

# Nanoaerosol Mass Spectrometry

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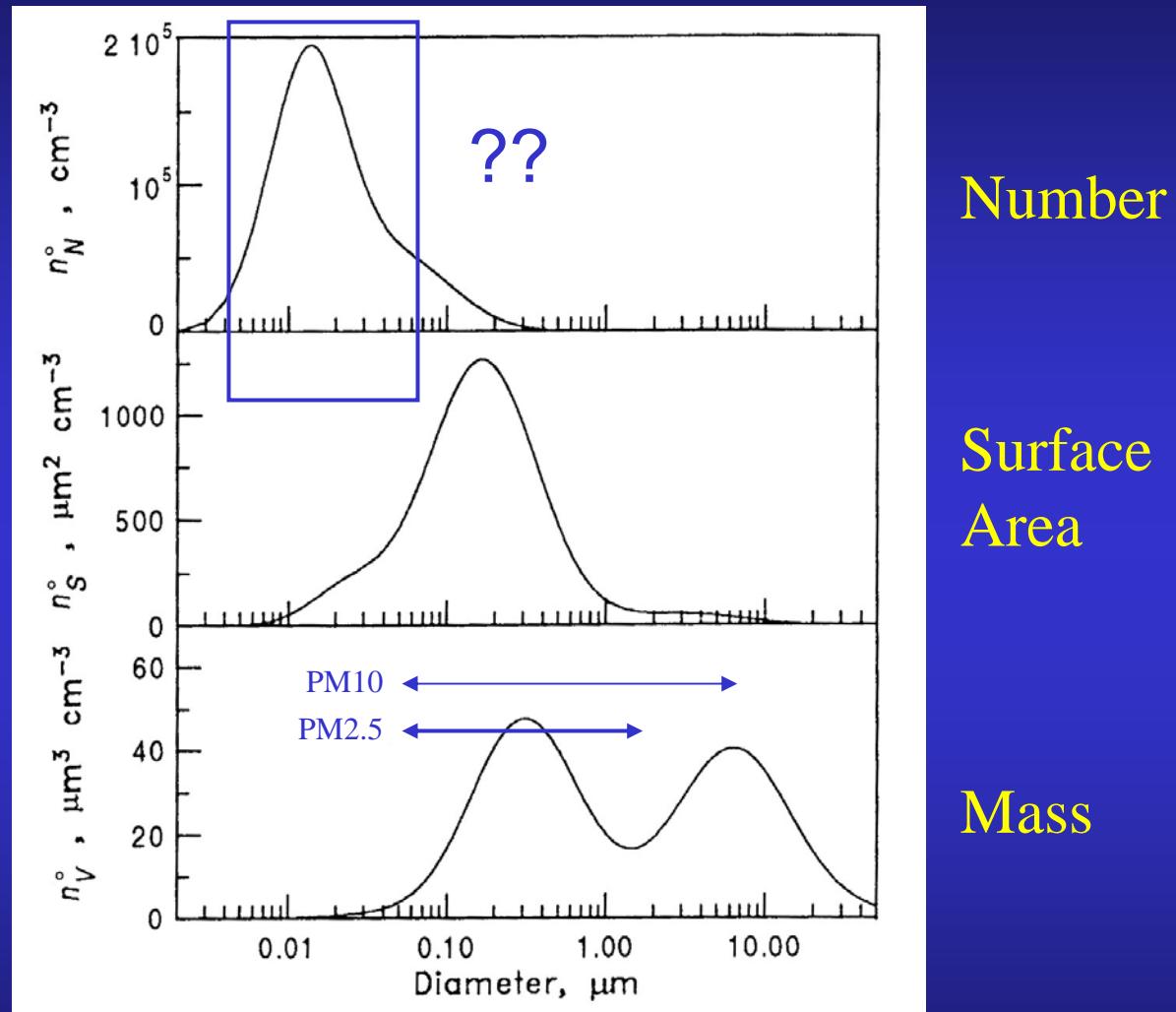


5<sup>th</sup> NIST Polymer MS Workshop  
March 6, 2008

# Outline

- Nanoparticles in the environment and workplace
- Mass spectrometers for determining nanoparticle size and composition
- Ionization mechanisms of single particles
- Applications

# Nanoparticles in the Environment



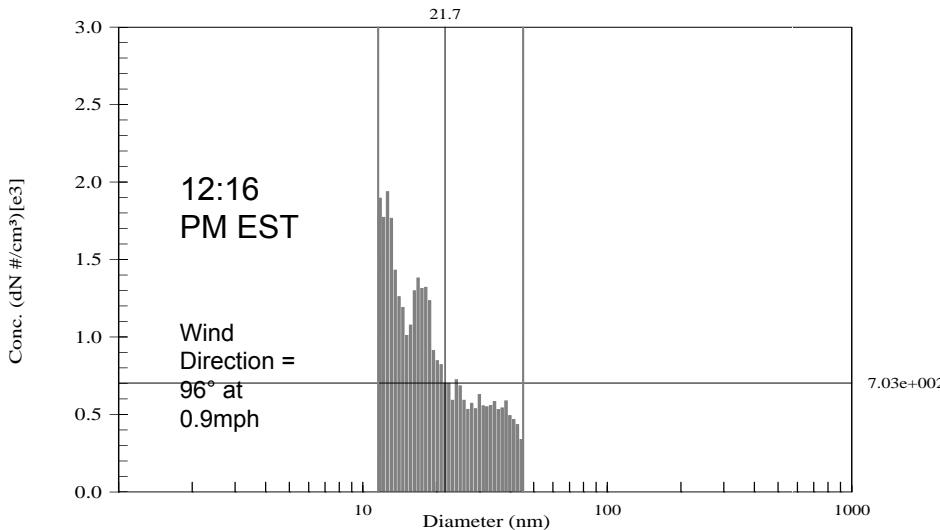
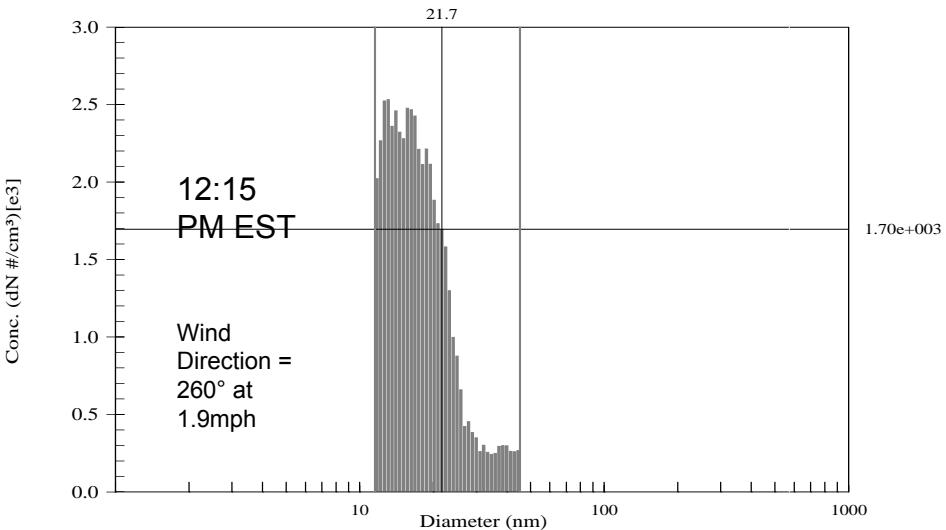
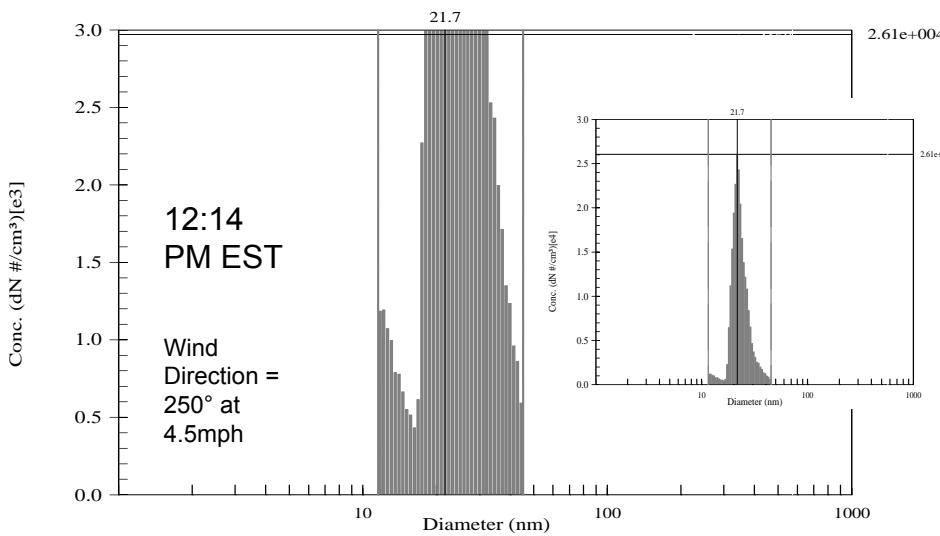
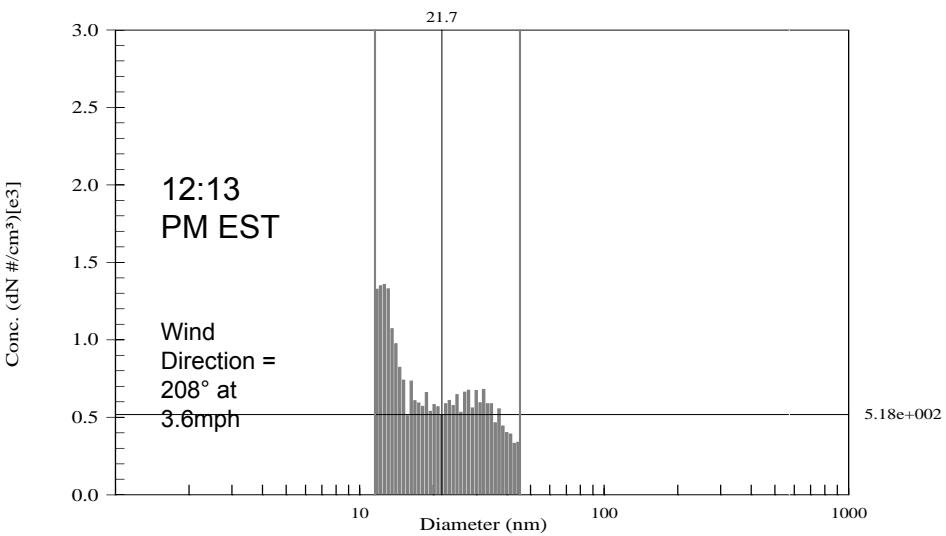
**Nuclei**  
New particle formation

**Accumulation**  
coagulation and growth

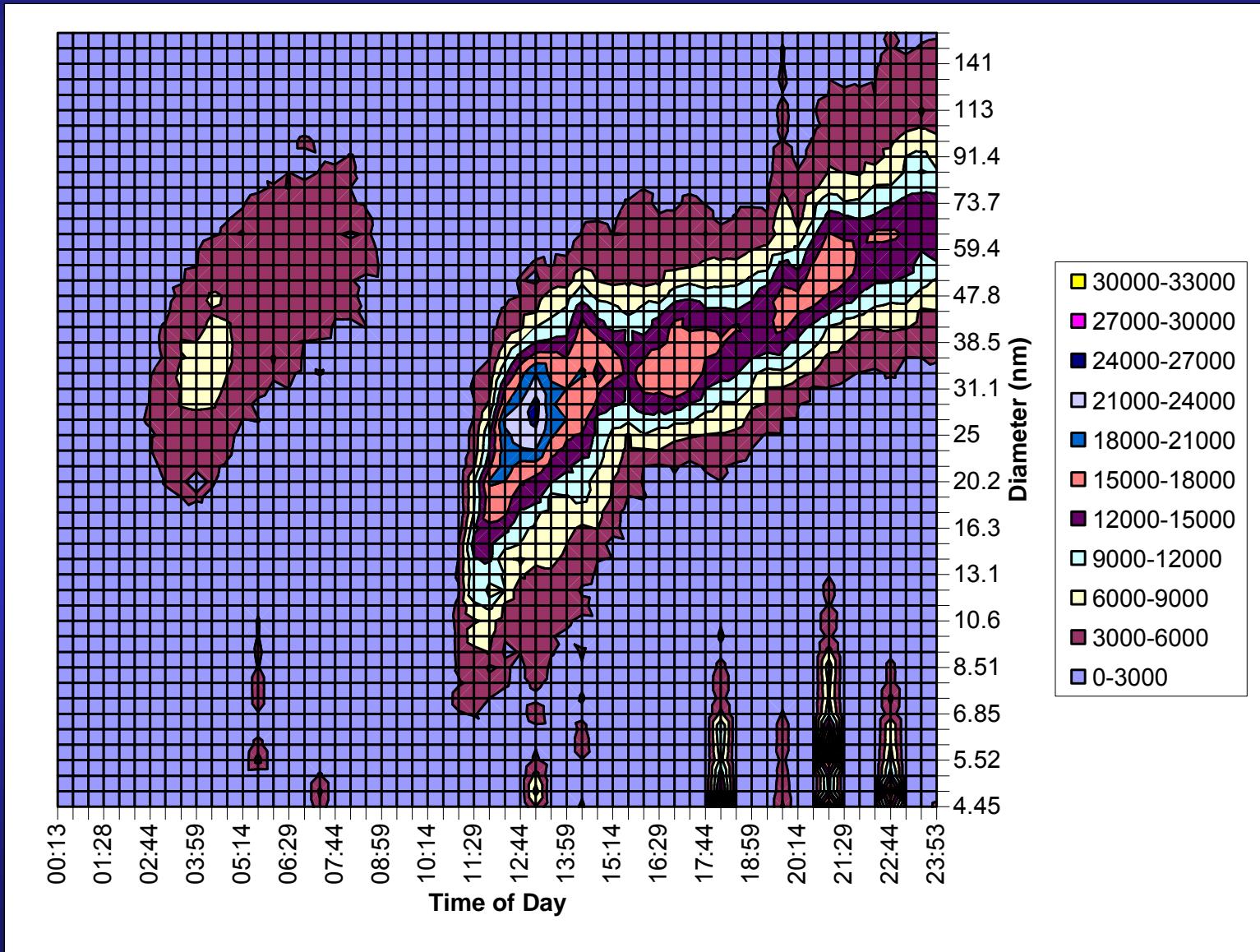
**Coarse**  
abrasion

# Particle Emission from a Diesel Locomotive

## Diesel engine passes monitoring site at 12:14 PM EST (6/08/05)



# Particle Nucleation in Lewes, DE 10/21/06



# Nanoparticles in the Work Place

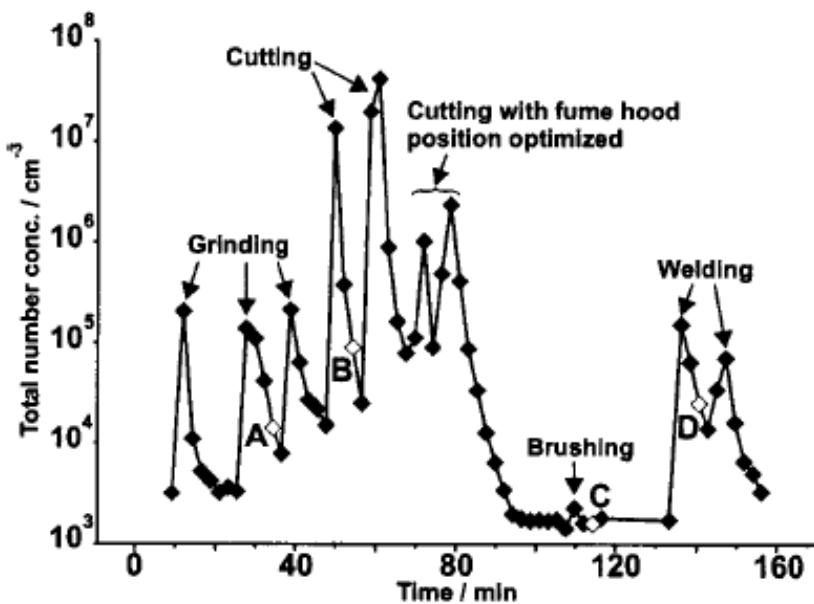


Fig. 7 The total particle number concentration ( $D_p = 0.014\text{--}0.7\ \mu\text{m}$ ) during grinding, cutting and welding on painted car metal sheet. The duration of each work task was about 5 min. The car repair shop was recently built and had a mechanical displacement type ventilation. Each data point indicates samples taken during 135 s each, about 40 cm from the working area. The size distributions for samples A–D are seen in Fig. 8. Air levels of isocyanates in the breathing zone of the worker are seen in Fig. 6.

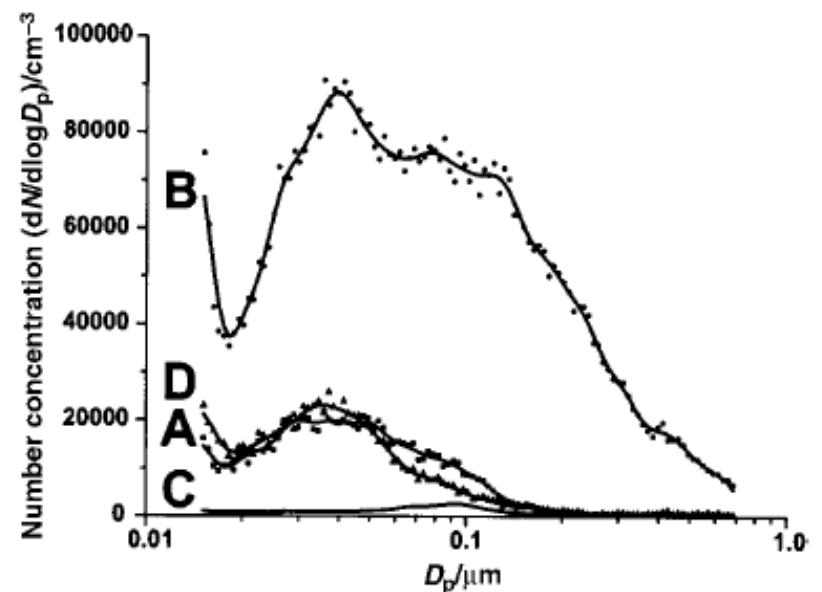
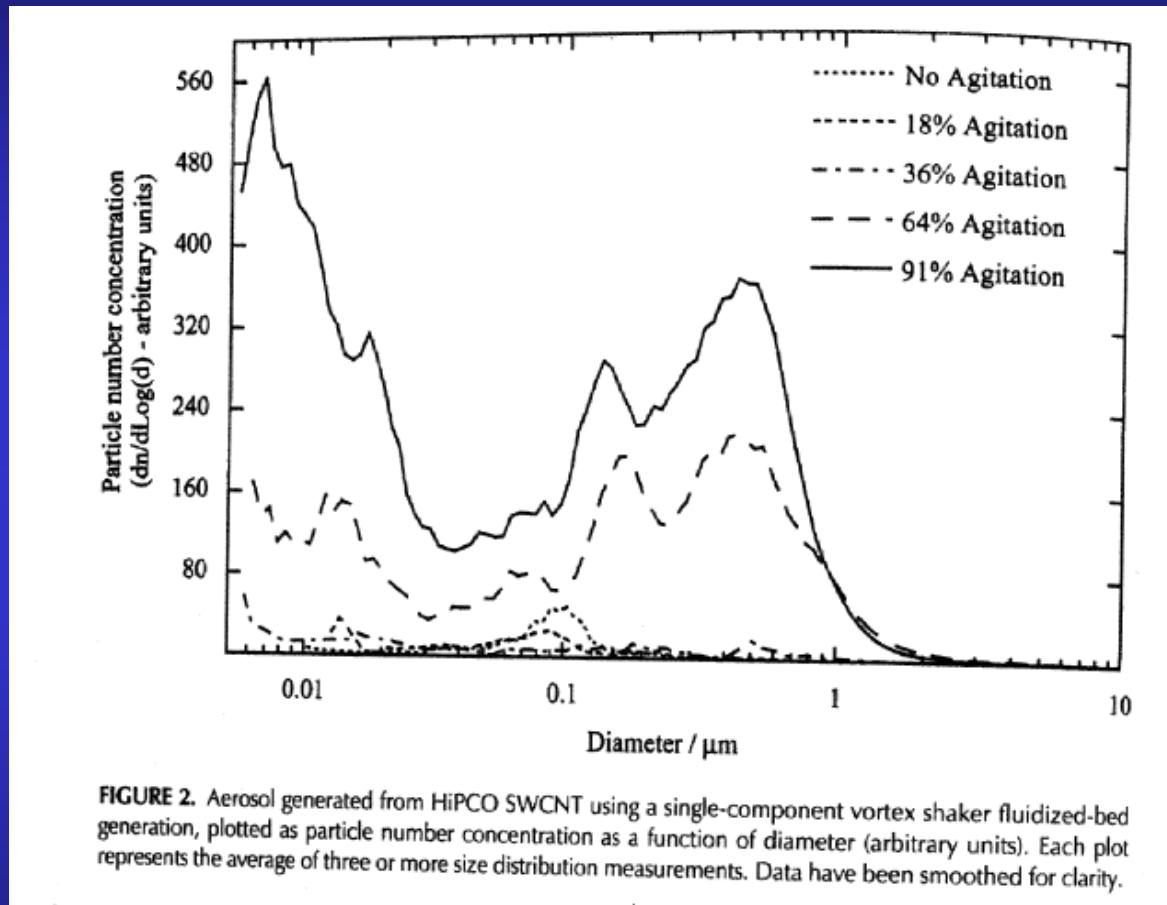


Fig. 8 Particle size distribution during grinding (A), cutting (B) and welding (D) of a painted car metal sheet and the particle size distribution of the background (C). The samples were taken during 135 s about 40 cm from the working area. The geometric mean diameter for the aerosol formed during grinding, cutting and welding was 0.05  $\mu\text{m}$  (geometric standard deviation = 1.9). After the aerosol had aged, a mode with geometric mean diameter of 0.2  $\mu\text{m}$  was formed. This mode was also seen in the background measurement (C).

# Airborne Particles from SWCNT Agitation

(Maynard et al., J. Toxicol. Environ. Health, Part A (2004) 67, 87)



1. What are the contributions of SWCNT, catalyst (Fe-Ni nanoparticles), and “laboratory” ultrafine particles from other sources?
2. How does laboratory exposure compare to environmental exposure?

# COMMENTARY

## Safe handling of nanotechnology

The pursuit of responsible nanotechnologies can be tackled through a series of grand challenges, argue Andrew D. Maynard and his co-authors.

**W**hen the physicist and Nobel laureate Richard Feynman challenged the science community to think small in his 1959 lecture 'There's Plenty of Room at the Bottom', he planted the seeds of a new era in science and technology. Nanotechnology, which is about controlling matter at near-atomic scales to produce unique or enhanced materials, products and devices, is now maturing rapidly with more than 300 claimed nanotechnology products already on the market<sup>1</sup>. Yet concerns have been raised that the very properties of nanostructured materials that make them so attractive could potentially lead to unforeseen health or environmental hazards<sup>2</sup>.

The spectre of possible harm — whether real or imagined — is threatening to slow the development of nanotechnology unless sound, independent and authoritative information is developed on what the risks are, and how to avoid them<sup>3</sup>. In what may be unprecedented pre-emptive action in the face of a new technology, governments, industries and research organizations around the world are beginning to address how the benefits of emerging nanotechnologies can be realized while minimizing potential risks<sup>4</sup>. Yet despite a clear commitment to support risk-focused research, opportunities to establish collaborative, integrated and targeted research programmes are being missed<sup>5</sup>. In September, Sherwood Boehlert, chair of the US House Science Committee, commented in a hearing that "we're on the right path to dealing with the problem, but we're sauntering down it when a sense of urgency is required". And in October, Britain's Royal Society raised concerns that the UK government had not made enough progress on reducing the uncertainties surrounding the health and environmental impacts of nanomaterials<sup>6</sup>.

### The risks

As research leaders in our respective fields, we recognize that systematic risk research is needed if emerging nano-industries are to thrive. We cannot set the international research agenda on our own, but we can inspire the scientific community — including government, industry, academia and other stakeholders — to move in the right direction. So we propose five



D. MAYNARD

Potential health risks from exposure to engineered nanomaterials must be understood and minimized.

grand challenges to stimulate research that is imaginative, innovative and above all relevant to the safety of nanotechnology.

Fears over the possible dangers of some nanotechnologies may be exaggerated, but they are not necessarily unfounded. Recent studies examining the toxicity of engineered nanomaterials in cell cultures and animals have shown that size, surface area, surface chemistry, solubility and possibly shape all play a role in determining the potential for engineered nanomaterials to cause harm<sup>7</sup>. This is not surprising: we have known for many years that inhaled dusts cause disease, and that their harmfulness depends on

both what they are made of and their physical nature. For instance, small particles of inhaled quartz lead to lung damage and the potential development of progressive lung disease, yet the same particles with a thin coating of clay are less harmful<sup>8</sup>. Asbestos presents a far more dramatic example: thin, long fibres of the material can lead to lung disease if inhaled, but grind the fibres down to shorter particles with the same chemical make-up and the harmfulness is significantly reduced<sup>9</sup>.

It is generally accepted that, in principle, some nanomaterials may have the potential to

cause harm to people and the environment. But the way science is done is often ill-equipped to address novel risks associated with emerging technologies. Research into understanding and preventing risk often has a low priority in the competitive worlds of intellectual property, research funding and technology development. And yet there is much at stake in how potential nano-specific risks are understood and managed. Without strategic and targeted risk research, people producing and using nanomaterials could develop unanticipated illness arising from their exposure; public confidence in nanotechnologies could be reduced through real or perceived dangers; and fears of litigation may make nanotechnologies less attractive to investors and the insurance industry.

The science community needs to act now if strategic research is to support sustainable nanotechnologies, in which risks are minimized and benefits maximized. Our five grand challenges are chosen to stimulate such research, as well as bring focus to a range of complex multidisciplinary issues. The challenges span the next 15 years, and their successful achievement will depend on coordination, collaboration, resources and ingenuity. They are not comprehensive — there is essential research that is not covered here — but they do form a framework on which others can build.

Maynard et al., Nature (2006) **444**(16), 267-269

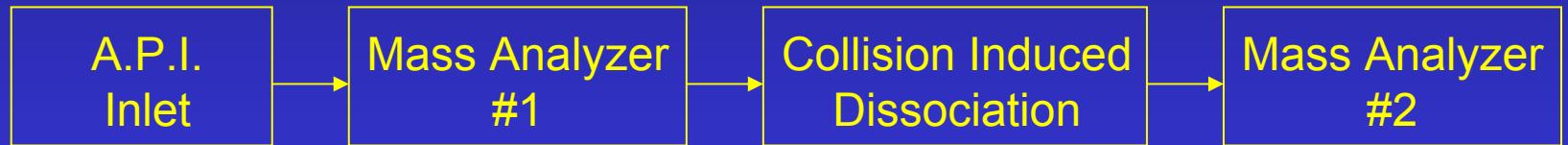
Grand Challenge #1:  
Instruments to monitor nanoparticle emissions and assess exposure

# Characteristics of Nanoparticles

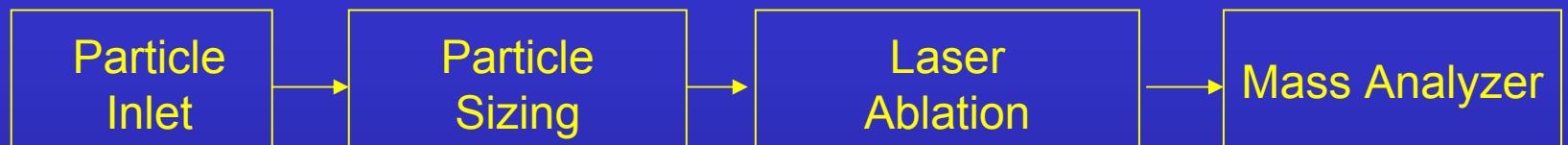
Particle Diameter (nm)	Mass (g)	Mass (Da)	Atmospheric Source	Biological Equivalent
5	$6.5 \times 10^{-20}$	40,000	Homogeneous nucleation; Emission from high temperature source	Proteins
10	$5.2 \times 10^{-19}$	310,000		
50	$6.5 \times 10^{-17}$	40,000,000	Emission from high temperature source;  Growth of smaller particles via secondary components or coagulation	Virons
100	$5.2 \times 10^{-16}$	310,000,000		

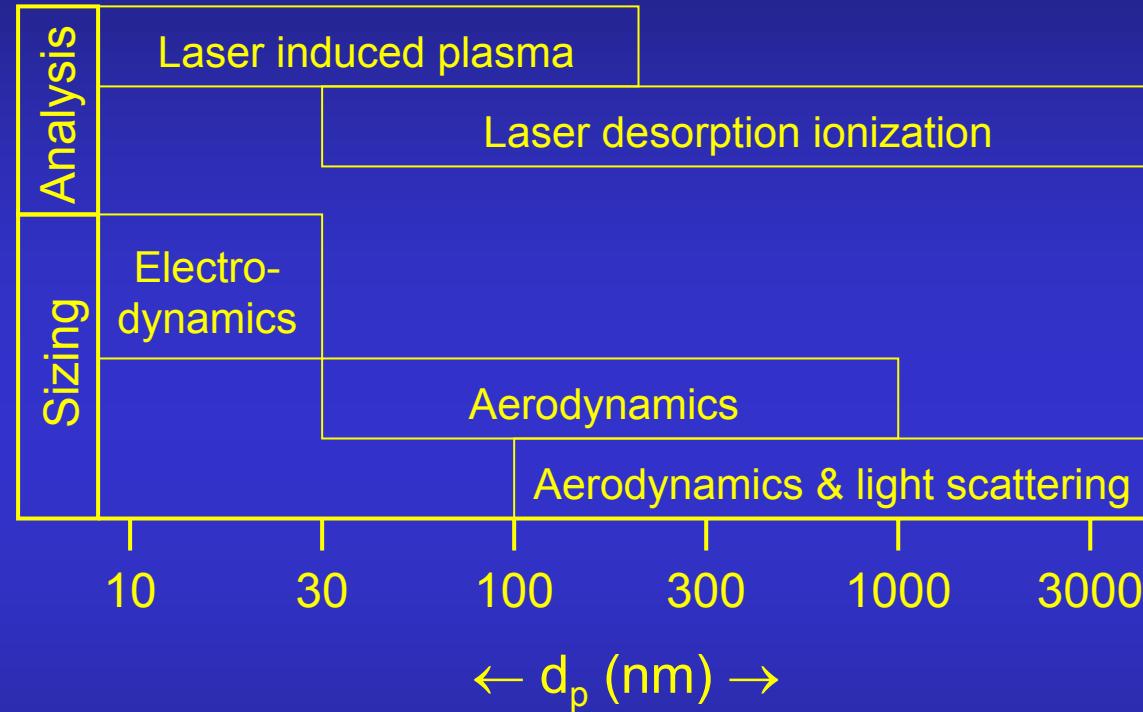
# Aerosol vs. Conventional Mass Spectrometry

## Tandem Mass Spectrometry



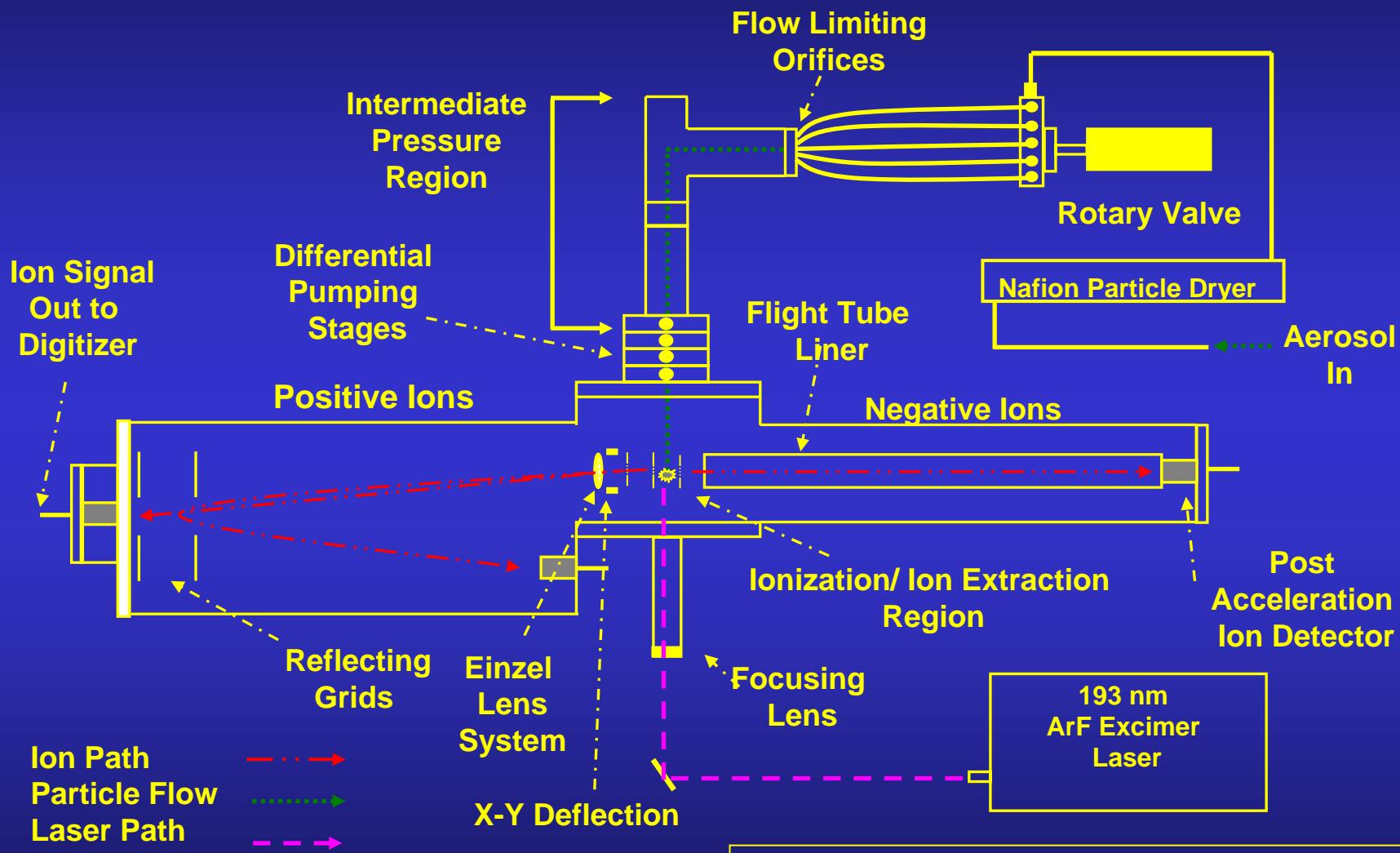
## Single Particle Mass Spectrometry





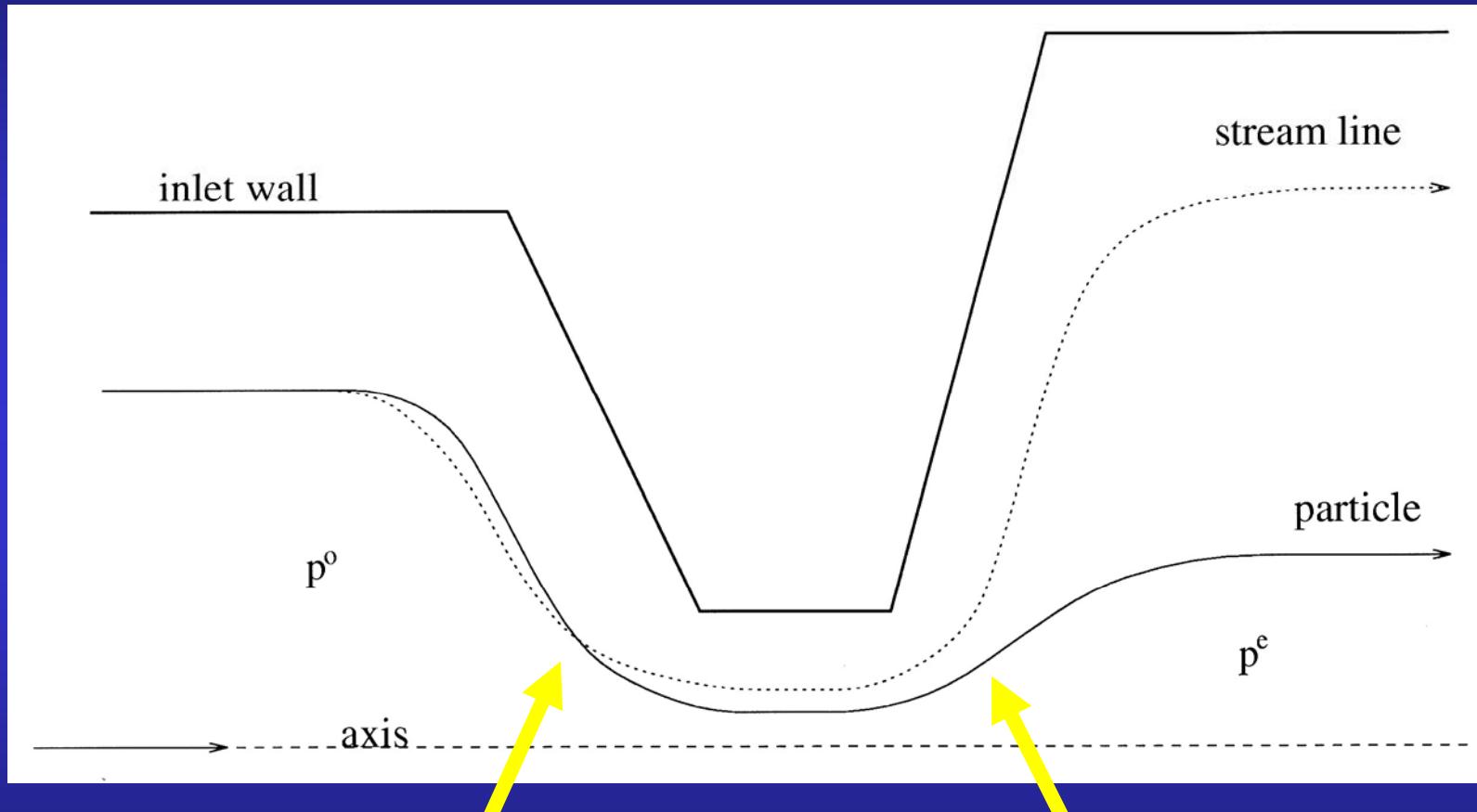
# Real-Time Single Particle Mass Spectrometer (RSMS)

( $d_{va} = 50\text{-}700 \text{ nm diameter}$ )



**Sizing – aerodynamic focusing**  
**Analysis – uv laser desorption ionization**

# Inlet Aerodynamics



low pass filter  
(small particles)

High pass filter  
(large particles)

# Stokes Number (St)

$$St \propto \frac{\rho_p d_p^2}{D_o} \left( 1 + \frac{K}{d_p P} \right)$$

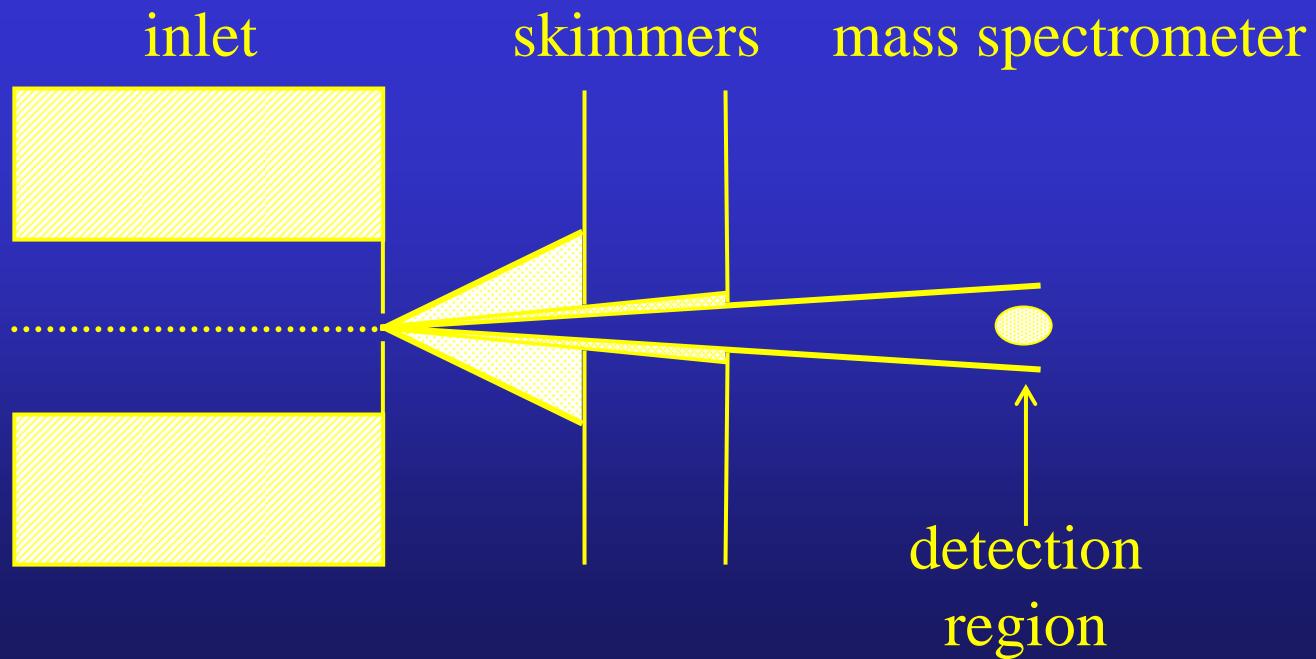
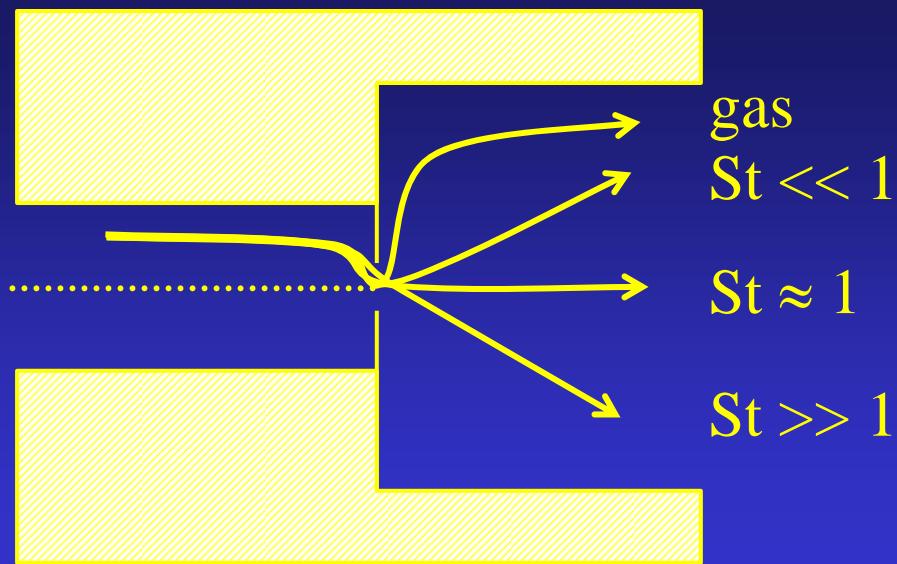
$\rho_p$  = particle density

$d_p$  = particle diameter

$D_o$  = orifice diameter

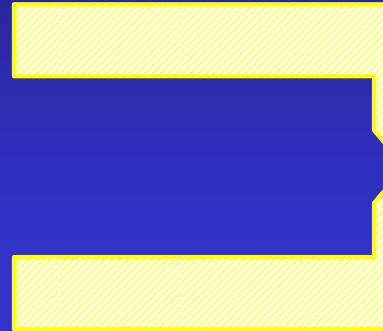
$P$  = gas pressure at orifice

$K$  = constant



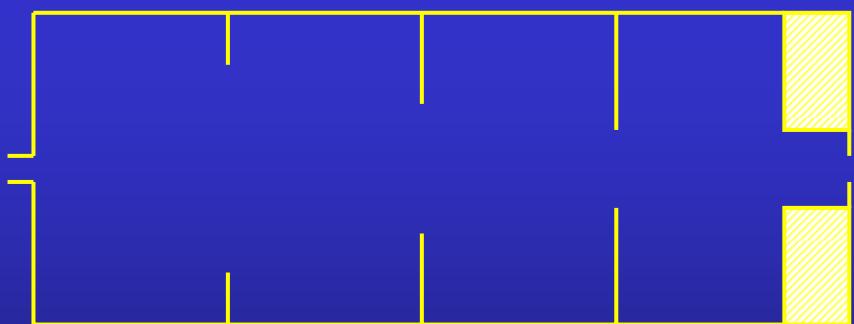
## Sharp Orifice (Single Lens Element) Size Selective Focusing

Mallina et al, Aerosol Sci. Technol. (2000) 33, 87-104



## Aerodynamic Lens (Multiple Lens Elements) Size Independent Focusing

Liu et al, Aerosol Sci. Technol. (1995) 22, 314-322



# Stokes Number (St)

$$St \propto \frac{\rho_p d_p^2}{D_o} \left( 1 + \frac{K}{d_p P} \right)$$

$\rho_p$  = particle density

$d_p$  = particle diameter

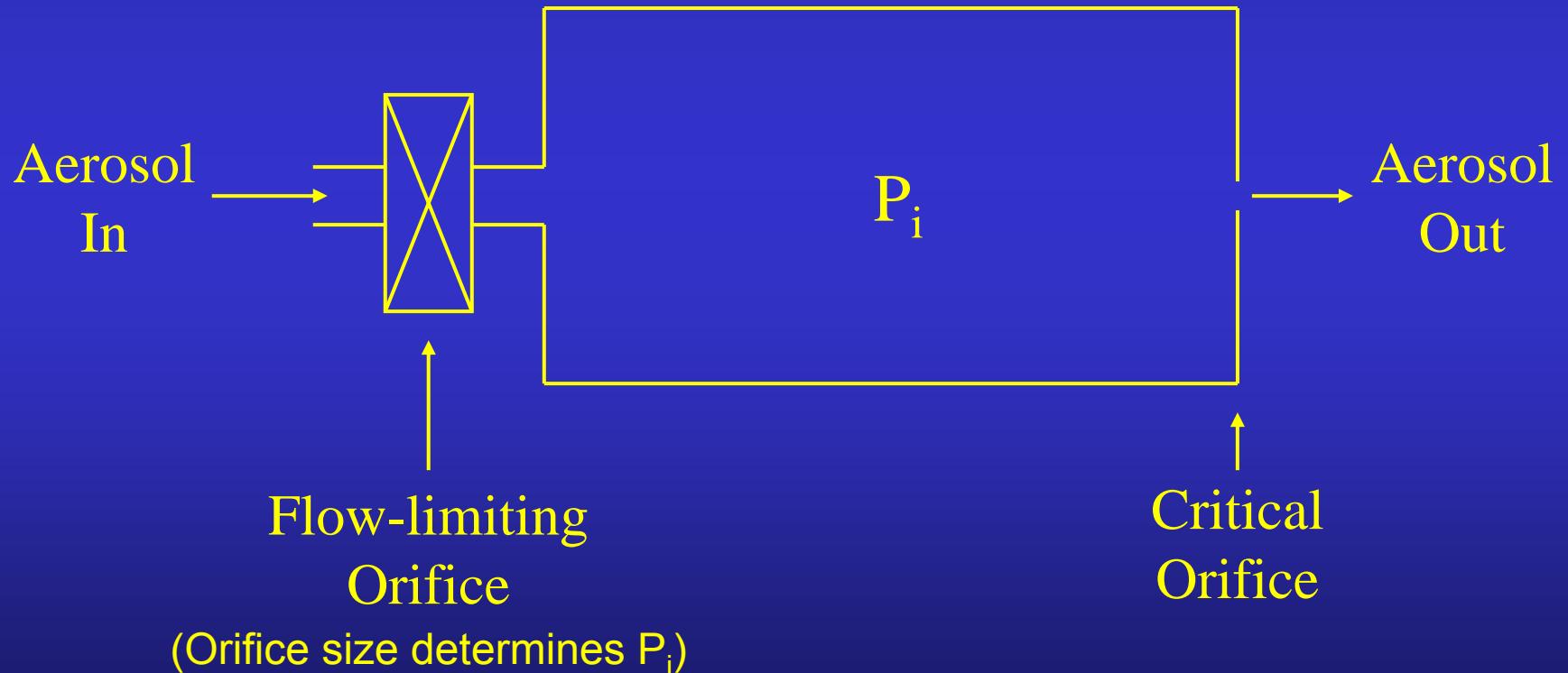
$D_o$  = orifice diameter

$P$  = gas pressure at orifice

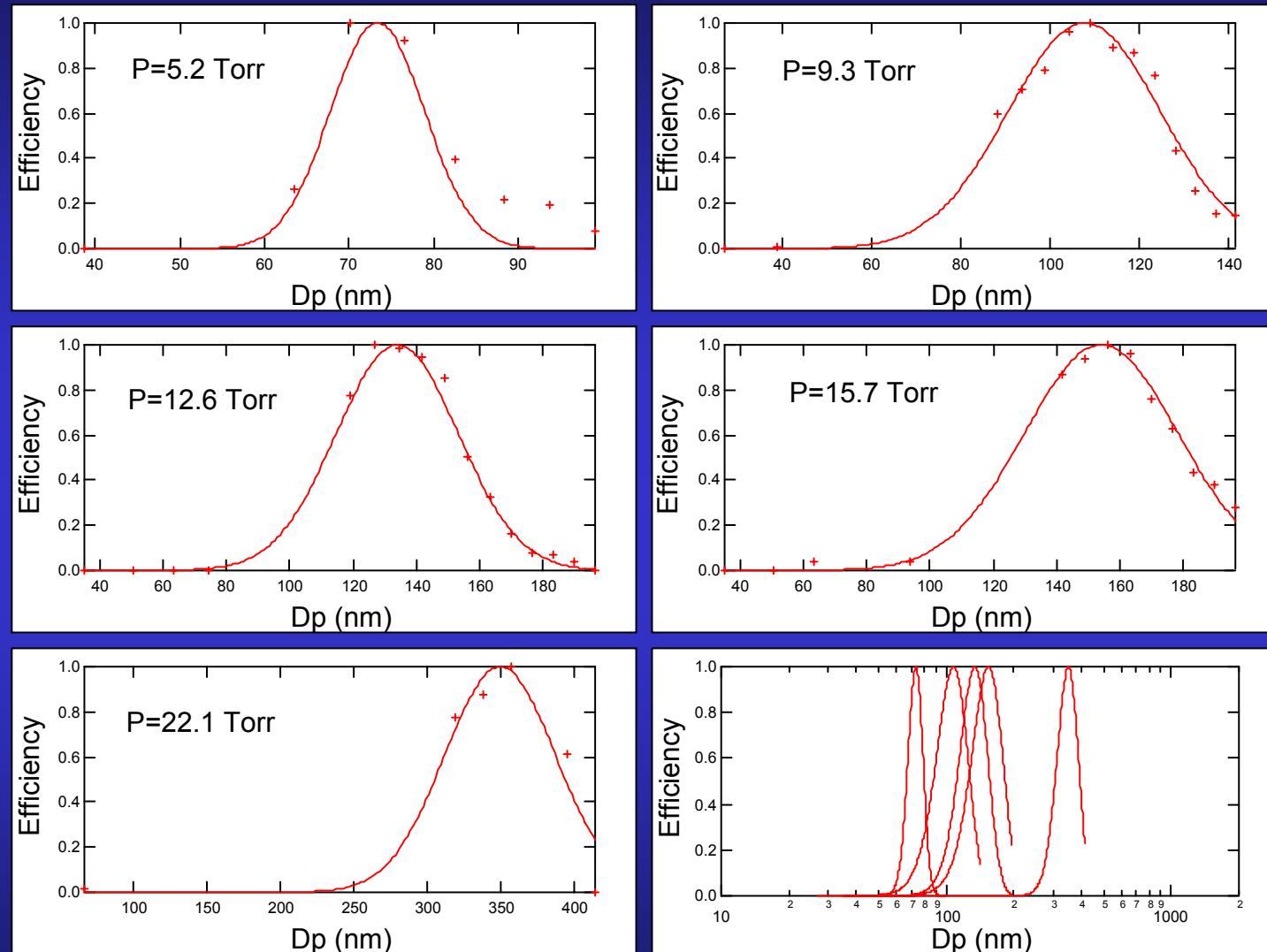
$K$  = constant

## Particle Selection by Dynamic Focusing:

$$d_p \propto P_i$$



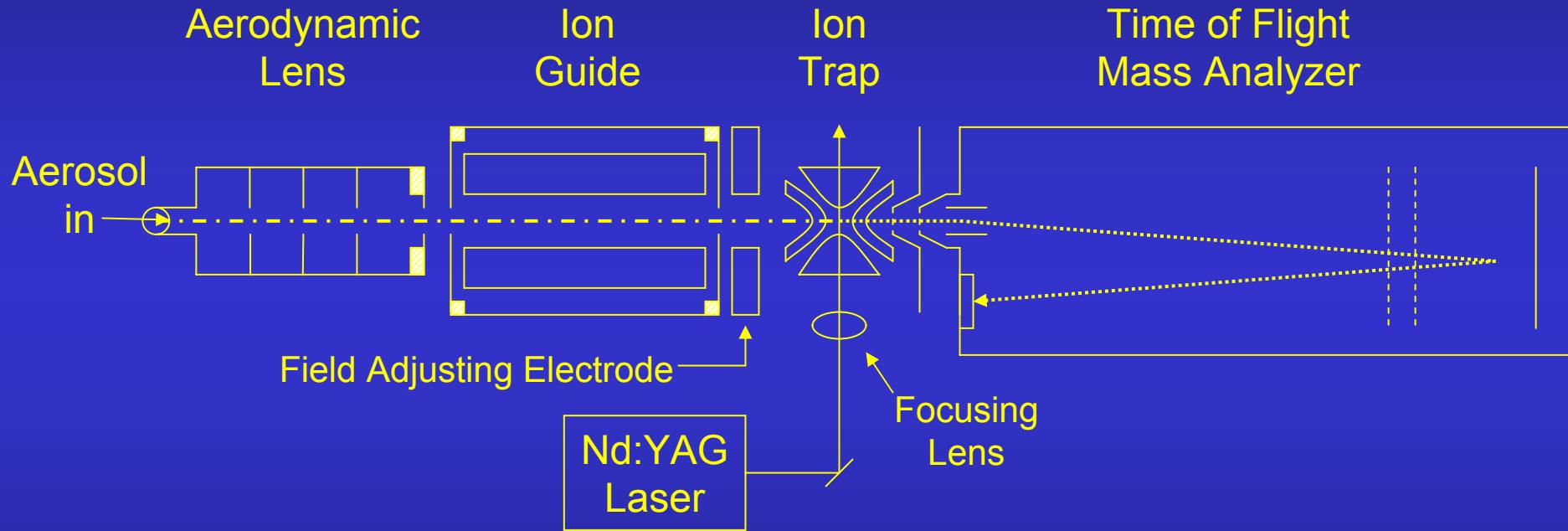
# Particle Sizing by Aerodynamic Focusing



Data are for oleic acid droplets selected with a DMA;  $\sigma_g = 1.1$   
Adapted from: Phares et al, AS&T (2002) 36, 583-592

# Nanoaerosol Mass Spectrometer (NAMS)

( $d_{mn} = 10\text{-}30 \text{ nm}$ )



Particle Inlet = aerodynamic lens + quadrupole ion guide

Particle Sizing/Confinement = ion trap ( $d_{mn} = 7\text{-}30 \text{ nm}$ )

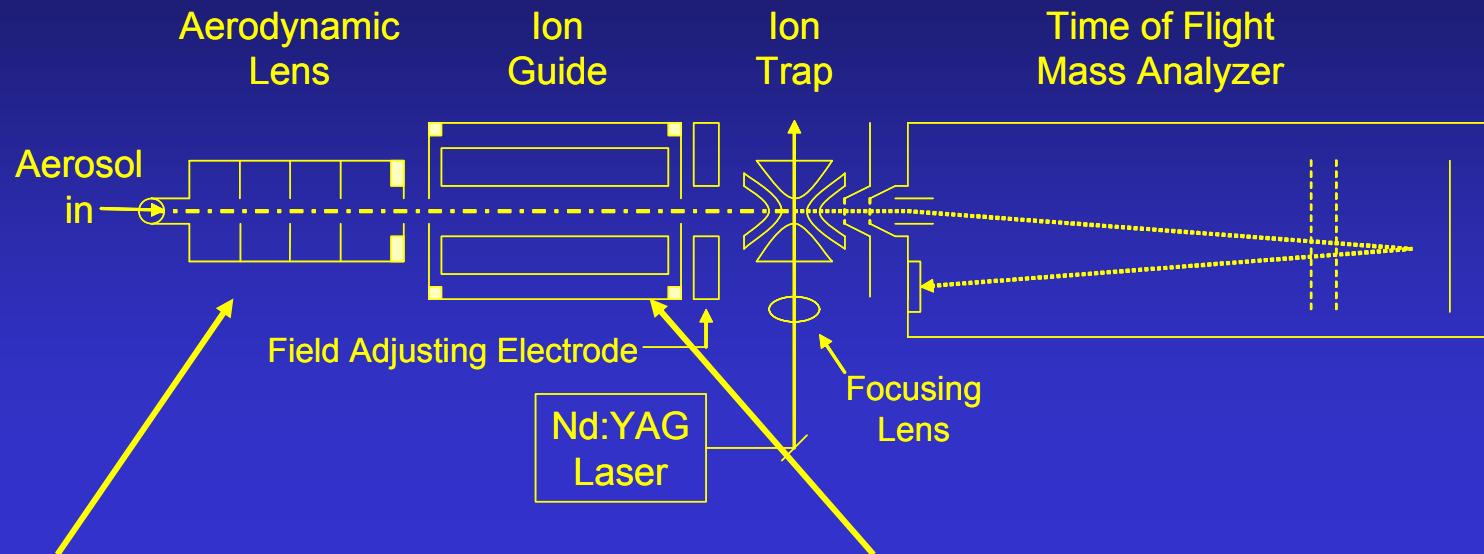
Chemical Analysis = laser plasma formation ( $70 \text{ J/cm}^2$ ) + TOFMS

Wang et al., Anal. Chem. (2006) 78, 1750-1754

Wang and Johnston, Int. J. Mass Spectrom. (2006) 258, 50-57

Johnston et al., Appl. Spectrosc. (2006) 60, 264A-272A

# Particle Inlet



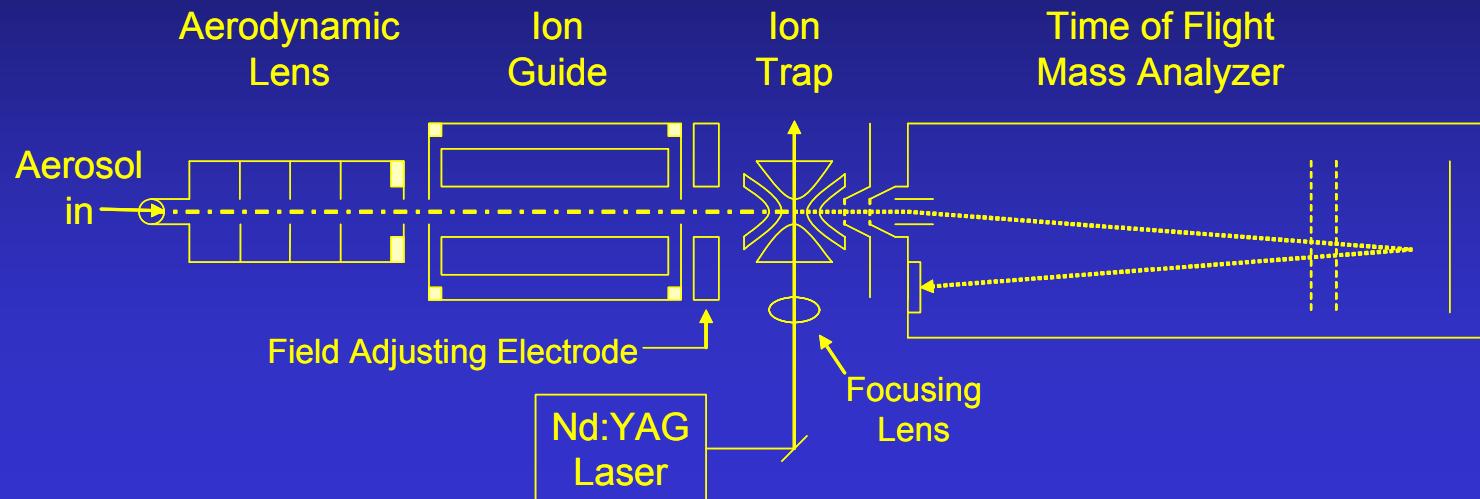
## Aerodynamic lens

- Nanoparticle lens “A” in Wang, McMurry, et al., AS&T (2005) 39, 624
- Efficient focusing above ca. 20 nm

## Quadrupole ion guide

- 140 kHz, 800 V<sub>p-p</sub>,  $2.5 \times 10^{-2}$  mbar Ar
- Efficient focusing below ca. 20 nm
  - On/off hit rate = 100 (12 nm)
  - 35 (18 nm)
  - 6 (22 nm)

# Quadrupole Ion Trap (1)



- “Digital” Ion Trap = square wave potential applied to ring electrode; floated at -2 V  
+504V, -507 V (frequency = 4-150 kHz; selects particle size)
- Field adjusting electrode (-40 to -200 V) facilitates trapping by optimizing the electric field gradient at the entrance end cap

## Quadrupole Ion Trap (2)

- Particle trapping is based on m/z
- Mass Normalized Diameter ( $d_{mn}$ ) assumes a single charge and unit density

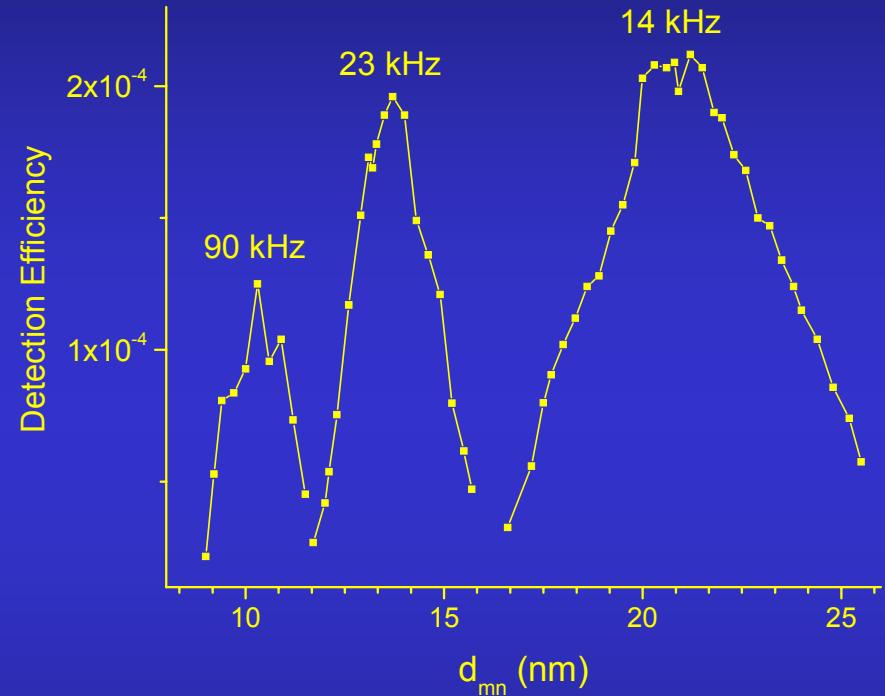
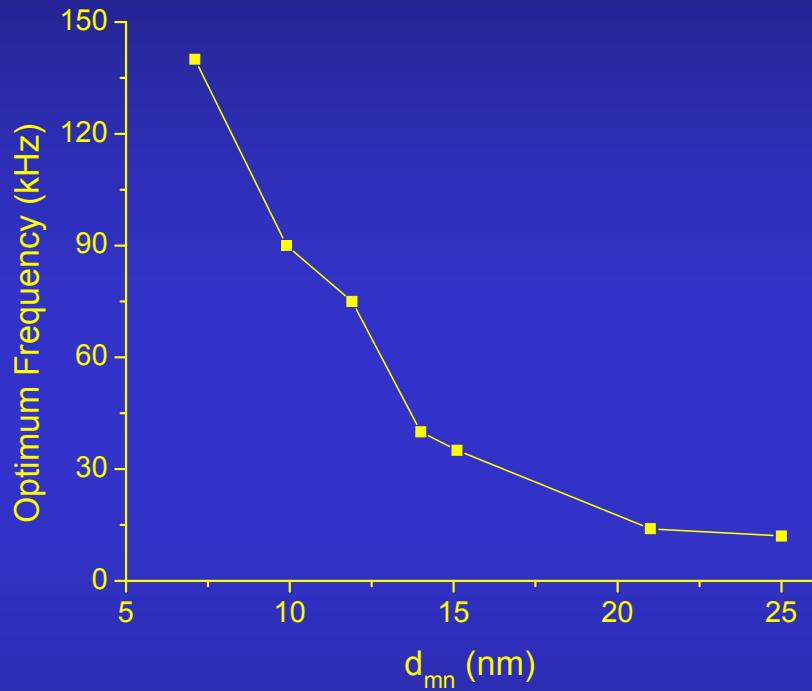
$$d_{mn} = \left( \frac{\rho_p}{\rho_0} \right)^{1/3} d_m$$

- Stable motion determined by  $q_z$ :

$$(q_z)_{\max}: \quad q_z = \frac{4eV}{mr_o^2(2\pi f)^2} = \frac{(6 \times 10^{-3})eV}{\pi^3 d_{mn}^3 r_o^2 f^2} \leq 0.712$$

$$(q_z)_{\min}: \quad D_z \approx 0.206(q_z V)$$

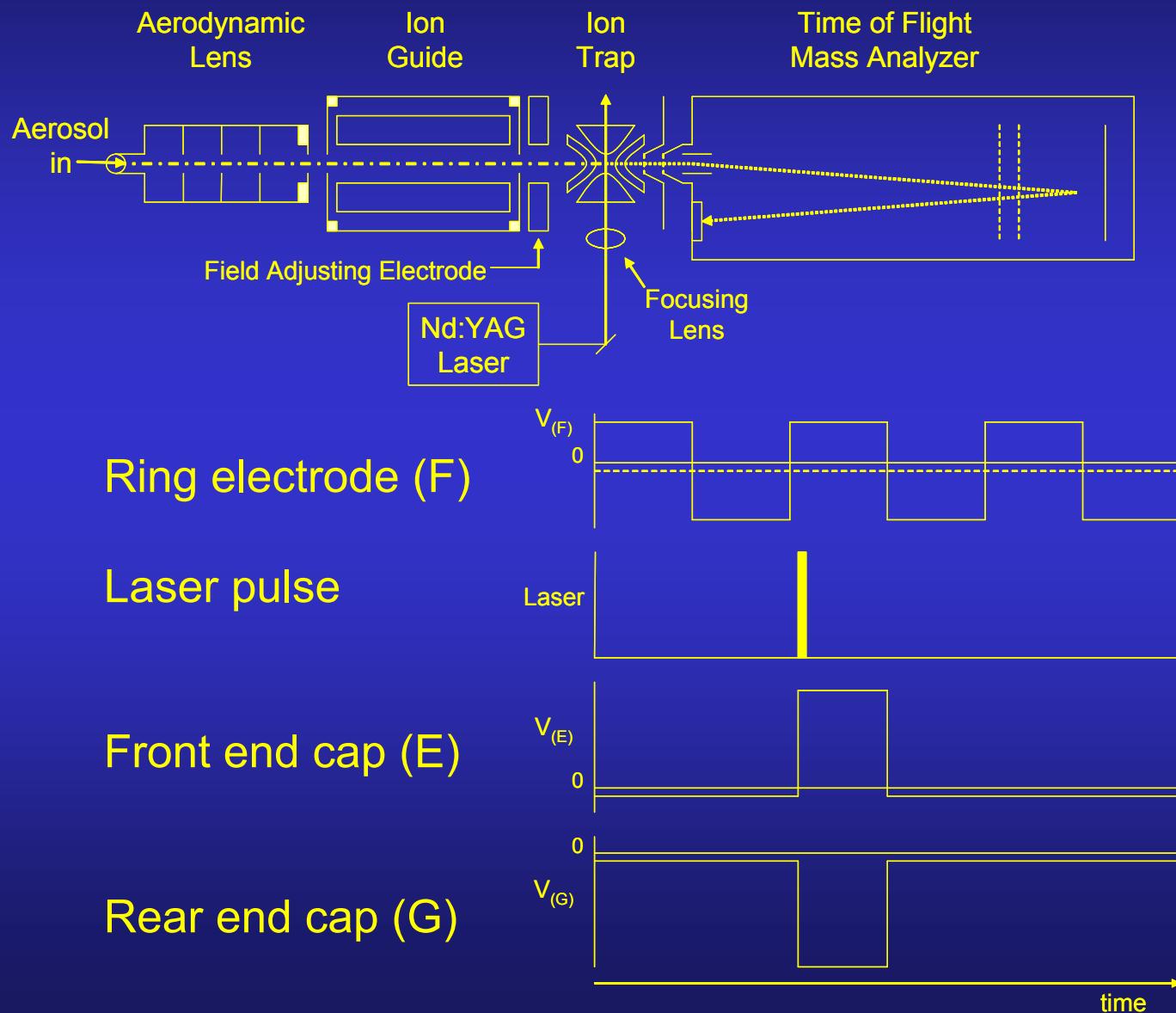
# Quadrupole Ion Trap (3)



$$f \propto (d_{mn})^{-2/3}$$

$$\sigma_g \approx 1.1$$

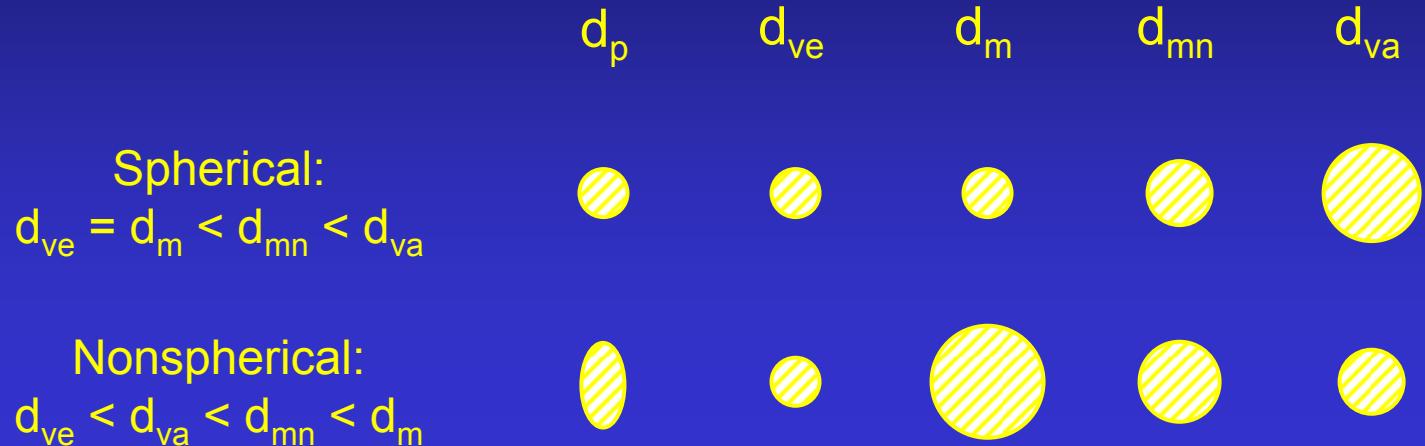
# Extraction of Laser-Produced Ions



# Particle Size Definitions

Symbol	Name	Definition	Relationship
$d_p$	Physical Diameter	Actual size/dimension of the particle	
$d_{ve}$	Volume equivalent diameter	Diameter of a spherical particle having the same mass as the actual particle and the same density as bulk material	
$d_{va}$	Vacuum aerodynamic diameter	Diameter of a spherical particle with a density of 1 g/cm <sup>3</sup> that has the same settling velocity as the actual particle; evaluated in the free-molecular regime	$d_{va} = \frac{\rho_p}{\rho_0 \chi_v} d_{ve}$
$d_m$	Electrical mobility diameter	Diameter of a spherical particle having the same electrical mobility (migration rate in an electric field) as the actual particle	$d_m = \frac{C_c(d_m)}{C_c(d_{ve})} \chi_v d_{ve}$
$d_{mn}$	Mass normalized diameter	Diameter of a spherical particle having the same mass as the actual particle but with a density of 1 g/cm <sup>3</sup>	$d_{mn} = \left( \frac{\rho_p}{\rho_0} \right)^{1/3} d_{ve}$

# The reported particle size depends on the definition!



Size relationships are depicted for  $\rho_p = 1.7 \text{ g/cm}^3$

Particle density and/or shape can be determined from simultaneous measurement of two or more “diameters”

# Ionization Strategies:

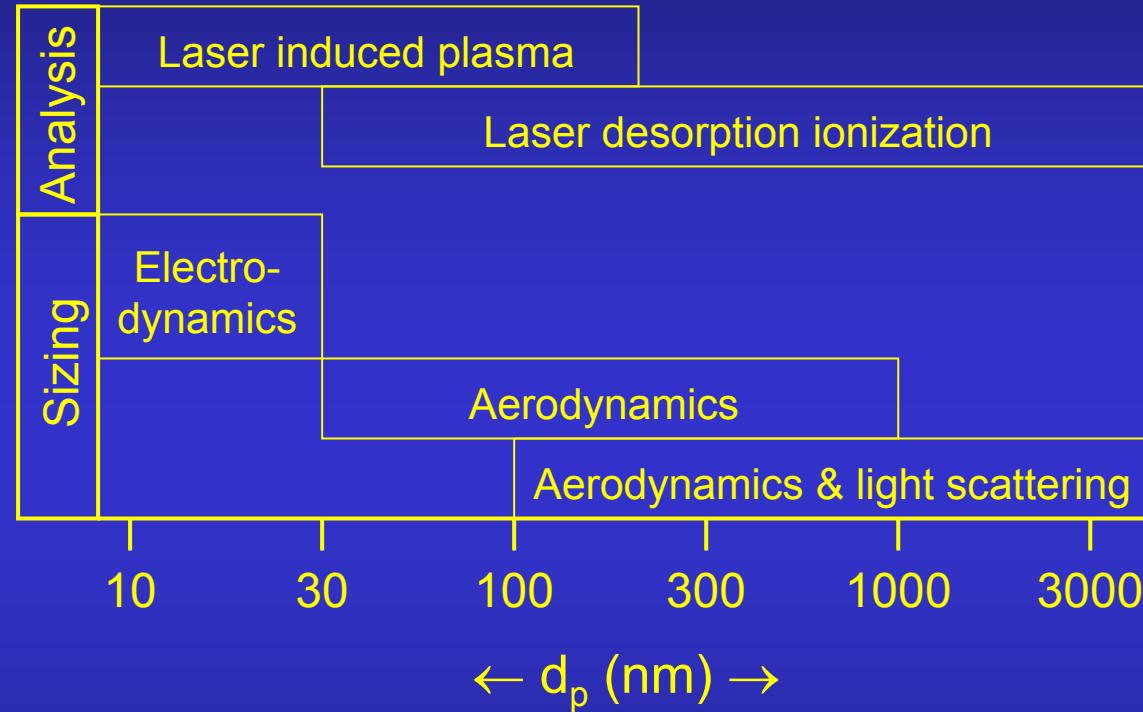
## Single Particle Mass Spectrometry (w/o surfaces)

Most useful for  $d_p < 1 \mu\text{m}$

- Laser Desorption Ionization (LDI)
- Laser Induced Plasma (LIP)

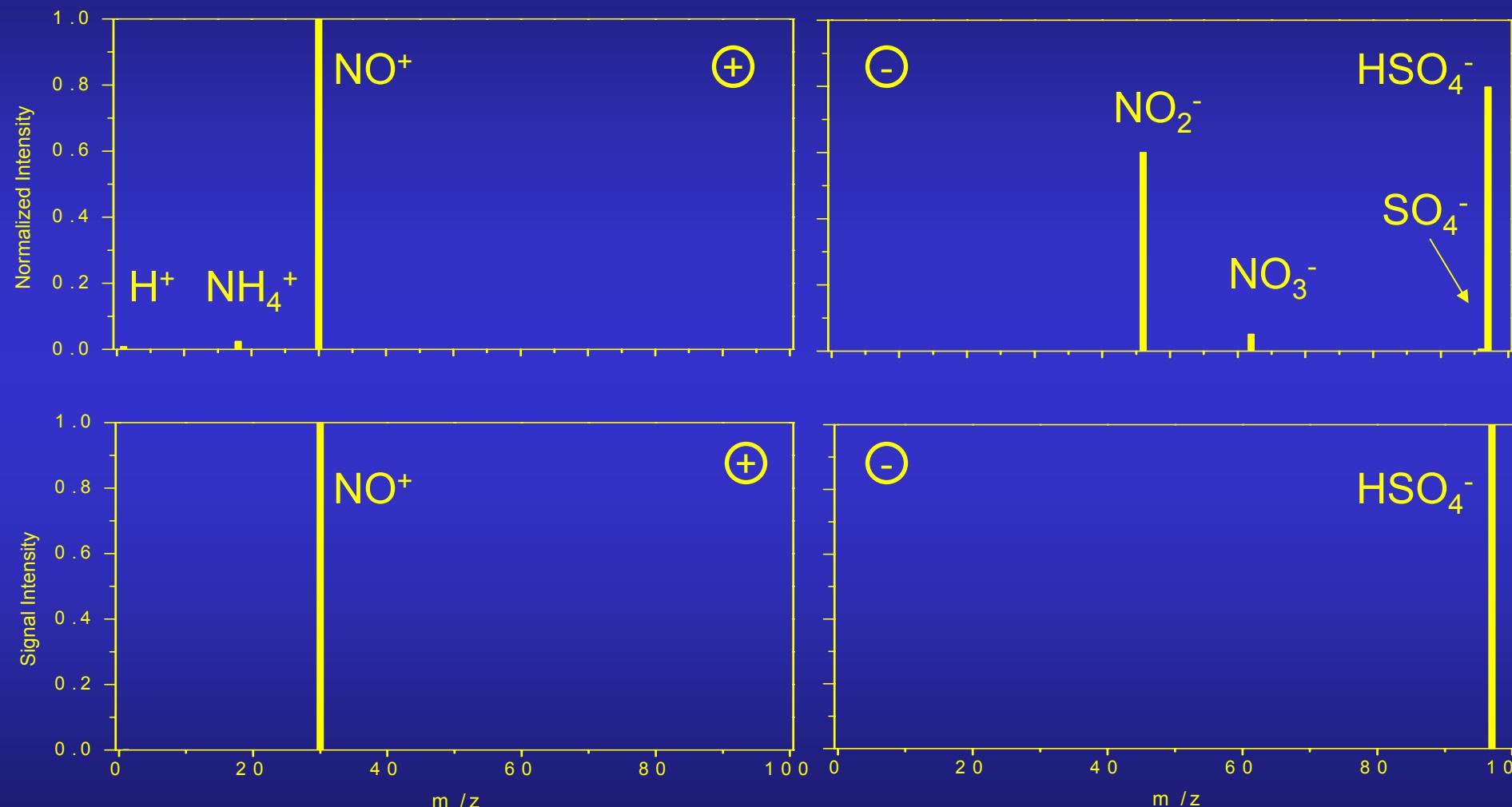
Reasonable possibilities for  $d_p > 1 \mu\text{m}$

- Matrix-Assisted Laser Desorption/Ionization (MALDI)
- Two-Step Laser (or Thermal) Desorption – Laser Ionization (LD-PI)



# Particle-to-Particle Variations in LDI Mass Spectra

(1:1 molar ratio  $\text{NH}_4\text{NO}_3:(\text{NH}_4)_2\text{SO}_4$ )



# Ion Formation Mechanism in Single Particle LDI

1. Particle Disintegration



2. Laser Assisted Ionization



3. Electron Capture



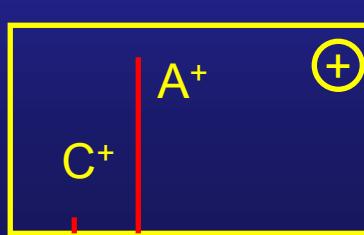
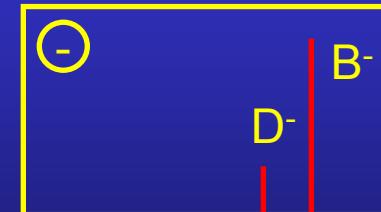
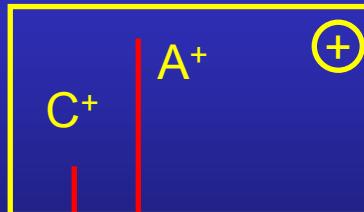
4. Charge Transfer



Dense plume:  
processes 3, 4 dominant

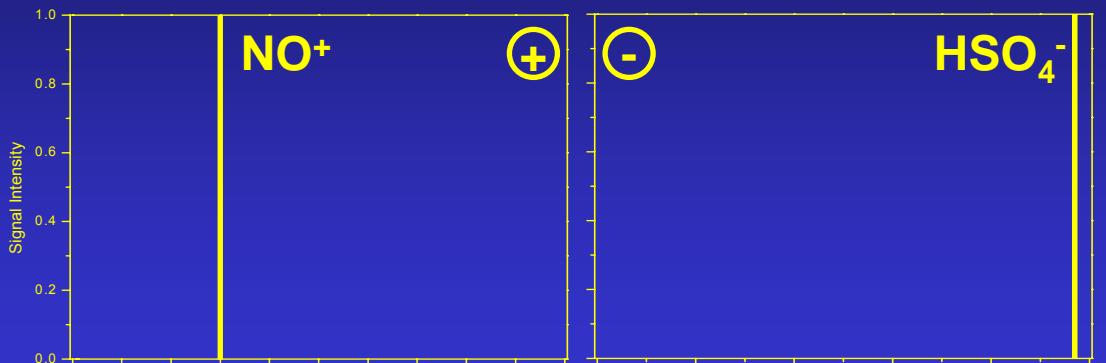


Dispersed plume:  
processes 3, 4 less dominant

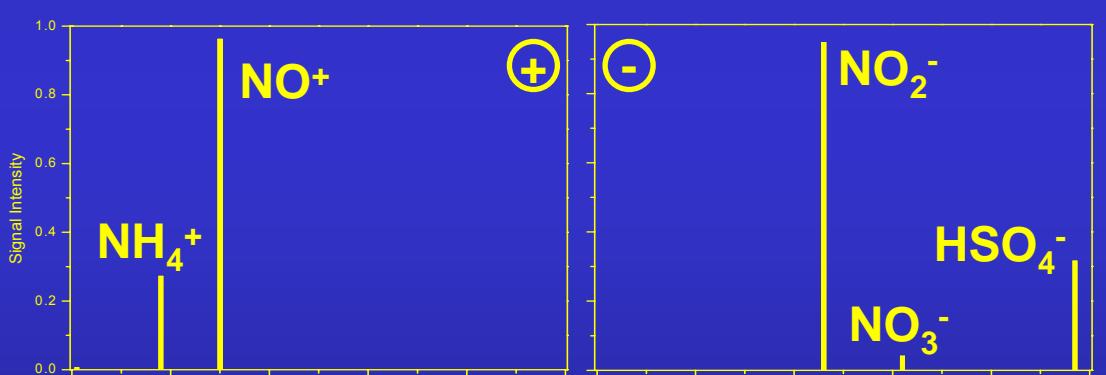


or

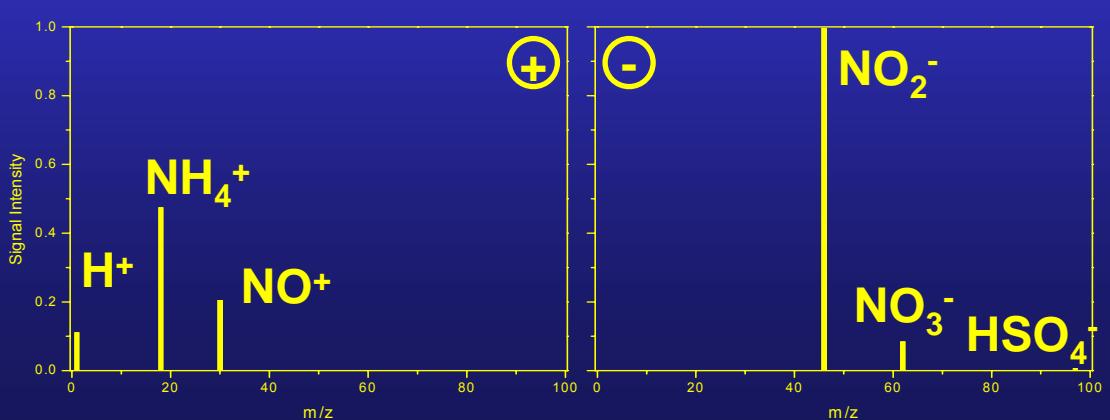
# Varying Plume Conditions



1:1 Mole Ratio of  
 $\text{NH}_4\text{NO}_3:(\text{NH}_4)_2\text{SO}_4$



Species	Ionization Potential (eV)
NO	9.26
NH <sub>3</sub>	10.07
H	13.6

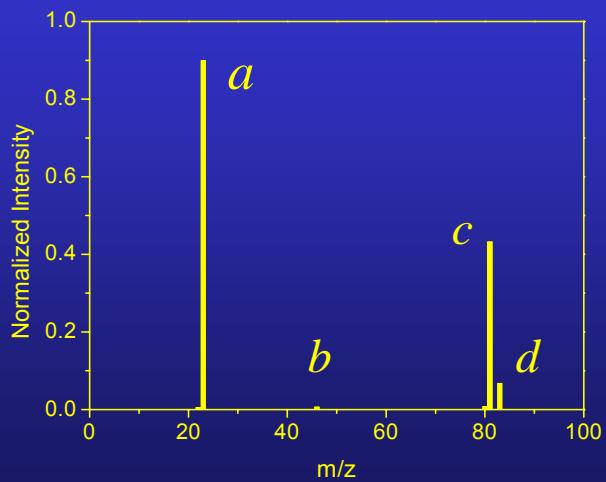


Species	Electron Affinity (eV)
HSO <sub>4</sub>	4.75
NO <sub>3</sub>	3.97
NO <sub>2</sub>	2.27

# Covariance Calculation

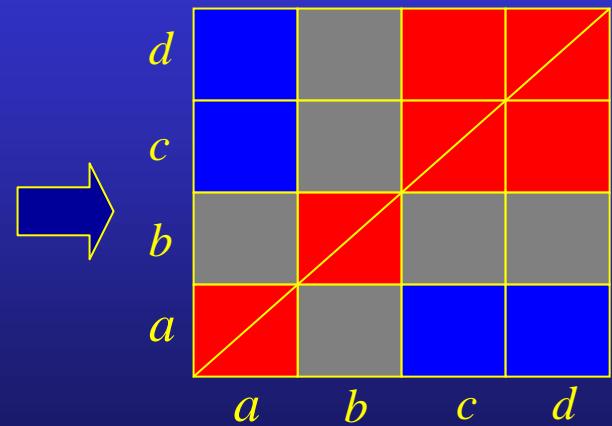
$$C(x, y) = \frac{1}{n} \sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})$$

$$\gamma(x, y) = \frac{C(x, y)}{[C(x, x)C(y, y)]^{1/2}}$$

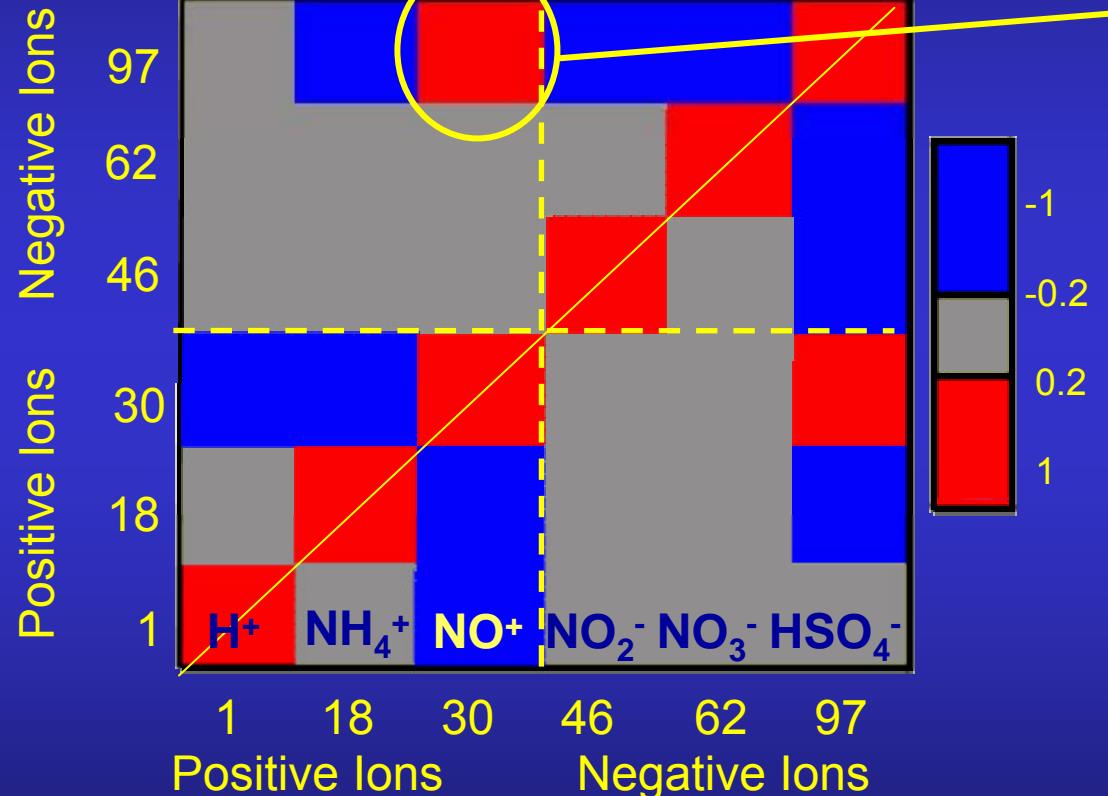


A correlation matrix for the peaks:

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
<i>d</i>	-0.5	0	0.4	1
<i>c</i>	-0.2	0.1	1	0.4
<i>b</i>	0	1	0.1	0
<i>a</i>	1	0	-0.2	-0.5



# 1:1 mole ratio $\text{NH}_4\text{NO}_3:(\text{NH}_4)_2\text{SO}_4$



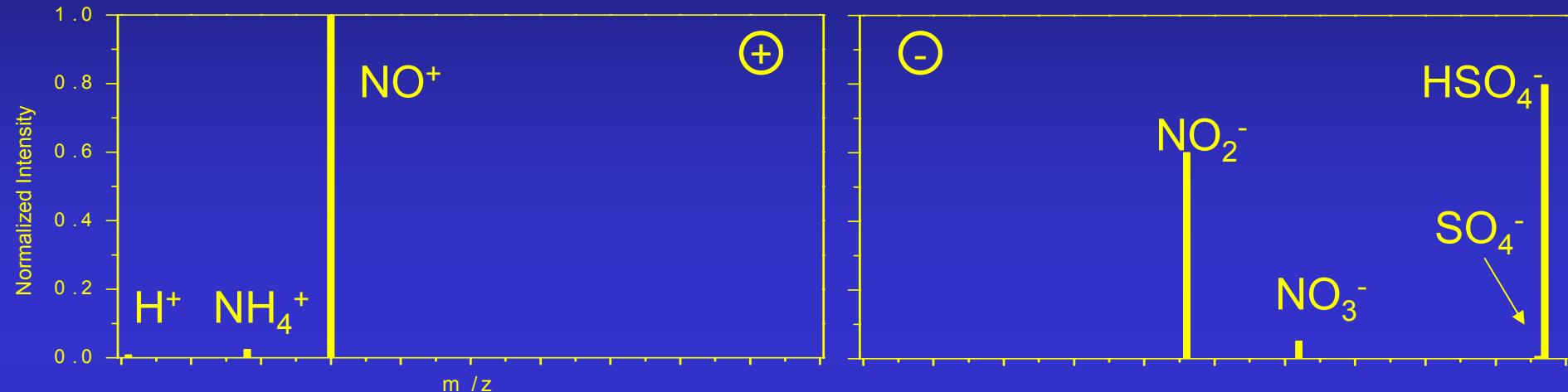
Positive Correlations:  
 $\text{NO}^+$  and  $\text{HSO}_4^-$

Negative Correlations:  
 $\text{NO}^+$  and  $\text{H}^+$ ,  $\text{NH}_4^+$   
 $\text{NH}_4^+$  and  $\text{HSO}_4^-$   
 $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{HSO}_4^-$

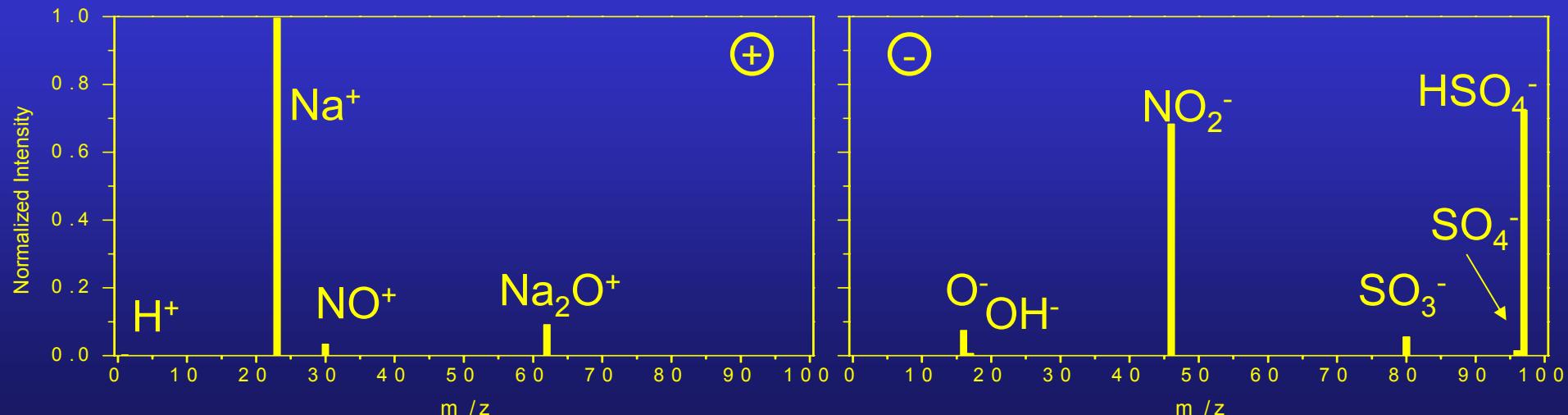
Charge Transfer Reactions:  
 $\text{NO} + \text{H}^+ \rightarrow \text{NO}^+ + \text{H}$   
 $\text{HSO}_4^- + \text{NO}_2^- \rightarrow \text{HSO}_4^- + \text{NO}_2$

# Averaged Mass Spectra

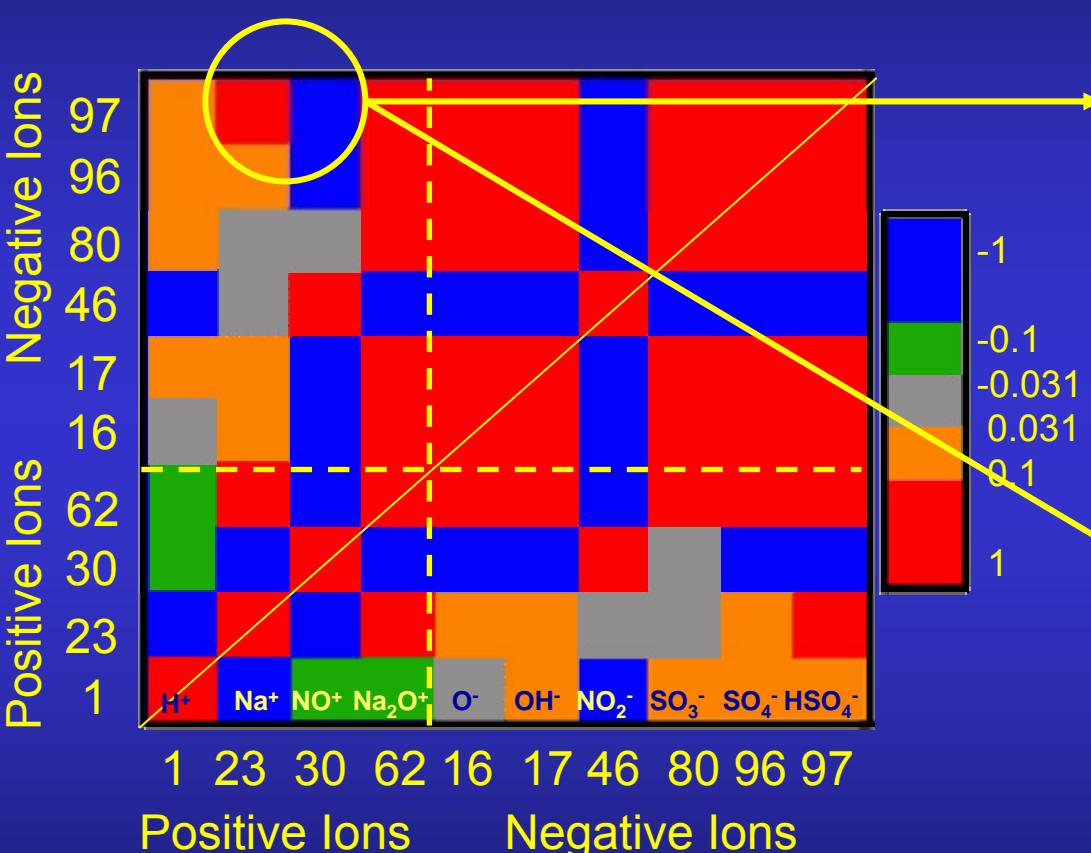
1:1 mole ratio  $\text{NH}_4\text{NO}_3:(\text{NH}_4)_2\text{SO}_4$



1:1 mole ratio  $\text{NH}_4\text{NO}_3:\text{Na}_2\text{SO}_4$



# 1:1 mole ratio $\text{NH}_4\text{NO}_3:\text{Na}_2\text{SO}_4$



## Positive Correlations:

$\text{Na}^+$ ,  $\text{Na}_2\text{O}^+$  and  $\text{HSO}_4^-$   
 $\text{SO}_3/\text{SO}_4/\text{HSO}_4^-$  and  $\text{O}/\text{OH}^-$   
 $\text{NO}^+$  and  $\text{NO}_2^-$

## Negative Correlations:

$\text{Na}^+$  and  $\text{H}^+$ ,  $\text{NO}^+$   
 $\text{NO}^+$  and  $\text{SO}_4/\text{HSO}_4^-$   
 $\text{NO}_2^-$  and  $\text{SO}_3/\text{SO}_4/\text{HSO}_4^-$

## Charge Transfer Reactions:

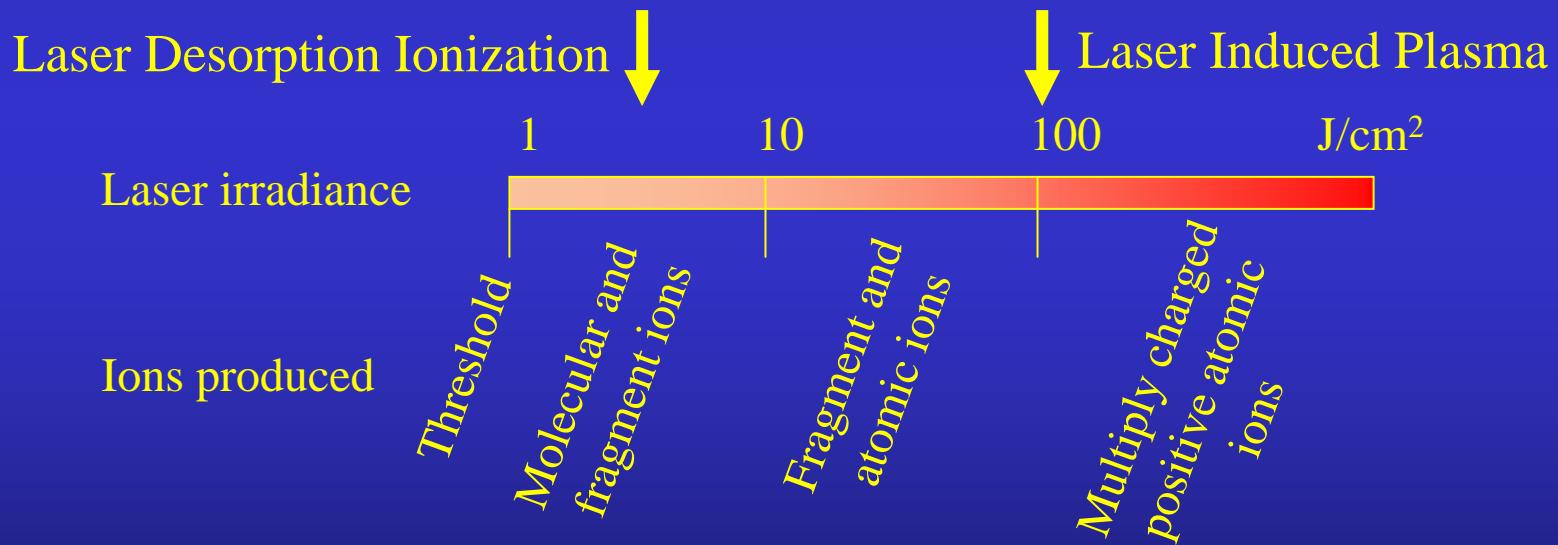


Ionization potential of Na: 5.14 eV  
 Ionization potential of NO: 9.46 eV

# Laser Induced Plasma Formation

## (“Complete Ionization Limit”)

High energy laser radiation produces an extremely hot plasma  
(Reents et al, 2001; Mahadevan et al 2002)



# “Complete Ionization Limit”

## Characteristics of the Laser Induced Plasma

- Particle is quantitatively converted to atoms which are quantitatively converted to positively charged atomic ions
- Absolute signal is related to particle mass (can be used for particle sizing)
- Relative signals of different ions give the elemental composition

Examples:

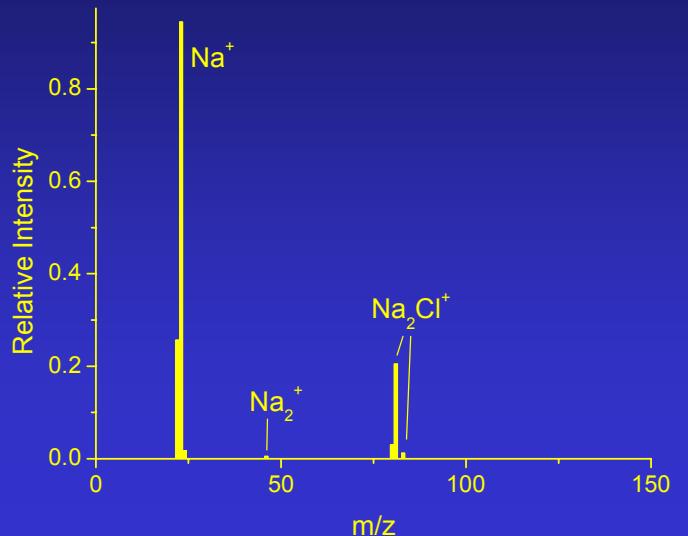
Reents and Gee, Aerosol Sci. Technol. (2000) 33, 122-134

Mahadevan et al, J. Phys. Chem. A (2002) 106, 11083-11092

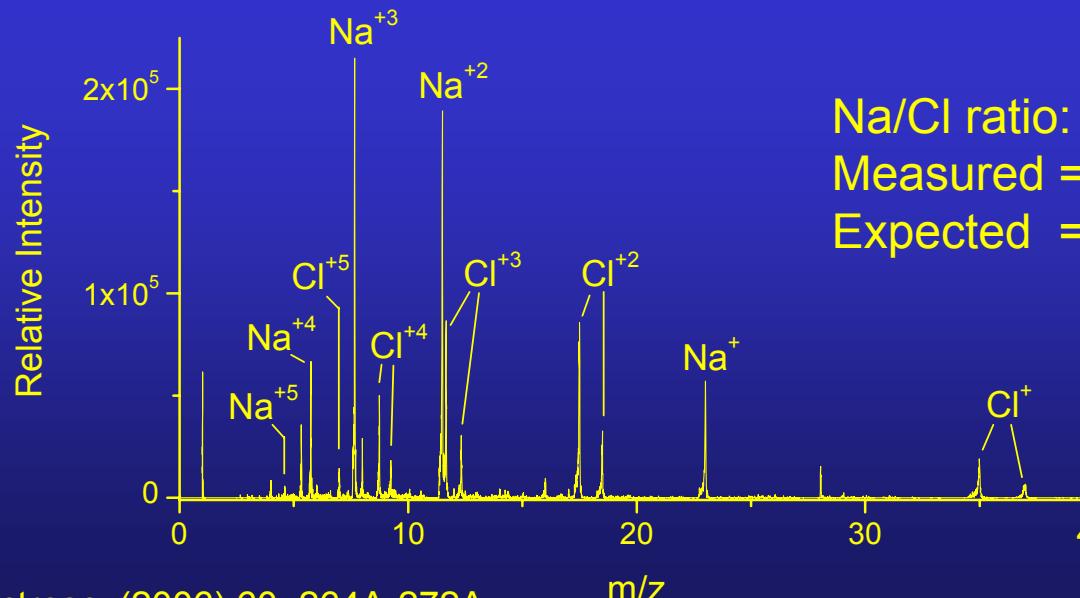
Lee et al, Aerosol Sci. Technol. (2005) 39, 162-169

# Atomic Analysis in the Complete Ionization Limit

Laser  
Desorption  
Ionization  
(193 nm, 2 J/cm<sup>2</sup>)

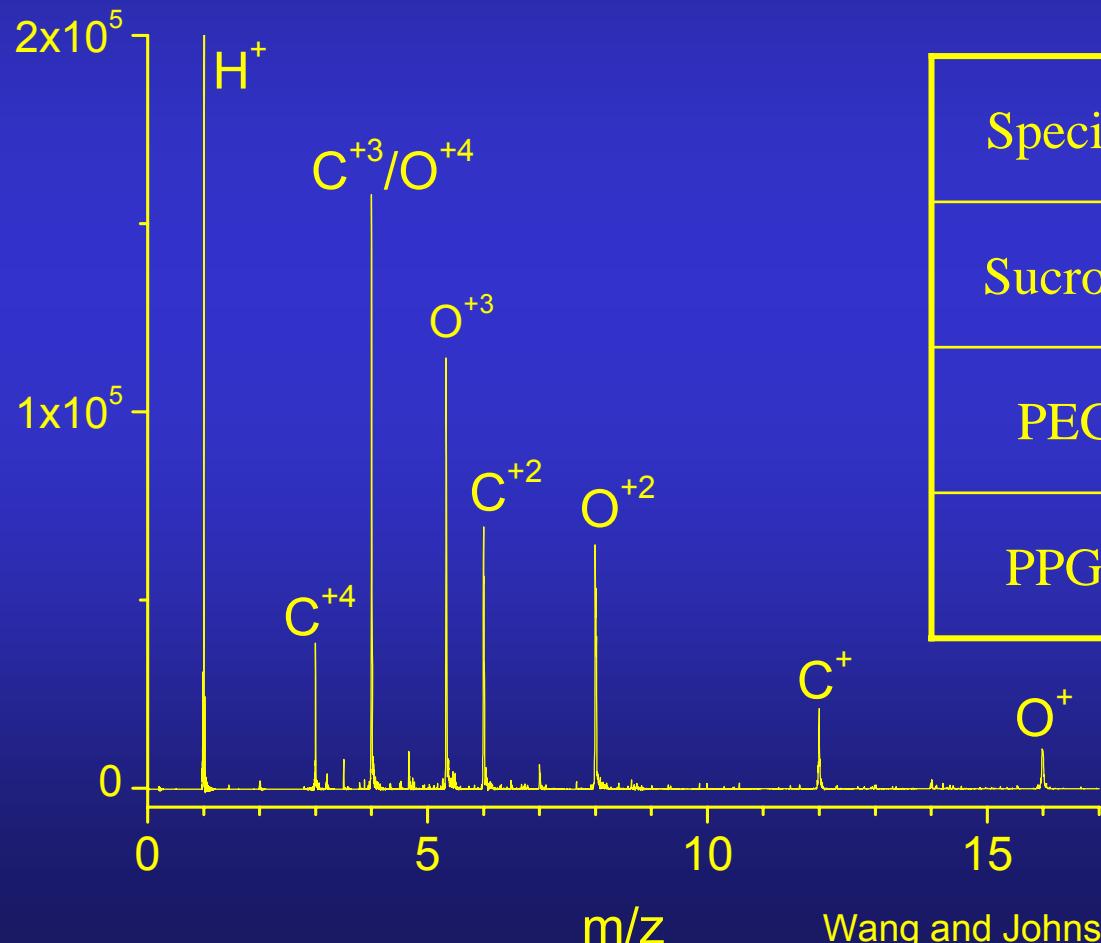


Laser  
Induced  
Plasma  
(532 nm, 70 J/cm<sup>2</sup>)



# C:O Atomic Ratios by NAMS

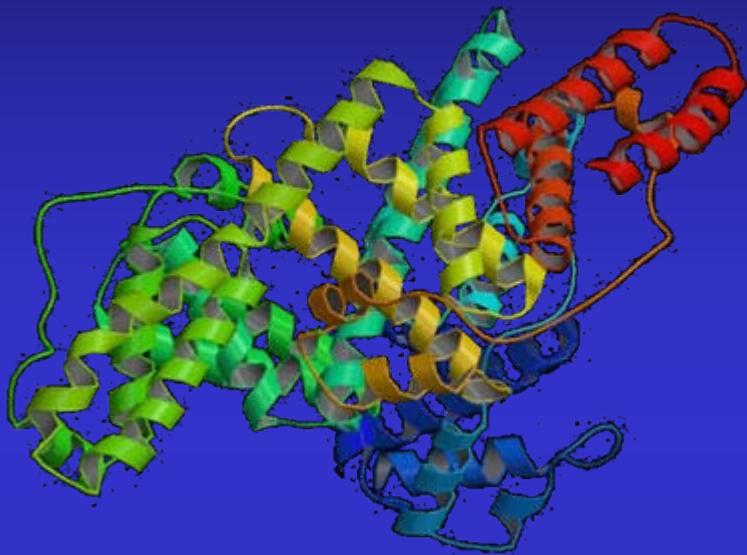
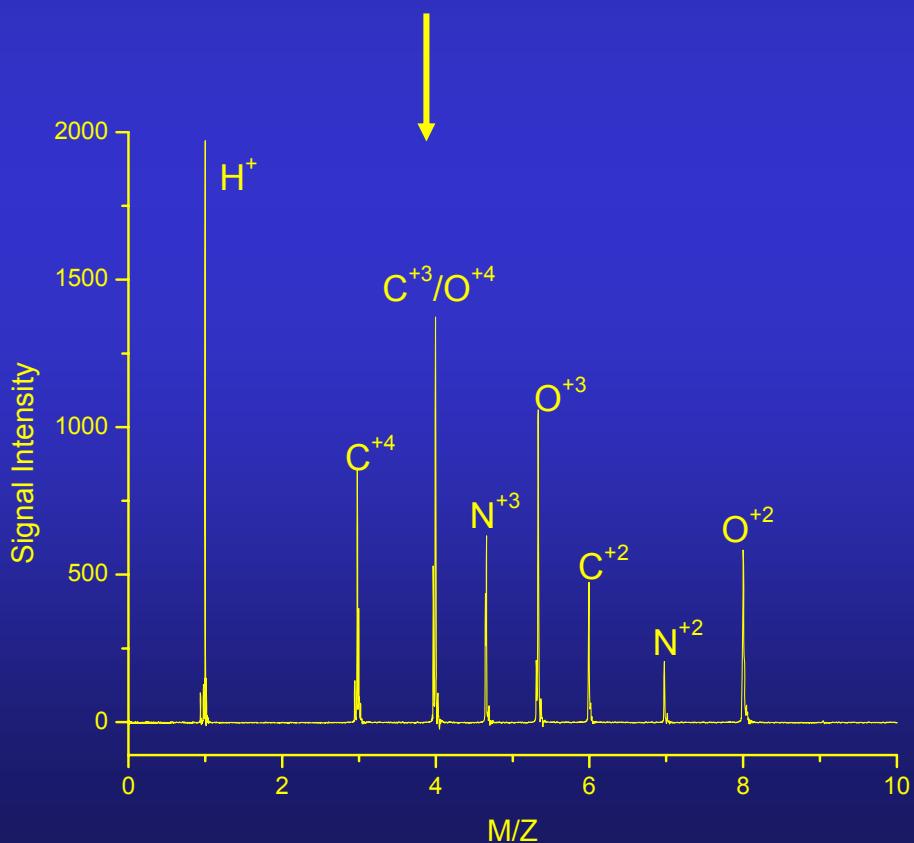
10 nm dia. sucrose particles



Species	C:O Expected	C:O Measured
Sucrose	1.09	$1.06 \pm .03$
PEG	2.00	$1.93 \pm .04$
PPG*	2.62	$2.60 \pm .04$

# Single particle analysis can be single molecule analysis

Mass Spectrum of a  
Single BSA Molecule  
( $C_{3071}H_{4826}N_{816}O_{927}S_{40}$ )



$MW = 66,000$  (7 nm diameter)

Mass of one molecule =  $1 \times 10^{-19}$  g

Wang et al., Anal. Chem. (2006) 78, 1750-1754

# Ambient Nanoparticle Measurements



State of Delaware  
Air Quality Monitoring Site  
Wilmington, Delaware

# Particle Size Reconciliation

$$\text{RSMS} - 50 \text{ nm } d_{va} \longrightarrow d_{va} = \frac{\rho_p}{\rho_0 \chi_v} d_{ve}$$

$$\text{NAMS} - 25 \text{ nm } d_{mn} \longrightarrow d_{mn} = \left( \frac{\rho_p}{\rho_0} \right)^{1/3} d_{ve}$$

Average Ambient Density

$$\rho_p = 1.7 \text{ g/cm}^3$$

Average Shape Factor

$$\chi_v = 1$$

$$d_{ve} \text{ RSMS} = 29 \text{ nm}$$
$$d_{ve} \text{ NAMS} = 21 \text{ nm}$$

Khlystov et al., A., *Aerosol Sci. Technol.* (2004) 38 (S1), 229-238

Zelenyuk, A., Cai, Y., Imre, D. *Aerosol Sci. Technol.*, (2006) 40, 197-217

Wang and Johnston, *Int. J. Mass Spectrom.* (2006) 258, 50-57

Johnston et al., *Appl. Spectrosc.* (2006) 60, 264A-272A

# Nanoparticle Measurements in Wilmington, Delaware

## RSMS

May 2005 – February 2006

Total Particles – 482,659

50 nm ( $d_{va}$ ) Particles – 38,087

## NAMS

May 9 – 19, 2006

Total Particles – 19,403

25 nm ( $d_{mn}$ ) Particles - 9,842

### “Secondary Aerosol” – 60%

Ammonium sulfate, nitrate, organics

→ Particles with C, N > 94%

89%

→ Particles with O 73%

73%

### “Primary Aerosol” – 40%

Biomass Burning (K)

29%

→ Particles with S > 94%

89%

Fossil Fuel Combustion (C)

5%

→ Particles with ~100% C 3%

73%

### *Industrial Sources*

Alkali Metals (Na, K)

3%

→ Particles with Na, K 1%

1%

Amine

2%

→ Particles with Transition/Heavy

Transition/Heavy Metals

1%

Metals (V, Fe, Zn) 1%

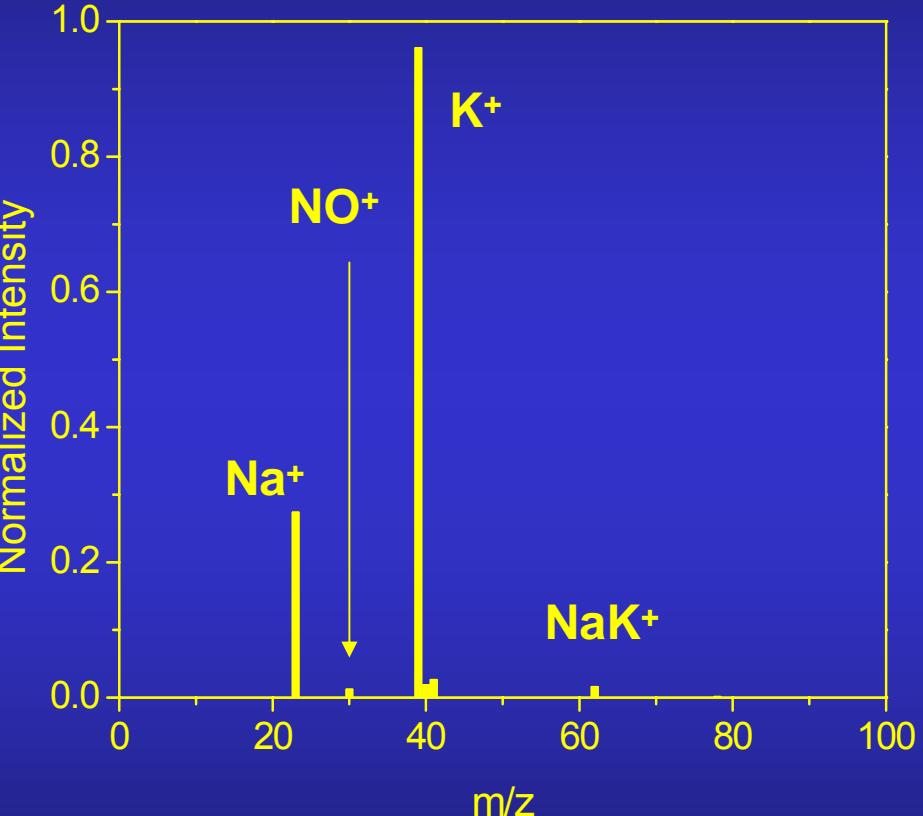
1%

*V, Fe, Zn, Sn, Ce/La, Pb*

**Particles with Si**

**46%**

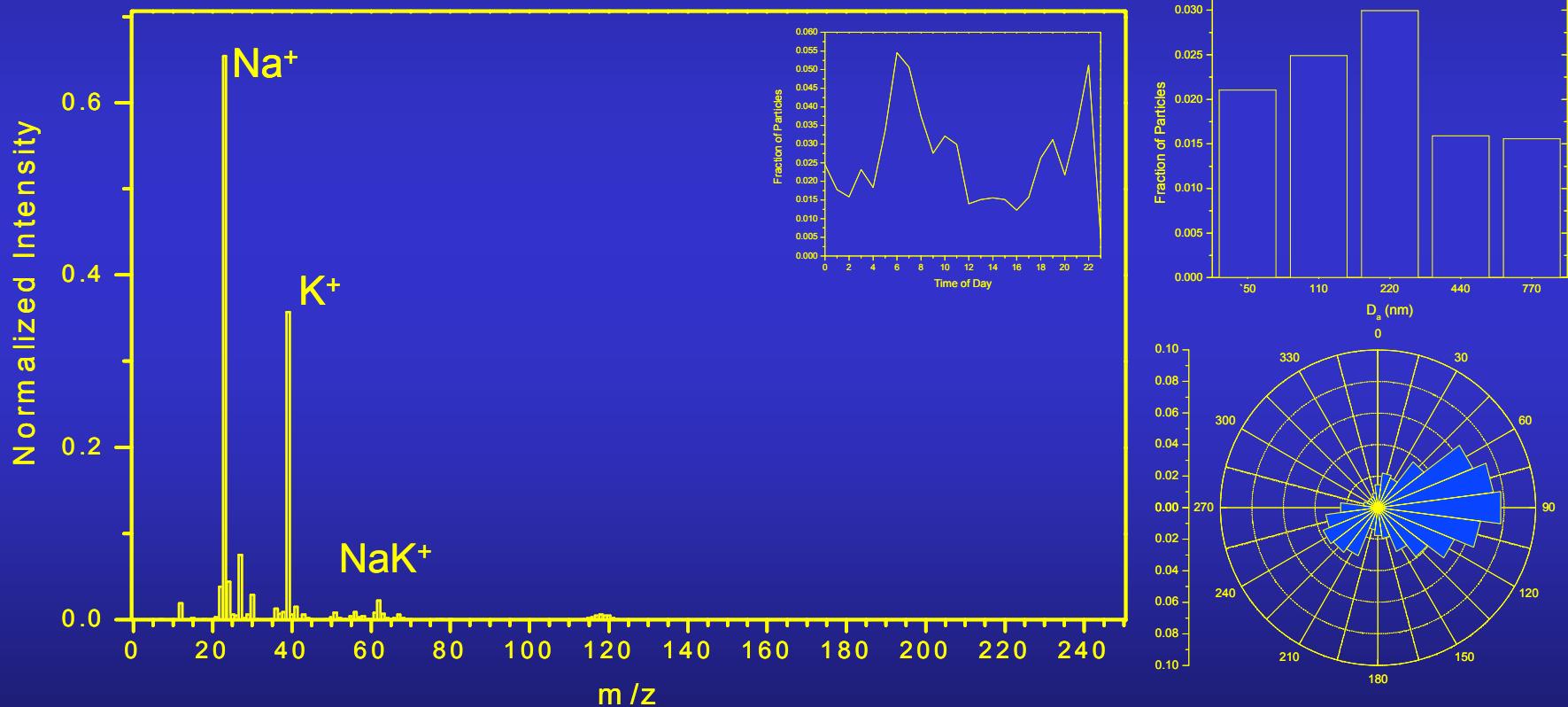
# Primary Aerosol - RSMS



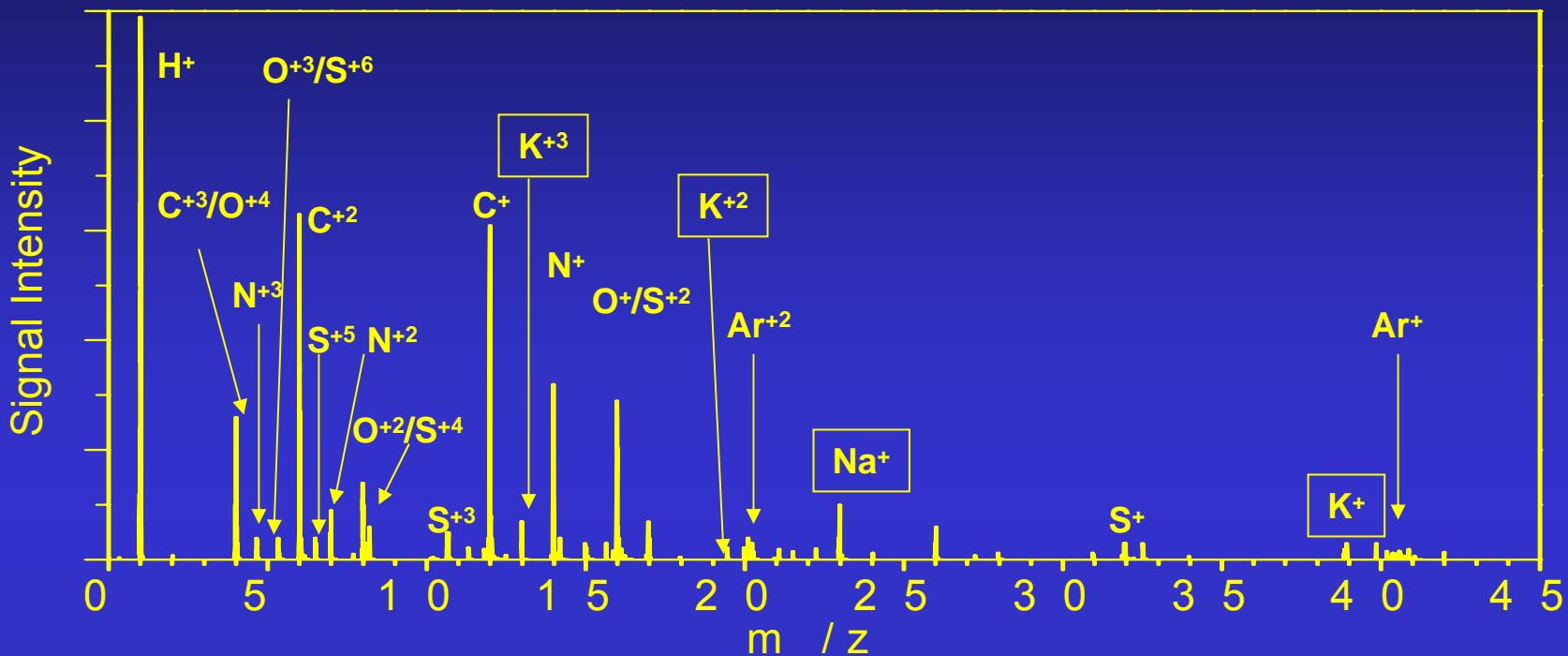
Alkali metals, transition metals are efficiently ionized by RSMS

Trace elements are markers for specific emission sources

Na-K Class: 2% of particles analyzed in RSMS dataset  
Emission Sources: Power Plant ( $90^\circ$ ), Refinery ( $210^\circ$ )



# Primary Aerosol - NAMS



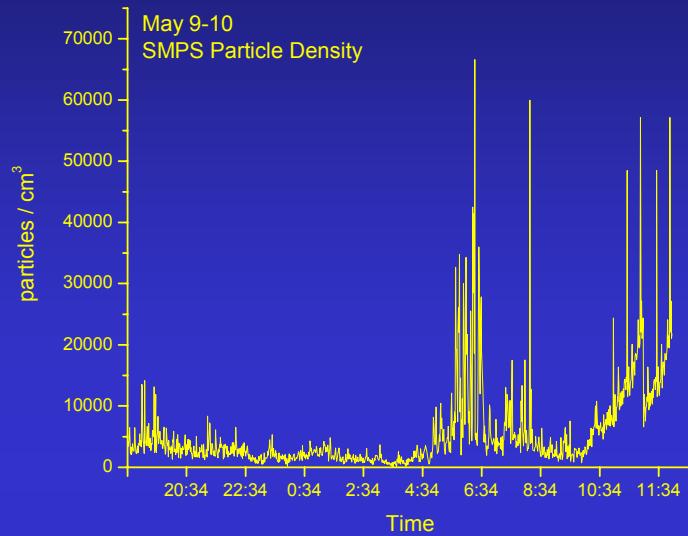
- Different elements are detected with the same sensitivity
- Trace elements are difficult to detect

## K-Na Single Particle

Carbon	65%
Oxygen	15%
Nitrogen	6%
Sulfur	5%
Sodium	5%
Potassium	4%

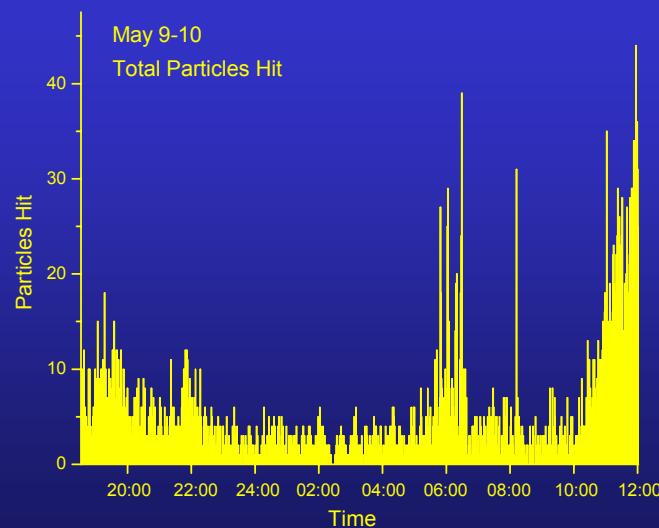
# Ambient Nanoparticle Characterization with NAMS

May 9-10, 2006: 5002 particles in 17 hr



$dN/d(\log d_p)$  vs. Time

$$d_m = 21 \text{ nm} \quad (d_{mn} = 25 \text{ nm} \text{ for } \rho = 1.7 \text{ g/cm}^3)$$

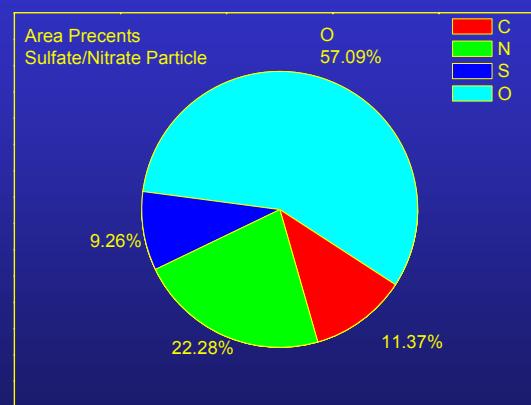
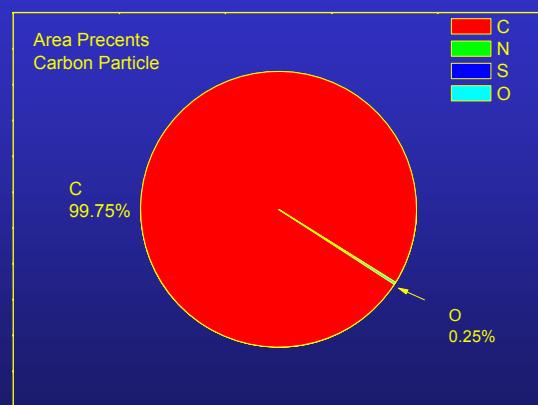
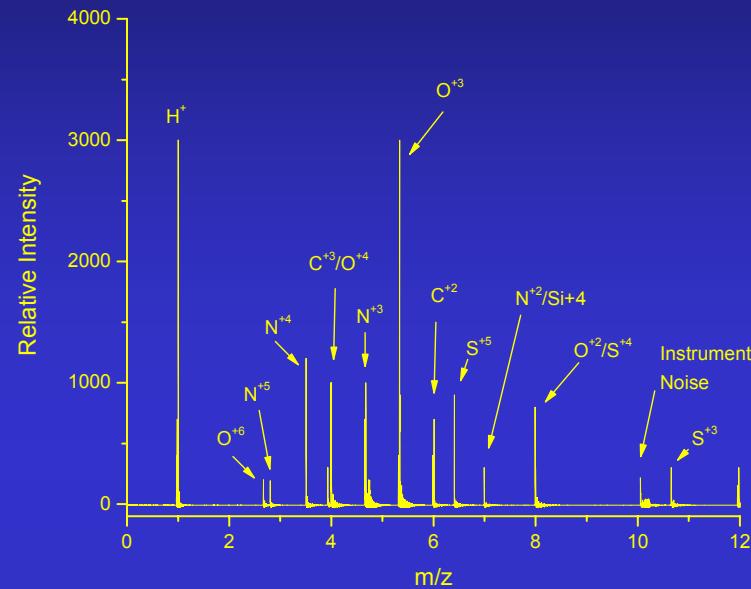
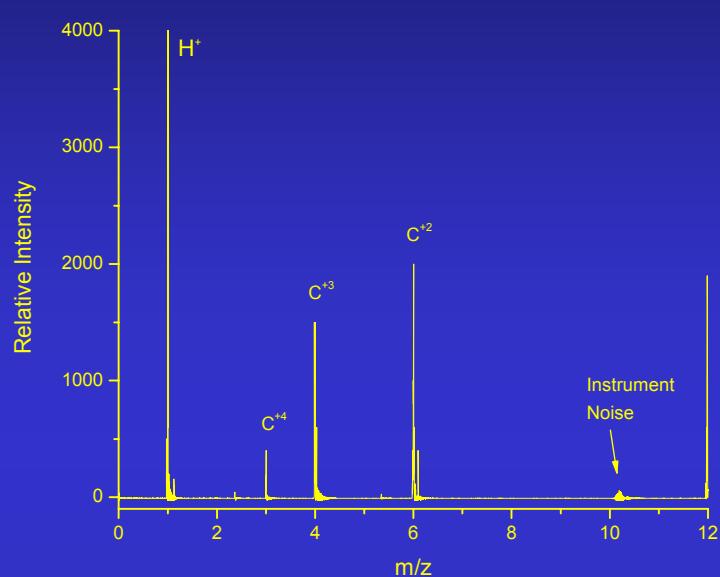


NAMS Particle Hits per min vs. Time

$$d_{mn} = 25 \text{ nm} \quad (f = 10 \text{ kHz})$$

# Single Particle Mass Spectra

( $d_{mn}=25$  nm, 6:33 PM, 9 May 2006)



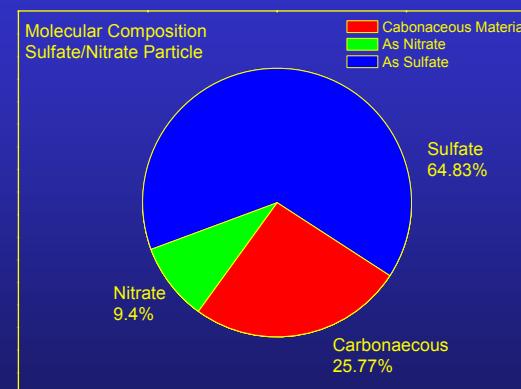
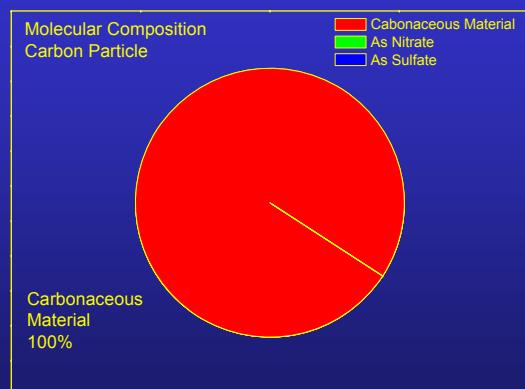
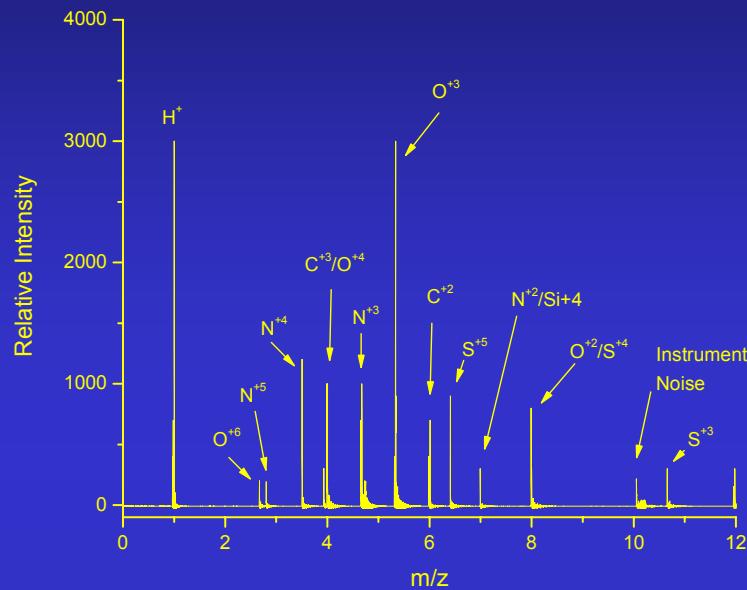
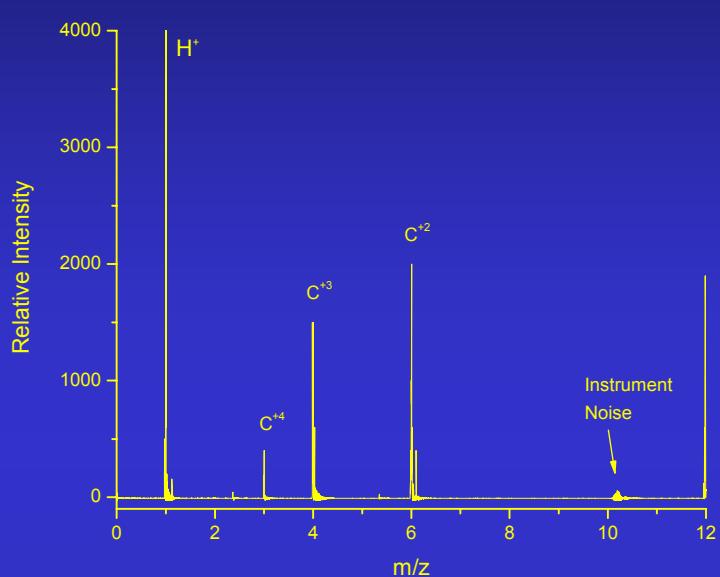
# Inferring Molecular Composition from Atomic Composition

## Total Integrated Area for: C, O, N, S, Si

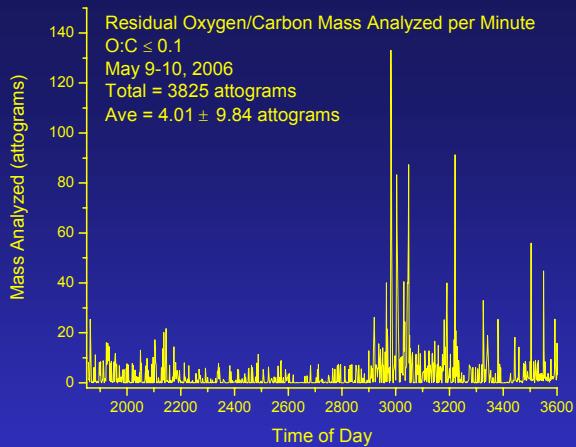
- ↳ Apportion O as  $\text{SiO}_2$  from Si signal
- ↳ Apportion N and residual O as  $(\text{NH}_4)_2\text{SO}_4$  from S signal
- ↳ Apportion residual O as  $\text{NH}_4\text{NO}_3$  from residual N signal
- ↳ Combined residual O with C signal for Organic Carbon

# Single Particle Mass Spectra

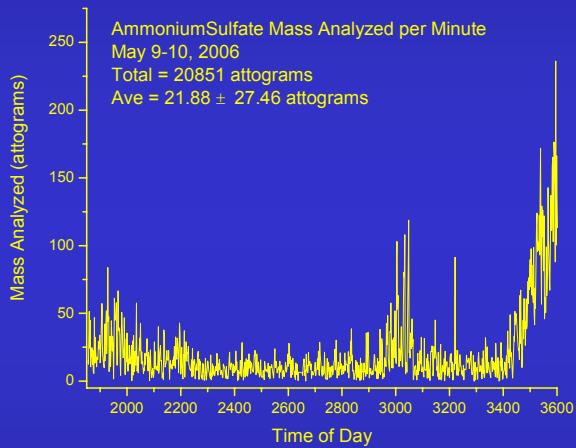
( $d_{mn}=25$  nm, 6:33 PM, 9 May 2006)



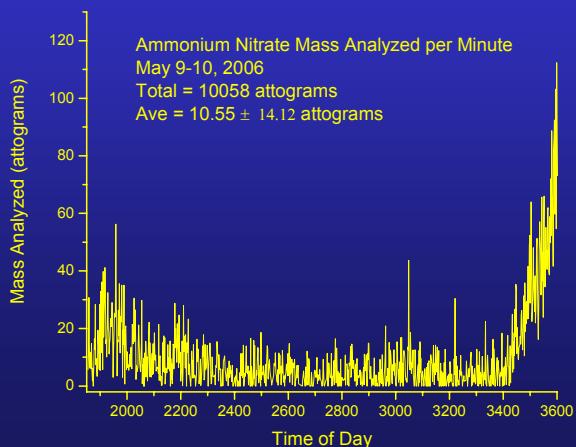
Primary Organic Carbon – most of the mass is in the morning “spikes” (individual vehicles?)



Ammonium Sulfate – present both in the morning “spikes” (diesel vehicles?) and midday “ramp” (secondary aerosol)



Ammonium Nitrate – present only in the midday “ramp” (secondary aerosol)



# Conclusions

1. Single particle mass spectrometry allows the size, shape, density and composition of nanoparticles to be determined in flowing systems.
2. RSMS and NAMS analyze a wide range of particle sizes:
  - Particles above about 50 nm in diameter are most easily size selected by aerodynamics (RSMS)
  - Particles below about 30 nm in diameter are most easily size selected by electrodynamics (NAMS)
3. RSMS and NAMS give complementary measures of composition:
  - Laser desorption ionization is sensitive to trace metals that can act as signatures for primary aerosol
  - Laser induced plasma permits quantitative characterization of secondary aerosol (sulfate, nitrate, organics).
4. Single particle detection gives insight into ionization processes (e.g. covariance analysis).
5. Ambient monitoring with single particle mass spectrometry gives insight into nanoparticle sources.

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DOE