Multidimensional Characterization of Individual Aerosol Particles

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**Importance:**
Aerosols are ubiquitous: Atmospheric aerosols impact climate and human health, aerosols are used for drug delivery. While Nanotechnology relies on their unique properties to produce novel materials aerosolized pathogens have the potential to be used as terror agents. The study of chemistry and microphysics of particles is central to the advancement in each of these fields.

**Fundamental Science:**
The chemical and physical properties and behavior of nanomaterials differ from the bulk or the isolated molecules. The field of nanoscience aims to develop the knowledge that bridges the gap between the isolated molecule to the bulk.
**Measurements of Aerosol Properties**

**Challenges**
- Most aerosols have low number concentrations of small particles that come in many sizes, compositions, shapes, and phases.
- Aerosols that are composed of *internally* or *externally* mixed particles have very different properties.

**Solution**
- Develop an ultra-sensitive, high-precision instrument that can characterize small particles with high temporal resolution.
- Measure simultaneously many of the relevant attributes for each individual particle.

Particle behavior, including its chemical reactivity, is a function not only of its composition, but also depends on its size, shape, morphology and phase.
SPLAT II on an aircraft

SPLAT : Laboratory, Field, and Aircraft Compatible

- Laboratory and field deployable
- Compact, portable, and aircraft-compatible
- Provides quantitative multidimensional information for individual particles
  - Number concentration
  - Size
  - Composition
  - Density
  - Shape (dynamic shape factor, asphericity, asymmetry)
  - Morphology
  - Hygroscopicity
  - Fractal dimension
  - CCN activity
  - IN activity
- Uses unique data classification, mining and visualization software

SPLAT: An Ultra-Sensitive, High Precision Instrument for Multidimensional Single Particle Characterization

- Characterizes particles with sizes from 50 nm to 3 µm
- Characterizes 50% of 85 nm particles
- Sizes 2000 particles/sec
- Measures the composition of 100 particles/sec
- Sizes particles with 0.5% precision
- Uses IR/UV ion formation mode to generate quantitative particle composition

Number Concentrations – 1 sec resolution

Asphericity – 1 sec resolution

High Precision Sizing & Size Distributions

- SPLAT sizing resolution is better than 0.5%
- Particle size distributions are measured with high temporal resolution, even for very low particle concentrations
- Size distributions can be used to measure particle density

Particle Density from SPLAT (no DMA)

We can measure particle density directly from SPLAT measured size distributions. We can do it for all particles or for composition resolved data.

High Precision Density Measurements

**Molten Salts**
- Nanoparticles are ultra-pure and form metastable phases that can exist far from equilibrium.
- We reported the first density measurements for a number of hygroscopic particles in highly metastable phases.

<table>
<thead>
<tr>
<th>System</th>
<th>Predicted g/cm³</th>
<th>Observed g/cm³</th>
<th>Crystal g/cm³</th>
<th>Δ**%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(NO₃)₂</td>
<td>—</td>
<td>2.16 ± 0.02</td>
<td>2.54</td>
<td>15</td>
</tr>
<tr>
<td>NaHSO₄</td>
<td>2.22</td>
<td>2.19 ± 0.02</td>
<td>2.43</td>
<td>9</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>2.09</td>
<td>2.10 ± 0.01</td>
<td>2.26</td>
<td>7</td>
</tr>
<tr>
<td>NH₄HSO₄</td>
<td>1.74</td>
<td>1.77 ± 0.02</td>
<td>1.79</td>
<td>1</td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>—</td>
<td>1.57 ± 0.025</td>
<td>1.73</td>
<td>8</td>
</tr>
</tbody>
</table>

**SOA**
- We reported the first high precision density measurements for Secondary Organic Aerosols (SOA) particles formed by oxidation of α-pinene.

\[ \rho = 1.215 \pm 0.005 \text{ g cm}^{-3} \]

\[ R = 0.99999 \]

Aspherical Particles: Dynamic Shape Factors (DSF)

Determined the effect of flow regime and orientation on DSFs for PSL agglomerates.

The first measurements of the DSF in the free-molecular regime for a number of particle systems.

Electric field induced dipole can result in particle alignment.
Alignment depends on particle shape, size and electric field.
We used this method to separate, for the first time, particles on the basis of shape.

**A New Real-Time Method for Determining Particle Asymmetry and Shape Separation**

Zelenyuk, A. and Imre, D. Aerosol Science and Technology 2007, 41, 112-124
A New Real-Time Method for Determining Particles Sphericity and Density

Line-width makes it possible to distinguish between spherical and aspherical particles

Particle Morphology: “Depth-profiling”

Particle Composition Measured by Laser Desorption/Ionization

What Else Can We Determine About these NaCl Coated Particles

<table>
<thead>
<tr>
<th>$d_{ve}$ NaCl seed (nm)</th>
<th>$d_m$ (nm)</th>
<th>$d_{va}$ (nm)</th>
<th>DOP $V_f$</th>
<th>DOP $W_f$</th>
<th>Meas. $\rho$ (g/cm$^3$)</th>
<th>Calc $\rho$ (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>139</td>
<td>212</td>
<td>272</td>
<td>0.72</td>
<td>0.535</td>
<td>1.284</td>
<td>1.32</td>
</tr>
<tr>
<td>139</td>
<td>257</td>
<td>298</td>
<td>0.84</td>
<td>0.71</td>
<td>1.164</td>
<td>1.17</td>
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<tr>
<td>139</td>
<td>408</td>
<td>427</td>
<td>0.96</td>
<td>0.92</td>
<td>1.046</td>
<td>1.03</td>
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<tr>
<td>215</td>
<td>272</td>
<td>420</td>
<td>0.50</td>
<td>0.32</td>
<td>1.542</td>
<td>1.57</td>
</tr>
<tr>
<td>215</td>
<td>312</td>
<td>420</td>
<td>0.67</td>
<td>0.48</td>
<td>1.346</td>
<td>1.37</td>
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</table>

<table>
<thead>
<tr>
<th>$d_{ve}$ NaCl seed (nm)</th>
<th>$d_m$ (nm)</th>
<th>$d_{va}$ (nm)</th>
<th>Pyr. $V_f$</th>
<th>Pyr. $W_f$</th>
<th>$\rho_{ef}$</th>
<th>DSF</th>
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<tbody>
<tr>
<td>139</td>
<td>241</td>
<td>272</td>
<td>0.743</td>
<td>0.63</td>
<td>1.13</td>
<td>1.155</td>
</tr>
</tbody>
</table>

- Size
- Composition
- What is on the surface
- Shape
- Precise composition
- Density
- Effective density
- Dynamic Shape Factor

Morphology of SOA/DOP: Is it a Homogeneous Solution Droplet?

- It has widely been assumed that secondary organic aerosol (SOA) and all other organics form solution droplets, which acts to increase SOA formation yield.
- Our data clearly show that they do not mix and form layered particles.
- We generated SOA-coated DOP particles (a), which have a second 1.5 nm thick layer of DOP at the surface, and DOP-coated SOA particles (b).
- We demonstrated that both forms are stable for many hours.

Kinetics of Evaporation and Phase of SOA

- Models assume that SOA evaporates in minutes, when gas phase concentrations decrease.
- Our findings show that SOA evaporates so slow that it can be ignored.
- SOA is assumed to be liquid
- Our findings show that SOA is not in liquid form
- Spectator atmospheric organics thus far been ignored
- Our findings show that these organics adsorb on SOA particles, increase their mass, and inhibit evaporation.

Many More Applications to Atmospheric Science

- Sources, properties, evolution of atmospheric aerosol
- SOA formation, properties, transformations
- Hygroscopic properties of aerosols
- Warm clouds: cloud condensation nuclei (CCN), interstitial and background aerosols
- Ice clouds: only 1 in $10^4$-$10^6$ particles become ice nuclei resulting in extremely low IN concentration (~0.1-10 p/Liter)

Zelenyuk et al. (2010b). *Analytical Chemistry* DOI: 10.1021/ac1013892
Zelenyuk et al. (2009). *Aerosol Science and Technology* 43:411-424
Exhaust PM Characterization

<table>
<thead>
<tr>
<th>Class</th>
<th>EC1</th>
<th>EC2</th>
<th>EC3</th>
</tr>
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<tbody>
<tr>
<td>%EC</td>
<td>93.5</td>
<td>86.5</td>
<td>79.7</td>
</tr>
<tr>
<td>%OC</td>
<td>5.7</td>
<td>12.6</td>
<td>16.4</td>
</tr>
<tr>
<td>%PAH</td>
<td>0.4</td>
<td>0.7</td>
<td>2.3</td>
</tr>
<tr>
<td>%Ca</td>
<td>0.2</td>
<td>0.6</td>
<td>1.0</td>
</tr>
<tr>
<td>%Nit</td>
<td>0.2</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>%other</td>
<td>6.5</td>
<td>14.5</td>
<td>20.3</td>
</tr>
</tbody>
</table>
The properties of SIDI PM are very different from those emitted from diesel engines. In SIDI PM organics, PAHs, and inorganics – are all part of the fractal soot particles, and none come on separate compact particles.
Acknowledgments

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