CHEM-5181
Graduate Course on
Mass Spectrometry & Chromatography

Aerosol Mass Spectrometry: Instrumentation & Applications

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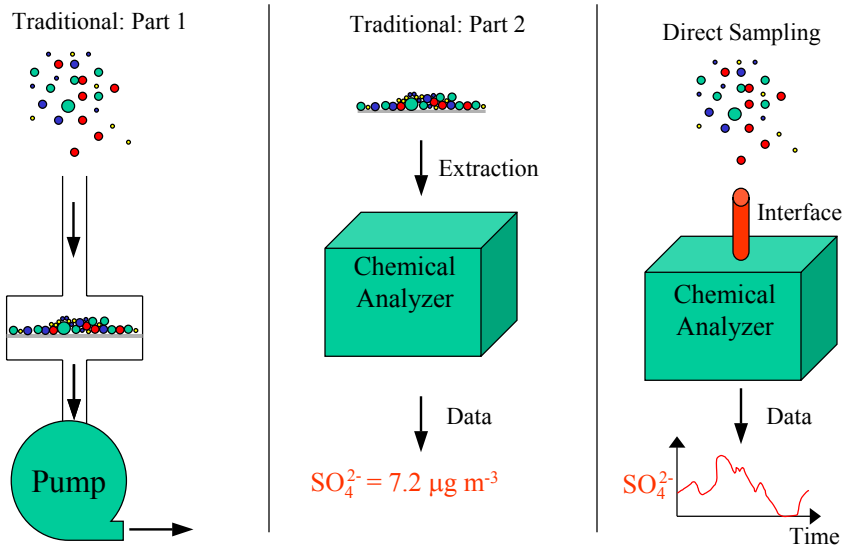
Outline

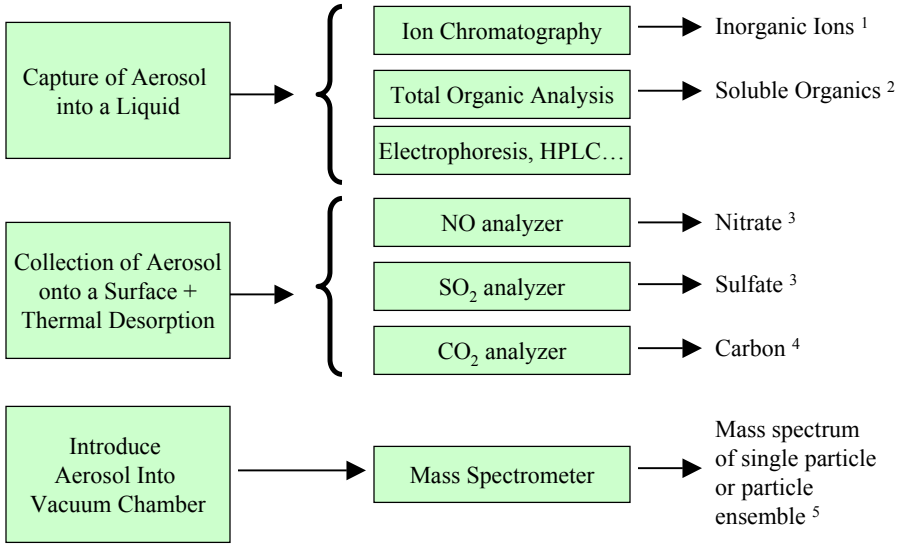
Introduction

1. Building Blocks
2. Implementations
3. Quantification
4. Applications
5. The Future

Aerosol Chemical Analysis



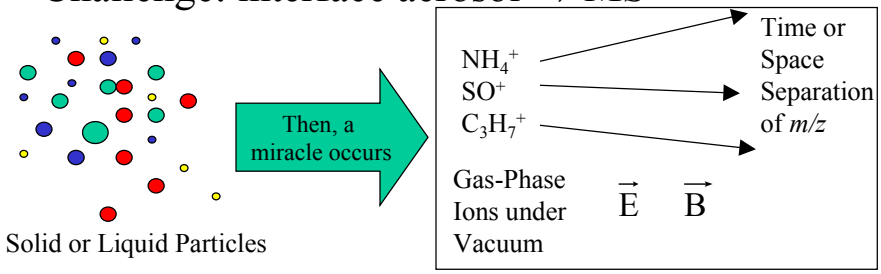
Real-Time Aerosol Chemistry Instruments



1: Dasgupta et al.; Weber et al; Slanina et al. // 2: Weber et al. // 3: Hering et al.; Edgerton et al; Koutrakis et al.; R&P Commercial Instrument // 4: Turpin et al; Hering et al. // 5: The rest of this talk.

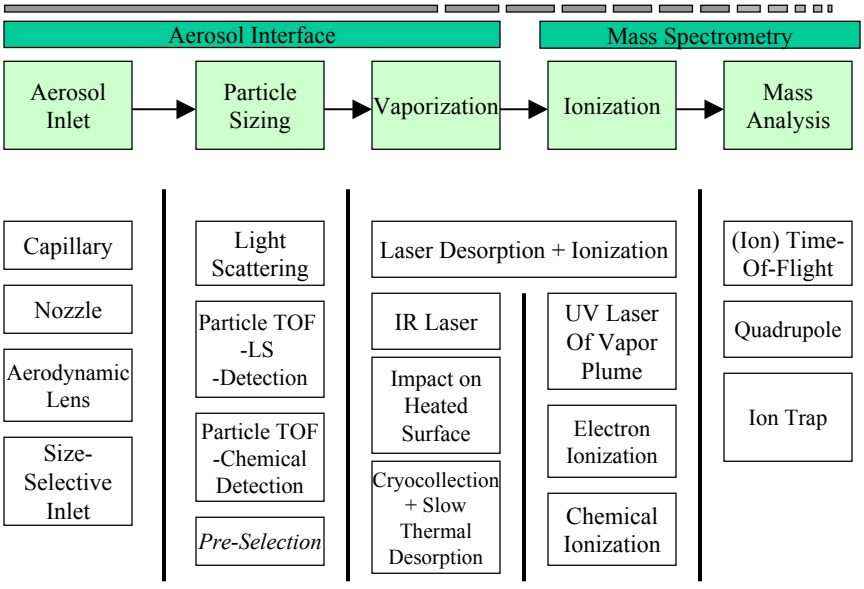
Why Aerosol Mass Spectrometry?

- Mass Spectrometry
  - Extreme sensitivity
  - Very fast response (down to ms)
  - Universal detection
  - Field deployable
- Challenge: interface aerosol → MS



Part 1: Instrumentation Building Blocks

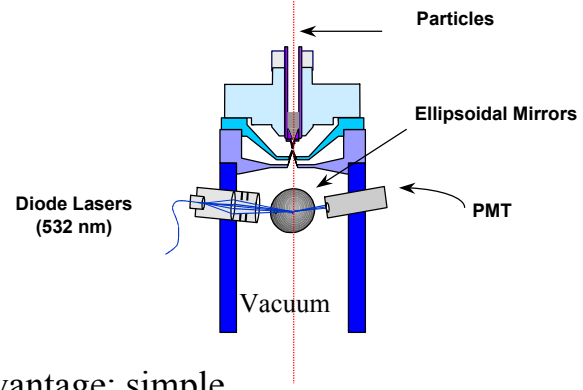
Conceptual Schematic of an Aerosol MS



Aerosol Inlets

- Objectives:
  - Introduce the particles into vacuum
  - Concentrate aerosols from gas-phase
    - ~10^{-8} mass ratio in ambient air
  - Impart size-dependent velocity
    - Use to measure size by particle time-of-flight

Aerosol Inlets: Nozzle



- Advantage: simple
- Disadvantages:
  - Somewhat finicky
  - Highly nonlinear (α D^3) transmission of particles vs. size

  (Number of detected particles is proportional to particle mass)

Aerodynamic Forces on a Particle

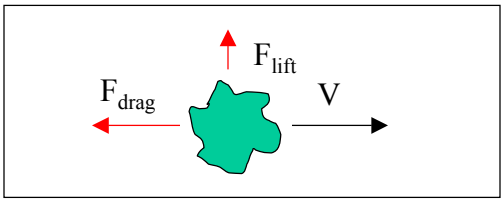
v: relative velocity between the gas and the particle

$F_{drag} \alpha d^2 v^2$

$F_{drag} = m a$

$m \alpha d^3$

$a \alpha d^{-1}$



Aerosol Inlets: Size-Selective Inlet

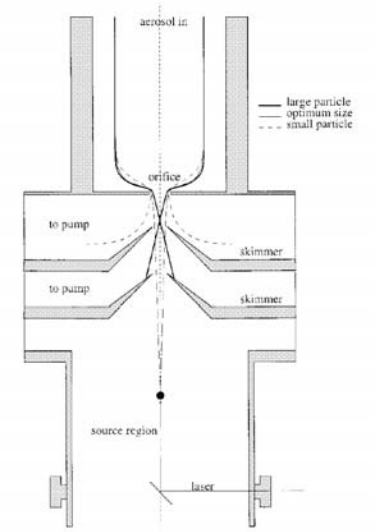


FIGURE 3. Working principle of a variable pressure inlet.

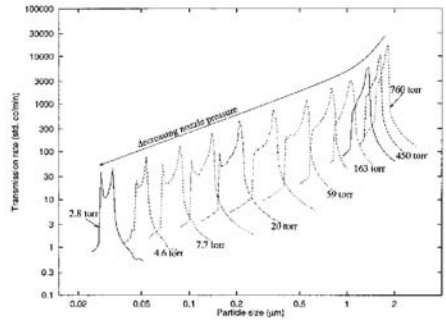


FIGURE 4. Transmission curves for the RSMS-II inlet for a 600 µm slice at 26 cm downstream of the orifice for various nozzle pressures.

Ramakrishna V.Mallina, Anthony S. Wexler, Kevin P. Rhoads, and Murray V. Johnston. High Speed Particle Beam Generation: A Dynamic Focusing Mechanism for Selecting Ultrafine Particles Aerosol Science and Technology 33:87-104, 2000.

Aerosol Inlets: Aerodynamic Lenses

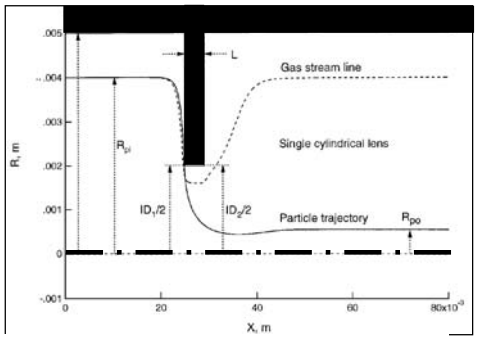


Figure 2. Schematic of a single thin cylindrical lens showing a gas streamline and the trajectory of a 500 nm particle. Q = 60 scc/min, L = 4 mm, $ID_1 = ID_2$ = 2 mm, OD = 10 mm, Re_0 = = 12.5, P_{up} = 280 Pa, R_{pi} = 4 mm, R_{po} = 0.5 mm.

Note: original lens design by Liu, Ziemann, and McMurry (1995).

Xuefeng Zhang, Kenneth A. Smith, Douglas R. Worsnop, Jose Jimenez, John T. Jayne, and Charles E. Kolb. A Numerical Characterization of Particle Beam Collimation by an Aerodynamic Lens-Nozzle System: Part I. An Individual Lens or Nozzle Aerosol Science and Technology 36: 617–631 (2002)

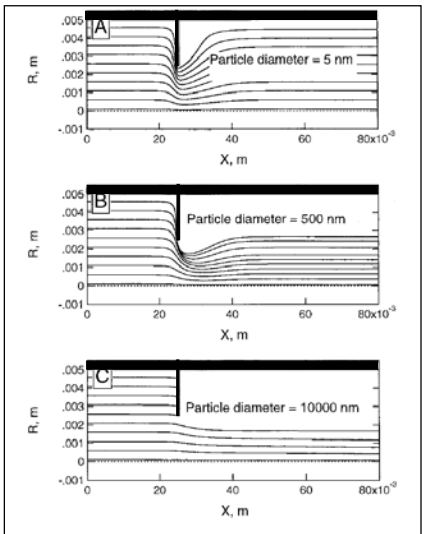
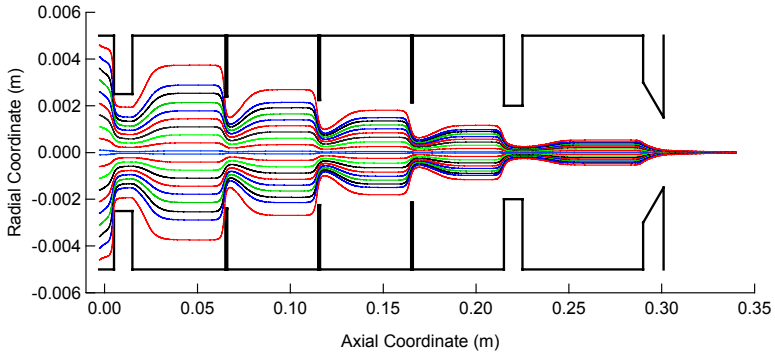


Figure 3. Particle trajectories through a single thin cylindrical lens (D_p = 5,500, 1000 nm). L = 0.5 mm, $ID_1 = ID_2$ = 5 mm, OD = 10 mm, Q = 60 scc/min, Re_0 = 12.5, and P_{up} = 280 Pa.

Aerodynamic Lenses



2.4 Torr inlet

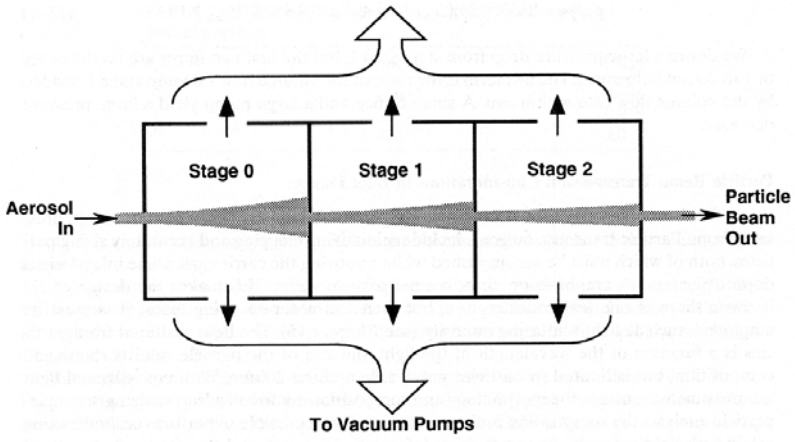
10^{-3} Torr Exit

Calculated Particle Trajectories, 100 nm Diameter Unit Density Spheres (Fluent ver 4.47)

Note: original lens design by Liu, Ziemann, and McMurry (1995).

Xuefeng Zhang, Kenneth A. Smith, Douglas R. Worsnop, Jose Jimenez, John T. Jayne, and Charles E. Kolb. A Numerical Characterization of Particle Beam Collimation by an Aerodynamic Lens-Nozzle System: Part II. An Integrated Lens-Nozzle System. Aerosol Science and Technology, submitted, (2002).

Differential Pumping of the Gas



Wexler, A. S., and Johnston, M. V. (2001). "Real-time single-particle analysis." Aerosol Measurement: Principles, Techniques, and Applications, P. A. Baron and K. Willeke, eds., Wiley-Interscience, New York, 365-386.

Shape Effects on Aerodynamic Lenses

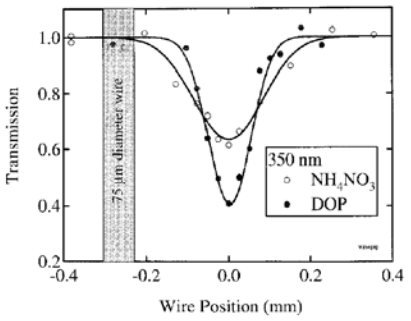


FIGURE 11. Particle beam width measurement for spherical DOP and nonspherical NH_4NO_3 particles. Beam widths are determined by passing a 75 μm diameter wire across the particle beam path and calculating particle transmission from the ratio of the single particle count rates measured by the mass spectrometer to the count rates measured by the CPC. Beam broadening is observed for nonspherical particles. The solid lines represent a Gaussian fit to the inverted data yielding FWHM values of 0.13 mm for DOP and 0.23 mm for NH_4NO_3.

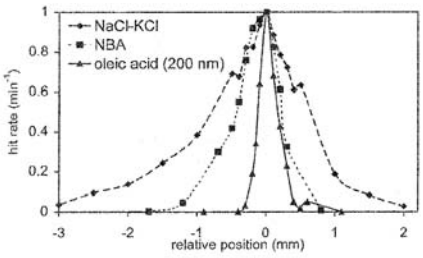


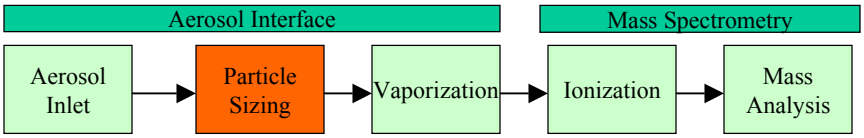
Figure 2. Particle beam profile measurements for NaCl-KCl, NBA, and oleic acid aerosols. NaCl-KCl and NBA aerosols are polydisperse with the average diameter of the detected particles approximately 85 nm. The oleic acid aerosol is monodisperse with a diameter of 200 nm.

This effect can bias the detection of all instruments against irregularly shaped particles. The smaller the solid angle of collection, the worse the bias. In general laser instruments will be more affected because of the need to focus the laser very tightly on the center of the particle beam.

• Jayne, J.T., D.C. Leard, X. Zhang, P. Davidovits, K.A. Smith, C.E. Kolb, and D.R. Worsnop, Development of an aerosol mass spectrometer for size and composition. analysis of submicron particles, Aerosol Sci. Technol., 33, 49-70, 2000.

• David B. Kane, Berk Oktem, and Murray V. Johnston. Nanoparticle Detection by Aerosol Mass Spectrometry. Aerosol Science and Technology 34: 520–527 (2001)

Conceptual Schematic of an Aerosol MS



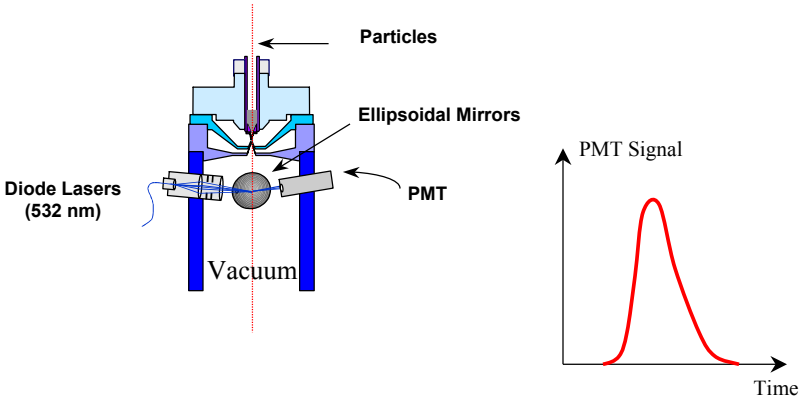
Light Scattering

Particle TOF -LS -Detection

Particle TOF -Chemical Detection

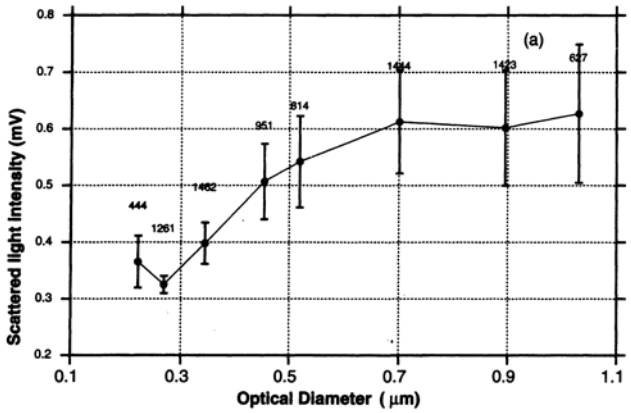
Pre-Selection

Particle Sizing: Light Scattering



- Principle: Intensity of light scattering increases with particle size

Particle Sizing: Light Scattering Intensity

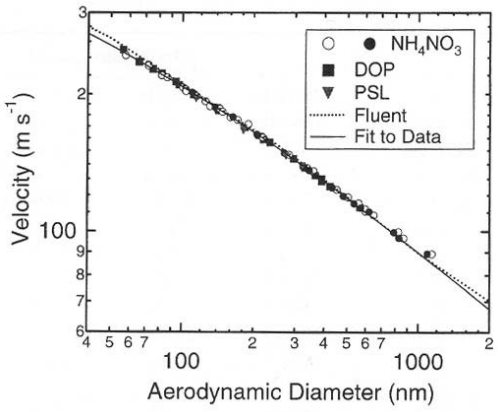


- Disadvantage: low resolution & dependence on optical properties

Shan-Hu Lee, Daniel Murphy, David S. Thomson, and Ann M. Middlebrook. Chemical Components of Single Particles Measured with Particle Analysis by Laser Mass Spectrometry (PALMS) during the Atlanta Supersite Project: Focus on Organic/Sulfate, Lead, Soot, and Mineral Particles. Journal of Geophysical Research, Vol. 107, D1, 10.1029/2000JD000011, 2002.

Size-Dependent Velocity

- Upon expansion into vacuum, particles acquire size-dependent velocity
- It's there, so you may as well use it to measure particle size



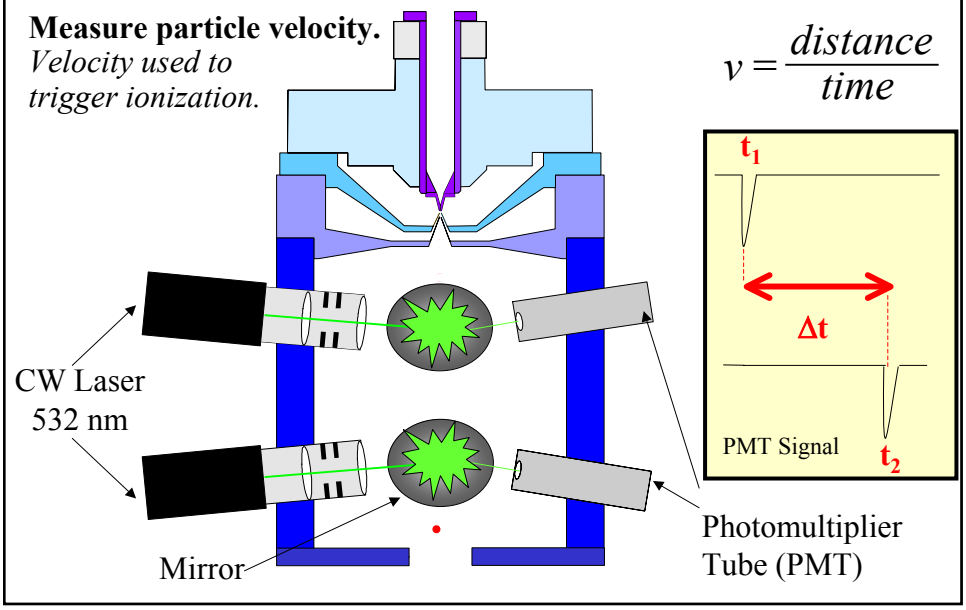
Jayne, J.T., D.C. Leard, X. Zhang, P. Davidovits, K.A. Smith, C.E. Kolb, and D.R. Worsnop, Development of an aerosol mass spectrometer for size and composition. analysis of submicron particles, Aerosol Sci. Technol., 33, 49-70, 2000.

Deborah Gross
Carleton College

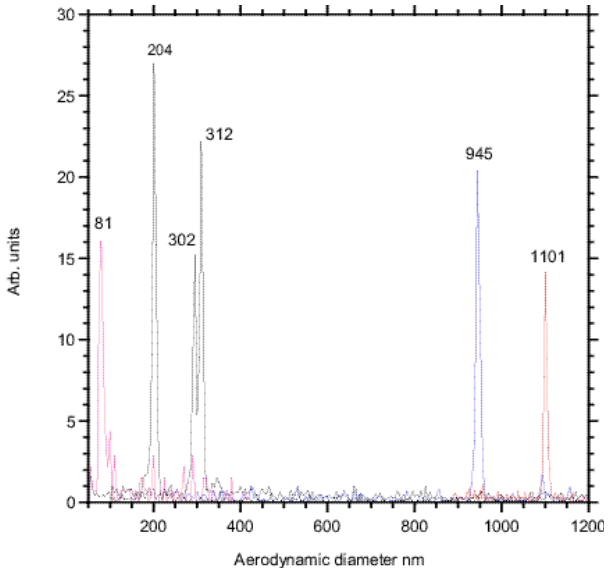
Particle TOF with LS Detection

Measure particle velocity.
Velocity used to trigger ionization.

$$v = \frac{distance}{time}$$



Two-Laser TOF: Resolution

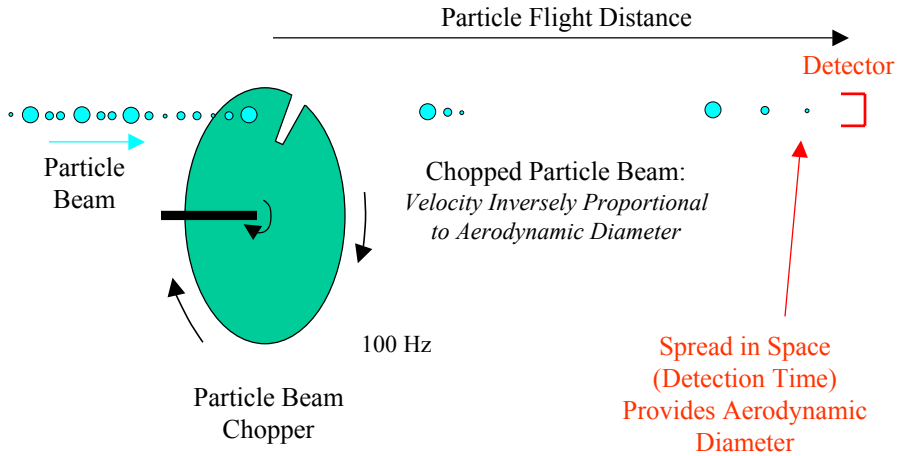


- Very high size resolution

  $R = D/\Delta D \sim 30$

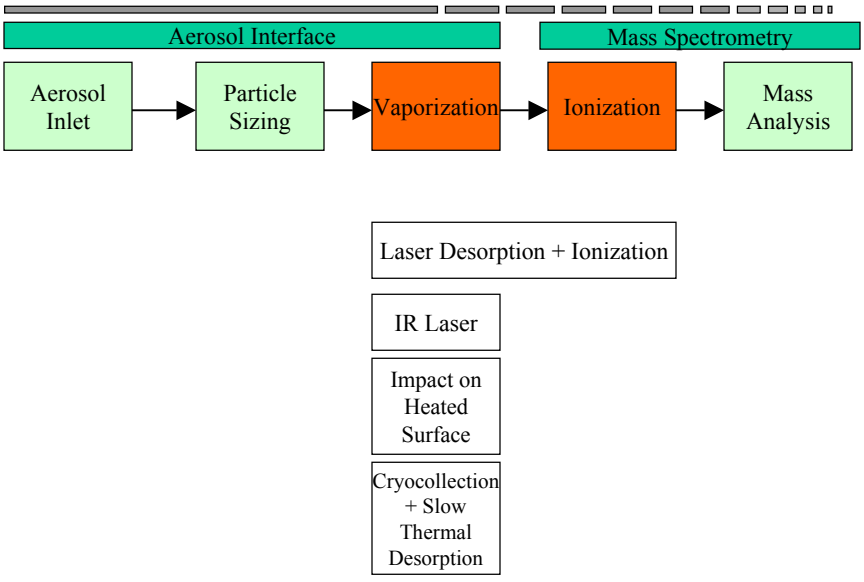
Courtesy of Dan Imre, Brookhaven National Lab, 2000.

Particle TOF with MS Detection



Jayne, J.T., D.C. Leard, X. Zhang, P. Davidovits, K.A. Smith, C.E. Kolb, and D.R. Worsnop, Development of an aerosol mass spectrometer for size and composition. analysis of submicron particles, Aerosol Sci. Technol., 33, 49-70, 2000.

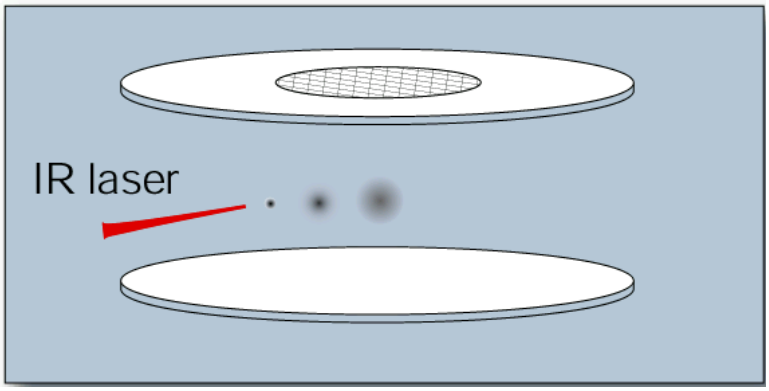
Conceptual Schematic of an Aerosol MS



Vaporization Objectives

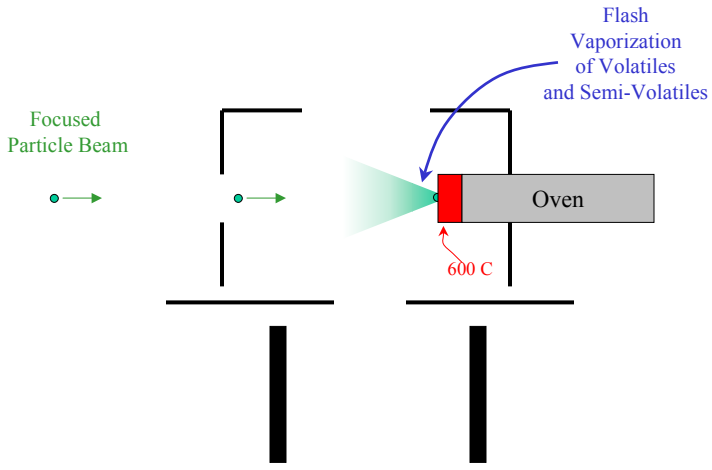
- Desorption + ionization
  - Simpler
- Two steps
  - Vaporization
  - Later Ionization
  - Easier to quantify mass (below)
  - Tradeoff:
    - some labile species will decompose if heating fast
    - refractory material (sea salt, dust…) will not evaporate unless at very high T

Vaporization: Infrared Laser

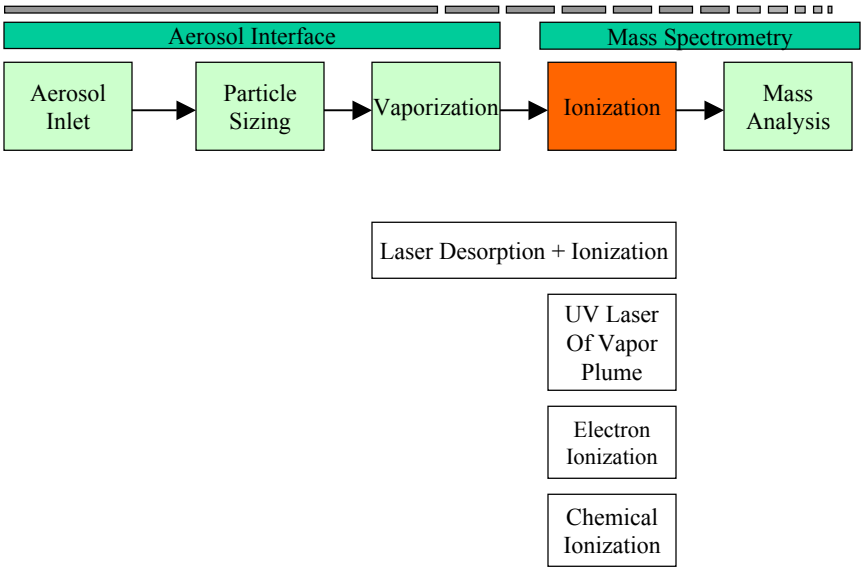


Courtesy of Tomas Baer, University of North Carolina, 2002.

Vaporization: Heated Surface



Conceptual Schematic of an Aerosol MS



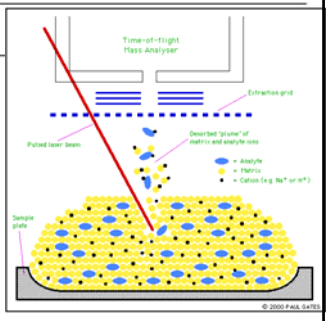
Ionization Objectives

- Produce ions from solid (LDI) or gas-phase neutral molecules
- Desirable properties
  - High efficiency (ions / molecule)
  - Number of ions linear with number of molecules
  - Universality / Selectivity
  - Fragmentation
    - Good and bad

LDI: Ion Formation Mechanisms

TABLE 6. Mechanistic Summary: Primary and secondary ionization mechanisms discussed in the text, and their activities in different forms of MALDI.

	UV MALDI		
	P+	NP+	P−
Primary			
MPI	●	●	●
Pooling	●●	●●	●●
ESPT	?		??
Disproportionation	??		??
Performed	●●	●	●
Thermal			
Spallation			
Secondary			
H^+ Transfer	●●		●●
e^- Capture & H^+ Transfer			●●
Cationization	●●	●●	
e^- Transfer	●	●	??
Ejection	●		●

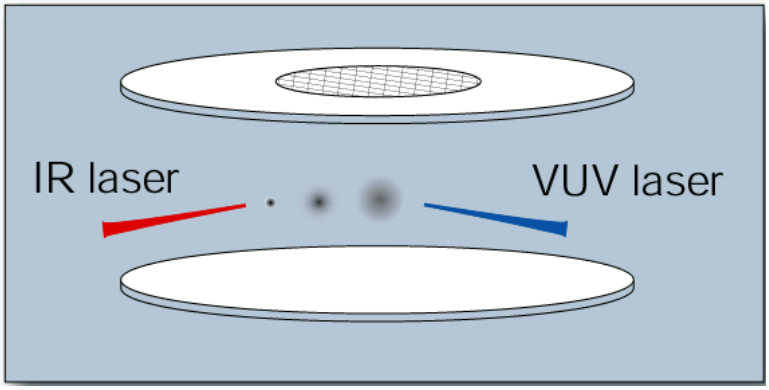


UV = ultraviolet excitation, IR = infrared excitation. Polarity of observed ions is indicated by + or −. P = polar analytes, NP = non-polar analytes. ●● = probably highly active, or active in many cases; ● = probably active, or active in some cases; ? = possibly sometimes active; ?? = possibly active, but not well-studied. No entry indicates probable lack of activity. MPI = multiphoton ionization, ESPT = excited-state proton transfer. Due to relative lack of experimental data, the UV NP− and IR− categories are not included, although the conclusions for IR+ may carry over to IR− with little change.

Sensitivity = f(matrix, analyte, concentration,…)

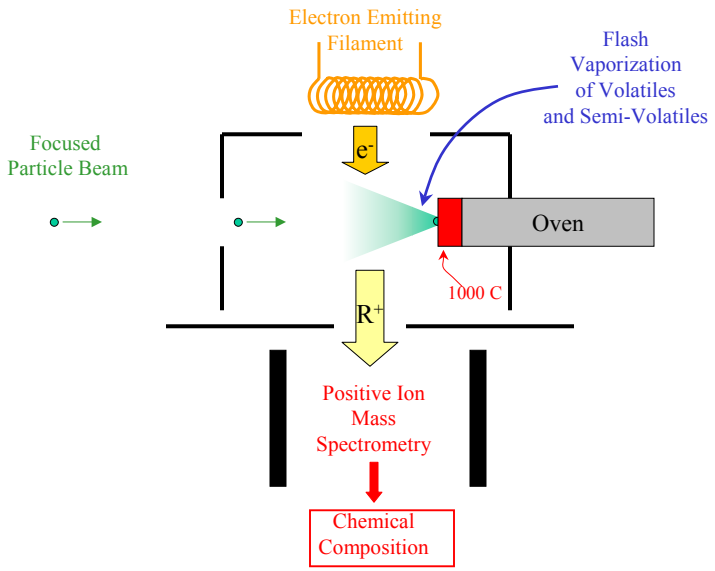
Renato Zenobi, and Richard Knochenmuss. Ion Formation in MALDI Mass Spectrometry. Mass Spectrometry Reviews, 1998, 17, 337-366.

Ionization: UV Laser Ionization of Vapor Plume



Courtesy of Tomas Baer, University of North Carolina, 2002.

Ionization: Electron Impact



Ionization: Chemical

- Charge exchange: $M + Ar^+ \rightarrow M^{+\cdot} + Ar$
- Electron capture: $M + e^- \rightarrow M^{-\cdot}$
- Proton transfer: $M + CH_5^+ \rightarrow (M+H)^+ + CH_4$
- Adduct formation: $M + TiCl_2^+ \rightarrow (M+TiCl_2)^+$

- Need Collisions!
  - $\lambda < 0.1$ mm ($P > 0.6$ mbar)
  - Sometimes at 1 atm (AP-CI)

Efficiency of Ion-Molecule Reactions

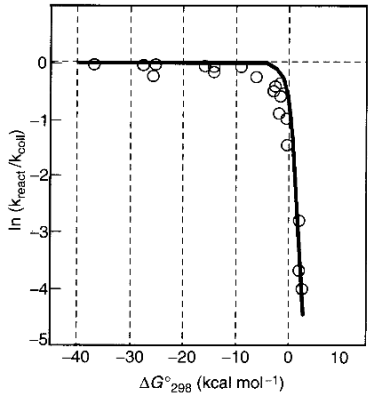
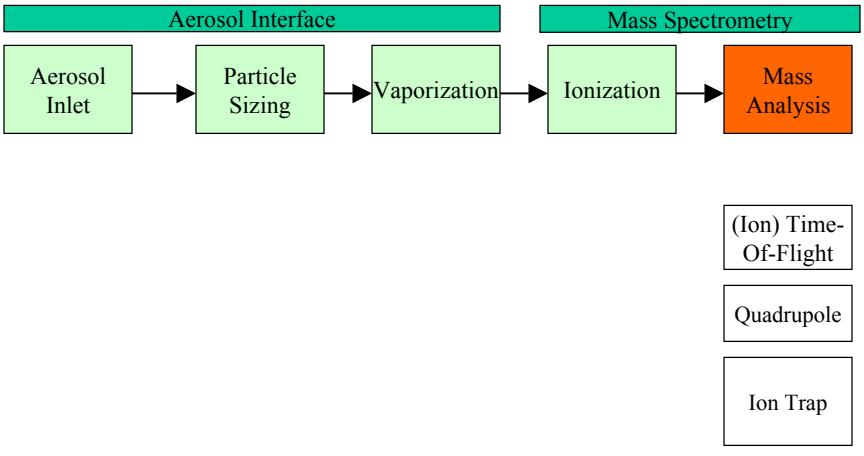


Figure 1.38
The natural logarithm of the number of reactions per collision ratio indicates that the proton transfer is almost 100% efficient when the process is exergonic. When it becomes endergonic, the efficiency drops sharply. (Reproduced (modified) from Ref. 77 with permission)

- Approx. every collision leads to a proton transfer, if $\Delta G^0 < 0$

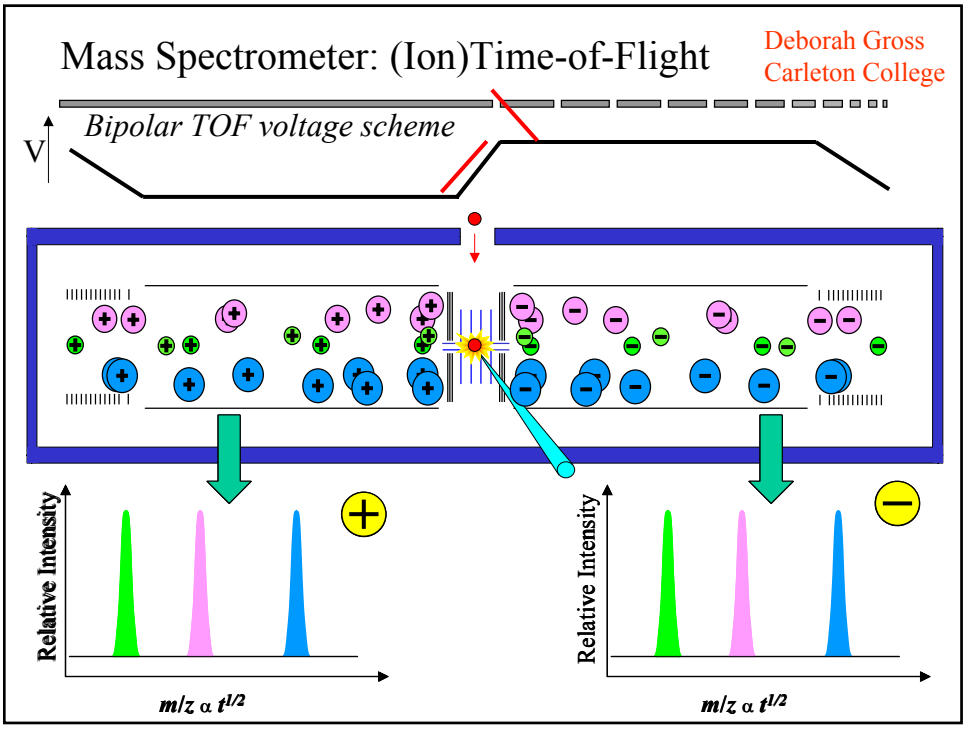
Edmon de Hoffmann and Vincent Stroobant. Mass Spectrometry: Principles and Applications. John Wiley & Sons, 2002.

Conceptual Schematic of an Aerosol MS

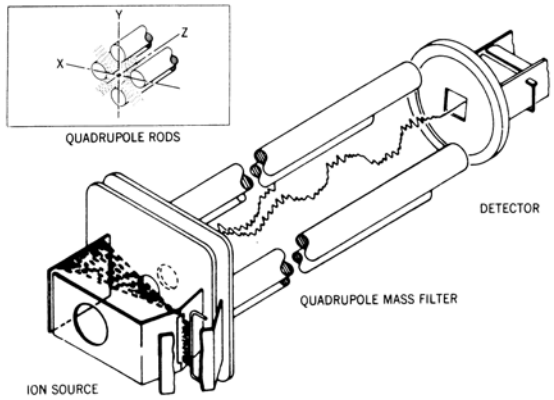


Mass Spectrometer

- Use electrical and/or magnetic forces to separate ions according to *m/z*
- In aerosol mass spectrometers
  - (Ion) Time-of-Flight
  - Quadrupole
  - Ion Trap
  - (Electric fields only!)
- Not used so far in Aerosol MS
  - Magnetic sector
  - Fourier Transform – Ion Cyclotron Resonance
  - Use magnetic fields



Mass Spectrometer: Quadrupole



J. Throck Watson: Introduction to Mass Spectrometry. Lippincott-Raven, 1997.

FIG. 4.7. Schematic diagram of quadrupole mass spectrometer illustrating irregular flight path of ions from the ion source through the central space between the quadrupole rods to the detector. (Courtesy of Finnigan Corporation.)

- Advantage: simple, rugged, lightweight
- Disadvantage: only one *m/z* at a time

Mass Spectrometer: Ion Trap

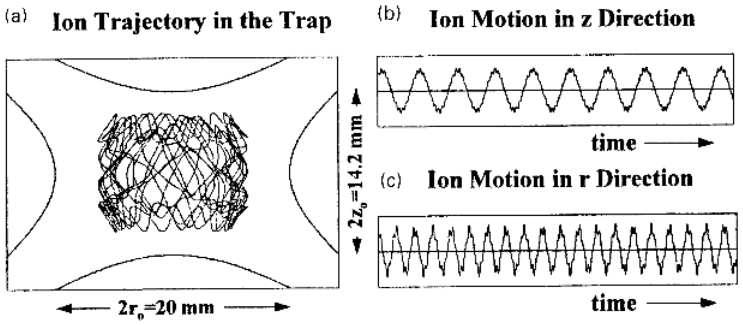
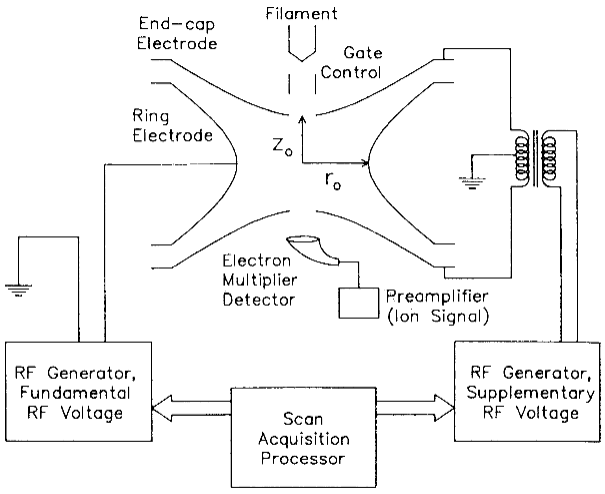


Figure 13-24 Simulation of motion of a single trapped ion in an ion trap: (a) shows the overall motion within the trap in cross section, (b) shows the time-dependent component of motion in the axial direction, and (c) shows the radial-direction component.

J.B. Lambert, H.F. Shurvell, D.A. Lightner, R. G. Cooks, Organic Structural Spectroscopy. Prentice-Hall, 2002.

Mass Spectrometer: Ion Trap II



J. Throck Watson: Introduction to Mass Spectrometry. Lippincott-Raven, 1997.

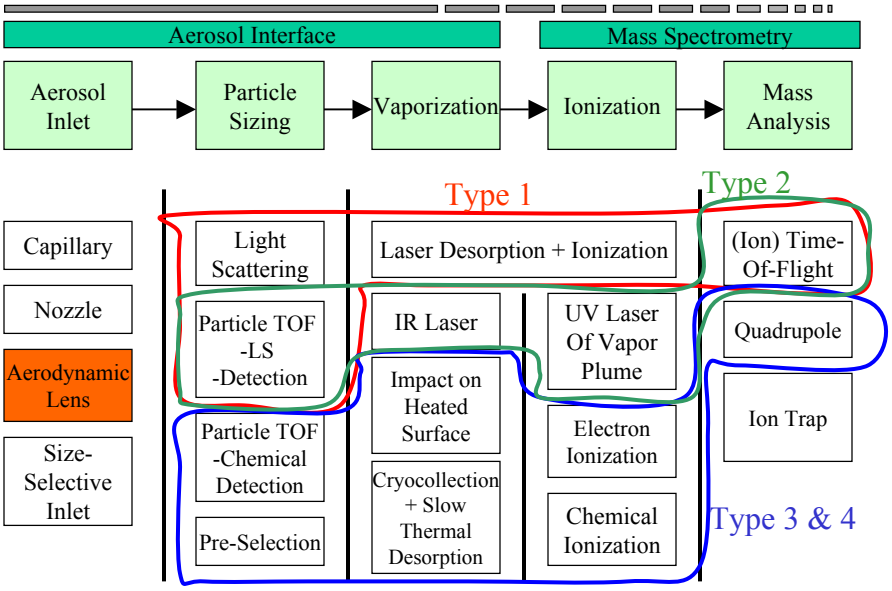
FIG. 4.10. Schematic diagram of ion-trap mass spectrometer.

Part 2: Instrumentation Implementations

Types of Implementations

- All combinations: 480 implementations
  - In practice only ~25 have been used
- Type 1: Laser-Desorption Ionization
  - Most attempted by research groups
  - Many variations
- Type 2: Two-Laser Systems
- Type 3: Thermal Vaporization + Electron Ionization
- Type 4: Thermal Vaporization + Chemical Ionization

Implementations: "Clusters" of Designs



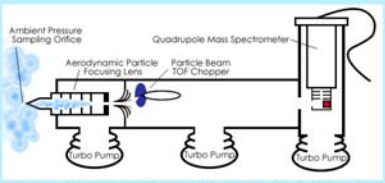
http://cires.colorado.edu/~jjose/ams.html

Aerosol Mass Spectrometry Web Page - Microsoft Internet Explorer

File Edit View Favorites Tools Help

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

Aerosol Mass Spectrometry Web Page



Animation of the Aerodyne AMS. Credit: Matt Thyson (Lexington, Massachusetts)

This page is maintained by Jose L. Jimenez. Email me at jose.jimenez@colorado.edu if you have any questions, corrections, and/or items that you would like to me add to these pages

1. Introduction
2. Research Groups Involved in the Development and/or Application of the AMS
3. Other Aerosol Mass Spectrometers Based on Thermal (Non-Laser) Vaporization
4. Aerosol Mass Spectrometers Based on Laser Vaporization
5. AMS User's Meetings
6. AMS Pictures
7. Journal Papers about the AMS and its Application
8. Conference Presentations about the AMS and its Application
9. Resources for AMS Users
10. General Aerosol Resources

1. Introduction

This page contains information and links related to aerosol mass spectrometry. There is information about all types of on-line aerosol mass spectrometers.There is comparatively more information on the Aerosol Mass Spectrometer (AMS) developed at Aerodyne Research, Inc, basically because I know more about that system, since I was heavily involved in its development, and I have been able to compile more information about it.

News: The American Association for Aerosol Research (AAAR) has asked me to give a 2-hour tutorial lecture on Aerosol Mass Spectrometry (covering real-time systems, both laser and non-laser based) at their 2002 Annual Meeting. I obviously highly recommend this tutorial ;-) (as well as several other tutorials). It is scheduled for Monday, Oct. 7, 2002, and can be attended by anyone who is at the AAAR conference for a nominal fee (~$80)

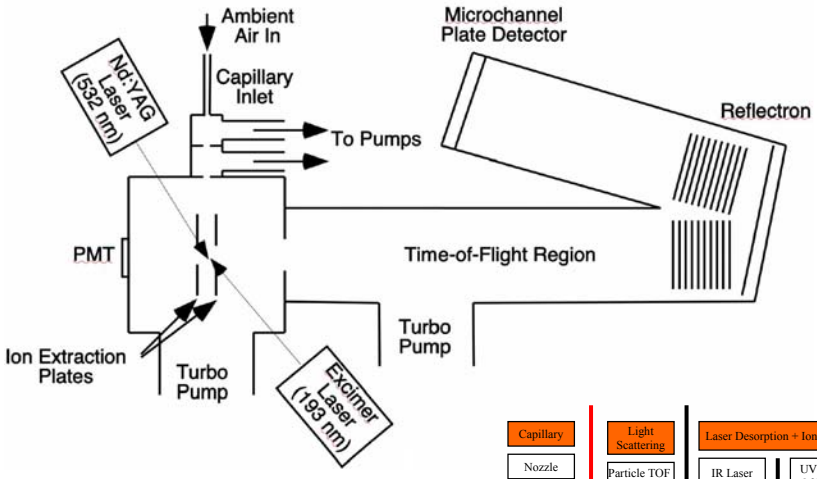
t1 and t2 implementations (Laser-Based)

Most are customized for a problem!

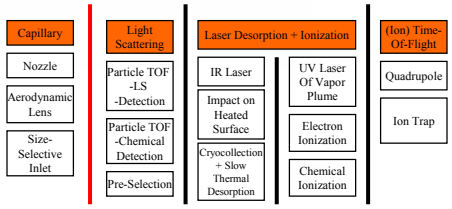
10. Aerosol Mass Spectrometers Based on Laser

Instrument	Principal Investigator	De		
PALMS	Dan Murphy (Papers)			
Aerosol Time of Flight Mass Spectrometer (ATOFMS)	Prof. Kim Prather	Department of Chemistry	University of California at San Diego	
Commercial version of the ATOFMS	Markus Galli		TSI, Inc.	St. Paul, Minnesota
RSMS	Murray Johnston & Tony Wexler	Department of Chemistry & Department of Mechanical Engineering	University of Delaware & University of California, Davis	
Single Particle Laser Ablation Time-of-Flight Mass Spectrometer (SPLAT-MS)	Dan Imre and Alla Zelenyuk	Atmospheric Chemistry Division	Brookhaven National Lab	Brookhaven, New York
Single Particle Laser Ablation Time-of-Flight Mass Spectrometer (SPLAT)	Stephan Borrmann	Cloud Physics and Chemistry	Max Plank Institute for Chemistry, Johannes Gutenberg-University Mainz, & Research Center Juelich	Mainz, Germany
Particle Blaster	Bill Reents		Bell Labs	Murray Hill, New Jersey
Single Particle Mass Spectrometer	Tomas Baer & Roger Miller	Department of Chemistry	University of North Carolina at Chapel Hill	Chapel Hill, North Carolina
Single Particle Mass Spectrometer (SPMS)	Michael Zachariah	Department of Chemical Engineering	University of Minnesota	Minneapolis, Minnesota
Laser Ablation Mass Spectrometer (LAMS)	Greg Evans		University of Toronto	Toronto, Canada
Single Particle Mass Spectrometer	Bernhard Spengler	Institute for Inorganic and Analytical Chemistry	University of Giessen	Giessen, Germany
Real-Time Mass Spectrometer	Peter Reilly	Chemical Sciences Division	Oak Ridge National Laboratory	Oak Ridge, Tennesee
Single Particle Mass Spectrometer	Denis Phares	Department of Mechanical Engineering	Texas A&M University	College Station, Texas
Aerosol Mass Spectrometer	Joe Petrucci	Department of Chemistry	University of Vermont	Burlington, Vermont
TSI 3800 (Commercial Instrument)	Deborah Gross	Department of Chemistry	Carleton College	Minnesotta
TSI 3800 (Commercial Instrument)	Eric Gard		Lawrence Livermore National Lab	Livermore, California

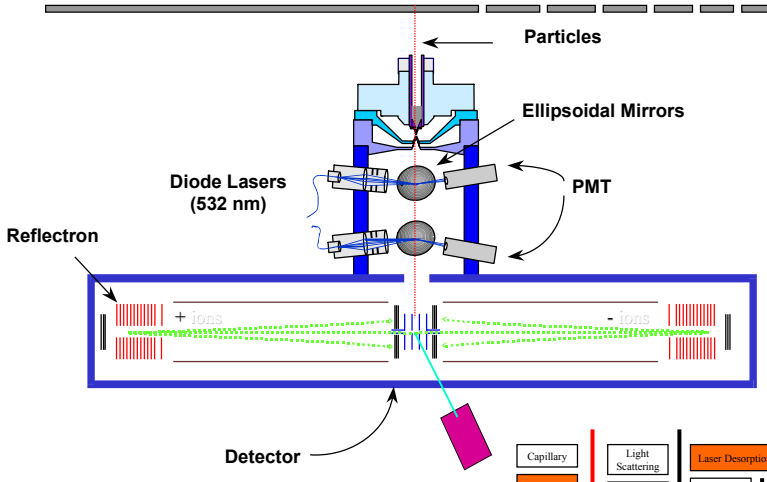
Type 1: PALMS (Murphy *et al.*)



Middlebrook, A., Murphy, D.M., Lee, S.-H., Thomson, D.S., Prather, K. A., Wenzel, R. J., Liu, D.-Y., Phares, D.J., Rhoads, K.P., Wexler, A. S., Johnston, M.V., Jimenez, J.L., Jayne, J.T., Worsnop, D.R., Yourshaw, I., Seinfeld, J.H., and Flagan, R.C. An intercomparison of Particle Mass Spectrometers During the 1999 Atlanta Supersite Project. Journal of Geophysical Research-Atmospheres, in press, 2002.

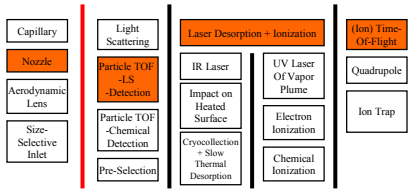


Type 1: ATOFMS (Prather *et al.*)

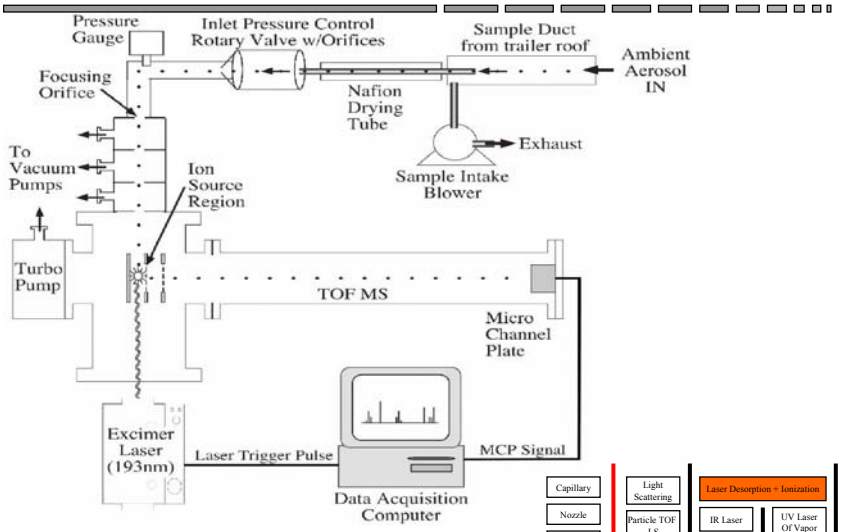


AAAR'02: Tue & Thu: PI1-02

Courtesy of Prof. Kim Prather



Type 1: RSMS (Johnston, Wexler *et al.*)



Middlebrook, A., Murphy, D.M., Lee, S.-H., Thomson, D.S., Prather, K. A., Wenzel, R. J., Liu, D.-Y., Phares, D.J., Rhoads, K.P., Wexler, A. S., Johnston, M.V., Jimenez, J.L., Jayne, J.T., Worsnop, D.R., Yourshaw, I., Seinfeld, J.H., and Flagan, R.C. An intercomparison of Particle Mass Spectrometers During the 1999 Atlanta Supersite Project. Journal of Geophysical Research-Atmospheres, in press, 2002.

Comparison of 3 Type-1 Systems

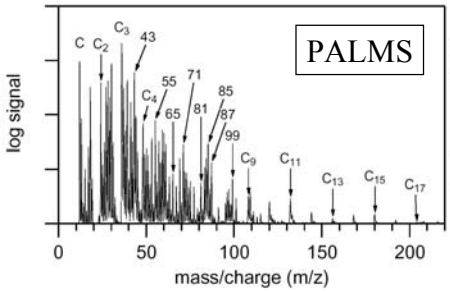
Table 1. Main Design Characteristics of the Four Particle Mass Spectrometers

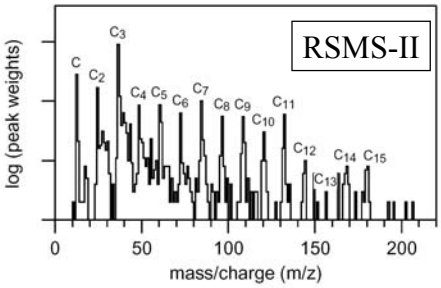
	particle detection/ sizing	aerodynamic size range (µm)	volatilization/ ionization method	mass spectrometer	single-particle classification methods
PALMS	light scattering	0.35[a]-2.5	LDI[b] $\lambda = 193$ nm $2\text{-}5 \times 10^9$ W/cm^2	single time of flight reflectron	peak ID[c]/ regression tree analysis
ATOFMS	aerosol time of flight	> 0.2	LDI[b] $\lambda = 266$ nm $\sim 10^8$ W/cm^2	dual time of flight reflectron	peak ID[c]/ artificial neural network
RSMS-II	aero-dynamic focussing	0.015-1.3	LDI[b] $\lambda = 193$ nm $1\text{-}2 \times 10^8$ W/cm^2	single linear time of flight	peak ID[c]/ artificial neural network
AMS	aerosol time of flight	0.05-2.5	T ~ 550 ºC with electron impact	quadrupole	not applicable

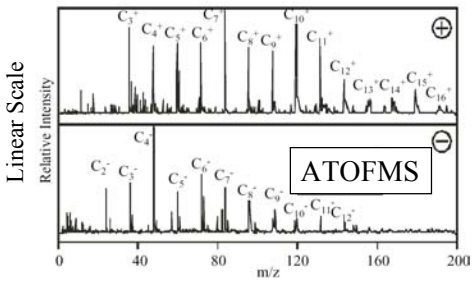
[a] PALMS' optical lower limit (0.22 µm) was converted into aerodynamic diameter, d_a, by assuming the optical diameter equals the Stoke's diameter, d_s, and $d_a = d_s \times \text{sqrt}(\rho_p C_c/\rho_0)$, where ρ_p is the particle bulk density = 1.5 g cm^{-3} (P. H. McMurry, personal communication), C_c is the Cunningham correction factor = 1.74 for d = 0.22 µm, and ρ_0 is the standard density = 1 g cm^{-3} [*Hinds*, 1982].
[b] LDI = laser desorption/ionization
[c] ID = identification

Middlebrook, A., Murphy, D.M., Lee, S.-H., Thomson, D.S., Prather, K. A., Wenzel, R. J., Liu, D.-Y., Phares, D.J., Rhoads, K.P., Wexler, A. S., Johnston, M.V., Jimenez, J.L., Jayne, J.T., Worsnop, D.R., Yourshaw, I., Seinfeld, J.H., and Flagan, R.C. An intercomparison of Particle Mass Spectrometers During the 1999 Atlanta Supersite Project. Journal of Geophysical Research-Atmospheres, in press, 2002.

Type 1: Soot/Hydrocarbon Single Particles

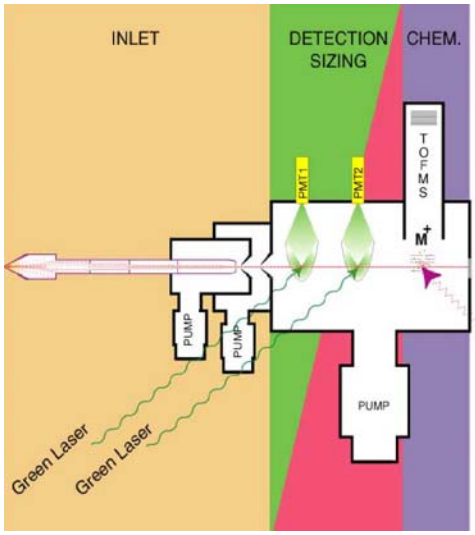


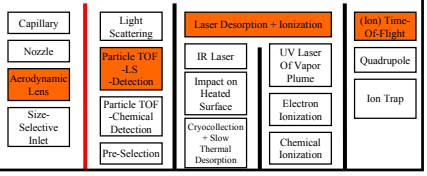




Middlebrook, A., Murphy, D.M., Lee, S.-H., Thomson, D.S., Prather, K. A., Wenzel, R. J., Liu, D.-Y., Phares, D.J., Rhoads, K.P., Wexler, A. S., Johnston, M.V., Jimenez, J.L., Jayne, J.T., Worsnop, D.R., Yourshaw, I., Seinfeld, J.H., and Flagan, R.C. An intercomparison of Particle Mass Spectrometers During the 1999 Atlanta Supersite Project. Journal of Geophysical Research-Atmospheres, in press, 2002.

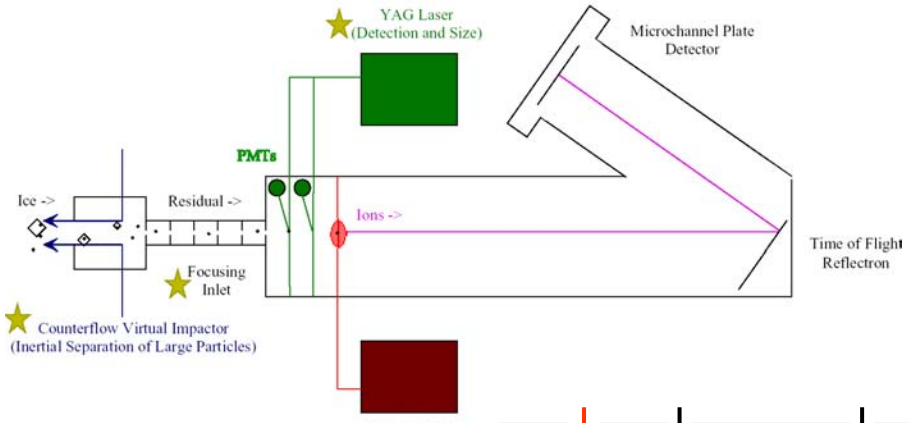
Type 1: SPLAT-MS (Imre *et al.*)





Courtesy of Dan Imre, Brookhaven National Laboratory, 2001.

Type 1: PALMS (Murphy *et al.*)



Courtesy of David Thomson, NOAA Aeronomy Laboratory, 2002.

Capillary	Light Scattering	Laser Desorption + Ionization	IR Laser	(Ion) Time-Of-Flight
Nozzle	Particle TOF -LS -Detection		Impact on Heated Surface	Quadrupole
Aerodynamic Lens	Particle TOF -Chemical Detection		Cryocollection + Slow Thermal Desorption	Ion Trap
Size-Selective Inlet	Pre-Selection		UV Laser Of Vapor Plume	
			Electron Ionization	
			Chemical Ionization	

Type 1: LAMPAS2 (Spengler et al.)

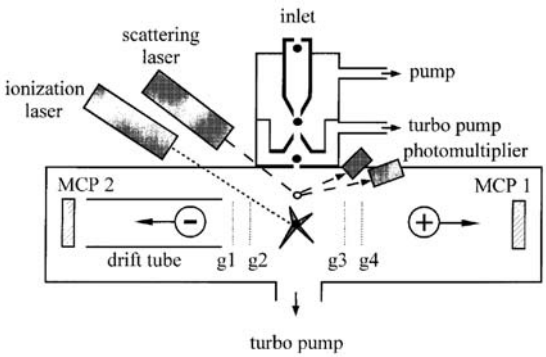
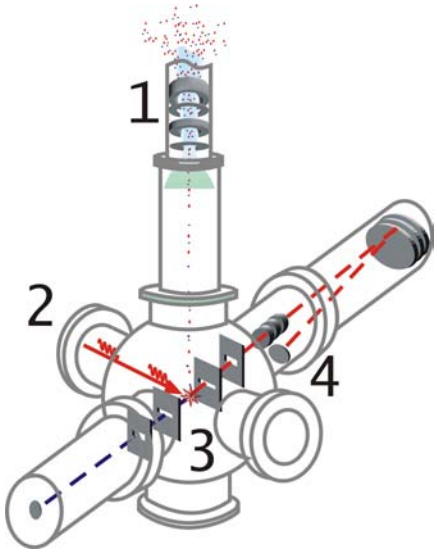


FIGURE 1. Scheme of the instrumental setup of the mobile aerosol mass spectrometer "LAMPAS 2."

A. Trimborn, K.-P. Hinz, and B. Spengler. Online Analysis of Atmospheric Particles with a Transportable Laser Mass Spectrometer. Aerosol Science and Technology 33:191-201, 2000.

Capillary	Light Scattering	Laser Desorption + Ionization	IR Laser	(Ion) Time-Of-Flight
Nozzle	Particle TOF -LS -Detection		Impact on Heated Surface	Quadrupole
Aerodynamic Lens	Particle TOF -Chemical Detection		Cryocollection + Slow Thermal Desorption	Ion Trap
Size-Selective Inlet	Pre-Selection		UV Laser Of Vapor Plume	
			Electron Ionization	
			Chemical Ionization	

Type 1: AMS (Petrucci *et al.*)

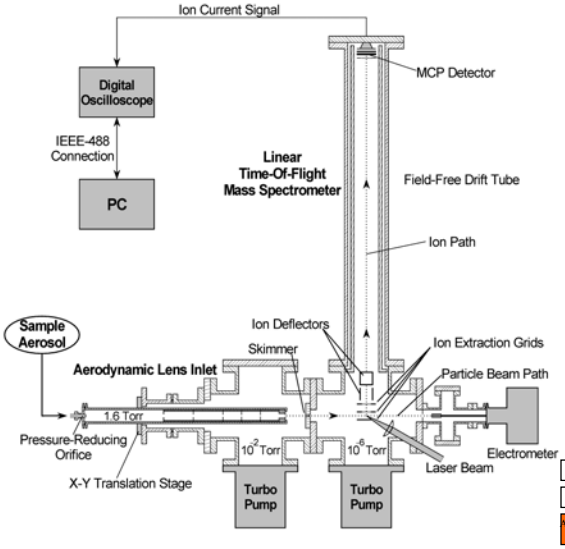


Courtesy of Joe Petrucci, University of Vermont, 2002.
http://www.uvm.edu/~gpetrucc/ams/amshome.html

Capillary	Light Scattering	Laser Desorption + Ionization	IR Laser	UV Laser Of Vapor Plume
Nozzle	Particle TOF -LS -Detection		Impact on Heated Surface	Electron Ionization
Aerodynamic Lens	Particle TOF -Chemical Detection		Cryocollection + Slow Thermal Desorption	Chemical Ionization
Size-Selective Inlet	Pre-Selection			

(Ion) Time-Of-Flight	
Quadrupole	
Ion Trap	

Type 1: SMPS (Zachariah *et al.*)

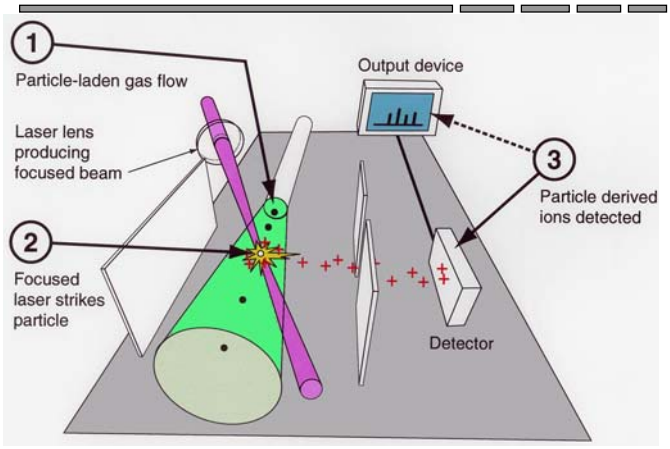


R. Mahadevan, D. Lee, H. Sakurai, and M. R. Zachariah, Measurement of Condensed-Phase Reaction Kinetics in the Aerosol Phase Using Single Particle Mass Spectrometry, Accepted for Publication, J. Phys. Chem. A, 2002.

Capillary	Light Scattering	Laser Desorption + Ionization	IR Laser	UV Laser Of Vapor Plume
Nozzle	Particle TOF -LS -Detection		Impact on Heated Surface	Electron Ionization
Aerodynamic Lens	Particle TOF -Chemical Detection		Cryocollection + Slow Thermal Desorption	Chemical Ionization
Size-Selective Inlet	Pre-Selection			

(Ion) Time-Of-Flight	
Quadrupole	
Ion Trap	

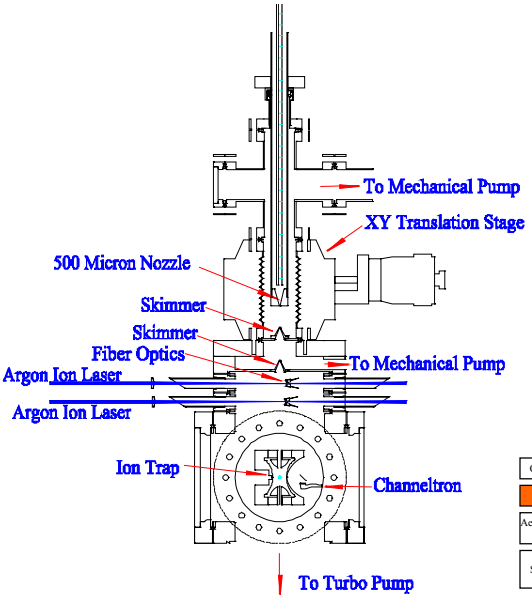
Type 1: Particle Blaster (Reents *et al.*)



Courtesy of Bill Reents, Bell Laboratories, 2002

Capillary	Light Scattering	**Laser Desorption + Ionization**	(Ion) Time-Of-Flight
Nozzle	Particle TOF -LS -Detection	IR Laser	Quadrupole
Aerodynamic Lens	Particle TOF -Chemical Detection	Impact on Heated Surface	Ion Trap
Size-Selective Inlet	Pre-Selection	Cryocollection + Slow Thermal Desorption	
		UV Laser Of Vapor Plume	
		Electron Ionization	
		Chemical Ionization	

Type 1: RTMS (Reilly *et al.*)

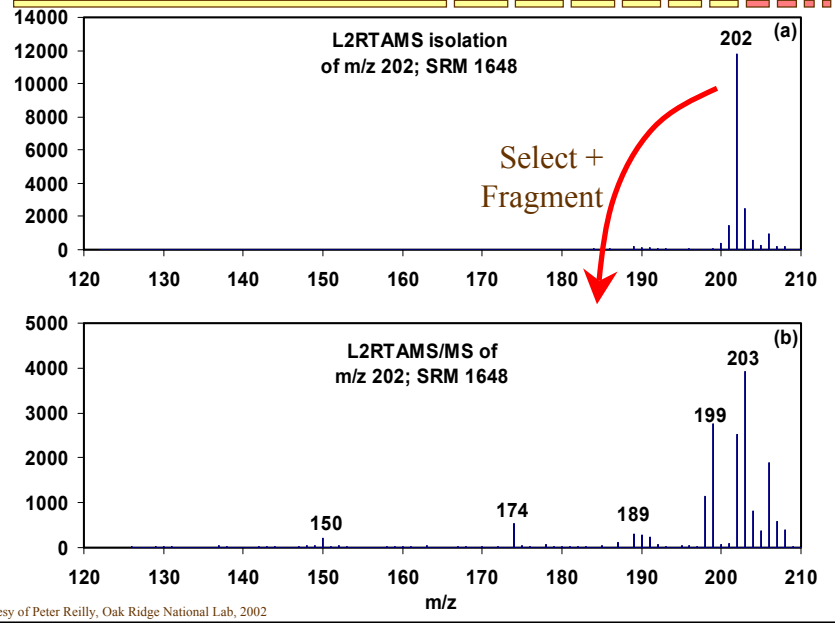


Courtesy of Peter Reilly, Oak Ridge National Lab, 2002

1. Reilly, P. T. A., Gieray, R. A., Whitten, W. B. , and Ramsey, J.M., Aerosol Sci. Technol. 33:135 (2000).
2. Lazar, A. C., Reilly, P.T. A., Whitten, W. B. , and Ramsey, J. M., Environ. Sci. Technol. 33: 3993 (1999).
3. Reilly, P. T. A., Gieray, R. A., Whitten, W. B. , and Ramsey, J. M., Combust. Flame 122:90 (2000).
4. Reilly, P. T. A.,Gieray, R. A., Whitten, W. B. , and Ramsey, J. M., J. Amer. Chem. Soc. 122:11596 (2000).

Capillary	Light Scattering	**Laser Desorption + Ionization**	(Ion) Time-Of-Flight
Nozzle	Particle TOF -LS -Detection	IR Laser	Quadrupole
Aerodynamic Lens	Particle TOF -Chemical Detection	Impact on Heated Surface	**Ion Trap**
Size-Selective Inlet	Pre-Selection	Cryocollection + Slow Thermal Desorption	
		UV Laser Of Vapor Plume	
		Electron Ionization	
		Chemical Ionization	

L2RTAMS/MS of m/z 202 desorbed from the surfaces of individual Urban Particulate Matter particles



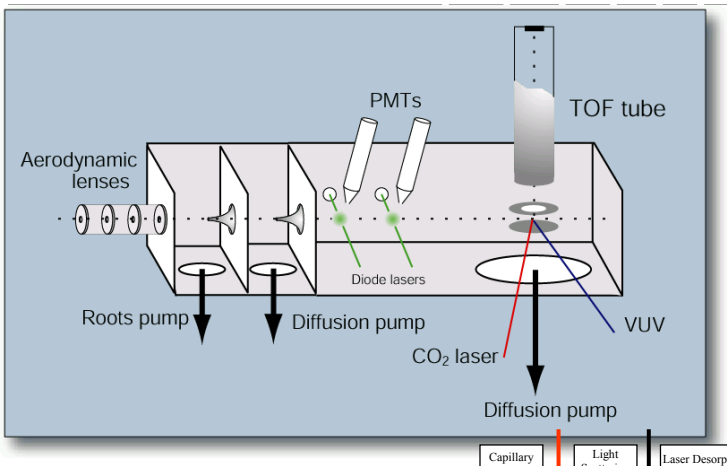
Courtesy of Peter Reilly, Oak Ridge National Lab, 2002

Type 1: Ion Trap vs. TOF-MS

Peter Reilly, Oak Ridge National Lab, 2002

- Advantages of Ion Trap
  - Ability to do MS/MS
  - A much greater tolerance of space charge effects
  - A stable linear mass scale.
  - Better mass resolution if needed.
  - The ability to average part or all of the aerosol MS data without having to worry about shifting mass scales and peak broadening that occur due to space charge, digitizer jitter, uncertainty in the precise starting point of the ions and broad variations in the laser hit
  - A lower pumping requirement due to the 10^{-3} Torr operating pressure.
  - A much smaller instrument package
  - A much greater facility for data handling, manipulation and storage
- In fairness to the TOF users, the disadvantages are:
  - A limited dynamic mass range due to the change in trap depth as a function of mass
  - An inability to detect species below 15 Da.
  - Ion trap instrumentation is much more complex--not for the instrumentally challenged
  - Trap manufacturers are not easily convinced to give you information to modify their instruments for your purposes

Type 2: Two-Laser. Baer, Miller, *et al.*



Capillary | Nozzle | Aerodynamic Lens | Size-Selective Inlet

Light Scattering | Particle TOF -LS -Detection | Particle TOF -Chemical Detection | Pre-Selection

Laser Desorption + Ionization | IR Laser | Impact on Heated Surface | Cryocollection + Slow Thermal Desorption

UV Laser Of Vapor Plume | Electron Ionization | Chemical Ionization

(Ion) Time-Of-Flight | Quadrupole | Ion Trap

Note: this approach was first demonstrated by Fergenson & Prather

Figure courtesy of Tomas Baer, Univ. North Carolina, 2002.

Type 2: "Gentle" VUV Ionization

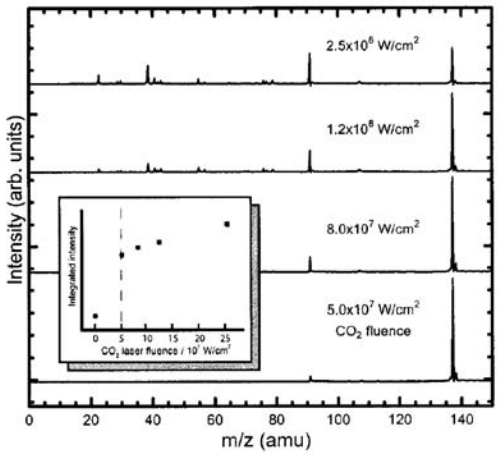


Figure 2. Mass spectra of *m*-nitrotoluene particles as a function of the CO_2 laser fluence. The inset shows the integrated intensity of the signal vs CO_2 laser fluence with the dashed vertical line indicating the threshold fluence of 5.0×10^7 W/cm^2. The leftmost point on the inset plot is the origin (0,0), and the other four points correspond to the four spectra shown in the figure.

D. Craig Sykes, Ephraim Woods, III, Geoffrey D. Smith, Tomas Baer, and Roger E. Miller. Thermal Vaporization-Vacuum Ultraviolet Laser Ionization Time-of-Flight Mass Spectrometry of Single Aerosol Particles. Anal. Chem.2002, 74,2048-2052.

Type 2: IR vs. Thermal vaporization

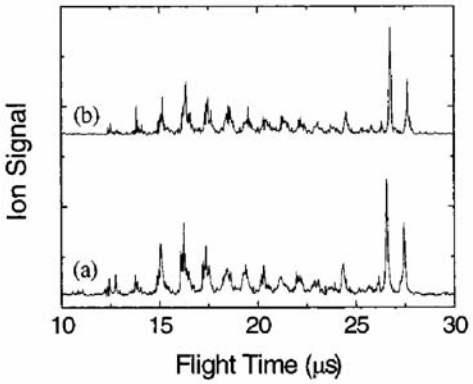
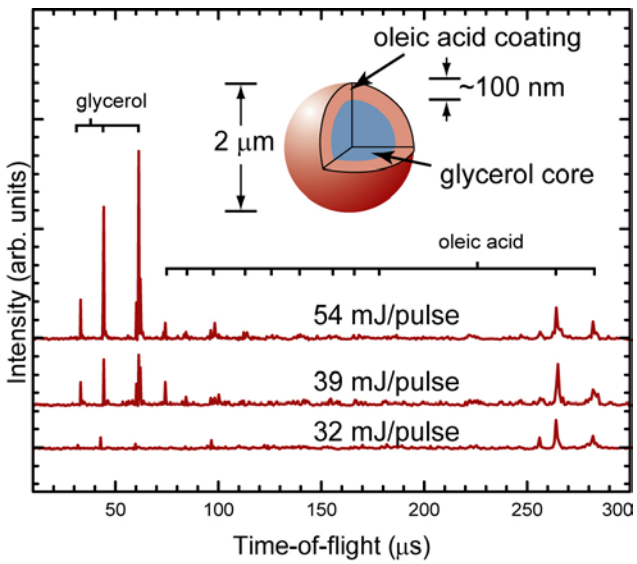


Figure 5. Comparison of oleic acid TOF mass spectra obtained by vaporizing the particles with the heater (a) and the infrared CO_2 laser (b). Note the similarity in the resulting mass spectra. Each spectrum is the average of 100 single-particle mass spectra.

D. Craig Sykes, Ephraim Woods, III, Geoffrey D. Smith, Tomas Baer, and Roger E. Miller. Thermal Vaporization-Vacuum Ultraviolet Laser Ionization Time-of-Flight Mass Spectrometry of Single Aerosol Particles. Anal. Chem.2002, 74,2048-2052.

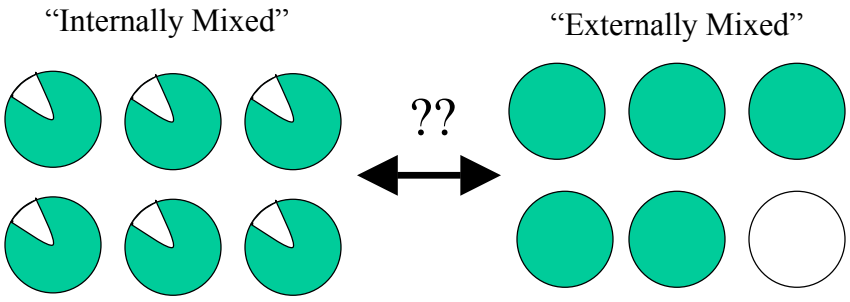
Type 2: Depth profiling with CO_2 laser



Woods, Smith, Miller, and Baer, *Anal. Chem.* **47** 1642-1649 (2002)

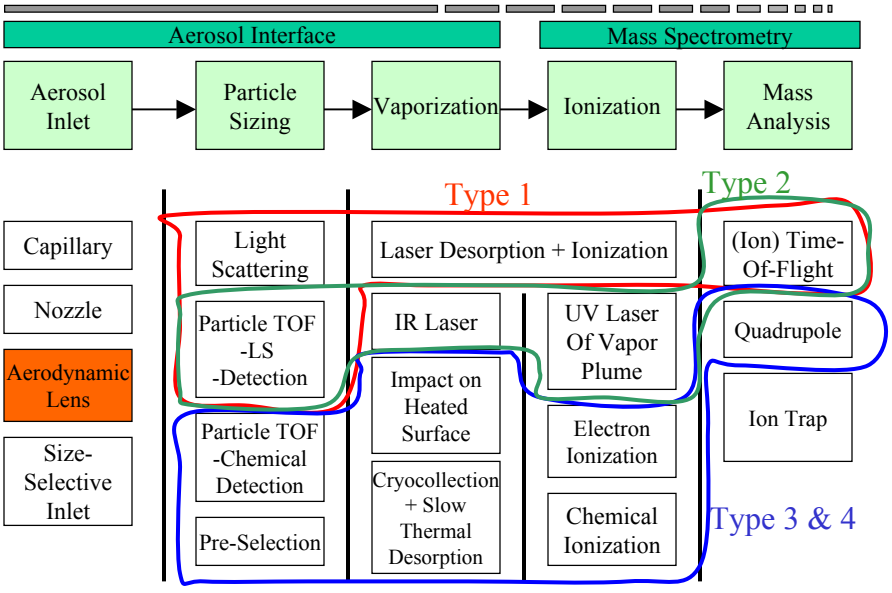
Type 1 + 2 vs. 3 + 4: Ensemble vs. Single Particle Analysis

For example: 17% of the mass is organics, 83% is sulfate



- Single Particle Instruments DIRECTLY detect the mixing state
- Ensemble Averaging Instruments can only answer the mixing question indirectly, and with lower precision

Implementations: "Clusters" of Designs

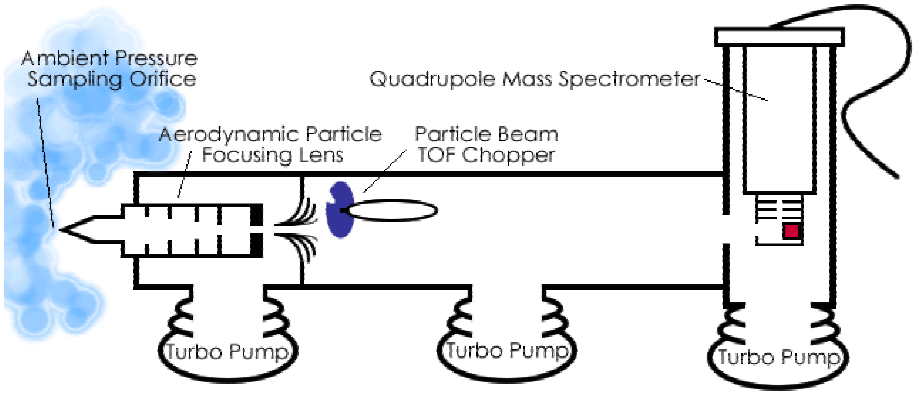


Types 3 + 4: Thermal Vaporization

9. Other Aerosol Mass Spectrometers Based on Thermal (Non-Laser) Vaporization

Instrument	Principal Investigator	Department	Institution	Location
Particle Beam Thermal Desorption Mass Spectrometer (PB-TDMS)	Paul Ziemann	Department of Environmental Sciences	University of California at Riverside	Riverside, California
Atmospheric Pressure - Chemical Ionization Mass Spectrometer (AP-CIMS)	Thorsten Hoffmann		Institute of Spectrochemistry and Applied Spectroscopy	Dortmund, Germany
Aerosol Composition Mass Spectrometer (ACMS)	Jochen Schreiner & Konrad Mauersberger		Max-Planck Institute for Nuclear Physics	Heidelberg, Germany
Gas & Particle-Phase Selected-Ion Chemical Ionization Mass Spectrometer (SI-CIMS)	Paul Wennberg	Depg. of Geological and Planetary Sciences	California Institute of Technology	Pasadena, California
Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS)	Jim Smith & Fred Eisele	Atmospheric Chemistry Division	National Center for Atmospheric Research (NCAR)	Boulder, Colorado

Type 3: Aerodyne AMS



Capillary
Nozzle
Aerodynamic Lens
Size-Selective Inlet

Light Scattering
Particle TOF -LS -Detection
Particle TOF -Chemical Detection
Pre-Selection

Laser Desorption + Ionization
IR Laser
Impact on Heated Surface
Cryocollection + Slow Thermal Desorption
UV Laser Of Vapor Plume
Electron Ionization
Chemical Ionization

(Ion) Time-Of-Flight
Quadrupole
Ion Trap

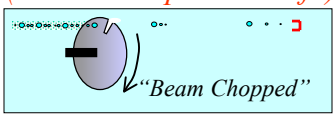
Jayne et al., Aerosol Science and Technology 33:1-2(49-70), 2000.
Jimenez et al., Journal of Geophysical Research, in press, 2002.

Type 3: AMS: Information Obtained

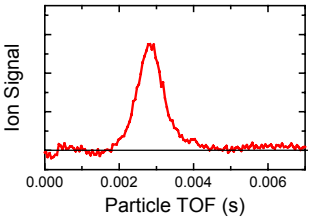
Dual Operating Modes

Size Distribution

(limited composition info)

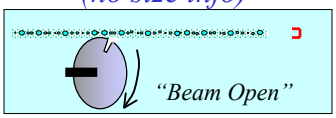


Spectrometer Setting is Fixed (small subset of 0-300 amu)

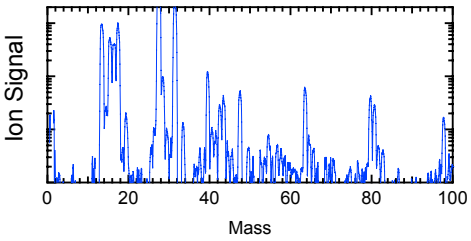


Average Composition

(no size info)



Spectrometer is Scanned (0-300 amu)



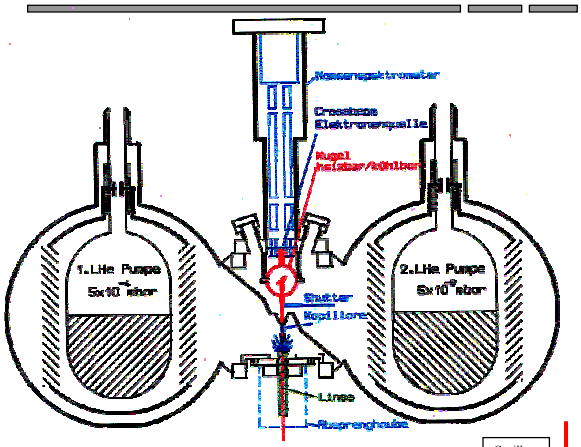
3. Research Groups Involved in the Development and/or Application of the Aerodyne AMS

AAAR'02: 5D on Wed

(t3) Aerodyne AMS Users

Serial No.	Principal Investigator	Department	Institution	Location
001	Drs. Doug Worsnop & John Jayne	Center for Aerosol and Cloud Chemistry	Aerodyne Research	Billerica, Massachusetts, USA
002	Prof. Paul Davidovits	Department of Chemistry	Boston College	Newton, Massachusetts, USA
	Prof. Ken Smith	Department of Chemical Engineering	Massachusetts Institute of Technology	Cambridge, Massachusetts, USA
003	Profs. John Seinfeld & Rick Flagan	Department of Chemical Engineering	California Institute of Technology	Pasadena, California, USA
004 & 012	Hugh Coe	Atmospheric Physics Group	UMIST	Manchester, UK
005	Prof. Darin Toohey	Program in Atmospheric and Oceanic Science	University of Colorado	Boulder, Colorado, USA
006	Prof. Jonathan Allen	Departments of Chemical and Environmental Engineering	Arizona State University	Tempe, Arizona, USA
007	Prof. Stephan Borrmann & Johannes Schneider	Cloud Physics and Chemistry	Max Planck Institute for Chemistry	Mainz, Germany
008	Prof. Ken Demerjian	Aerosol Science Lab, Department of Earth and Atmospheric Sciences	State University of New York at Albany	Albany, New York, USA
009	Dr. Yutaka Kondo	Center for Advanced Science and Technology	University of Tokyo	Tokyo, Japan
010	Dr. Ann Middlebrook	Aeronomy Laboratory	National Oceanic and Atmospheric Administration	Boulder, Colorado, USA
011	Prof. Jose L. Jimenez	Department of Chemistry & Biochemistry and CIRES	University of Colorado at Boulder	Boulder, Colorado, USA

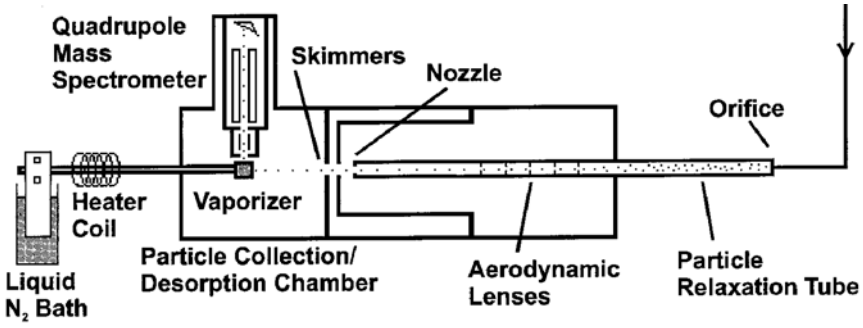
Type 3: ACMS (Schreiner *et al.*)



Courtesy of Jochen Schreiner
Max Plank Institute fur KernPhysik
http://www.mpi-hd.mpg.de/mauersberger/schreiner/index.htm

Capillary	Light Scattering	Laser Desorption + Ionization		(Ion) Time-Of-Flight
Nozzle	Particle TOF -LS -Detection	IR Laser	UV Laser Of Vapor Plume	Quadrupole
Aerodynamic Lens	Particle TOF -Chemical Detection	Impact on Heated Surface	Electron Ionization	Ion Trap
Size-Selective Inlet	Pre-Selection	Cryocollection + Slow Thermal Desorption	Chemical Ionization	

Type 3: PBTDMS (Ziemann *et al.*)



Herbert J. Tobias and Paul J. Ziemann. Compound Identification in Organic Aerosols Using Temperature-Programmed Thermal Desorption Particle Beam Mass Spectrometry. Anal. Chem.1999, 71, 3428-3435.

Capillary	Light Scattering	Laser Desorption + Ionization		(Ion) Time-Of-Flight
Nozzle	Particle TOF -LS -Detection	IR Laser	UV Laser Of Vapor Plume	Quadrupole
Aerodynamic Lens	Particle TOF -Chemical Detection	Impact on Heated Surface	Electron Ionization	Ion Trap
Size-Selective Inlet	Pre-Selection	Cryocollection + Slow Thermal Desorption	Chemical Ionization	

Type 3: PBTDMS Thermograms (Ziemann *et al.*)

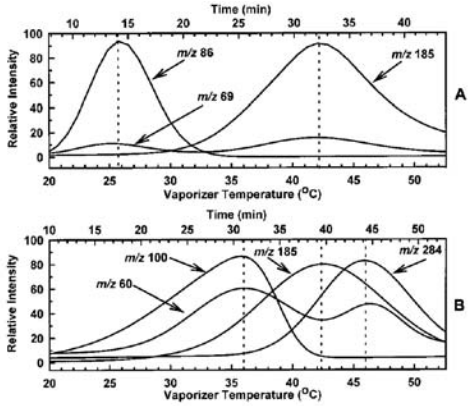
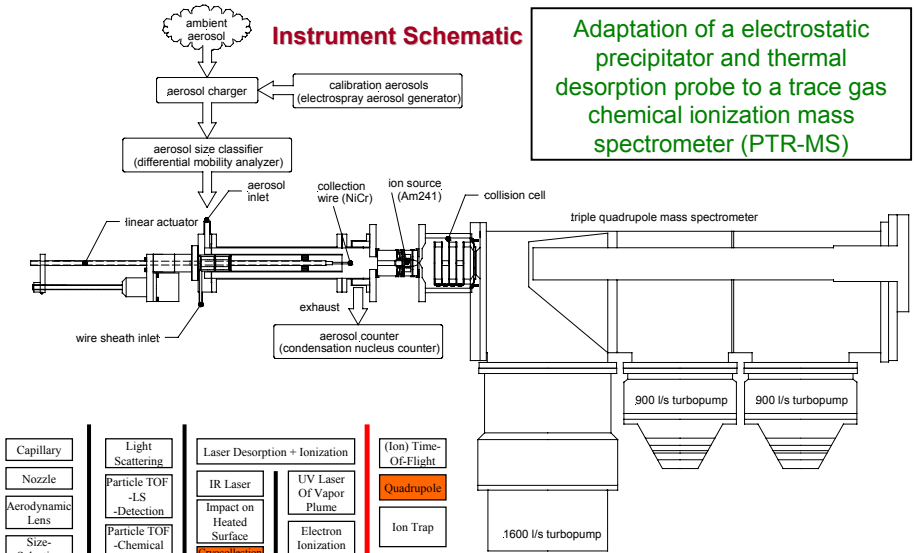


Figure 2. Mass thermograms of the TPTD of multicomponent aerosols. Thermogram A consists of glutaric acid (*m*/*z* 86) and DOS (*m*/*z* 185) measured at a temperature ramp rate of ~0.90 °C/min. The *m*/*z* 69 signal trace is due to both glutaric acid and DOS. Thermogram B consists of adipic acid (*m*/*z* 100), DOS (*m*/*z* 185), and stearic acid (*m*/*z* 284) measured at a temperature ramp rate of ~0.75 °C/min. The *m*/*z* 60 signal trace is due to both adipic acid and stearic acid but not DOS. For this figure, all the raw *m*/*z* signal traces were smoothed by curve fitting.

Herbert J. Tobias and Paul J. Ziemann. Compound Identification in Organic Aerosols Using Temperature-Programmed Thermal Desorption Particle Beam Mass Spectrometry. Anal. Chem.1999, 71, 3428-3435.

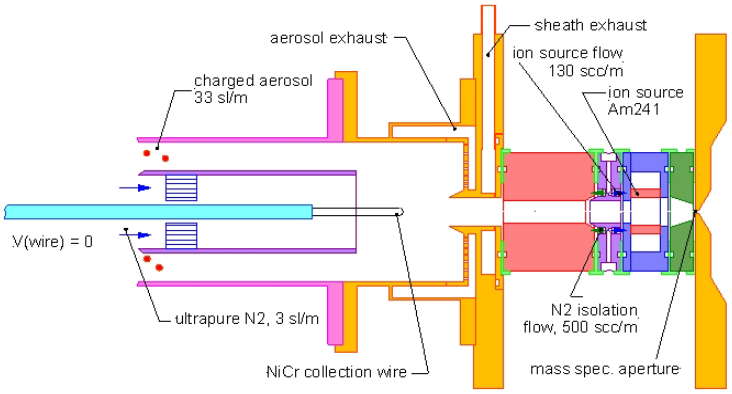
Type 4: Thermal Desorption Chemical Ionization Mass Spectrometry (TDCIMS)



Adaptation of a electrostatic precipitator and thermal desorption probe to a trace gas chemical ionization mass spectrometer (PTR-MS)

Courtesy of Jim Smith, NCAR
http://www.acd.ucar.edu/~jimsmith/POP

Type 4: TDCIMS: Schematic of Source Region



Capillary | Nozzle | Aerodynamic Lens | Size-Selective Inlet

Light Scattering | Particle TOF -LS -Detection | Particle TOF -Chemical Detection | Pre-Selection

Laser Desorption + Ionization | IR Laser | Impact on Heated Surface | Cryocollection & Thermal Desorption

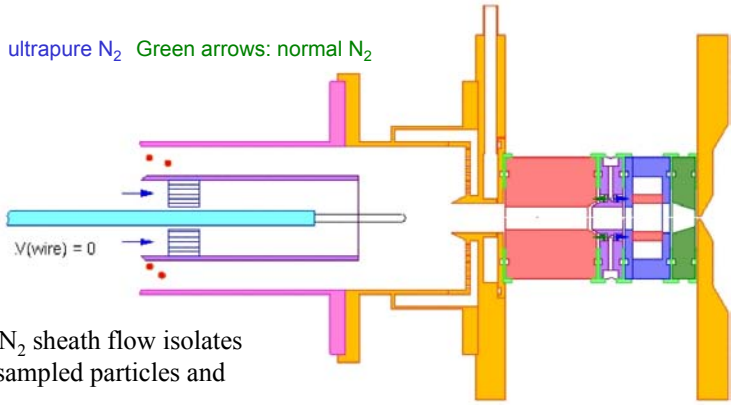
UV Laser Of Vapor Plume | Electron Ionization | Chemical Ionization

(Ion) Time-Of-Flight | Quadrupole | Ion Trap

Courtesy of Jim Smith, NCAR
http://www.acd.ucar.edu/~jimsmith/POP

Type 4: TDCIMS: Gas Flow in Source

Blue arrows: ultrapure N_2 Green arrows: normal N_2



- Ultra pure N_2 sheath flow isolates wire from sampled particles and gas
- Some contamination of the wire from gases is inevitable, so we periodically collect "background spectra" with no particles being collected (as above).

Capillary | Nozzle | Aerodynamic Lens | Size-Selective Inlet

Light Scattering | Particle TOF -LS -Detection | Particle TOF -Chemical Detection | Pre-Selection

Laser Desorption + Ionization | IR Laser | Impact on Heated Surface | Cryocollection & Thermal Desorption

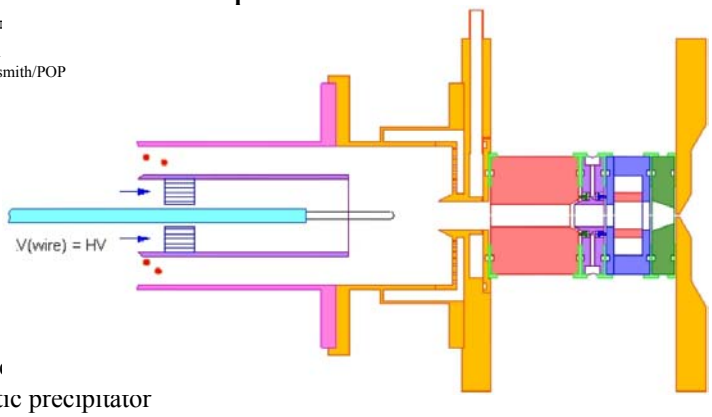
UV Laser Of Vapor Plume | Electron Ionization | Chemical Ionization

(Ion) Time-Of-Flight | Quadrupole | Ion Trap

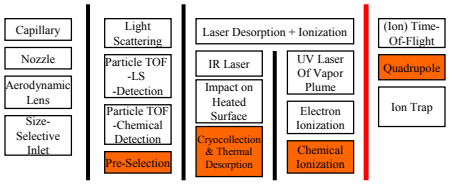
Courtesy of Jim Smith, NCAR
http://www.acd.ucar.edu/~jimsmith/POP

Type 4: TDCIMS: Step 1 – Particle Collection

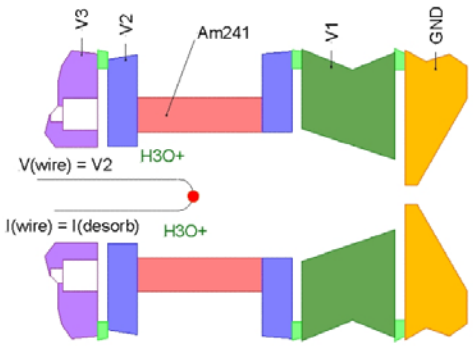
Courtesy of Jim Smith, NCAR
http://www.acd.ucar.edu/~jimsmith/POP



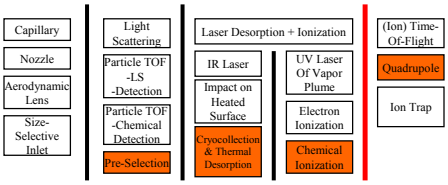
- Sample air with
  enters electrostatic precipitator
- Collection filament is biased at a ca. 4 Kvolts with respect to chamber walls.
- Particles cross flow streamlines to collect on metal filament
- After a few minutes, wire is inserted into ion source for sample analysis



Type 4: TDCIMS: Step 2 – Sample Desorption and Analysis

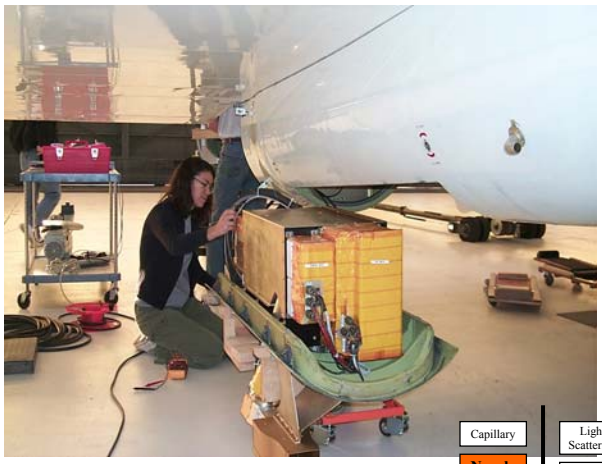


- Wire momentarily heated at temperatures up to 300 °C to desorb sample
- Neutral compounds are ionized using chemical ionization, e.g.: $H_3O^+ + NH_3 \rightarrow NH_4^+ + H_2O$
- Reagent ions are created by α particles emitted from the source, generating mostly H_3O^+, O_2^- and CO_3^-
- Ionized analyte injected into a quadrupole mass spectrometer for analysis



Courtesy of Jim Smith, NCAR
http://www.acd.ucar.edu/~jimsmith/POP

Type 4: SI-CIMS (Wennberg *et al.*)

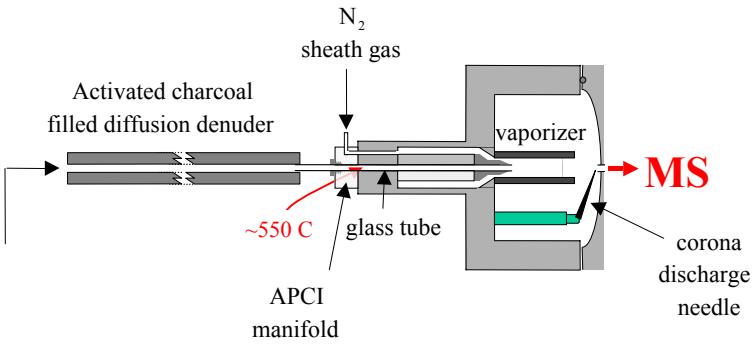


Dr. Karena McKinney of Caltech preparing the SI-CIMS on the ER-2

Courtesy of Paul Wennberg
Caltech
http://www.gps.caltech.edu/~wennberg/cims.html

Capillary	Light Scattering	Laser Desorption + Ionization		(Ion) Time-Of-Flight
Nozzle	Particle TOF -LS -Detection	IR Laser	UV Laser Of Vapor Plume	Quadrupole
Aerodynamic Lens		**Gas Heating**	Electron Ionization	Ion Trap
Size-Selective Inlet	Particle TOF -Chemical Detection	Cryocollection + Slow Thermal Desorption	**Chemical Ionization**	
	Pre-Selection			

Type 4: APCI-MS (Hoffman *et al.*)



Courtesy of Thorsten Hoffmann, Institute of Spectrochemistry, Dortmund, Germany

Capillary	Light Scattering	Laser Desorption + Ionization		(Ion) Time-Of-Flight
Nozzle	Particle TOF -LS -Detection	IR Laser	UV Laser Of Vapor Plume	Quadrupole
Aerodynamic Lens		**Gas Heating**	Electron Ionization	**Ion Trap**
Size-Selective Inlet	Particle TOF -Chemical Detection	Cryocollection + Slow Thermal Desorption	**Chemical Ionization**	
	Pre-Selection			

Comparison of Commercial Instruments

	Aerodyne AMS (Type 3)	TSI 3800 (Type 1)
Single Particle Information?		
Quantitative Size Information?		
Quantitative Single Particle Composition?		
Quantitative Ensemble Composition?		
Detection of SO4, NH4, NO3, Organics		
Detection of Refractory Material (dust…)		
Ability to Perform MS/MS		
Sensitivity (μg/m^3)		
Lower Size Limit (nm)		
Upper Size Limit (nm)		
Relative Transmission Efficiency vs. Size		
Weight (kg)		
Power Consumption (W)		
Line Voltage Needed (V)		
Instrument Volume (m3)		
Operated in the field (ground sites)?		
Operated in Aircraft?		
Perform in Vibrating Environment?		

Disclaimer: this comparison represents my opinion (not that of AAAR) on the state of both commercial instruments as of Oct. 2002. Both instruments are "moving targets" in that they are constantly being improved. Talk to representatives of both companies about how THEIR instrument matches YOUR application.

Comparison of Commercial Instruments

	$260k ~19 deliveries	Aerodyne AMS (Type 3)	TSI 3800 (Type 1)	$360k ~6-12 (?) deliveries*
INFORMATION OBTAINED				
Single Particle Information?		Only one m/z	Yes	
Quantitative Size Information?		Yes	Yes	
Quantitative Single Particle Composition?		Yes, but only one m/z	Very difficult, except when matrix does not change	
Quantitative Ensemble Composition?		Yes (Single Cal. Fact.)	Very difficult, except when matrix does not change	
Detection of SO4, NH4, NO3, Organics		Yes	Yes	
Detection of Refractory Material (dust…)		No	Yes	
Ability to Perform MS/MS		No	No	
Sensitivity (μg/m^3)		~0.01	< 0.001	
PARTICLE SIZE RANGE				
Lower Size Limit (nm)		40	300	
Upper Size Limit (nm)		~2000	10,000	
Relative Transmission Efficiency vs. Size		~100% (50-600 nm), decaying to ~0 at 2,000 nm	as D^3	
SPECIFICATIONS				
Weight (kg)		230	360	
Power Consumption (W)		600	>= 4000	
Line Voltage Needed (V)		110 or 220	220 only	
Instrument Volume (m3)		0.65	1.73	
Operated in the field (ground sites)?		Yes	Yes	
Operated in Aircraft?		Yes	No	
Perform in Vibrating Environment?		Yes		

*: Those are rumors, since TSI considers this Information confidential

Disclaimer: this comparison represents my opinion (not that of AAAR) on the state of both commercial instruments as of Oct. 2002. Both instruments are "moving targets" in that they are constantly being improved. Talk to representatives of both companies about how THEIR instrument matches YOUR application.

Part 3: Quantification

Two Types of Quantification

- Particle size distribution
  - Number
  - Mass
- Species mass concentration
  - Single particle (harder)
  - Particle ensemble (easier)

Size Distribution Quantification I

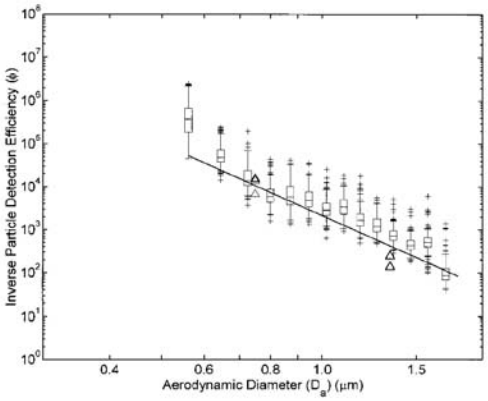


FIGURE 1. Inverse particle detection efficiency (ϕ) versus aerodynamic diameter (D_a) for the transportable ATOFMS instrument sampling ambient aerosols at Long Beach based on comparisons with impactor (△) and OPC (box and whisker) measurements. The solid line represents the best power law fit to the impactor data according to eqs 6 and 7. Note that the △ symbols are plotted at the logarithmic mean D_a value within each impactor bin but apply across the entire width of the impactor bin (see text).

Nozzle
Inlet

JONATHAN O. ALLEN, DAVID P. FERGENSON, ERIC E. GARD, LARA S. HUGHES, BRADLEY D. MORRICAL, ‡MICHAEL J. KLEEMAN, DEBORAH S. GROSS, MARKUS E. GALLI, KIMBERLY A. PRATHER, AND GLEN R. CASS. Particle Detection Efficiencies of Aerosol Time of Flight Mass Spectrometers under Ambient Sampling Conditions. Environ. Sci. Technol.2000, 34,211-217.

Size Distribution Quantification II

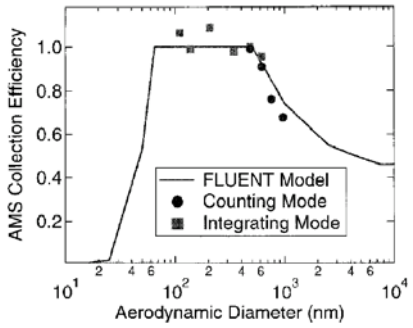


FIGURE 9. Summary of the AMS particle collection/detection efficiency as a function of aerodynamic diameter. Solid line is FLUENT model prediction. Circles are efficiencies determined by comparing AMS and CPC counting rates (data from Figure 8). Squares are collection efficiencies determined from the ratio of the measured to the calculated integrated area of the TOF data shown in Figure 4 (note that the data points originating from Figures 4 and 8 have been converted from mobility to aerodynamic diameter using particle density of 1.72 and a shape factor of 0.8).

Aerodynamic
Lens Inlet

Jayne, J.T., D.C. Leard, X. Zhang, P. Davidovits, K.A. Smith, C.E. Kolb, and D.R. Worsnop, Development of an aerosol mass spectrometer for size and composition. analysis of submicron particles, Aerosol Sci. Technol., 33, 49-70, 2000.

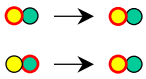
The Key to Mass Quantification

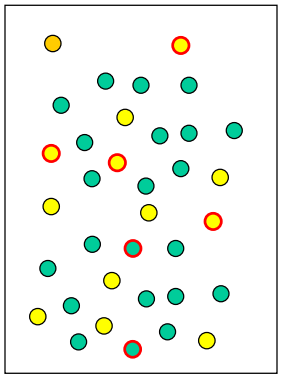
Limit 1: High local Pressure => many collisions

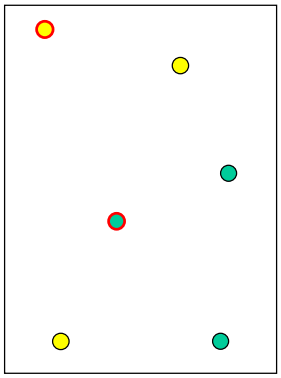
Limit 2: Very Low Local Pressure: no collisions

Neutrals	Ions
A	A^+
B	B^+

$IP_A > IP_B$



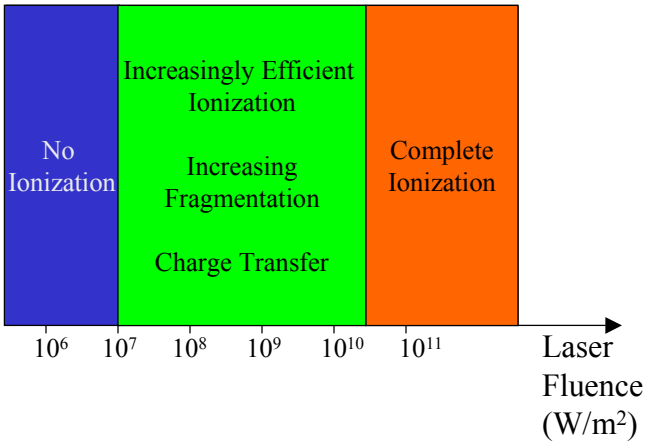




Extensive Charge Transfer

No Charge Transfer

(t1) LDI Laser Fluence vs. Quantification



- Note: this is a conceptual schematic. The processes are really more complex, and laser pulse energy (= fluence * duration), laser wavelength, and *particle composition* also play important roles

Species Mass Concentration Quantification

- LDI Tradeoff:
  - can quantify chemistry if the whole particle is turned into atomic ions
    - Very high laser fluences
  - Lose molecular information
- LDI at moderate fluences
  - Primary ions (+ electrons) formed
  - Ion-molecule reactions: species that are easier to ionize steal the charge. Results in differences in ionization efficiencies of up to *several orders of magnitude (2-6).*
- Two – Step processes:
  - separate vaporization and ionization
  - So that mean free path of ions and evaporated molecules is large => no collisions
  - Linear response

(t1) RSMS: Species Mass Quantification

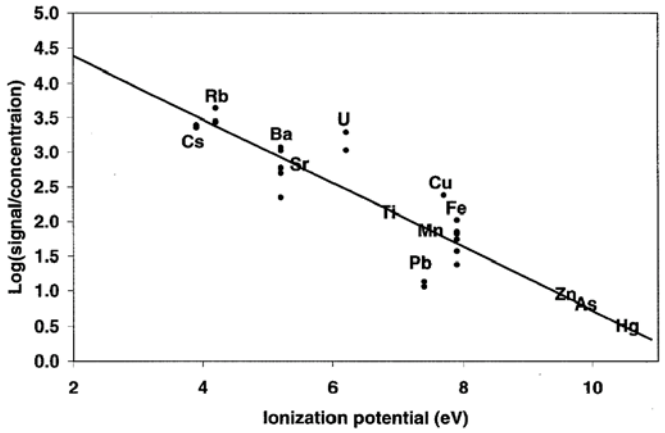


FIGURE 8. A plot of the log of the mass spectral signal intensity divided by the NIST provided concentrations versus the element ionization potential. The black line is a least squares fit to the data. The element symbols crossing the least squares line represent the projected positions in the plot of elements that were present in the sample but were not observed.

P. T. A. Reilly*, A. C. Lazar, R. A. Gieray,W. B.Whitten,and J. M. Ramsey. The Elucidation of Charge-Transfer-Induced Matrix Effects in Environmental Aerosols Via Real-Time Aerosol Mass Spectral Analysis of Individual Airborne Particles. Aerosol Science and Technology 33:135] 152 2000

(t1) ATOFMS: Ambient Nitrate

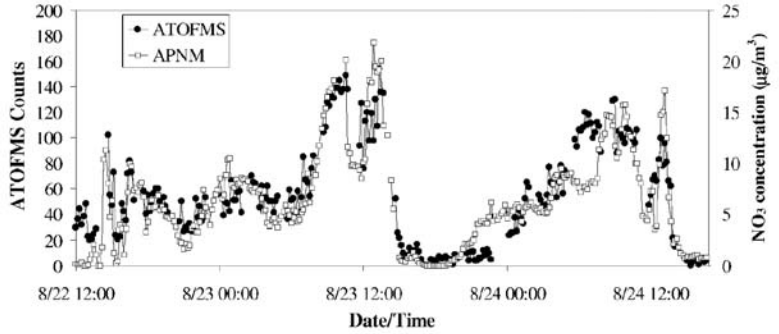


FIGURE 1. August, 1997 unscaled ATOFMS counts of particles and APNM nitrate mass concentration as a function of time. Temporal resolution is 10 min.

- LDI can be much more quantifiable *for the ensemble* when matrix does not change

Don-Yuan Liu, Kimberly A. Prather*, and Susanne V. Hering. Variations in the Size and Chemical Composition of Nitrate-Containing Particles in Riverside, CA. Aerosol Science and Technology 33:71-86 2000.

Field-Based Approach to ATOFMS Sensitivity Calibration (NO_3 and NH_4)

- Idea: scale *ensemble* to collocated MOUDI data
- Particle (inverse) detection efficiency fit:

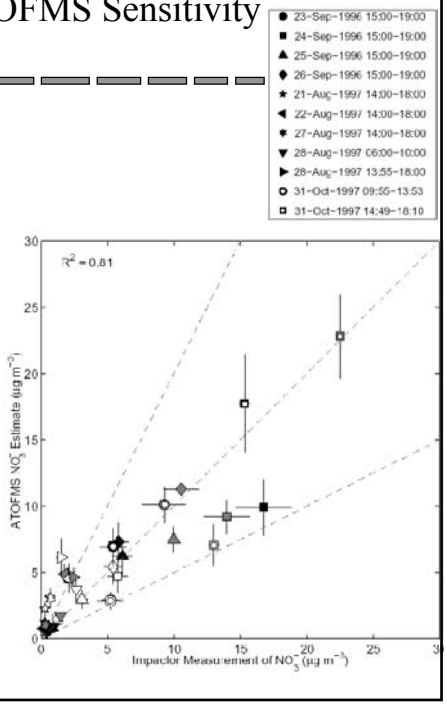
$$\phi = \alpha \, \mathrm{D}_a{}^{\beta}$$

β~ - 3.2 to - 4.7

- Species (*k*) & Size-Dependent (inverse) sensitivity fit:

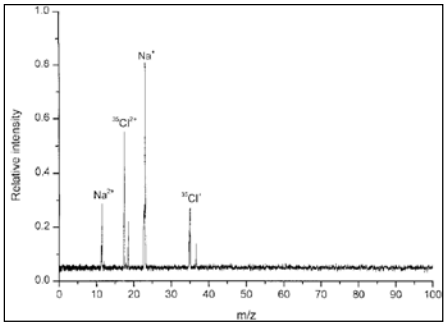
$$\psi_{jk} = \gamma_k \, \mathrm{D}_{a,j}{}^{\delta_k}$$

$\delta \sim 2.4$



P.V. Bhave, J.O. Allen, B.D. Morrical, D.P. Fergenson, G.R. Cass, and K.A. Prather.A Field-Based Aproach for Determining ATOFMS Instrument Sensitivities to NH4+ and NO3- in Size-Segregated Atmospheric Particles. Environmental Science and Technology, in press, 2002.

(t1) SP Elemental Quantification



Every atom in the particle is ionized. Atomic composition can be calculated from the ion counts.

TABLE 1. Measured ion ratios and elemental abundance for individual particles of sodium chloride (100 nm), silica (50 nm), and PSL spheres (64 nm).

Particle	Elemental Ratio Considered	Measured Ratio	True Ratio
100 nm sodium chloride	Chlorine/Sodium	1.12 ± 0.36[a]	1.00
50 nm silica	Oxygen/Silicon	1.93 ± 0.52[b]	2.00
64 nm PSL Sphere	Hydrogen/Carbon	1.13 ± 0.19[c]	1.00

[a] Results from 67 particles.
[b] Results from 28 particles.
[c] Results from 9 particles.

William D. Reents and Zhaozhu Ge. Simultaneous Elemental Composition and Size Distributions of Submicron Particles in Real Time Using Laser Atomization & Ionization Mass Spectrometry. Aerosol Science and Technology 33:122-134, 2000.

(t1) Single Particle Quantification: Reents *et al.*

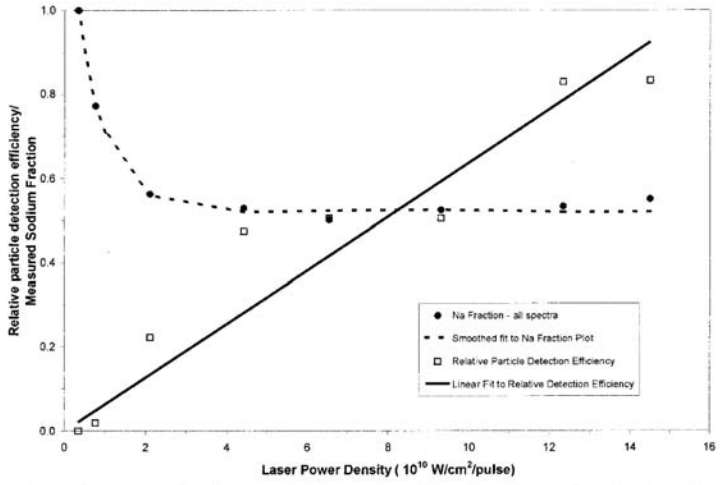
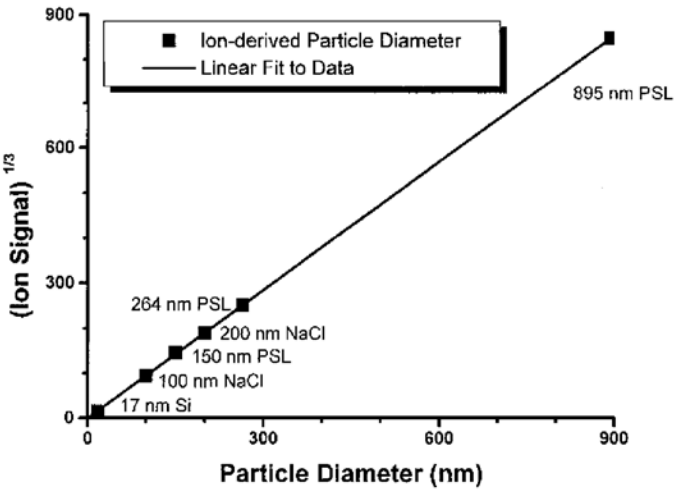


Figure 7. Dependence of measured sodium fraction and relative detection efficiency for ~70-nm sodium chloride particles on laser power density. Low laser power density results in inefficient ionization of chlorine relative to sodium. Increasing the laser power density beyond ~2 × 10^{10} W/cm^2 results in a constant sodium fraction. The particle detection efficiency increases with increasing laser power density.

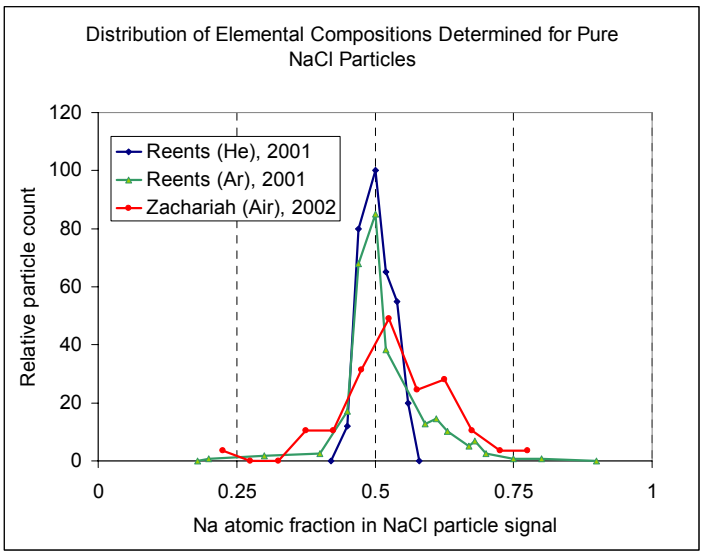
William D. Reents, Jr. and Michael J. Schabel. Measurement of Individual Particle Atomic Composition by Aerosol Mass Spectrometry. Anal. Chem.2001, 73,5403-5414

(t1) Single Particle Quantification: Reents *et al.*



Solid Particles can be sized by "counting" the number of atoms.

(t1) Single Particle Quantification: Influence of Gas



	IP (eV)
He	24.6
Ar	15.6
N_2	15.6
O_2	12.0
Cl	13.0
Na	5.1

(t2) IR + VUV Lasers: Quantification

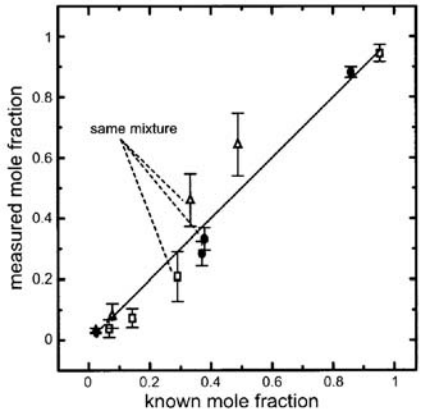
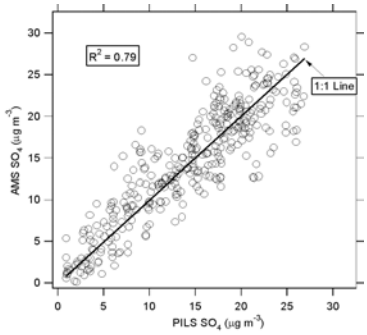


Figure 6. Plot comparing the measured mole fraction to the known mole fraction for a given component of one of four aniline/benzyl alcohol/*m*-nitrotoluene mixtures.(●, aniline; △, benzyl alcohol; □, *m*-nitrotoluene) The solid line represents identical measured and known concentrations, and the error bars reflect only the uncertainty in the ionization cross-section measurements. The dashed lines indicate the three different components of one of the four mixtures.

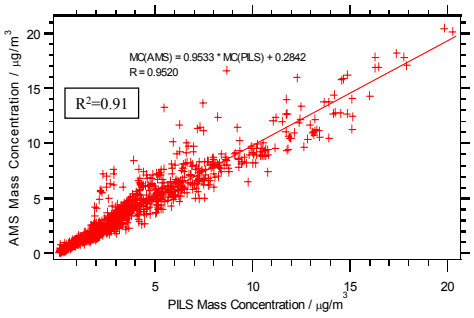
Ephraim Woods, III, Geoffrey D. Smith, Yury Dessiaterik, Tomas Baer, and Roger E. Miller. Quantitative Detection of Aromatic Compounds in Single Aerosol Particle Mass Spectrometry. Anal. Chem.2001, 73,2317-2322.

(t3) AMS: SO_4 Mass Conc.

Atlanta 1999
Jimenez et al.

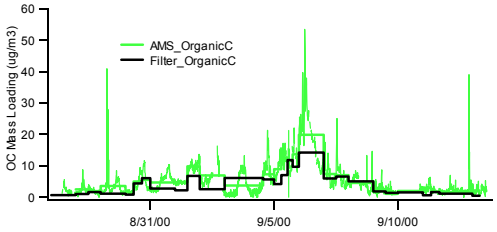


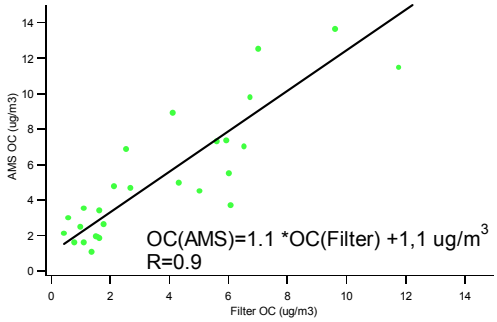
New York City 2001
Drewnick et al.



• A calibration factor (a single number for each species & the whole campaign) is determined by comparing to PILS semicontinuous instrument. This factor has been constant for all recent campaigns I am aware of.

(t3) AMS: Organic Mass Loading Comparisons

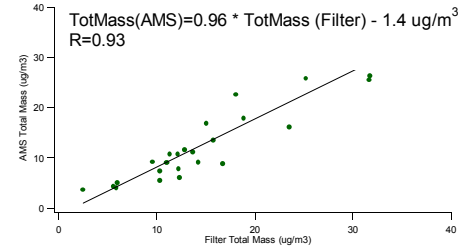




AMS vs. Filter

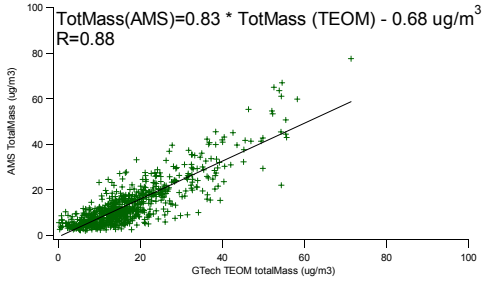
Filter: Karsten Bauman, GTech

(t3) AMS: Total Mass Loading Comparisons



AMS vs. Filter

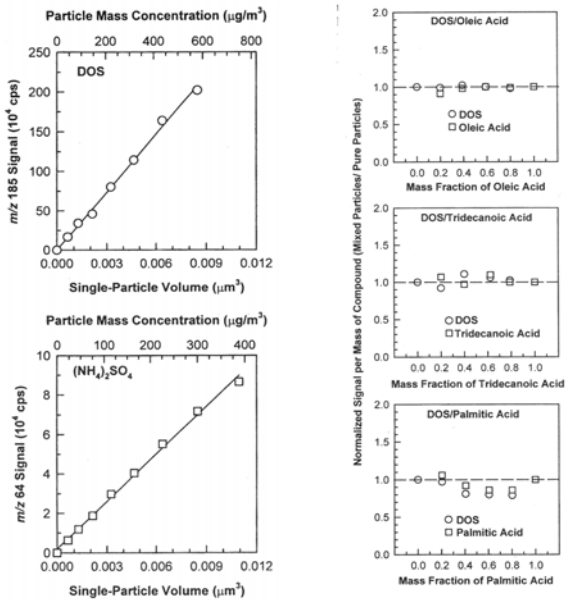
Filter: Karston Baumann, GTech



AMS vs. TEOM

TEOM (Tapered Element Oscillating Microbalance): Orsini et. al., Gtech

(t3) TDPBMS (Ziemann *et al.*): Quantification

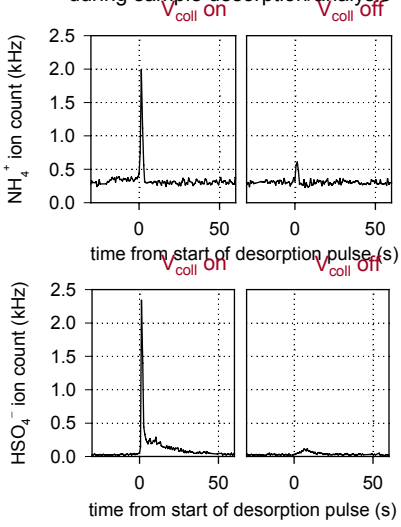


Herbert J. Tobias, Peter M. Kooiman, Kenneth S. Docherty, and Paul J. Ziemann. Real-Time Chemical Analysis of Aerosols Using a Thermal Desorption Particle Beam Mass Spectrometer. Aerosol Science & Technology, 33:1-2, 170 (2000).

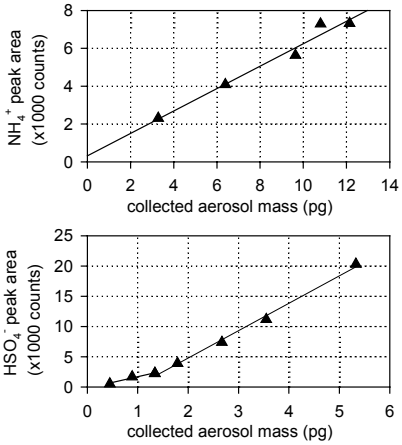
(t4) TD-CIMS: Quantification

Calibration with 14 nm (for NH_4^+) and 10 nm (for HSO_4^-) ammonium sulfate aerosol

Recorded ion abundance vs. elapsed time during sample desorption/analysis



Instrument response as a function of collected mass



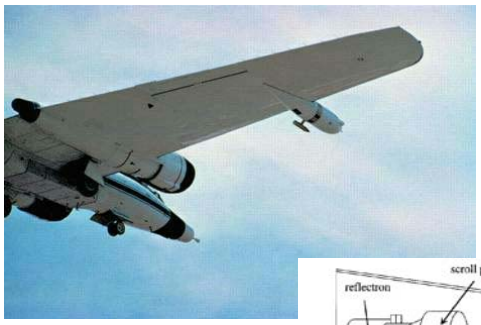
Voisin et al., submitted to Aerosol Sci. Technol., 2002

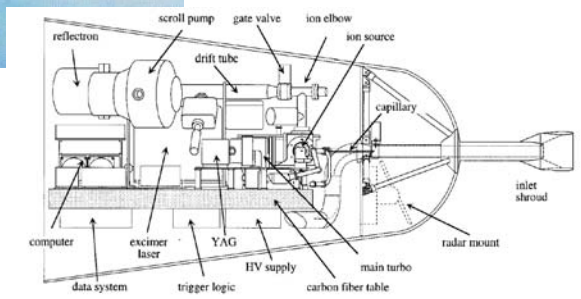
Part 4: Applications

Applications *(you name it!)*

- Atmospheric aerosols
  - Field: stratosphere, troposphere, urban areas
    - Airplanes, balloons, trucks, ground
  - Lab:
    - Gas-to-particle conversion
    - Heterogeneous chemistry
  - Aerosol Sources
    - Car & truck engines, incinerators, jet engines, cigarettes
    - Help design control technology
  - Health effects
- Industrial aerosols
  - Semiconductor manufacturing
  - Nanoparticle fabrication
  - Pharmaceutical aerosols

(t1) PALMS on Nose of WB-57



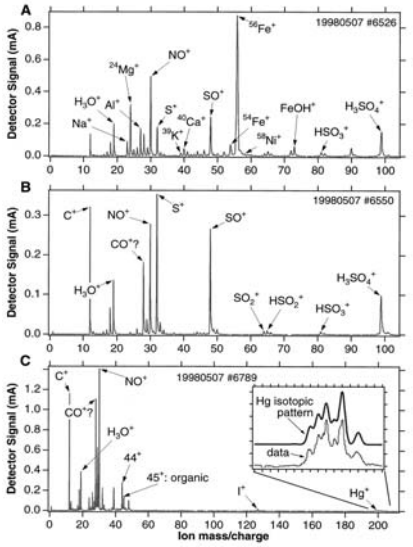


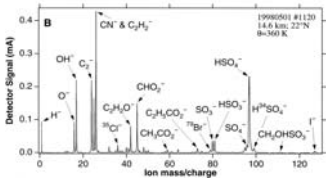
David S. Thomson*,Mike E. Schein, and Daniel M.Murphy. Particle Analysis by Laser Mass Spectrometry: WB-57F Instrument Overview. Aerosol Science and Technology 33:153-169 2000.

FIGURE 3. Schematic layout of the PALMS instrument components. For scale, the carbon fiber table is 122 cm (48″) long.

(t1) PALMS: Stratospheric Aerosols

Murphy et al. (1998) Science, 282, 1664



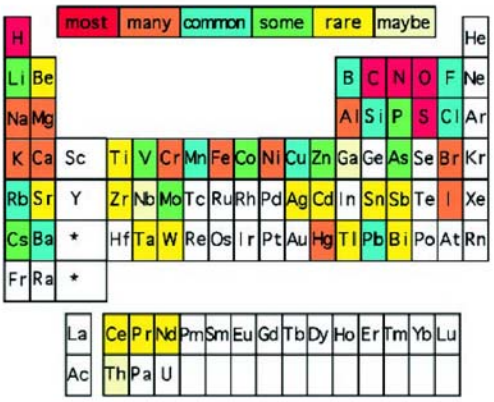


Upper tropospheric aerosols often contained more organic material than sulfate

Several common types of positive ion spectra in the stratosphere. The most common type contained iron, magnesium, and other metals as well as sulfate (A). About half of the stratospheric spectra had a large Fe peak. Between 20 and 40% of the spectra obtained more than 2 km above the tropopause showed little Fe, Hg, K, or other metals (B). Some organic material and NO^+ was almost always present. Some particles contained mercury (C), usually with a distinctive pattern of other peaks including a large C^+ peak and a peak at m/z = 127 that is presumed to be I^+. These spectra were obtained within minutes of each other in an otherwise fairly homogeneous air mass at 19 km

(t1) PALMS: Elements in Particles Above 5 km

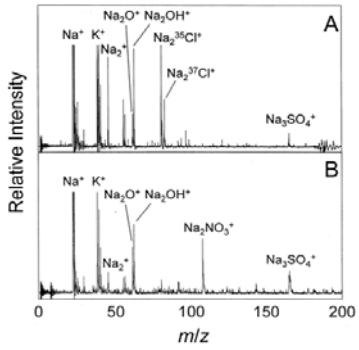
Fig. 9. Elements observed in aerosol particles at altitudes above 5 km. Frequencies are approximate because of differing ionization efficiencies. Elements with a distinctive signature of isotopes are also more likely to be unambiguously observed than those with only one isotope. Certain elements are likely to be undercounted because of spectral interferences. For example, the main isotopes of Si and Ti can be obscured by CO and SO, respectively.



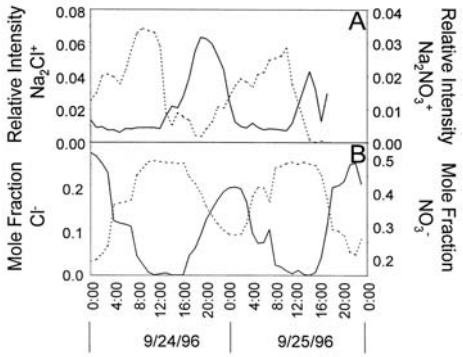
D. M. Murphy*, D. S. Thomson, M. J. Mahoney. In-Situ Measurements of Organics, Meteoritic Material, Mercury, and Other Elements in Aerosols from 5 to 19 km. Science 282: 1664-1668, 1998.

(t1) ATOFMS: Observation of Heterogeneous Chemistry

$$HNO_{3(g)} + NaCl_{(s\,or\,aq)} \rightarrow NaNO_{3(s\,or\,aq)} + HCl_{(g)}$$



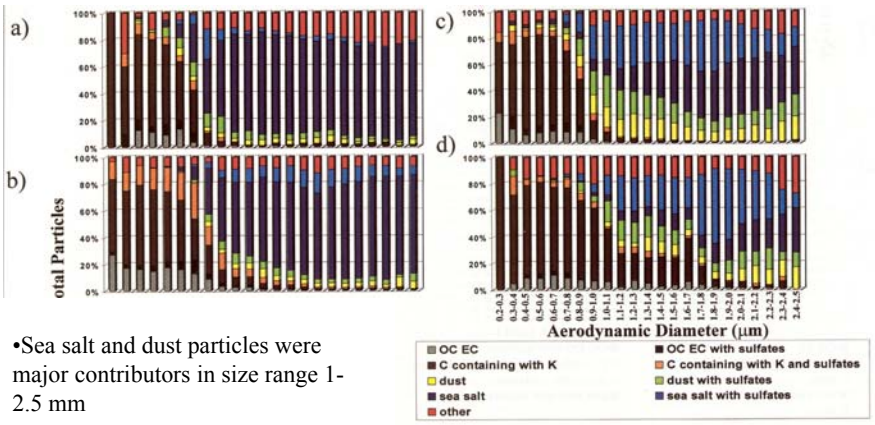
(A) Positive-ion mass spectrum of a 2.1-μm-diameter sea-salt particle acquired at Long Beach, California, on 24 September 1996 at 20:21 PST. The significant signal for the Na_2Cl^+ ion indicates that the particle is largely unreacted. (B) Positive-ion mass spectrum of a 1.9-μm-diameter sea-salt particle acquired at Long Beach on 24 September 1996 at 08:01 PST. Na^+ and K^+ are clearly present, as in (A); however, the Na_2Cl^+ cluster peak is undetectable, and a peak due to $Na_2NO_3^+$ is now present.



A strong diurnal trend in chloride replacement by nitrate on sea-salt particles. The solid curves represent the average intensity of chloride (or chloride marker) in the particles, and the dashed line indicates the average intensity of nitrate (or nitrate maker) in the particles. (A) The particles analyzed by the ATOFMS, (B) model calculations.

Gard et al. (1998) Science, 279, 1184

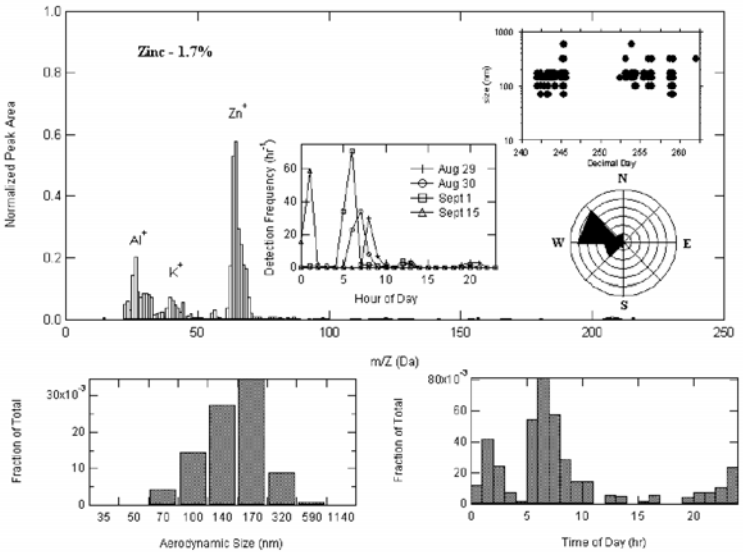
(t1) ATOFMS: Size-Resolved Chemistry in INDOEX



- Sea salt and dust particles were major contributors in size range 1-2.5 mm
- For smallest particles (0.2-1 mm), carbon-containing particles dominated
- Moving South (a) to North (d), carbon-containing particles increase.

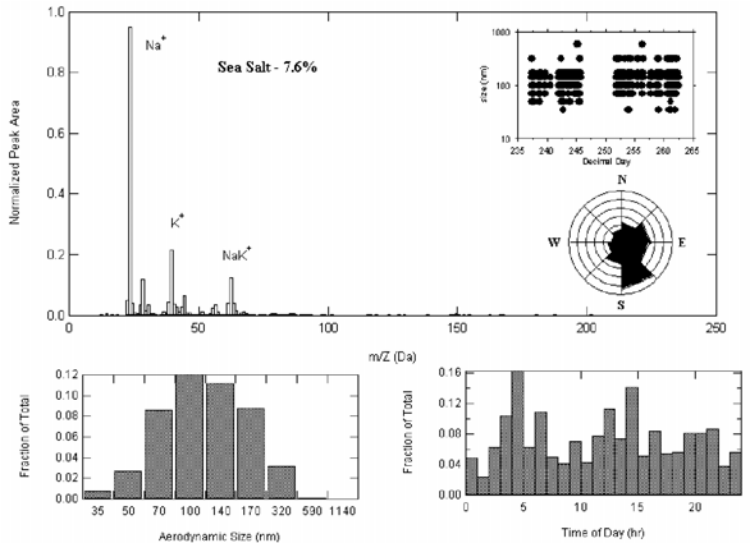
Guazzotti et al. (1998) JGR, 106, 28607

(t1) RSMS-II: Particle Types vs. Size, Time, Wind



Denis J. Phares, Kevin P. Rhoads, Murray V. Johnston, Anthony S. Wexler. Size-resolved ultrafine particle composition analysis Part 2: Houston. JGR special issue on the 1999 Atlanta Supersite Experiment, in press.

(t1) RSMS-II: Particle Types vs. Size, Time, Wind

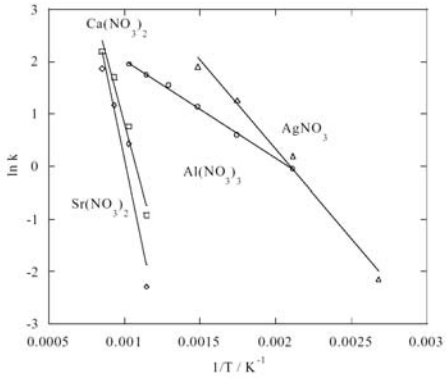


Denis J. Phares, Kevin P. Rhoads, Murray V. Johnston, Anthony S. Wexler. Size-resolved ultrafine particle composition analysis Part 2: Houston. JGR special issue on the 1999 Atlanta Supersite Experiment, in press.

(t1) SPMS: Nanoparticle Chemical Kinetics

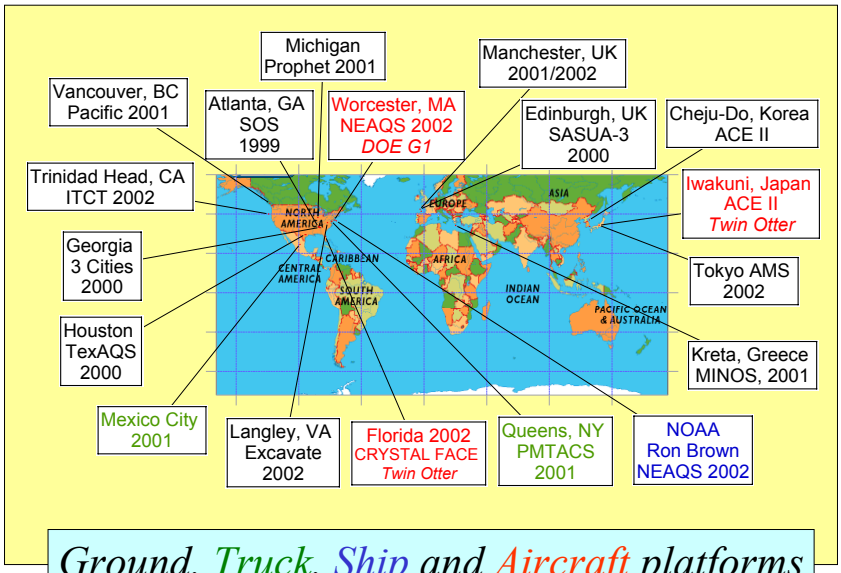
- Kinetics of thermal decomposition of metal nitrates in aerosol phase.
- Reaction carried out in furnace.
- Compared to traditional thermogravimetric analysis, observed significantly greater rates.
- The aerosol method is not prone to biases due to heat and mass transport. The thermogravimetric method is known to have such biases.

Arrhenius Plot



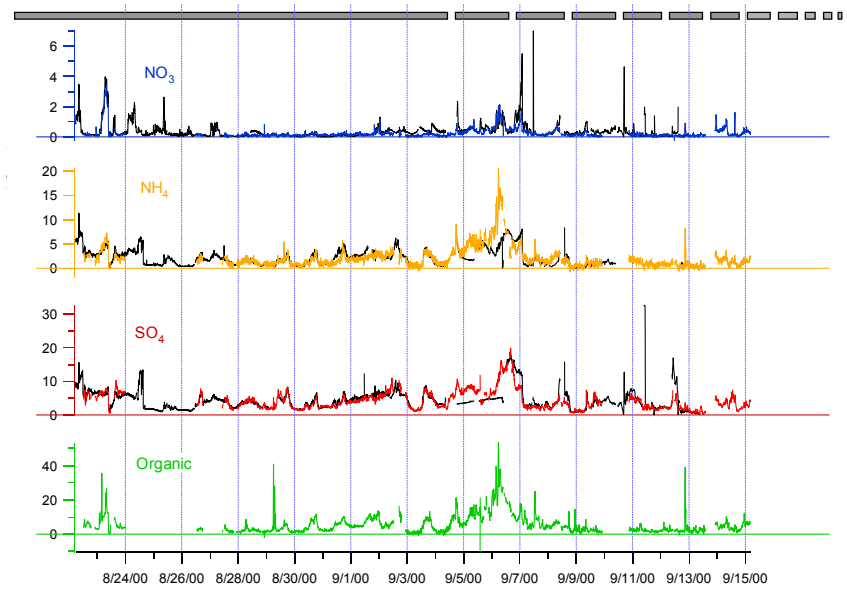
R. Mahadevan, D. Lee, H. Sakurai, and M. R. Zachariah, Measurement of Condensed-Phase Reaction Kinetics in the Aerosol Phase Using Single Particle Mass Spectrometry, Accepted for Publication, J. Phys. Chem. A, 2002.

(t3) AMS: Ambient Sampling

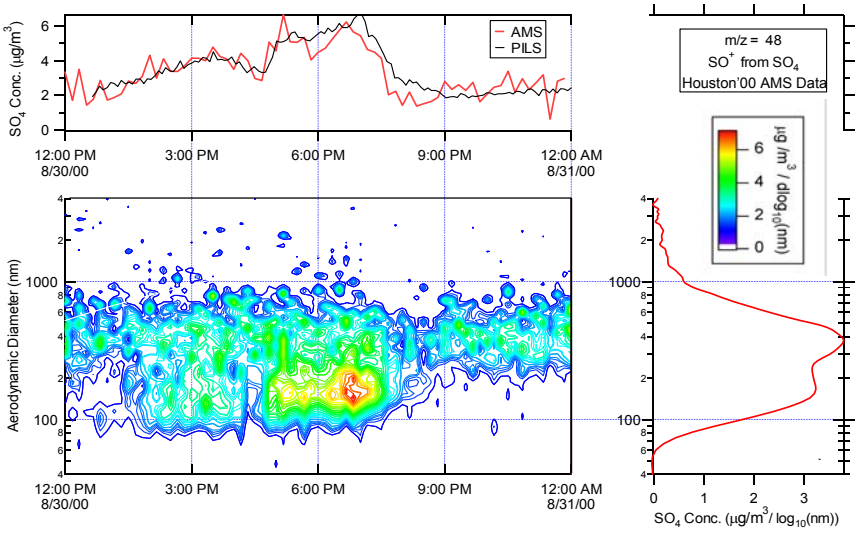


Ground, Truck, Ship and Aircraft platforms

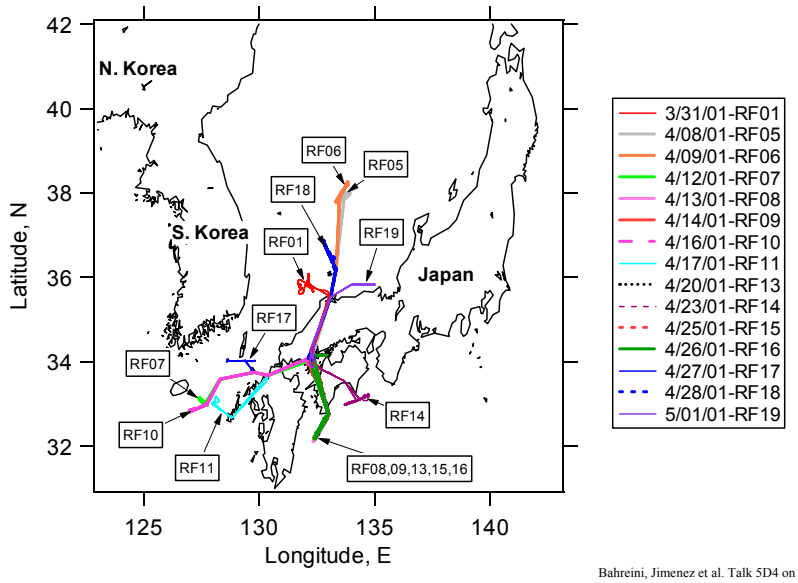
(t3) AMS: Aerosol Composition in Houston



(t3) AMS: Time and Size Separation in Houston

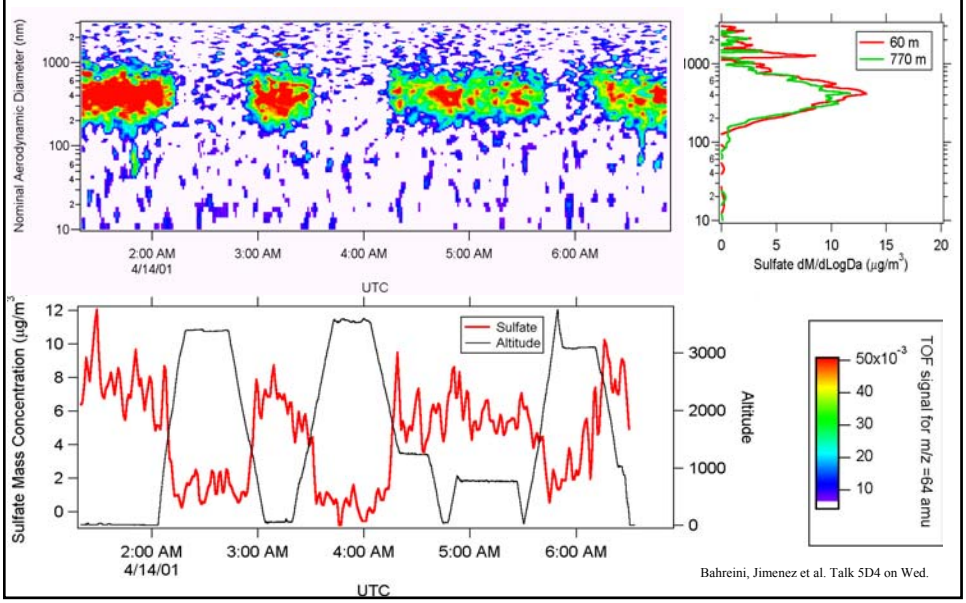


(t3) AMS: Twin Otter Flights in ACE-Asia



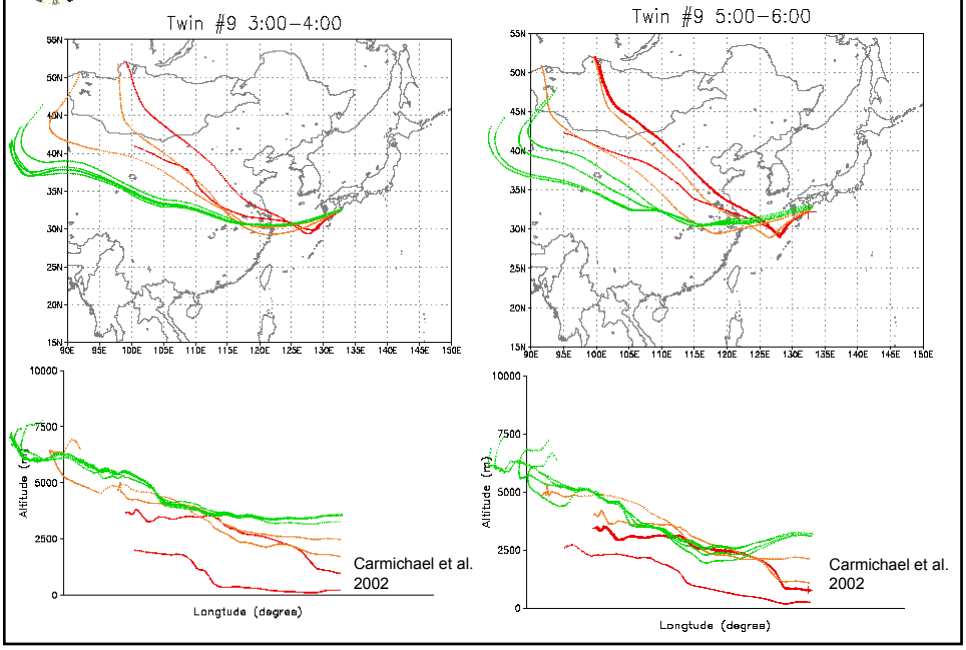
Bahreini, Jimenez et al. Talk 5D4 on Wed.

(t3) AMS: Sulfate Layers during ACE-Asia

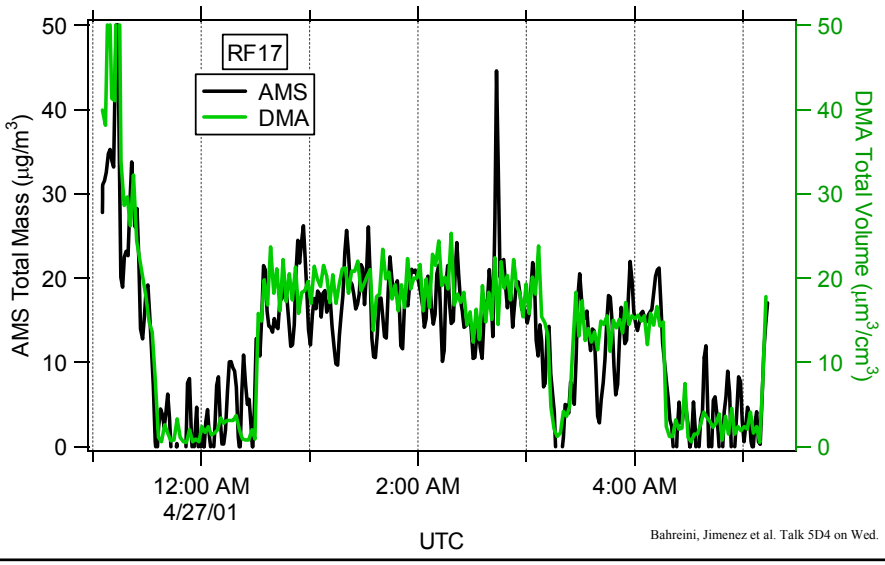


Bahreini, Jimenez et al. Talk 5D4 on Wed.

ACE-Asia- RF9-2001/04/14

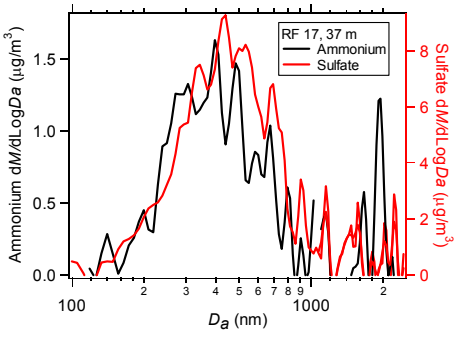


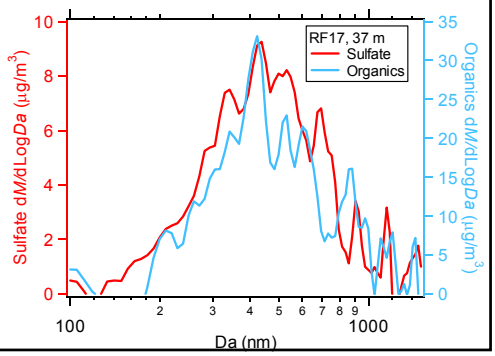
(t3) AMS vs. DMA during ACE-Asia Flight



Bahreini, Jimenez et al. Talk 5D4 on Wed.

(t3) AMS: Internally Mixed Aerosols

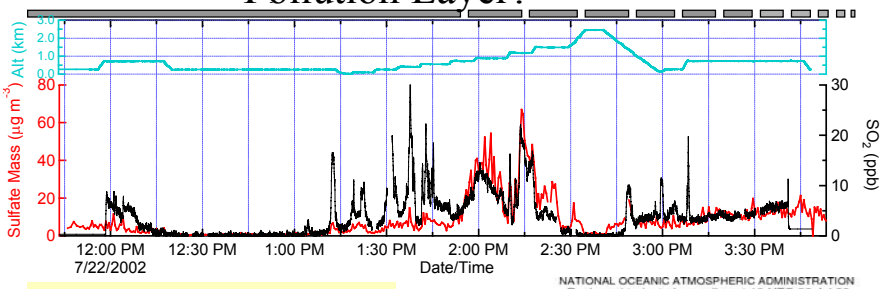


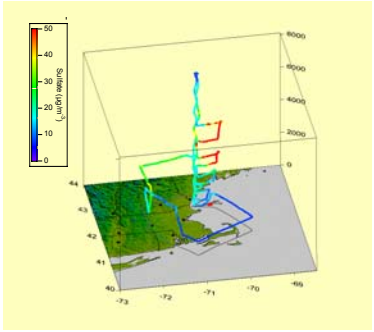


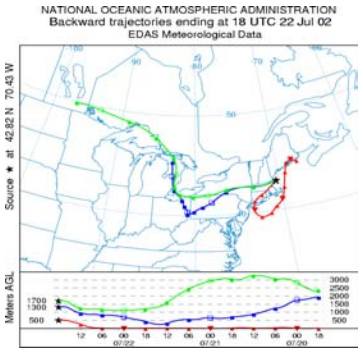
Bahreini, Jimenez et al. Talk 5D4 on Wed.

(t3) AMS: Ohio Valley Pollution Layer?

John Jayne, Manjula Canagaratna, Doug Worsnop: Summer 2002 Field Campaign in New England

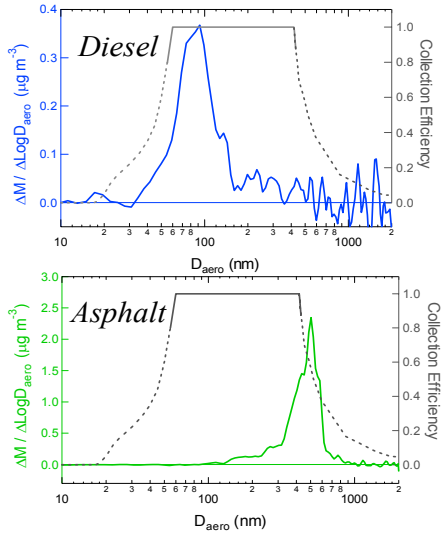






Courtesy of Aerodyne Research.

(t3) AMS: 4-Second Data Rate



Emission factors can be determined while chasing individual vehicles on road

Courtesy of Aerodyne Research.

Part 5: The Future

My Take on Near Future of Aerosol MS

- Technique is still in its infancy
- Inlets: improved and "tuned" aerodynamic lenses
- Thermal vaporization + EI + Time-of-Flight MS
- Chemical ionization
- Commercial Single Particle Elemental Composition
- Aerosol MS will be commonplace: e.g. at least one in each field study site / airplane…
- Commercial instruments will be used by non-specialists thanks to software & hardware improvements
  - Like evolution of DMA in the last 10-20 years
  - Price will still be limiting factor
- Custom-built instruments will be specialized for problems that the commercial instruments don't do well
- Bioterrorism developments?

Challenges Ahead

- Detection bias due to particle shape
  - Worse for instruments with small collection angles (generally laser-based)
- Quantitative detection of H_2O
- Evaporation / condensation artifacts
- Improved quantification
- Quantitative detection of dust, soot, trace metals
- Organic molecular information
- Ultrafine particles
- Miniaturization
- *Data analysis techniques & software!*

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- Deborah Gross
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- Jim Smith
- Michael Zachariah
- Paul Ziemann
- Pete Reilly
- Doug Worsnop
- Roya Bahreini
- John Jayne
- Manjula Canagaratna
- James Allan
- Bill Reents
- Tomas Baer
- Bernhard Spengler
- Klaus-Peter Hinz
- Frank Drewnick
- AMS Users
- TSI Inc. (M. Galli and R. Karlson)
- Qi Zhang
- *My CU mass spec. students*

Some References

- http://cires.colorado.edu/~jjose/ams.html
  - Lists of references in there
- Noble, C. A., and Prather, K. A. (2000). “Real-time single particle mass spectrometry: A historical review of a quarter century of the chemical analysis of aerosols.” Mass Spectrometry Reviews, 19(4), 248-274.
- Special issue on mass spectrometry of aerosols: Aerosol Science and Technology, 33(1-2), July/Aug. 2000.
- Wexler, A. S., and Johnston, M. V. (2001). “Real-time single-particle analysis.” Aerosol Measurement: Principles, Techniques, and Applications, P. A. Baron and K. Willeke, eds., Wiley-Interscience, New York, 365-386.