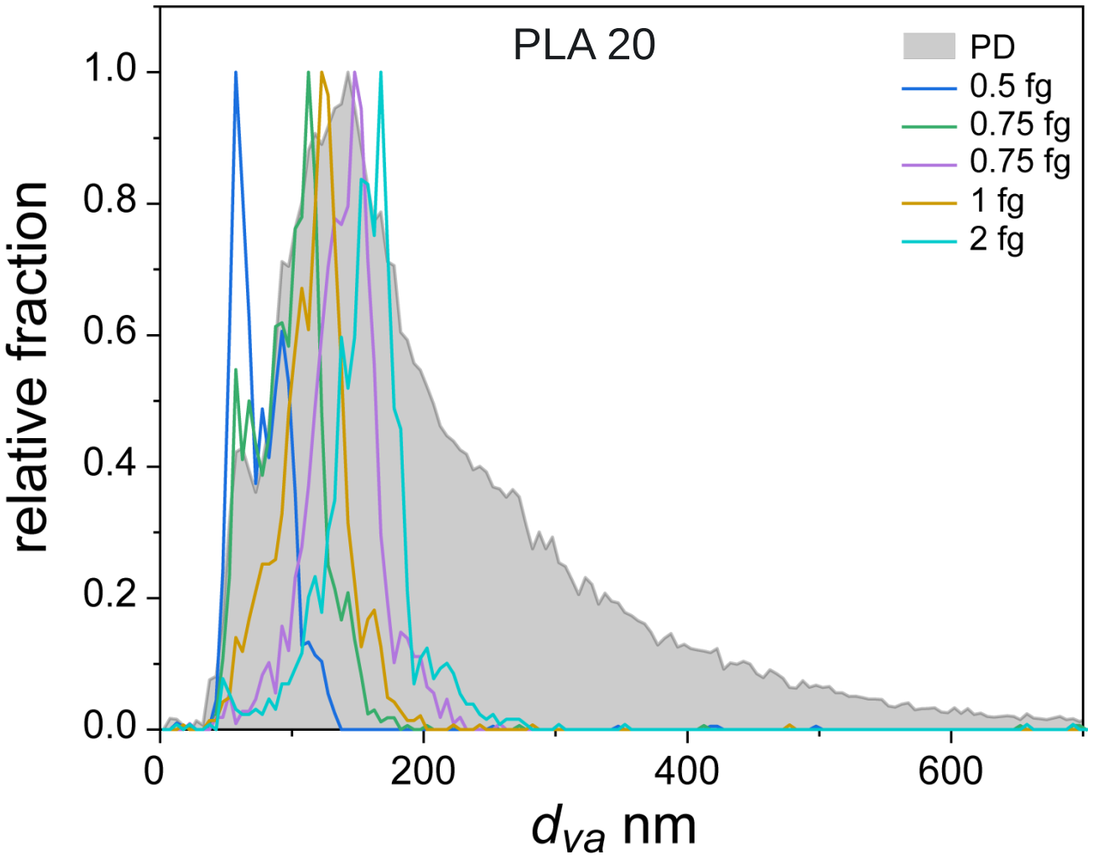
- Particles with mass of 0.1 fg have d_m of 40 nm and density of 3 g cm^{-3}, composed of ash
- d_{va} distributions of mass selected particles shows two distinct modes with lighter particles being mostly fractal and heavier particles being both: fractal and compact.

Size and Composition of Individual Exhaust Particles

- The presence of compact, larger particles is observed for many other PM sources
- These more compact, larger particles can significantly contribute to particulate mass loading

- Their presence can provide explanation for other observations: larger particle mode observed in the SMPS and EEPS scans, differences between Teflon filter and EC mass, higher values of Single Scattering Albedo (SSA), differences between the measured effective densities obtained in two different instrument configurations (DMA-CPMA-CPC vs. CPMA-SMPS





Conclusions

- Developed an ultra-sensitive, high-precision instrument and methods that can *quantitatively* characterize individual particles with high temporal resolution and measure simultaneously many of the relevant attributes for each individual particle
- Demonstrated the utility of this approach to characterize exhaust PM
- Characterized detailed properties of particles emitted by different engines, for a large number of operating conditions and fuels
- Measurements by single particle mass spectrometer make it possible to identify the presence of particles with different properties (compositions, sizes, masses, shapes, morphologies, and densities)
- Larger, more compact particles, with higher densities can significantly contribute to particulate mass loadings, light scattering signal
- The presence of larger, more compact particles can explain observations by EEPS, SMPS, CAPS, Teflon filters
- The presence of different particles types can result in the differences between the measured effective densities obtained in two different instrument configurations: mass → mobility and mobility → mass