What Can Single Particle Mass Spectrometers and Aerosol Mass Spectrometers Do and Not Do?

TSI Model 3800 'ATOFMS': SMPS

Daniel J. Cziczo

Aerodyne 'AMS': Thermal Desorption

AR ... hop on Advances in Airborne Instr...
University of Illinois, Champaign, IL, 14-16 October 2008

Special thanks to :
Dan Murphy, Dave Thomson, Berko Siero, Hanna Herich, Rami Alfarra

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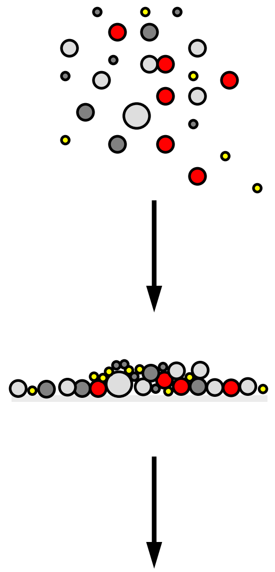
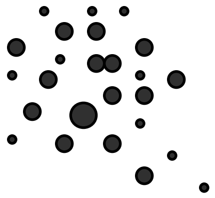
The Reason for Aerosol Mass Spectrometry?

Contemporary Aerosol Analysis



Analytical Chemistry

Or was it?



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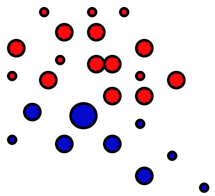

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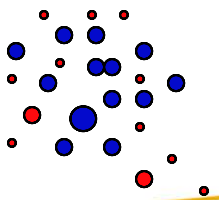
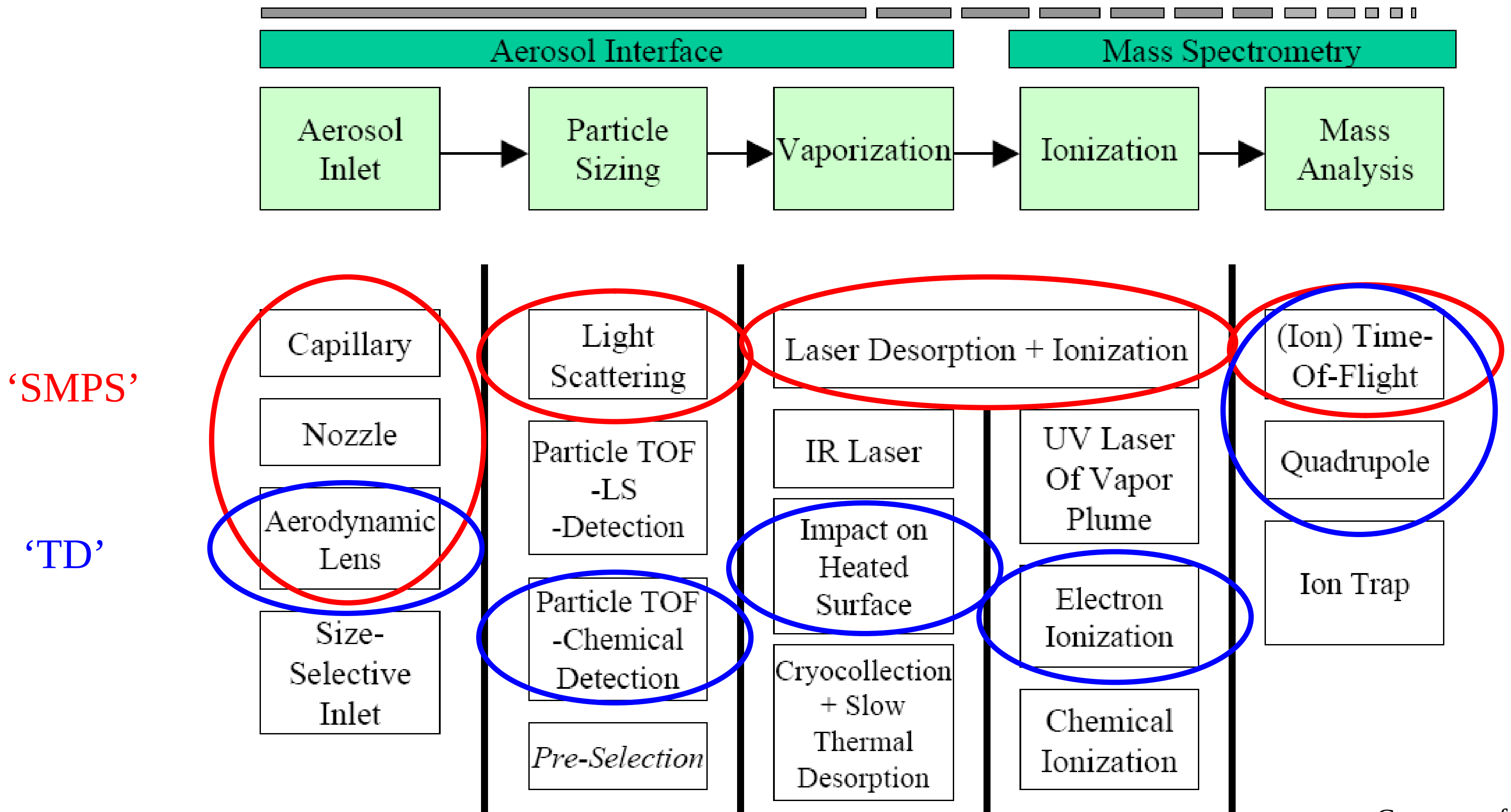
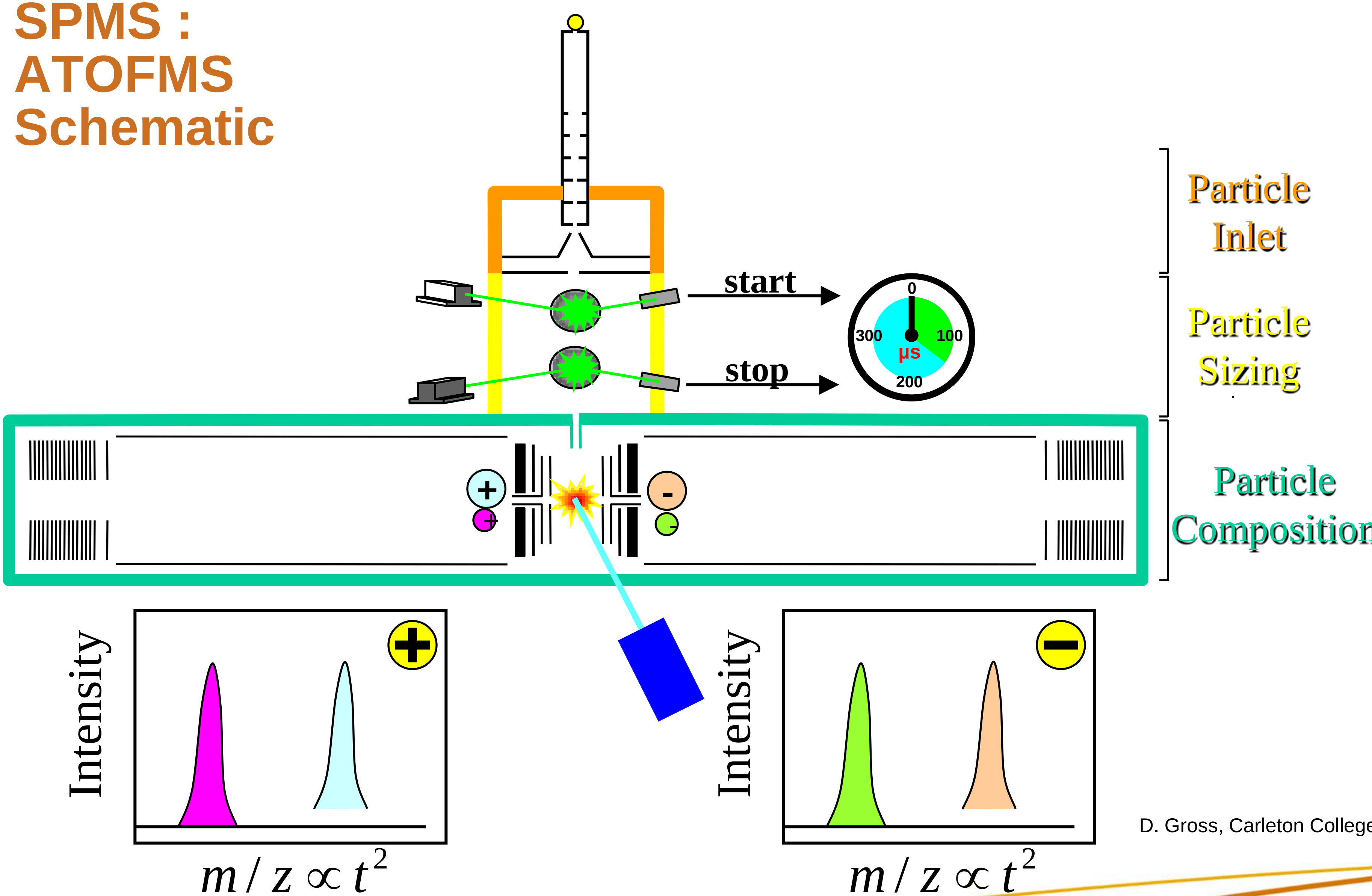


A Solution Matrix



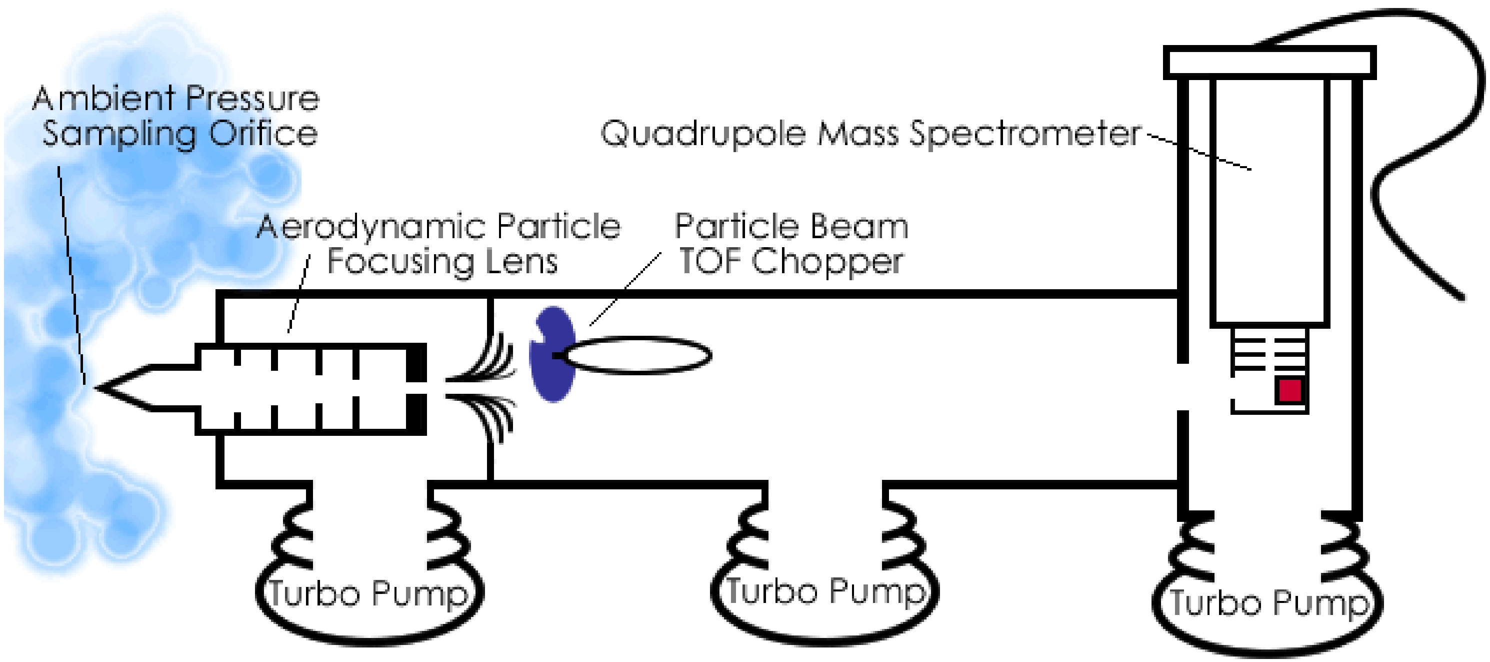
Courtesy of J. Jimenez

SPMS : ATOFMS Schematic



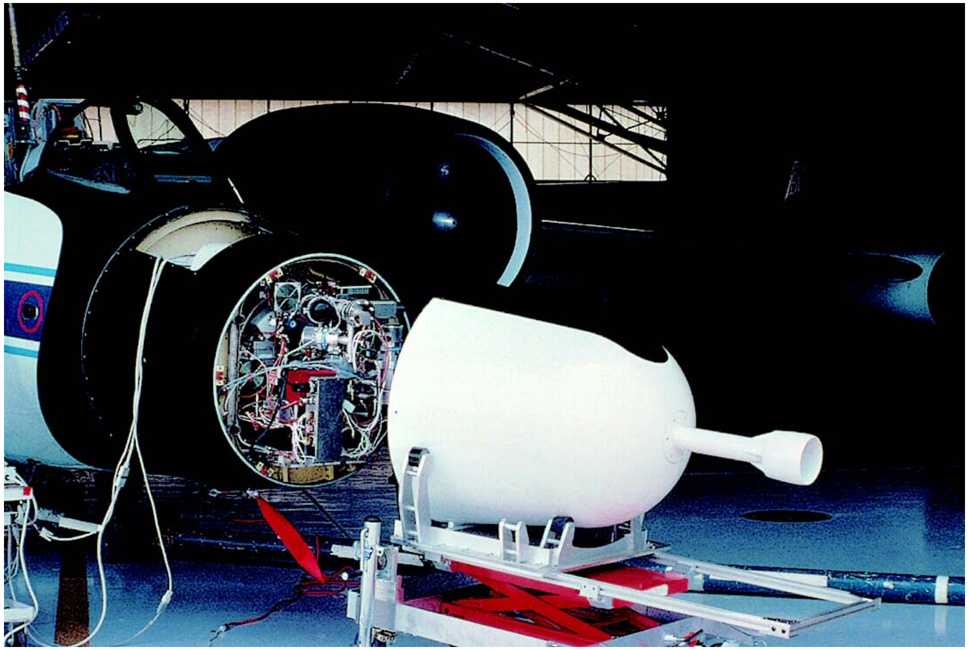
D. Gross, Carleton College

TD : AMS Schematic

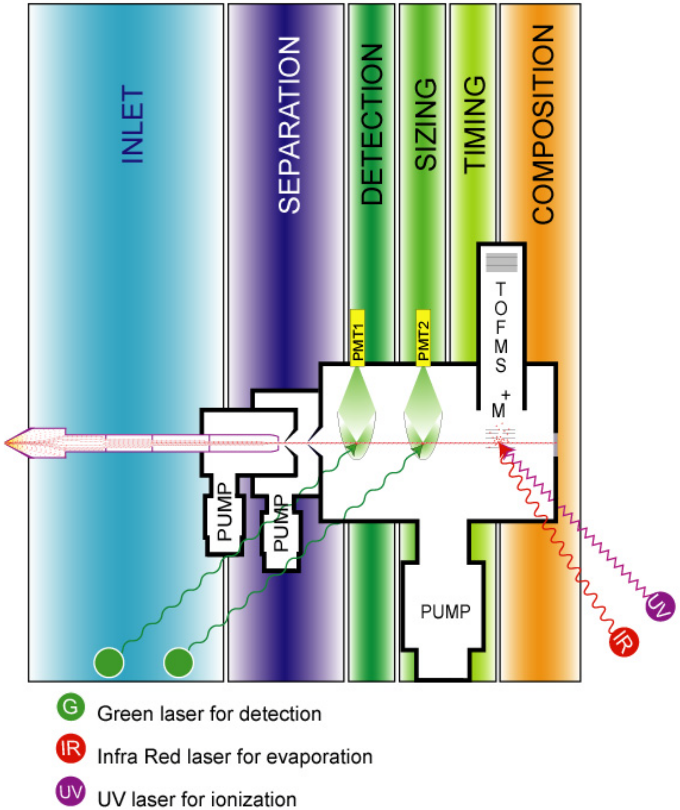


http://cires.colorado.edu/~jjose/ams.html

The Role of Custom Instruments…



‘PALMS’

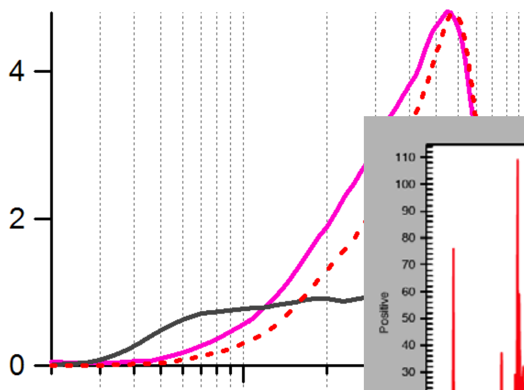


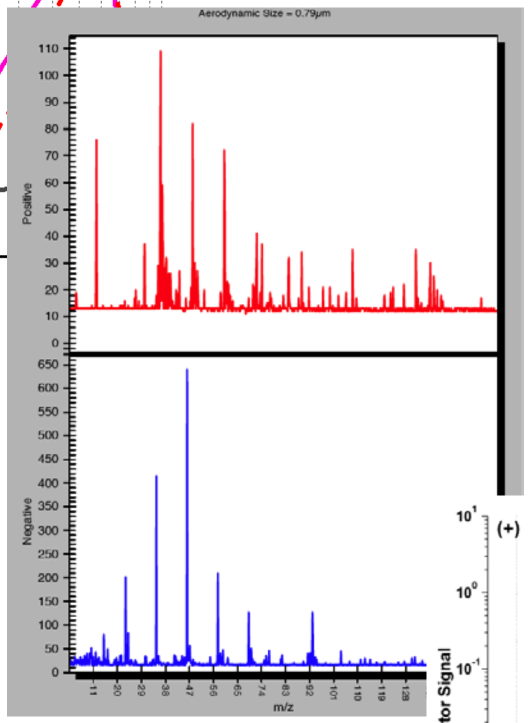
‘SPLAT’

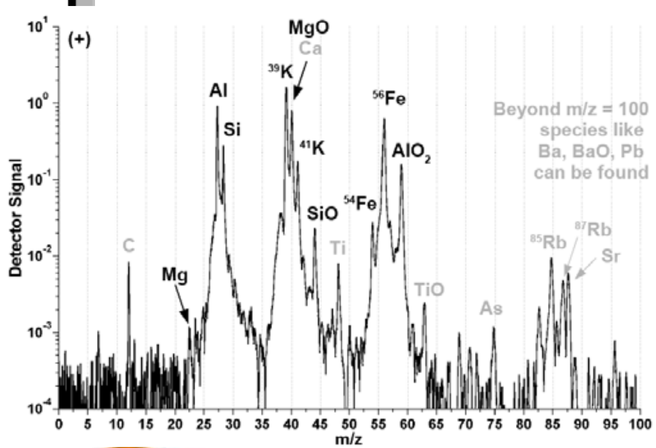
Side by Side Comparison

- Completed at ETH – Zurich, Fall 2007
- Model 3800 ATOFMS, PALMS 'lab' instrument, Aerodyne Q-AMS
- Sulfate (ammonium sulfate), organics (oleic, humic material, etc.) from aqueous solutions in custom atomizer
- Mineral dust from a custom powder disperser
- Soot from a Jing-Cast burner
- Size selection with DMA. Measurement of number (and mass) with SMPS

Data







-Detection and analysis frequency (SPMS)
-Mass loading (AMS)

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‘Sensitivity’ Matrix

	PALMS	ATOFMS	AMS
Ammonium Sulfate	x	low rate	efficiency
Organics	x	low rate	x
Soot	x	x	0
Mineral Dust	x*	x*	0

Notes :
*Except SiO_2
-‘Low rate’ reflects a lower analyzed vs. detected ‘hit rate’ for this material (<10% vs. 50%)
-‘Efficiency’ reflects a lower signal for this material (the ‘bounce’ phenomenon)
-Size not reflected here. AMS detected to ~70 nm but only at high (non-atmospheric) particle loads; PALMS ~200 nm; ATOFMS ~250. AMS due to lens and mass, SPMS due to optical.
-Opinion of group : PALMS required the most training; AMS software highly capable but required considerable training; ATOFMS operations and software simple.

What Can SMPS Do? Not Do?

- Sensitive at the single particle level
- Mass spectrum of entire particle is produced
- Depending on DI laser most atmospheric materials can be analyzed : includes mineral dusts and soot
- Dual polarity provides complementary information (e.g., mineral dust identification : Gallavardin et al., 2008)
- Not inherently quantitative ; need for a ‘pin’ and more research (Murphy et al., 2006)
- Must be clear about size dependence! Not ‘PM1’

What Can TD Do? Not Do?

- Sensitive to a suite of particles, single particles if large (or with new TOF detector – not used here)
- A single mass peak defined at a time (or new TOF detector)
- ‘Refractory’ material is not detected. Mixed materials (biomass) give *partial* signal. Temperature of impactor cup sets what is seen (normally not PSL or NaCl)
- Must also be clear about size dependence!
- Somewhat more quantitative ; TD also needs a ‘pin’ but some of this can be ‘assumed’ (CAUTION: complex behavior like ‘bounce’ and mixed refractory particles)

Conclusions

- SPMS and TD are *complementary*, not competitive, techniques!
- The mission planner must consider what is to be measured and which, if not both, techniques should be used (no AMS in a dust storm, no ATOFMS at a smog chamber, please).
- There is no perfect instrument. Every technique, including custom instruments, has strengths and weaknesses.
- The ease of use/purchase must be tempered with increased training and fundamental research.
- Let's not forget caveats and error bars!

Questions?

Discussion

Quantitation

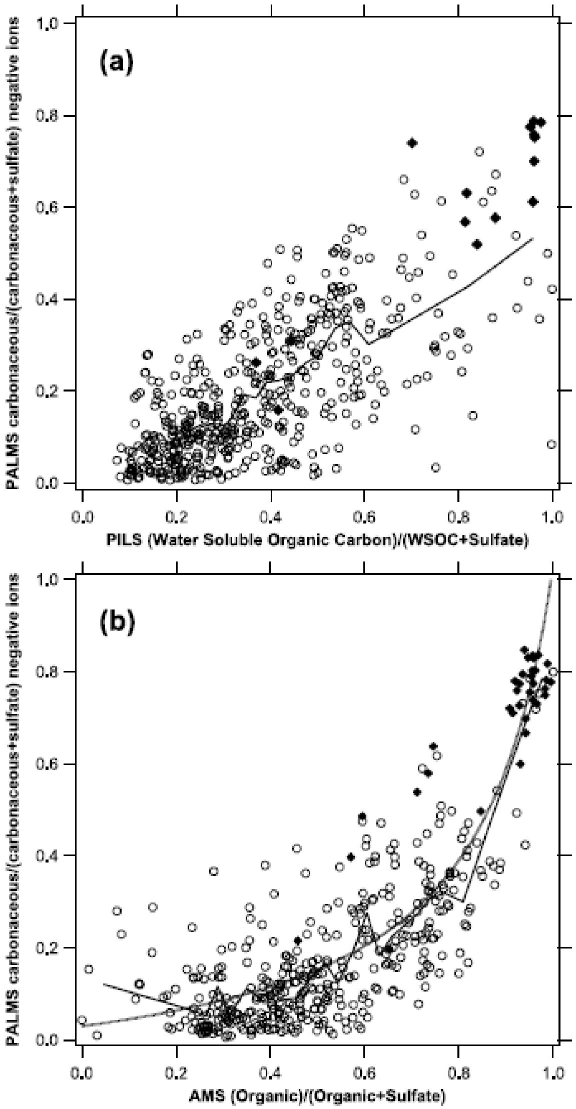

Figure 4. Comparisons of PALMS carbonaceous and sulfate ion fractions to (a) PILS and (b) AMS mass fractions during the 2004 P3 flights. Each point is an average of 300 mass spectra, or the spectra are averaged down to 25 bins (solid lines). Solid points are times when acetonitrile was greater than 300 ppb, indicating biomass burning influence. In an attempt to use comparable size cuts, PALMS mass spectra were not included for particles with aerodynamic diameters larger than 750 nm for the AMS comparison and 1 μm for the PILS comparison. Only times with organic plus sulfate loadings of greater than 1 μg m^{-3} for AMS or 0.5 μg m^{-3} for PILS were included. The dotted line in Figure 4b shows a smooth fit used in Figure 5.

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Single-particle mass spectrometry of tropospheric aerosol particles

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The Issue With Inlets

- Inlets based on the design of Liu et al. 1995. CFD simulations shows nearly 100% transmission efficiency in the range 70-500 nm, substantial transmission the 30-70 nm and 500 nm – 2.5 μm ranges for spherical particles. Irregularly shaped particles may have lower transmission.
- THIS IS NOT 'PM 1' !
- Every instrument has its own efficiency curve and we must make this clear (ATOFMS and PALMS dropped quickly below an optical threshold; AMS could only detect small particles if the mass loading was above threshold).