Composition of Freshly Nucleated Ultrafine Particles

Nanoparticle collection: Minnesota Group

Mass Spectroscopy Analysis: UC Riverside and NCAR

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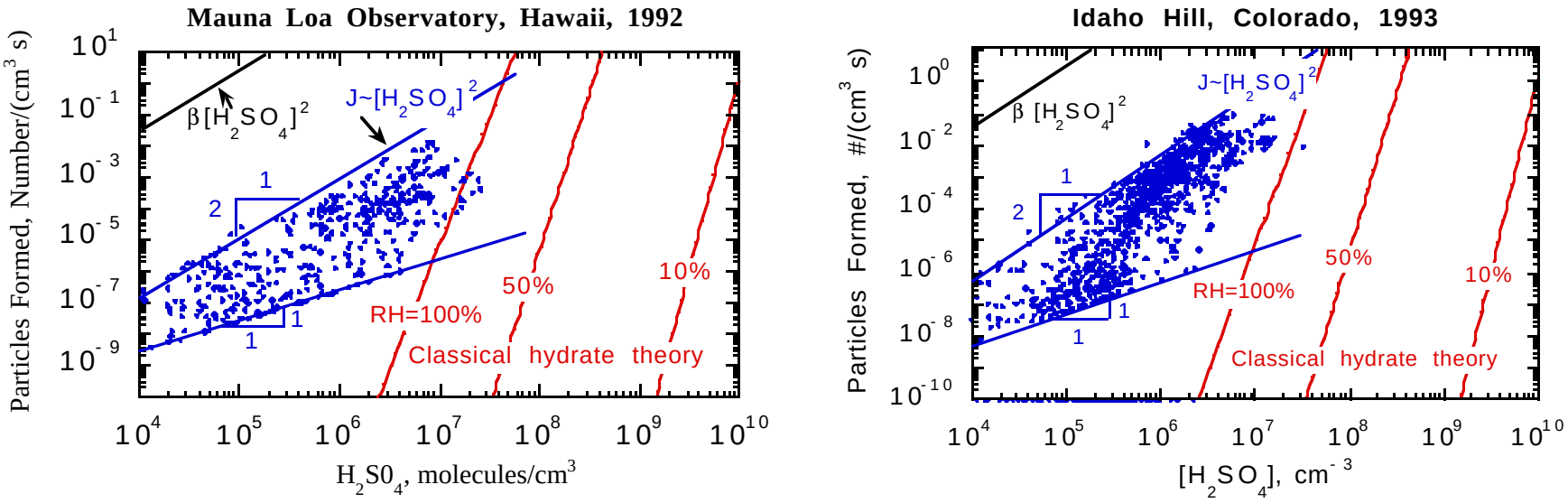
Atmospheric Measurements -The Motivation

Nanoparticle Growth Rates

* Measured growth rates and particle nucleation in atmospheric aerosols are consistently larger then predicted by H_2SO_4 condensation theory

Dependence of New Particle Formation Rates on $[H_2SO_4]$



- Actual particle productions rates >> values predicted by binary H_2O H_2SO_4 theory
- Observed functional dependence on [H2SO4] is weaker than predicted by nucleation theory

Conclusions About Atmospheric New Particle Formation Rates and Particle Growth Rates

* Measured NPF Rates >> Binary (H_2SO_4 +H_2O) Theory Nucleation Rates

* Rate~$[H_2SO_4]^2$, not ~$[H_2SO_4]^{\sim 10}$ as predicted by Binary (H_2SO_4] +H_2O) Nucleation Theory

* NPF rates tend to be lower when preexisting aerosol surface area is high

* Growth rates of freshly nucleated nanopartices are ~10x rates that could be due to condensation of H_2SO_4 and its associated H_2O and NH_3

Goals

* To develop instrumentation for measuring chemical composition of freshly nucleated atmospheric particles (dp~3-10 nm)

Measurement Issues

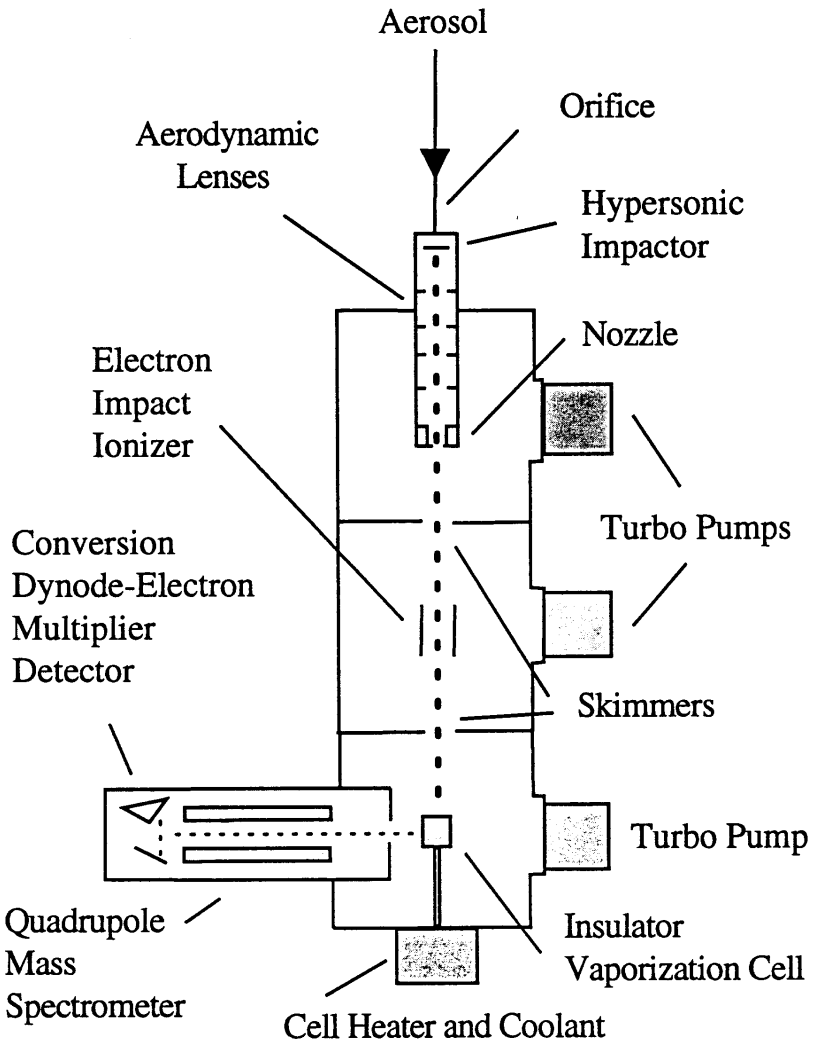
* Low atmospheric mass concentrations require high efficiency sampling systems to ensure short sample times

* Total elimination of large particles is essential to measure composition of small particles

Particle Beam Thermal Desorption Mass Spectrometer

* Particle Beam Formation
  - Aerodynamic lenses
  - Electrostatic Lenses
* Composition can be measured continuously or material can be collected for a period of time before measurement
* Issues
  - low mass concentration compounded by difficulty in focusing Ultrafine particles necessitates long sample times
  - incomplete particle separation or contamination from other sources
  - possible volatile evaporation at low pressure

PB-TDMS Schematic: Aerodynamic lens option



Particles enter the system through a critical orifice (76 sccm). Large particles are hypersonically impacted on an oiled impaction plate. Ultrafine particles are focused with the lens and passed through two skimmers and an optional electron impact ionizer. Particles impact on either an insulating or metal ionization cell. Molecules are thermally desorbed into the quadrupole mass spectrometer

-Molecular flux 10^8 for continuos analysis

-10^5 for flash vaporization with 10-1000 second collection time

-Metal collection cell kept at -20 °C to prevent evaporation during sampling

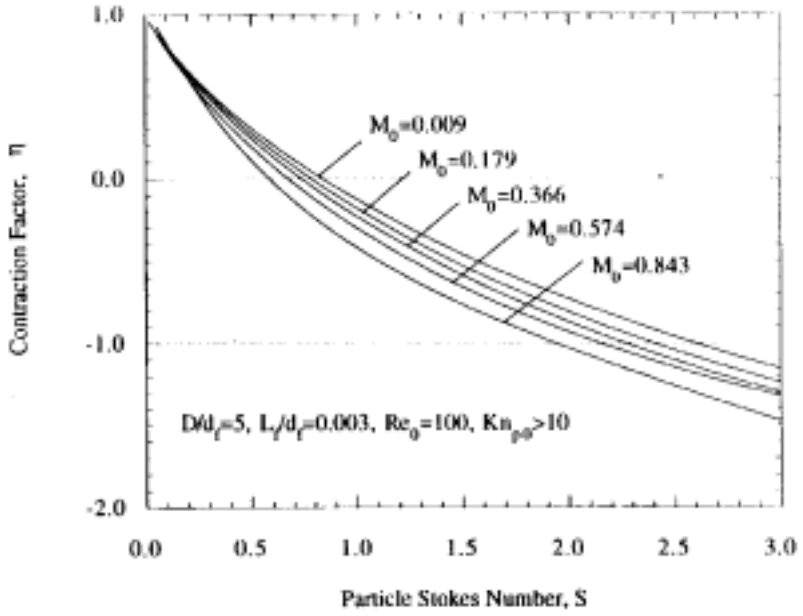
Design of Aerodynamic Lens

* Free molecular Stokes number

$$S = \frac{1}{\left(1+\frac{\pi\alpha}{8}\right)\sqrt{2\pi\gamma^3}} \frac{\pi\rho_p d_p c^3}{P^2 d_n^3}$$

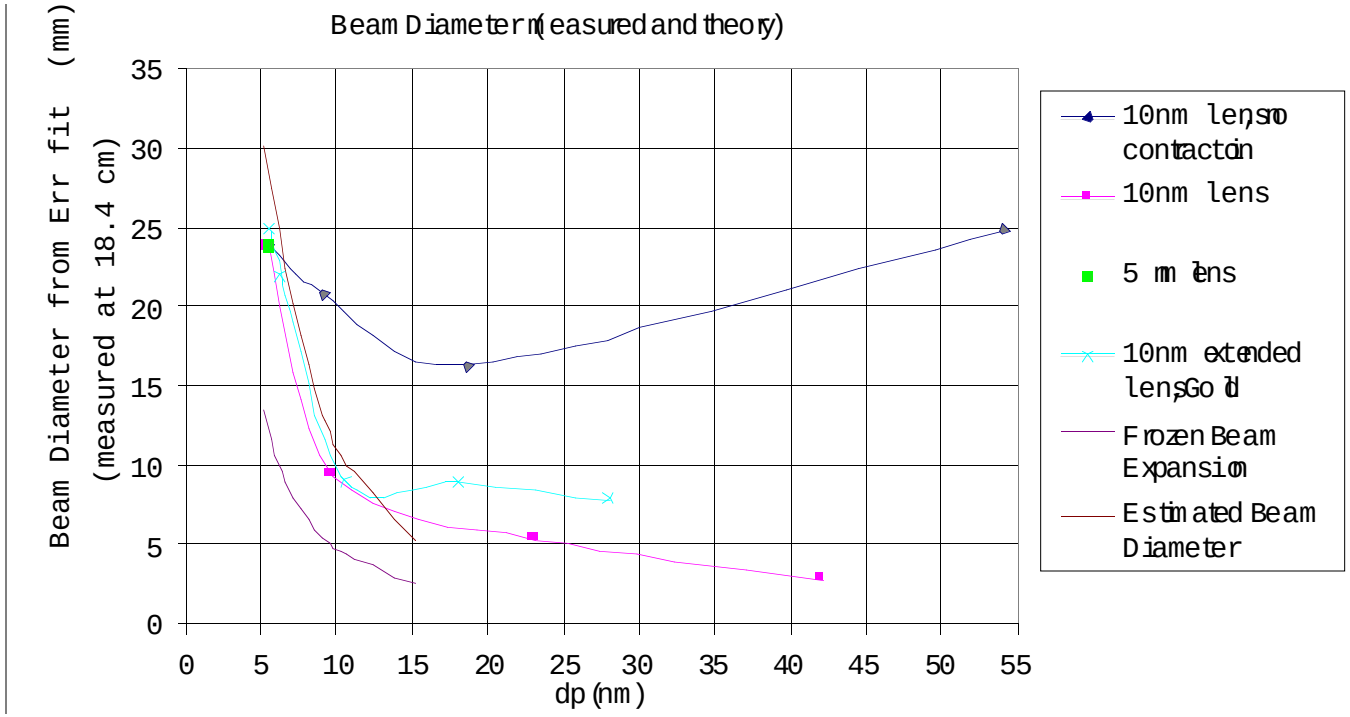
Orifice #	10 nm lens	10 nm extended lens	5 nm lens
1	0.186	0.186	0.253
2	0.236	0.236	0.333
3	0.298	0.298	0.441
4	0.395	0.395	0.585
5		0.500	
6		0.664	
Contration Diameter	1.020	1.700	1.700
Nozzle Diameter	0.519	0.850	0.774

Lens diameters (d_n)



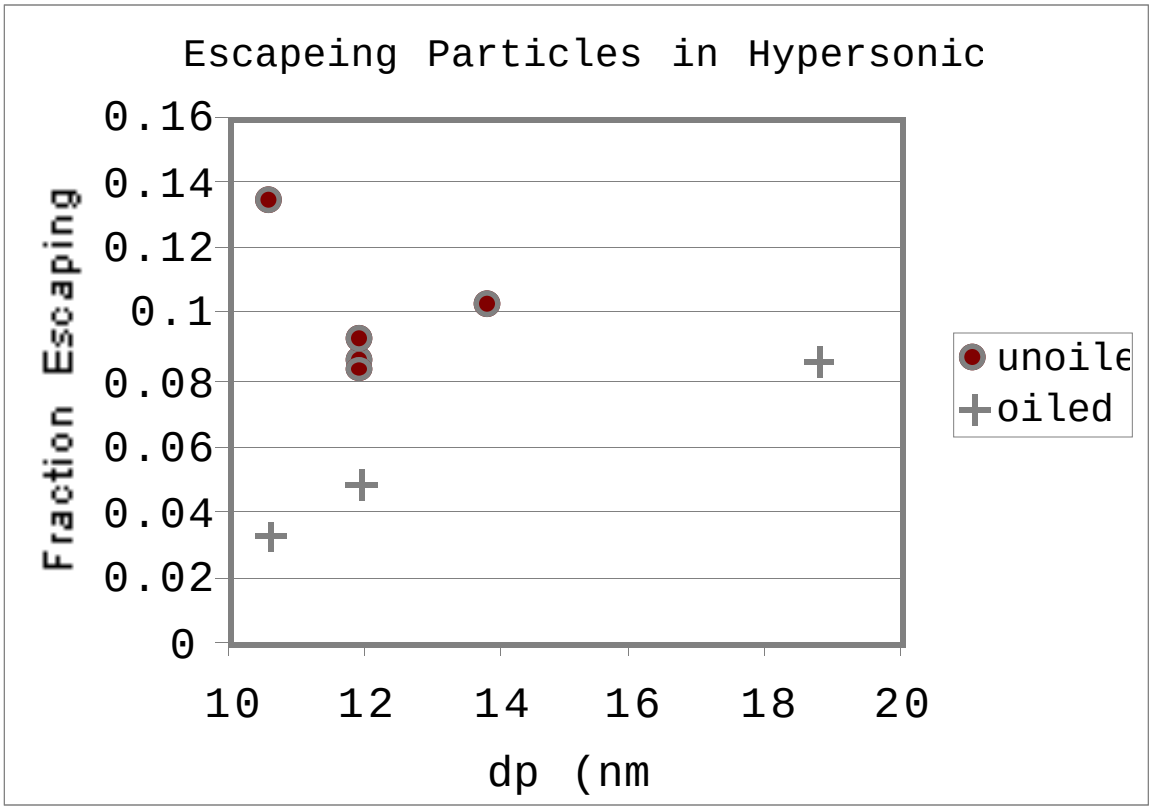
Lens Contraction factor from Peng Liu's Thesis

Aerodynamic Lens Beam Diameter Results



Conclusion: Diffusion leads to broad beams for sub-10 nm particles. Aerodynamic focusing is not the optimal approach for forming tightly collimated particle beams of nanoparticles.

Collection Efficiency of Hypersonic Impactor

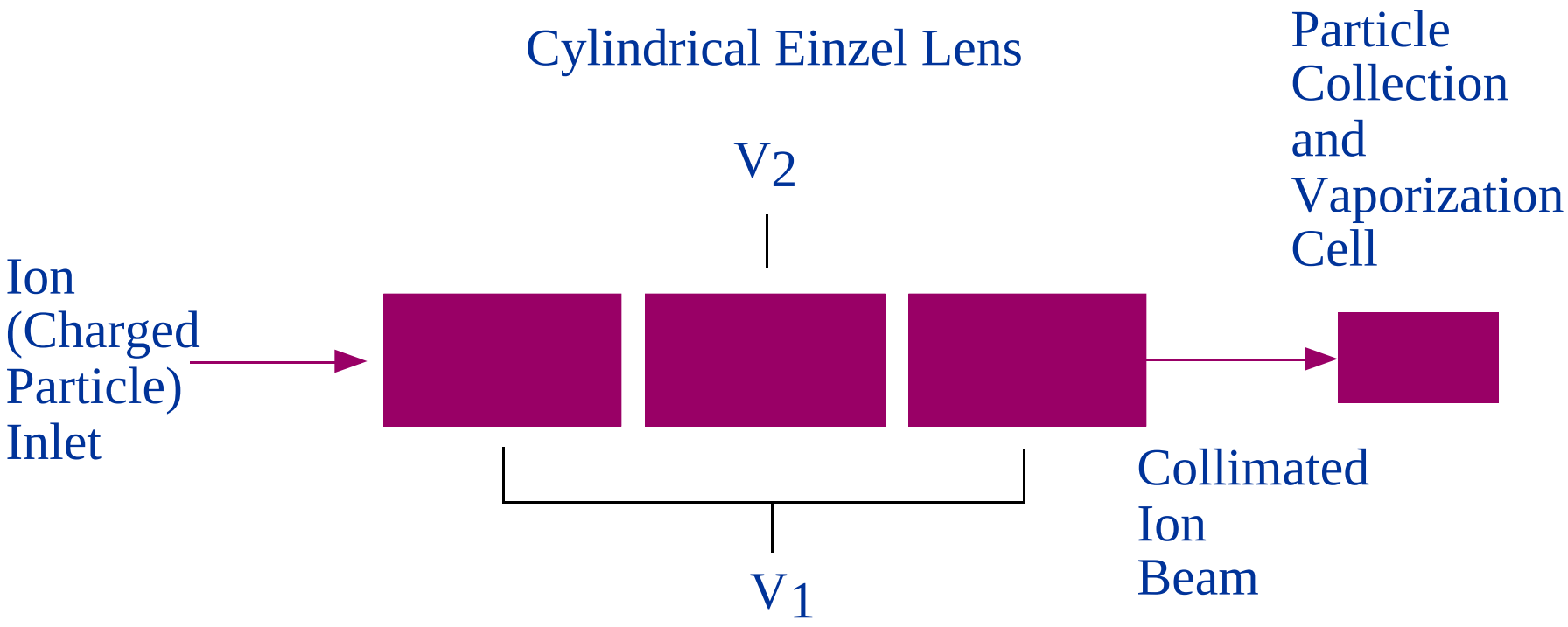


Conclusion: Hypersonic impactor does not collect all particles > 10 nm. Another means must be found to remove large particles.

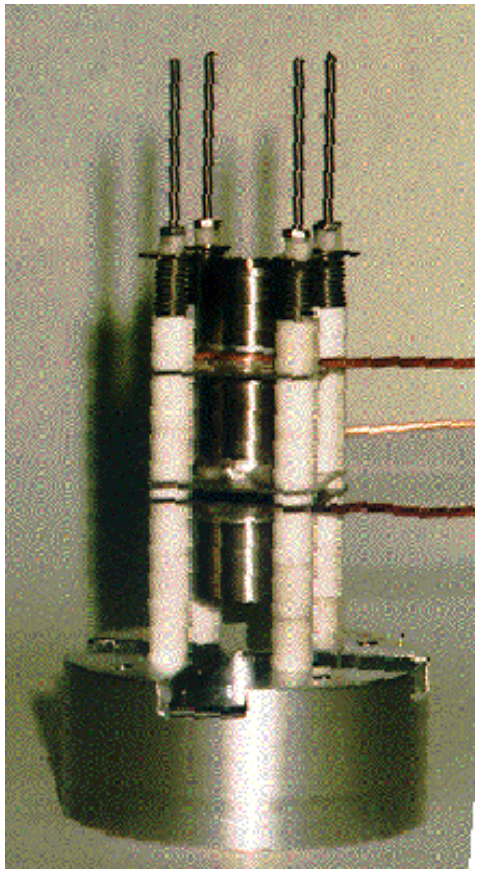
Conclusions Regarding Particle Beam Formation by Aerodynamic Lense

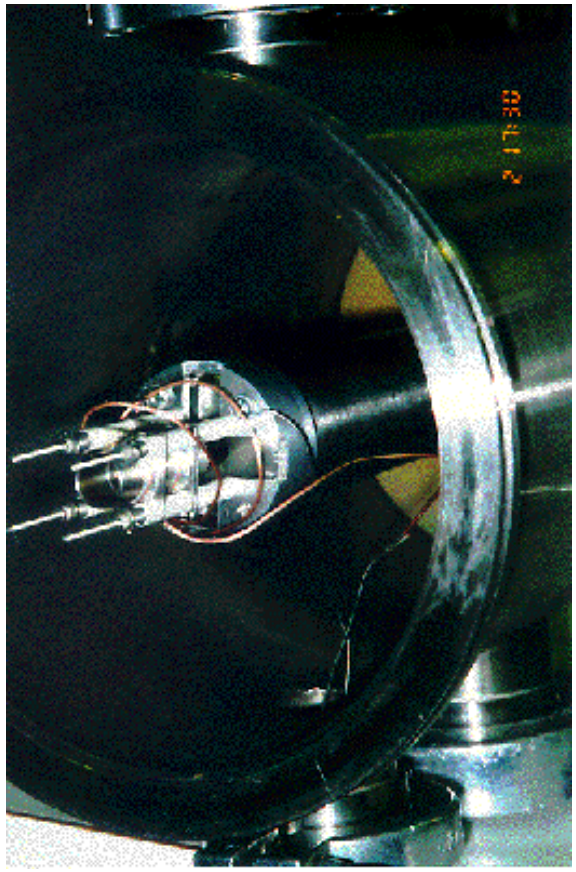
* Brownian diffusion limits the extent to which aerodynamic lenses can form tightly collimated beams of nanoparticles. Our goal is to form highly collimated lenses so as to improve collection efficiencies and decrease the size of the collection cup.
* The hypersonic impactor is not 100.0% effective at removing particles larger than 10 nm.

Schematic of Particle Beam Formation by Electrostatic Focusing



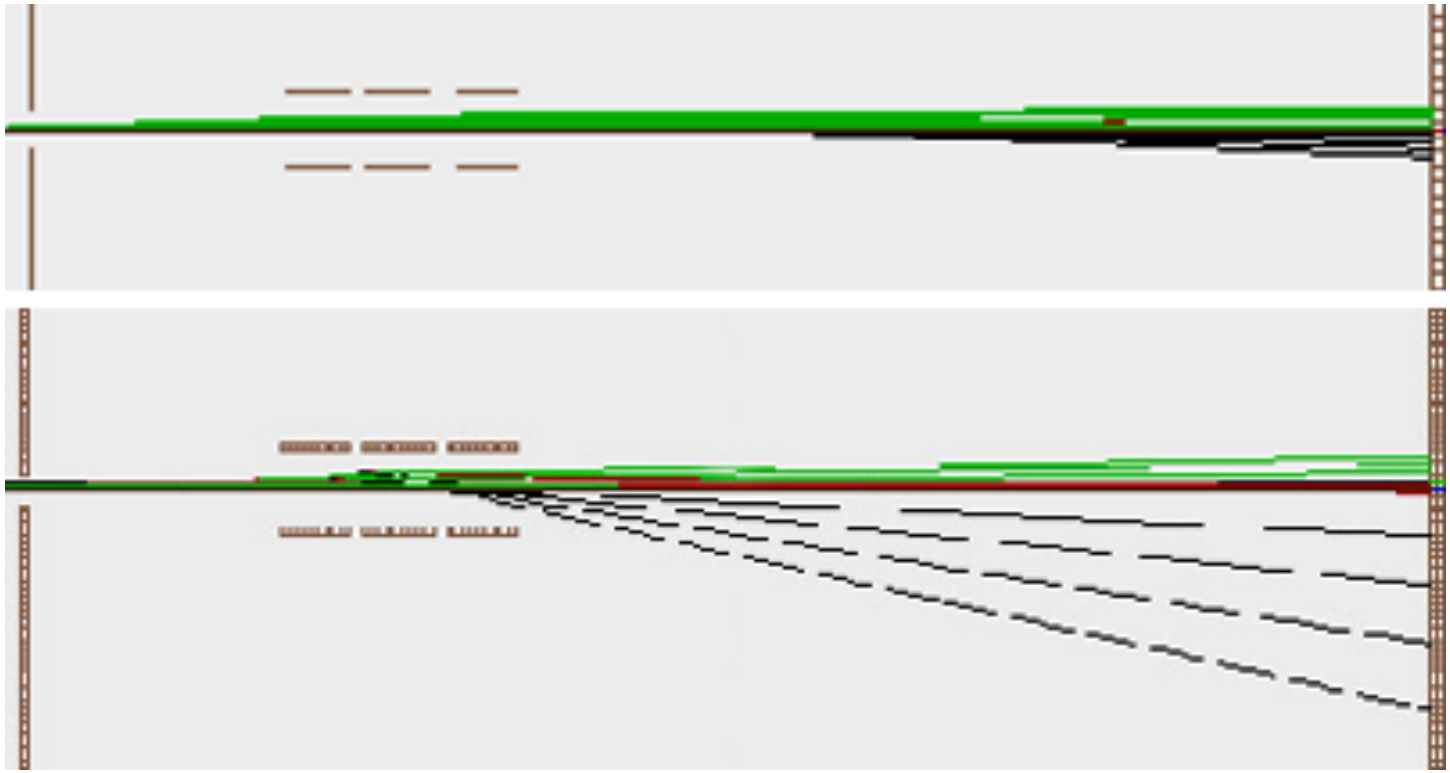
Photographs of Prototype Einzel Lens





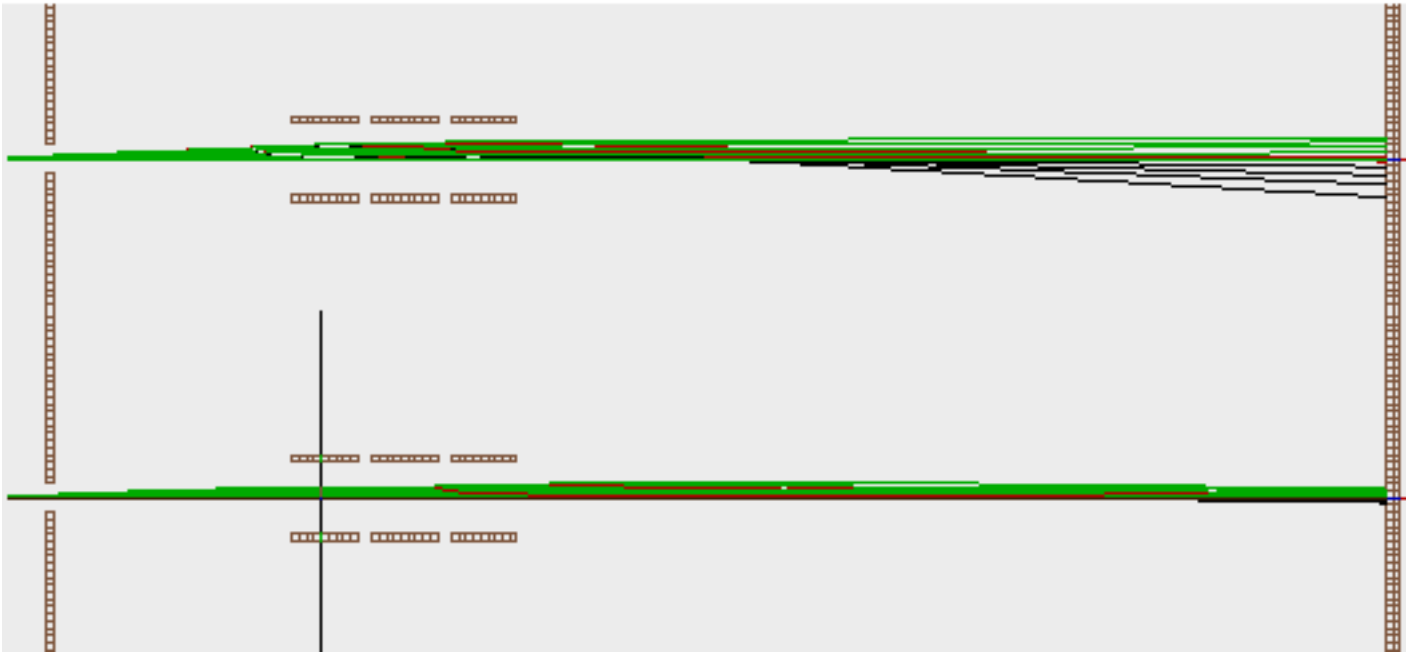
Effects of Energy Bandwidth: Comparison of Weak and Strong Electrostatic Lenses

14(black), 17 (red) and 20 (green) nm particles in
-a weak lens (top)
-a strong lens (bottom)



Accelerating Lenses

- **5 (black),6 (red),and 7 nm (green) particles in “weak” lenses.**
  - **Upper lens: V_2=-160 v, Beam Diameter=10.4 mm**
  - **Lower lens: V_1=-300 v, V_2=-700 v, Chamber grounded; Beam Diameter=2.4 mm**



Modeling Results

* Focusing is strongly effected by the energy bandwidth of the beam
* “Weak” lenses focus better then “Strong” lenses.
* Combining accelerating lenses with “weak” lenses yields even better results.
* Electrodynamic lenses show promising for producing tightly collimated nanoparticle beams, and further work on this topic is underway.

Particle Composition Analysis:

- Mass spectra of background gases are obtained by placing a filter upstream of the pressure-reducing orifice (Fig.1). Background ~detector noise ~100 cps.
- Mass spectra of $(NH_4)HSO_4$ and $(NH_4)_2SO_4$ and are indistinguishable, but differ from H_2SO_4 by strong NH_3^+ (*m/z* 17) peak (Fig 1).
- Mass spectra of organics (e.g. glutaric acid, $HOOC(CH_2)_3COOH$) contain such a variety of peaks as to be easily recognizable (Fig. 1).
- Metal vaporization cell allows rapid heating/vaporization of collected particles, resulting in larger mass peaks and increased signal/noise (Fig. 2). Metal also cools effectively, reducing particle evaporation.

Flash Desorption for Higher Sensitivity:

Figure 2 shows flash desorption results for DOS [dioctyl sebacate].

- DOS Particles collected in vaporization cell at –20°C for 360 s, then flash evaporated in ~0.45 and ~0.15 s.
- Constant total signal (peak area) indicates that molecular fragmentation is independent of vaporization time.
- No signal observed during collection, indicating no evaporative losses.
- Flash vaporization experiments confirm that signal/noise increases in proportion to collection time/ vaporization time. For 360 s collection time and 0.15 s vaporization time, signal/noise increases by 2.4×10^3.

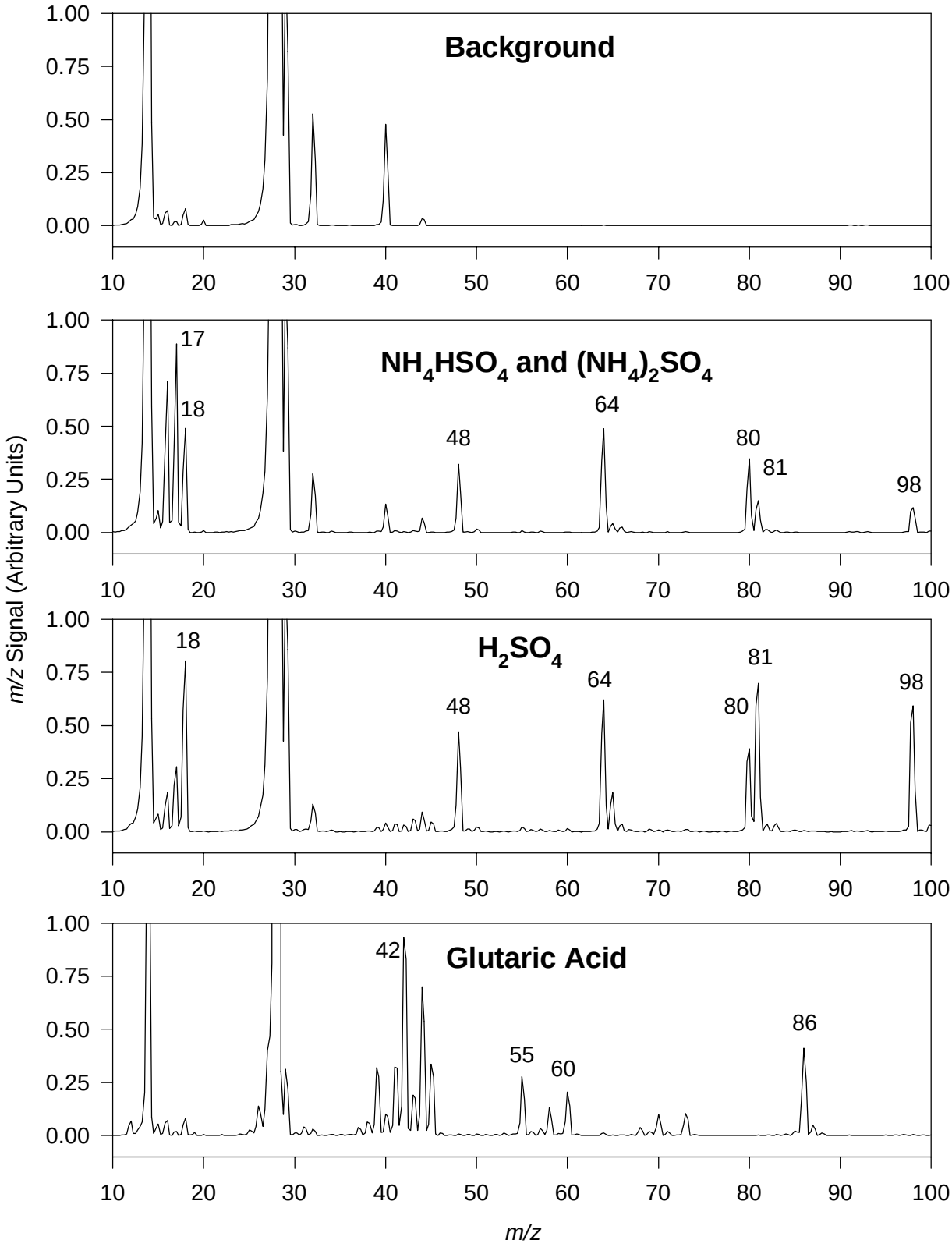


Figure 1. TDPBMS electron ionization mass spectra of laboratory-generated particles.

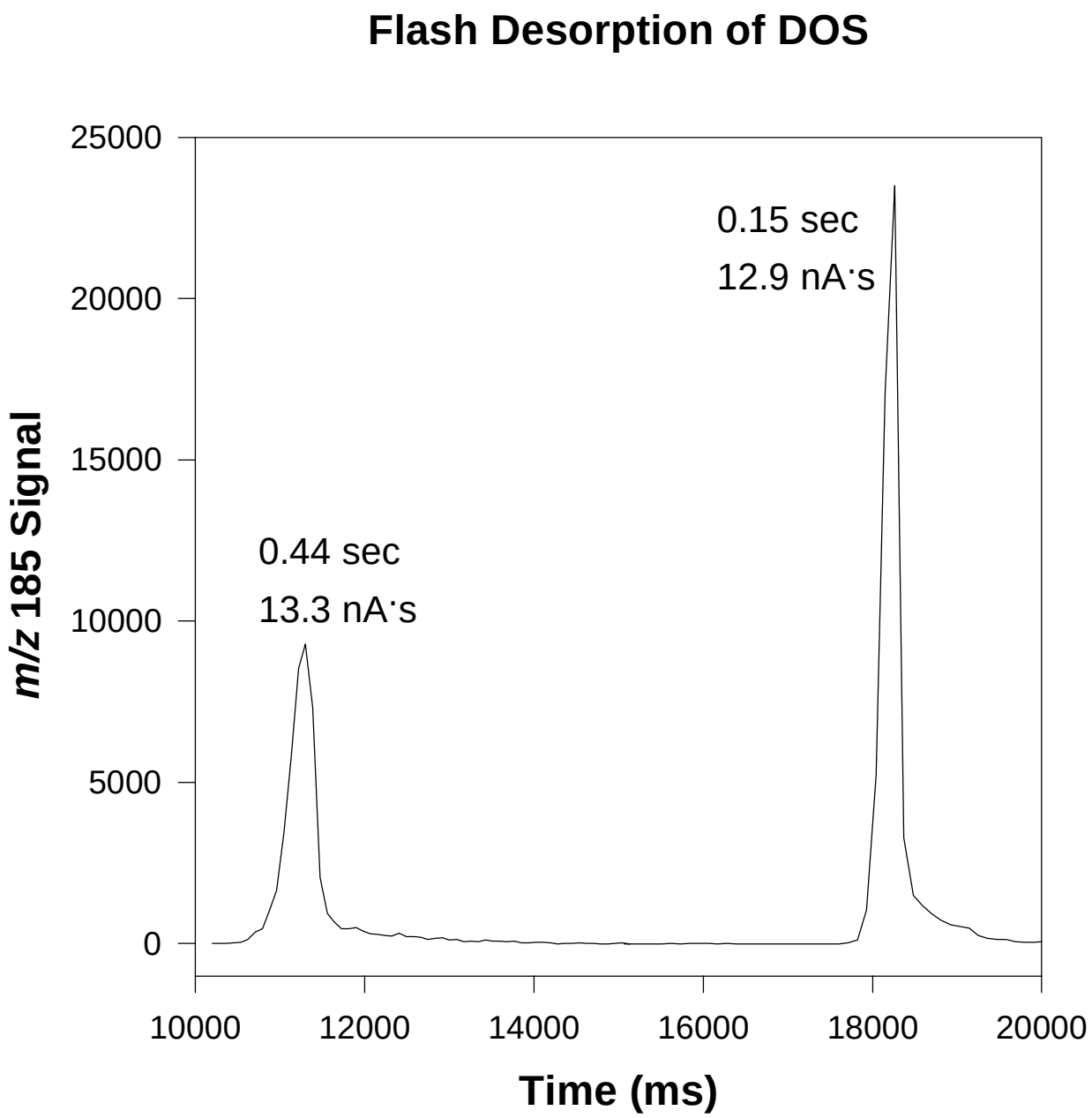


Figure 2. Flash desorption of DOS at two heating rates.

TDPBMS Results to Date

- Pumping scheme with cryotrap reduces background signal to pulse-counting detector limit (~100 cps).
- Present detection limit for continuous analysis of a single species corresponds to a flux of ~10^9 molecules/s into the vaporization cell.
- Vaporization cell can be pulsed in ~0.1 s, which is equal to limit set by data acquisition electronics.
- Flash vaporization experiments confirm that signal/noise increases in proportion to collection time/vaporization time. For proposed 10-10^3 s collection times and 0.1 s vaporization time, flux into the

vaporization cell must be ~10^5-10^7 molecules/s to exceed detection limit.

TDPBMS Results to Date

- Experimental results indicate that particle components with vapor pressures < 10^{-5} torr at -20°C can be collected in vacuum without significant evaporation. $(NH_4)_2SO_4$, H_2SO_4, and most ambient particulate organics are in this_catagory.
- TDPBMS mass spectra can distinguish $(NH_4)_2SO_4$, H_2SO_4, and organics, which are major species expected to be present.

Future TDPBMS Plans

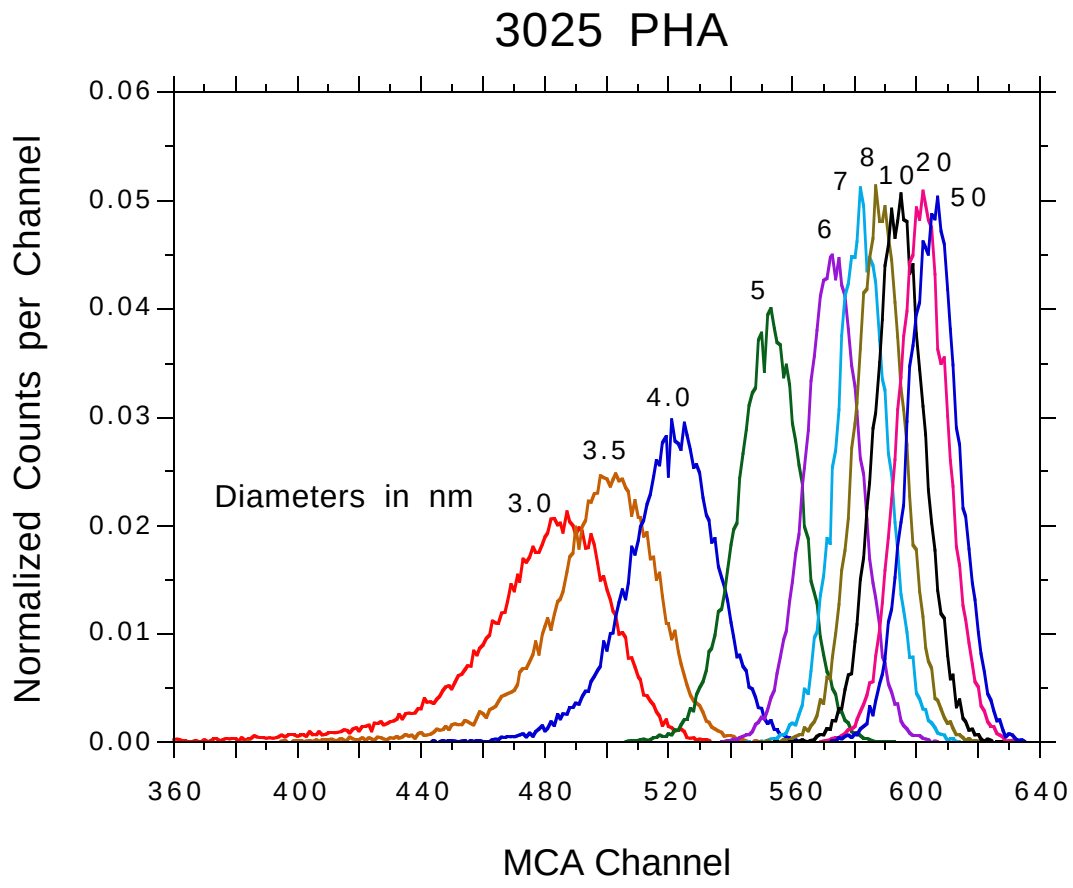
- Construct and test 45^{o} angled vaporization cell for higher efficiency vapor transport into mass spectrometer. Could reduce detection limit by ~10x.

- Add energy analyzer to mass spectrometer to reduce background. Could reduce detection limit by ~100x.

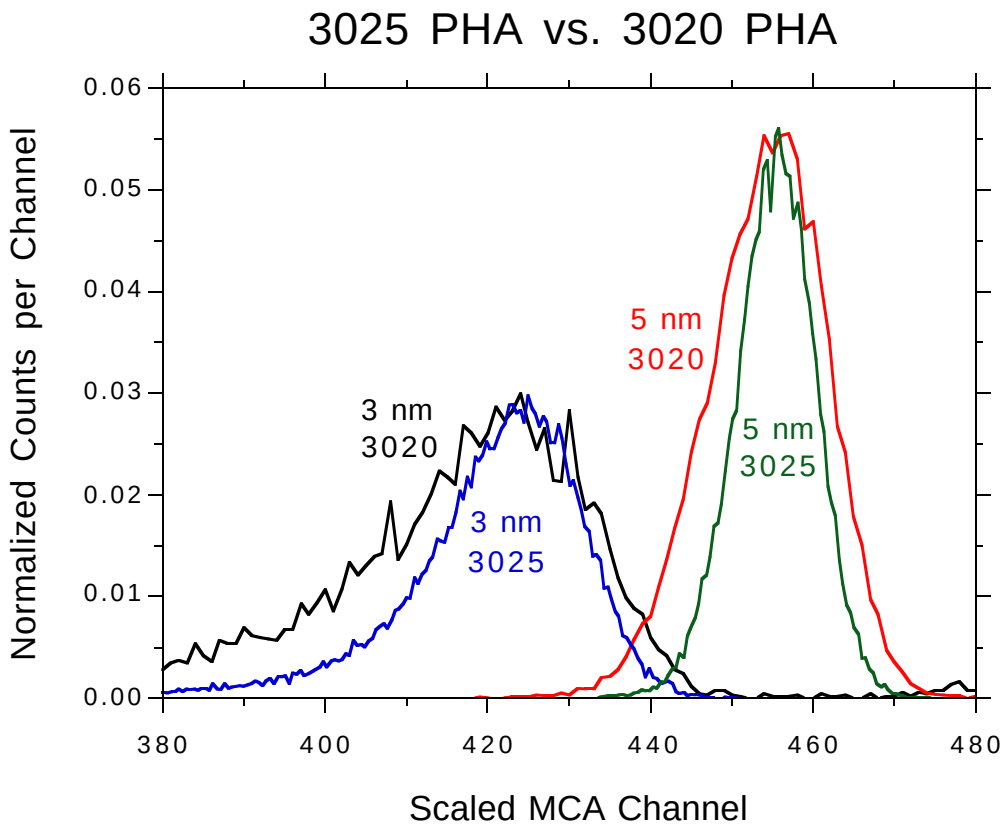
- Interface TDPBMS to hypersonic impactor-lens and test performance with laboratory particles (D_p<4 nm).

- Employ TDPBMS for field studies of the composition of freshly nucleated particles.

3025 Kernal Functions (Calibration)



3025
Relative to 3020 Prototype



Conclusions

* TSI 3025 UCPC has been modified to permit measurement of 3-10 nm size distributions by the PHA technique
* Sizing resolution of 3025 improved relative to resolution of 3020 prototype
* Microtherm LLC is able to provide this service on a commercial basis.