2010 International Aerosol Conference
Helsinki, Finland
Tutorial

Real-Time Aerosol Mass Spectrometry

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http://cires.colorado.edu/jimenez/ams.html

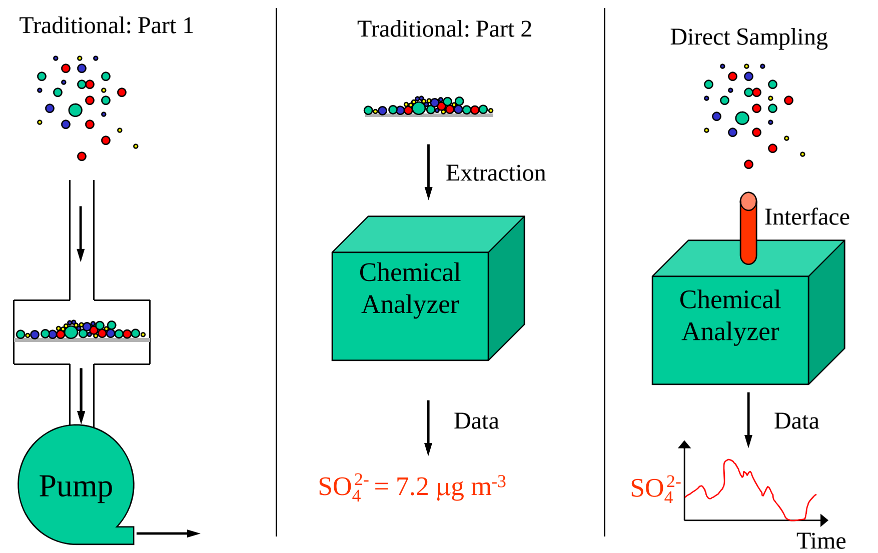
Outline

Introduction

1. Building Blocks
2. Instrument Designs
   - Main Properties
   - Example applications
   - Only most commonly used or useful ones, too many to cover them all here!
3. The Future

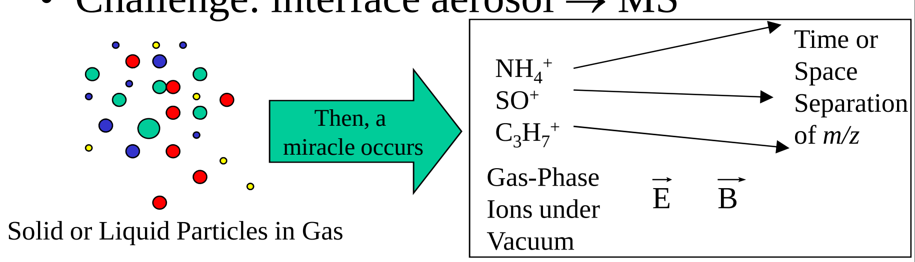
Note: focus on most common or useful instruments & last 10 years – don't have time to cover everything, or early work (see references)

Aerosol Chemical Analysis



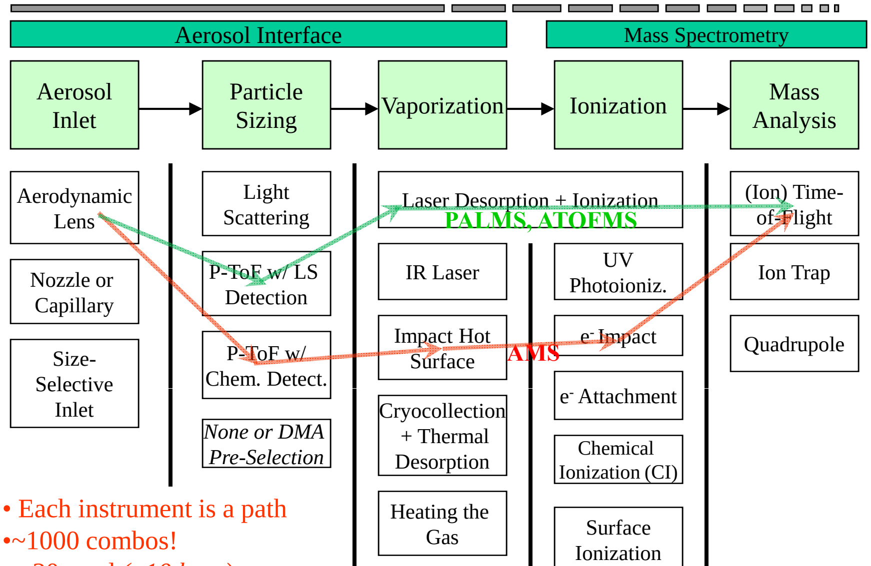
Why Aerosol Mass Spectrometry?

- Mass Spectrometry
  - Extreme sensitivity
  - Very fast response (down to 0.1 ms)
  - Universal detection
  - Field deployable
- Challenge: interface aerosol → MS



Part 1: Instrumentation Building Blocks

Conceptual Schematic of an Aerosol MS

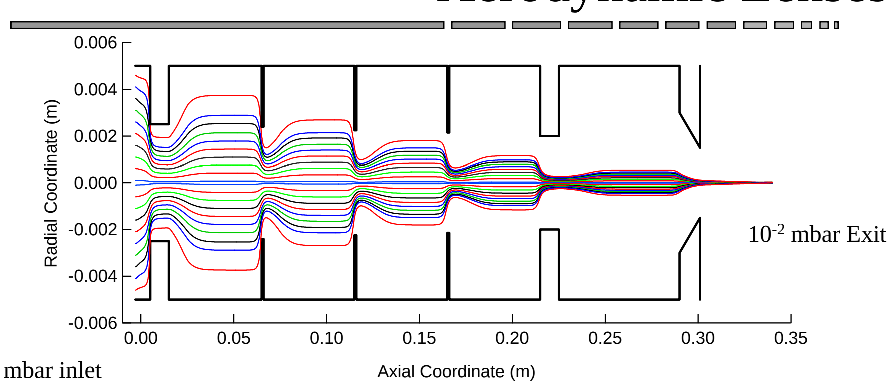


- Each instrument is a path
- ~1000 combos!
- ~30 used *(~10 here)*

Aerosol Inlets

- Particle Beam MS:
  - Introduce the particles into vacuum
  - Concentrate aerosols from gas-phase
    - ~10^{-8} particle (10 μg m^{-3}) / gas (1 kg m^{-3})
    - Reduce gas-phase interferences
  - Impart size-dependent velocity
    - Use to measure size by *particle* time-of-flight
- Other custom inlets

Aerodynamic Lenses



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

Original lens design:
- Liu, P., Ziemann, P. L., Kittelson , D. B., and McMurry, P. H. *Aerosol Sci. Technol.* 22:293–313, 1995.
- Liu, P., Ziemann, P. L., Kittelson, D. B., and McMurry, P.H. *Aerosol Sci. Technol.* 22:314–324, 1995.

CFD Simulations:
- Zhang, X., Smith, K.A., Worsnop, D.R., Jimenez, J.L., Jayne, J.T., and Kolb, C.E. *Aerosol Sci. Technol.*, 36: 617, 2002.
- Zhang, X., Smith, K.A., Worsnop, Jimenez, J.L., Jayne, J.T., D.R., Kolb, C.E., Morris, J., Davidovits, P., *Aerosol Sci. Technol.*, 38: 619, 2004.

Beam Width w/ Aerodynamic Lenses

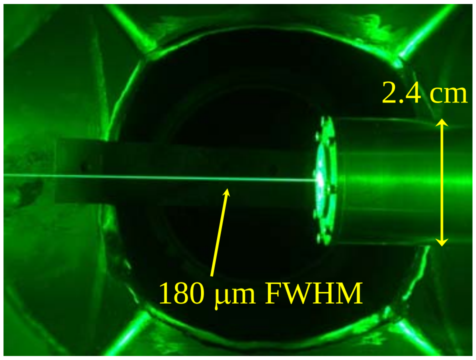


Figure courtesy of Guiseppe Petrucci, Univ. Vermont
http://www.uvm.edu/~gpetrucc

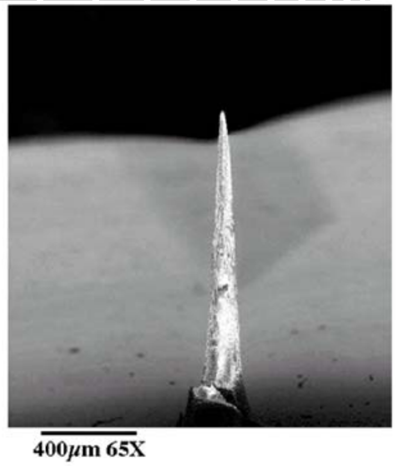
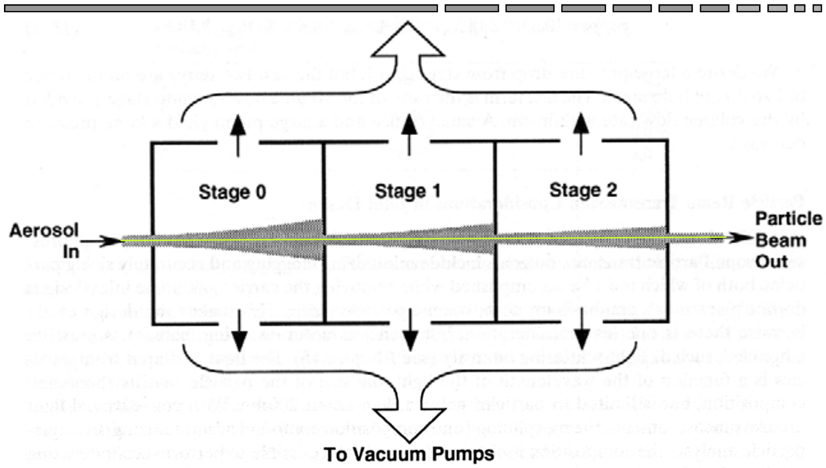


Fig. 6. SEM image of a silicon carbide 'tower' deposited by a focused nanoparticle beam [18].

Heberlein, J., O. Postel, S. Girshick, P. McMurry, W. Gerberichc, D. Iordanoglou, F.D. Fonzo, D. Neumann, A. Gidwani, M. Fan, and N. Tymiakc, Thermal plasma deposition of nanophase hard coatings. *Surface and Coatings Technology*, 2001. **142-144**: p. 265-271.

Differential Pumping of the Gas

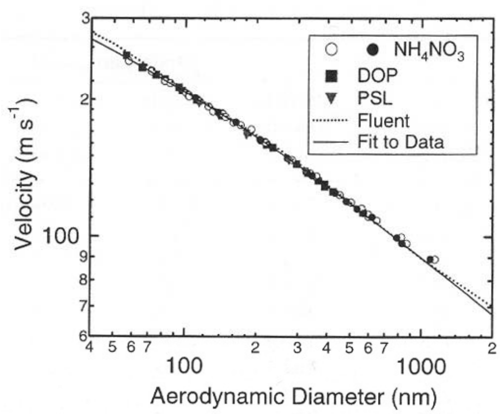


- E.g. in AMS: particles concentrated by 10^7 with respect to gas

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.

Drag: 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



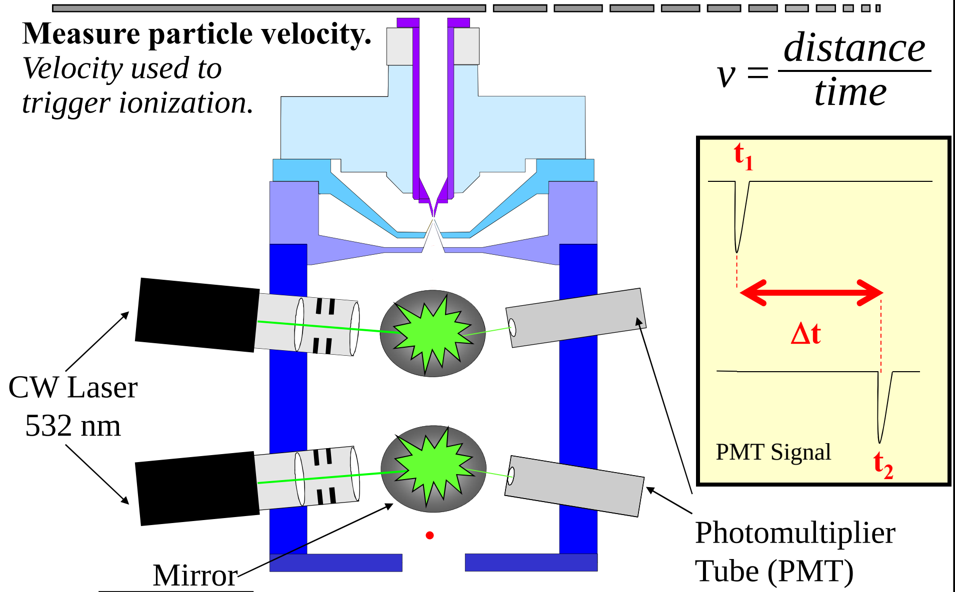
Jayne, J.T., D.C. Leard, X. Zhang, P. Davidovits, K.A. Smith, C.E. Kolb, and D.R. Worsnop, Development of an aerosol mass spectrometer for size and composition. analysis of submicron particles, Aerosol Sci. Technol., 33, 49-70, 2000.

Animation courtesy of
Deborah Gross
Carleton College

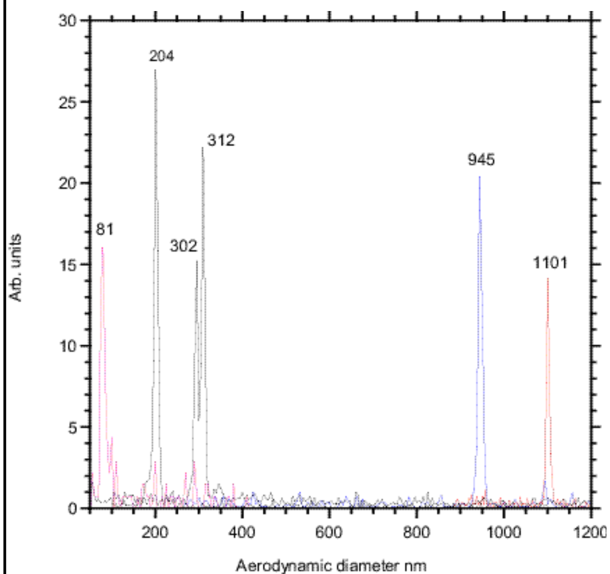
Particle TOF with LS Detection

Measure particle velocity.
Velocity used to trigger ionization.

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



Two-Laser TOF: Resolution



- Very high size resolution

  $R_d = d_{va}/\Delta d_{va} \sim 30$

$$d_{va} = \frac{\rho_p}{\rho_0}\frac{d_{ve}}{\chi_v}$$

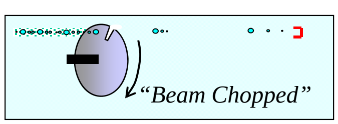
d_{va}: vacuum aerodynamic diameter (see DeCarlo et al., *Aerosol. Sci. Technol.*, 2004)

Zelenyuk, Alla and Imre. Beyond single particle mass spectrometry: multidimensional characterisation of individual aerosol particles, *International Reviews in Physical Chemistry*,28:2,309 -358, 2009.

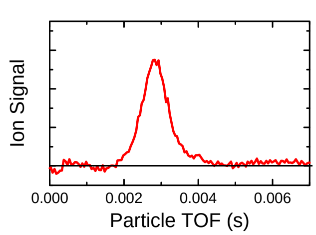
Figure courtesy of Dan Imre.

Size measurement: chopper + chemical detect.

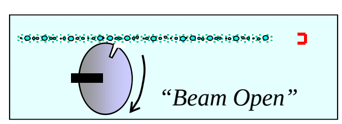
Size Distribution



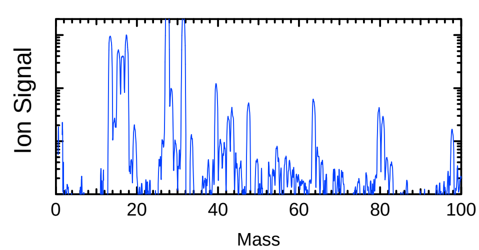
- Size distribution at each *m/z*
- Lower resolution than laser PToF
- But signal cut by ~25!



Ensemble Composition



- No size information
- Much higher signal-to-noise



Size Distribution Quantification

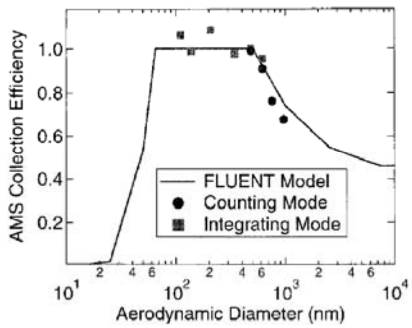


FIGURE 9. Summary of the AMS particle collection / detection efficiency as a function of aerodynamic diameter. Solid line is FLUENT model prediction. Circles are efficiencies determined by comparing AMS and CPC counting rates (data from Figure 8). Squares are collection efficiencies determined from the 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).

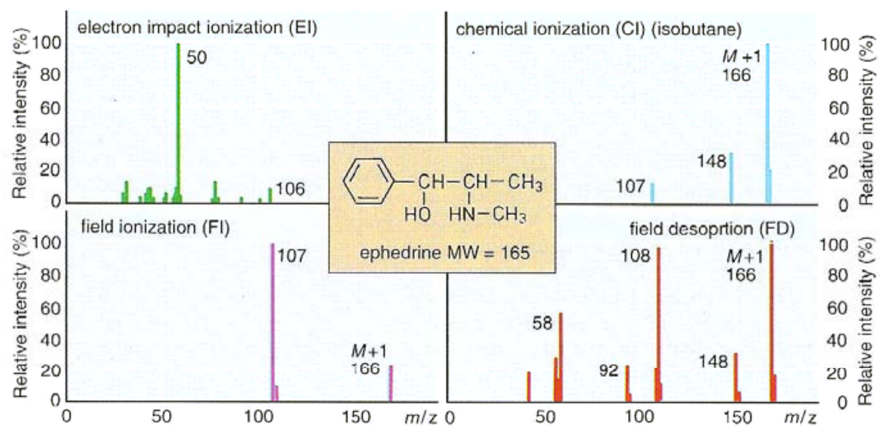
- No inlet can transmit all sizes
- Most common: submicron lenses
- Some custom lenses & others

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.

Ionization Objectives

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

Effect of Ionization Techniques



K. Comparison of mass spectra following different ionization methods

- Information is complementary
- Obtain data from more than one technique

From Schewdt, The Essential Guide to Analytical Chemistry, Wiley, 1997

EI Fragmentation vs. Molecular Structure

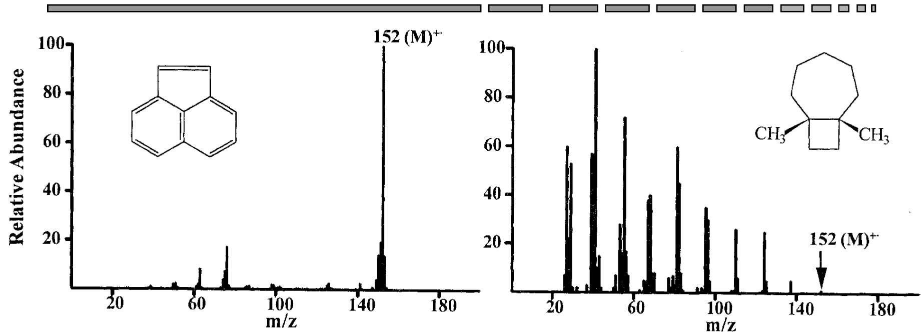
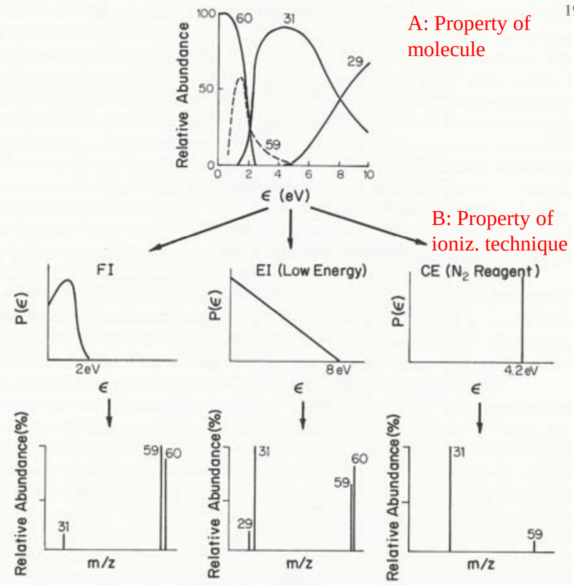


Figure 13-4 Contrasting degrees of fragmentation observed in the EI spectra of an aromatic and an alicyclic compound. The former resists dissociation and gives a molecular ion from which the molecular weight (152 Da) is measured. (From P.J. Ausloos, C. Clifton, O.V. Fateev, A.A. Levitsky, S.G. Lias, W.G. Mallard, A. Shamin, and S.E. Stein, NIST/EPA/NIH Mass Spectral Library—Version 1.5, National Institute of Standards and Technology, Gaithersburg, MD [1996].)

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

Breakdown Curve and Internal Energy Distribution



Result is convolution of A+B

Figure 14-29 Convolution of the breakdown curve (top, an intrinsic property) with the internal energy distribution (P[ε]) resulting from different ionization techniques under particular experimental conditions to produce mass spectra of 1-propanol. FI indicates field ionization, a soft ionization method used for vapor phase samples.

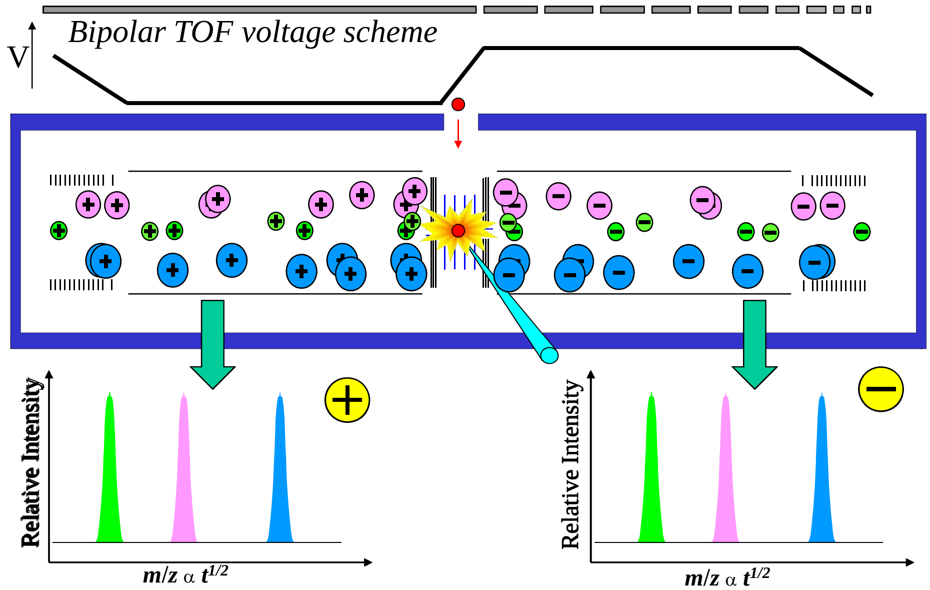
J.B. Lambert, H.F. Shurvell, D.A. Lightner, R. G. Cooks, Organic Structural Spectroscopy. Prentice-Hall, 2002.

Mass Spectrometer

- Now we have made some ions
- Electrical / magnetic forces to sort ions according to *m/z*
- In most aerosol mass spectrometers
  - **(Ion) Time-of-Flight**
  - Quadrupole or Ion Trap
- Not generally used so far in Aerosol MS
  - Electric & magnetic sectors
  - Fourier Transform – Ion Cyclotron Resonance
  - Orbitrap
- More info on:
  - http://www.colorado.edu/chemistry/chem5181 (my course)
  - http://en.wikipedia.org/wiki/Mass_spectrometry

Mass Spectrometer: (Ion)Time-of-Flight

Animation courtesy of Deborah Gross Carleton College



Mass Spectrometer: Quadrupole

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

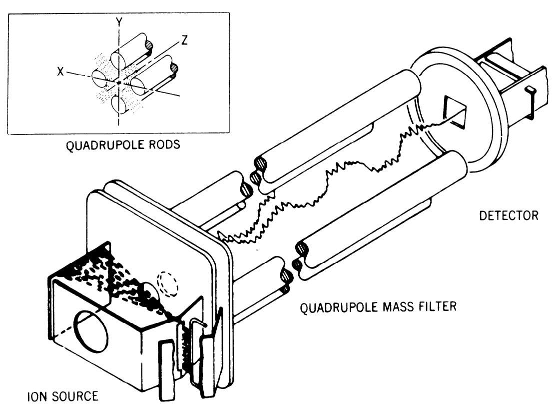


FIG. 4.7. Schematic diagram of quadrupole mass spectrometer illustrating irregular flight path of ions from the ion source through the central space between the quadrupole rods to the detector. (Courtesy of Finnigan Corporation.)

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

Mass Spectrometer: Ion Trap

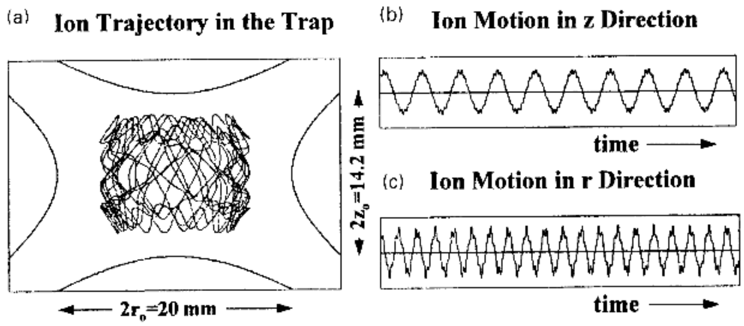
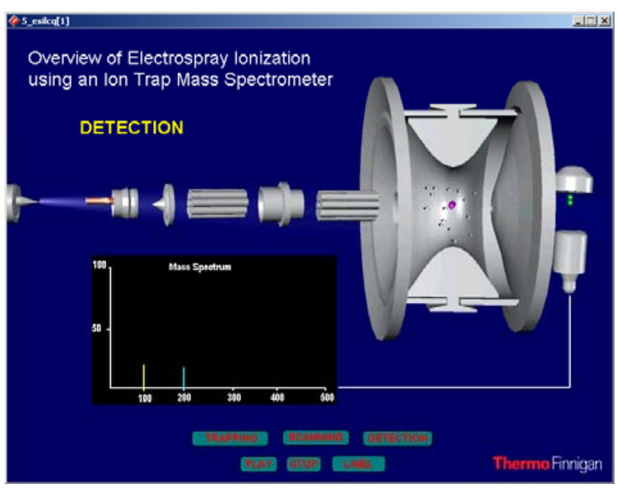


Figure 13-24 Simulation of motion of a single trapped ion in an ion trap: (a) shows the overall motion within the trap in cross section, (b) shows the time-dependent component of motion in the axial direction, and (c) shows the radial-direction component.

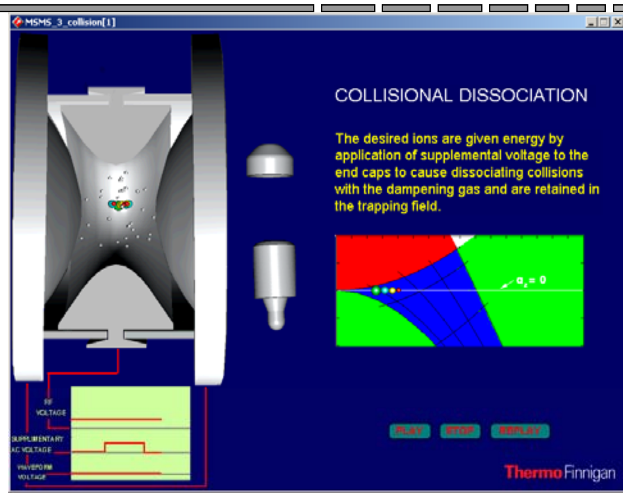
J.B. Lambert, H.F. Shurvell, D.A. Lightner, R. G. Cooks, Organic Structural Spectroscopy. Prentice-Hall, 2002.

Ion Trap Movie



- These and more available at:
  - http://www.colorado.edu/chemistry/chem5181

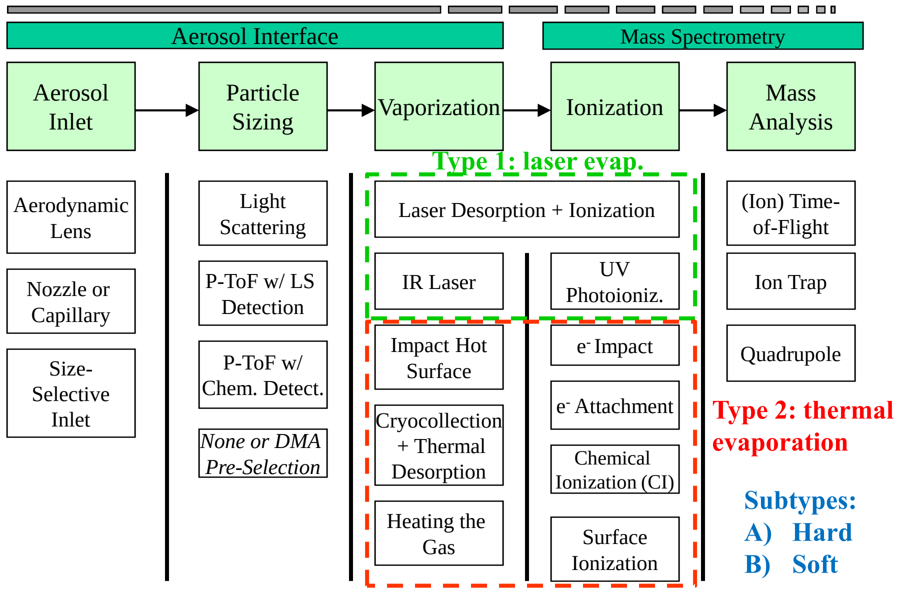
MS/MS with an Ion Trap



- MS/MS: isolate an ion, break it into pieces
  - Obtain its “mass spectrum”

Part 2: Instrument Implementations

Conceptual Schematic of an Aerosol MS



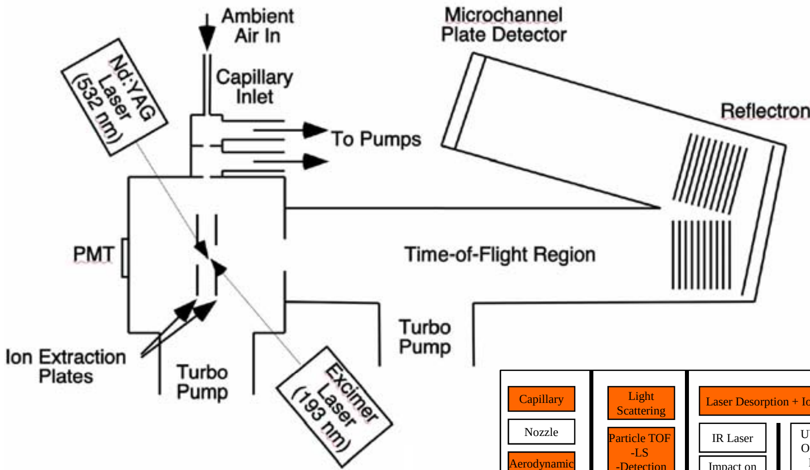
Type 1A: Laser Vaporization + Ionization

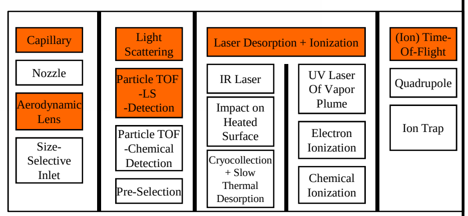
- Particle Analysis by Mass Spectrometry (PALMS): Dan Murphy et al., NOAA-Boulder
- Aerosol Time-of-Flight Mass Spectrometer (ATOFMS): Kim Prather et al., U. California (R/SD)
- Single-Particle Laser Ablation Mass Spectrometer (SPLAT): Alla Zelenyuk, Dan Imre et al., US DOE PNNL

Some Key Publications

- D.M. Murphy. The design of single-particle mass spectrometers. *Mass Spec. Rev.*, 26, 150– 165, 2007.
- D. M. Murphy, D. J. Cziczo, K. D. Froyd, et al., Single-particle mass spectrometry of tropospheric aerosol particles, J. Geophys. Res., 111, D23S32, doi:10.1029/2006JD007340, 2006.
- K.A. Pratt, J.E. Mayer, J.C. Holecek, R.C. Moffet, R.O. Sanchez, T.P. Rebotier, P. Thomas , H. Furutani, M. Gonin, K. Fuhrer, Y.X. Su, S. Guazzotti, K.A. Prather. Development and Characterization of an Aircraft Aerosol Time-of-Flight Mass Spectrometer. *Anal. Chem.*, 81, 1792-1800, 2009.
- A. Zelenyuk, and D. Imre. Beyond single particle mass spectrometry: multidimensional characterisation of individual aerosol particles, *International Reviews in Physical Chemistry*, 28:2,309 -358, 2009.

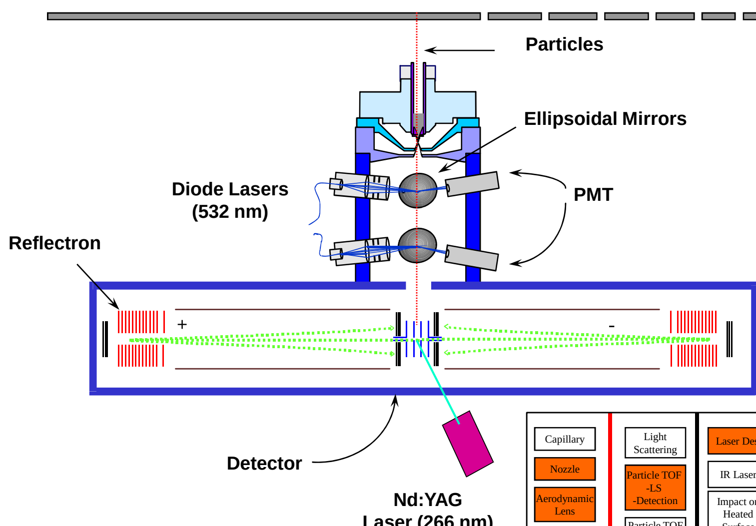
Type 1A: PALMS (Murphy *et al.*)





Middlebrook, A., Murphy, D.M., et al. An intercomparison of Particle Mass Spectrometers During the 1999 Atlanta Supersite Project. Journal of Geophysical Research-Atmospheres, 108(D7), 8424, doi:10.1029/2001JD000660, 2003.

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



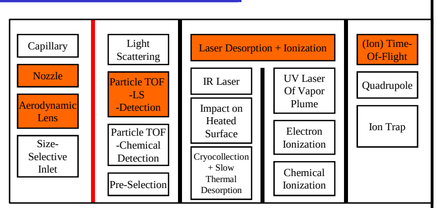
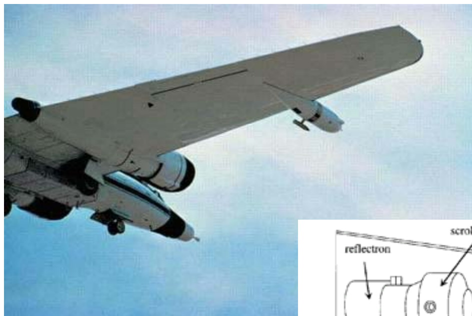


Figure courtesy of Prof. Kim Prather

Type 1A: PALMS on Nose of WB-57



- Very short inlet to minimize perturbation of particles (e.g. evaporation)
- Pilot has on/off switch

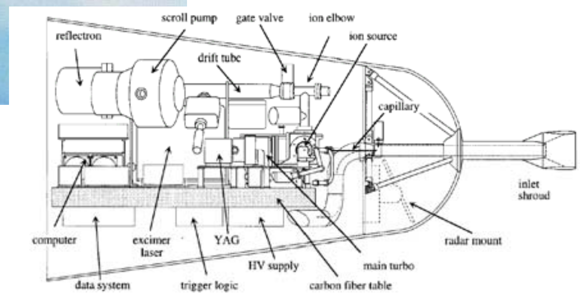
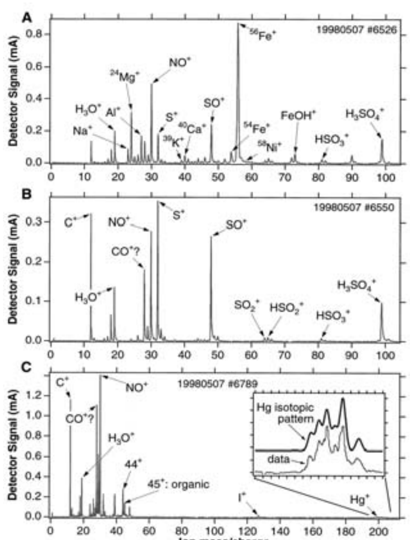


FIGURE 3. Schematic layout of the PALMS instrument components. For scale, the carbon fiber table is 122 cm (48″) long.

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.

Type 1A: PALMS: Stratospheric Aerosols

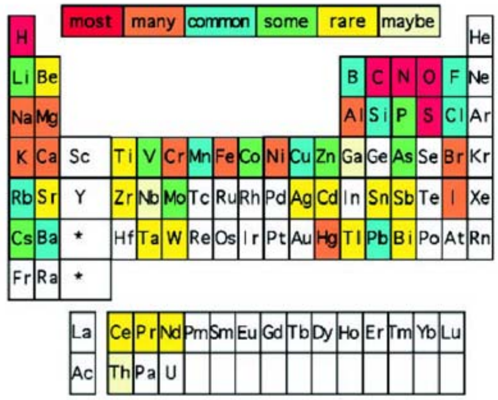
Murphy et al. (1998) Science, 282, 1664



- 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

Type 1A: PALMS: Elements in Part. 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.

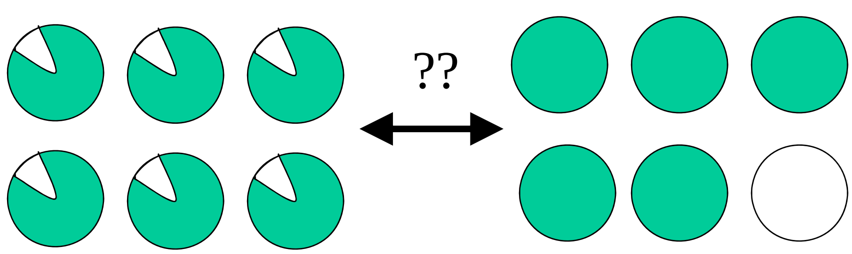


D. M. Murphy*, D. S. Thomson, M. J. Mahoney. In-Situ Measurements of Organics, Meteoritic Material, Mercury, and Other Elements in Aerosols from 5 to 19 km. Science 282: 1664-1668, 1998.

Ensemble vs. Single Particle Analysis

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

"Internally Mixed" "Externally Mixed"



- Single Particle instruments DIRECTLY detect the mixing state
  - Superior for e.g. ice nucleation studies (also refractory)
  - Ensemble averaging instruments only provide indirect info. on mixing state
- SP also superior for low number density situations

Type 1A: Nano Aerosol MS (NAMS)

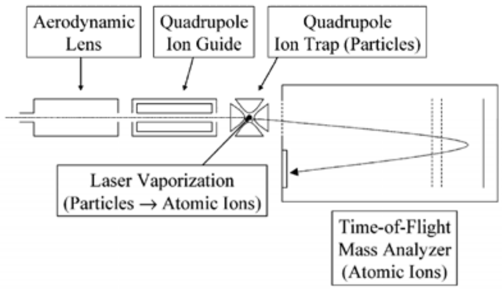


Figure 1. Basic design of the nanoaerosol mass spectrometer.

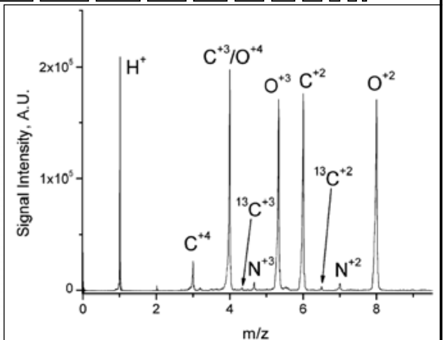
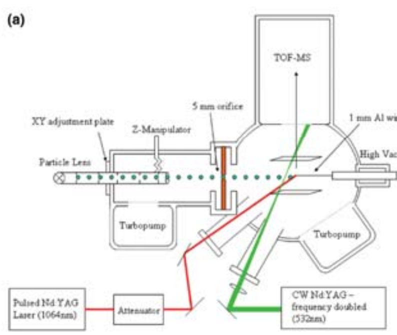


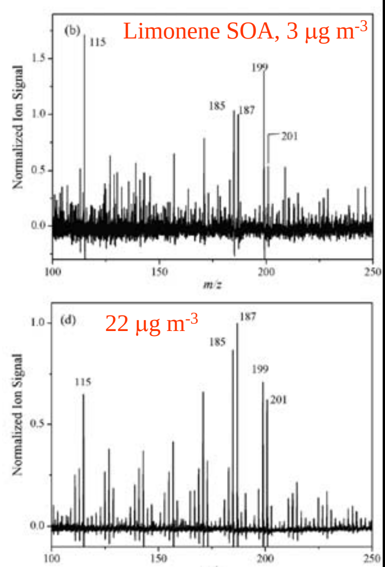
Figure 2. Low *m/z* region of the mass spectrum of ~10-nm-diameter sucrose particles, average of 50 individual spectra.

- Extremely high laser intensity
- Turn all atoms in the particle into multiply charged ions (high sens.)
- Determine elemental composition of nanoparticles

- S. Wang, C.A. Zordan, and M.V. Johnston. Chemical Characterization of Individual, Airborne Sub-10-nm Particles and Molecules. *Anal. Chem.* 2006, 78, 1750-1754
- NAMS follows up on earlier work from Reents and Ge, *Aerosol Sci. Technol.* 33, 122, 2000.

Type 1B: Near IR-LDI-MS





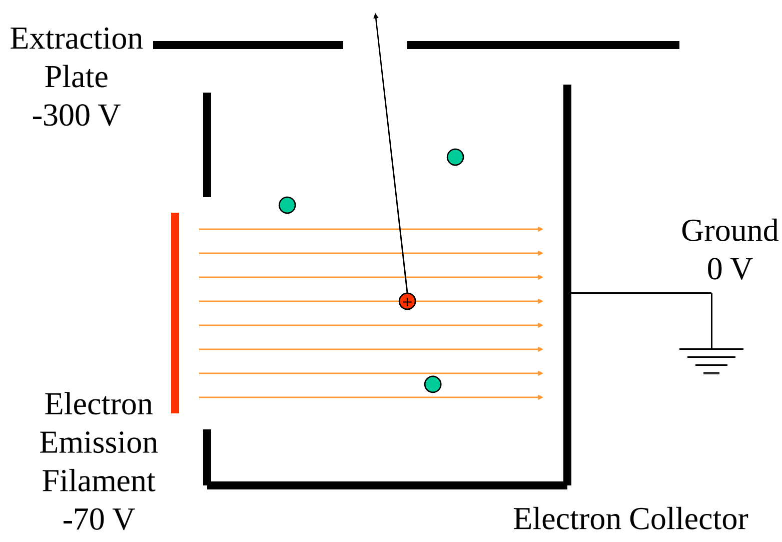
- Very recent, not well characterized
- Holy grial of soft-ionization: high signal w/ low fragmentation

S. Geddes, B. Nichols, S. Flemer, J. Eisenhauer, J. Zahardis, and G.A. Petrucci. Near-Infrared Laser Desorption/Ionization Aerosol Mass Spectrometry for Investigating Primary and Secondary Organic Aerosols under Low Loading Conditions. *Anal. Chem.*, ASAP paper, doi: 10.1021/ac1013354.

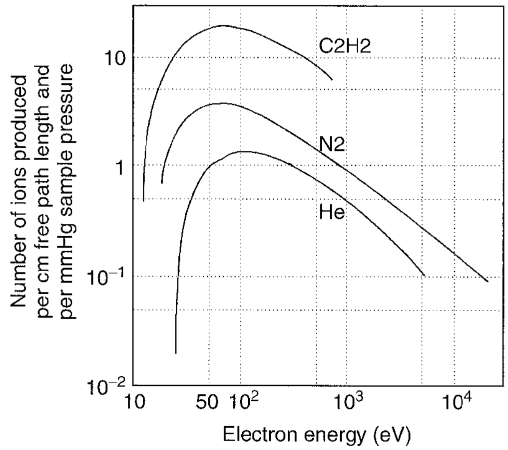
Type 2A:
TD + Electron Impact

- Aerosol Mass Spectrometer (AMS): Aerodyne + 70 groups, Worsnop, Jayne, *et al.*
- Thermal Desorption Particle Beam MS (TDPBMS): UC Riverside, Ziemann *et al.*
- Thermal Desorption Aerosol GC/MS (TAG): UC Berkeley, Goldstein *et al.*

Electron Ionization Source Scheme



Ionization Efficiency vs. Electron Energy

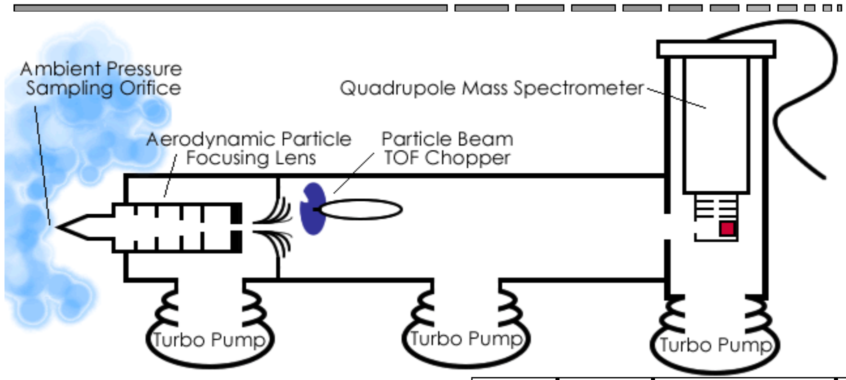


- Need ~70 eV electron energy for high ionization energy (= sensitivity)
- Ionization energy of most molecules ~10 eV
- energy of covalent bonds ~ 4 eV
- There is plenty of extra energy for breaking bonds! => high fragmentation in EI

Figure 1.2
Number of ions produced as a function of the electron energy. A wide maximum appears at around 70 eV

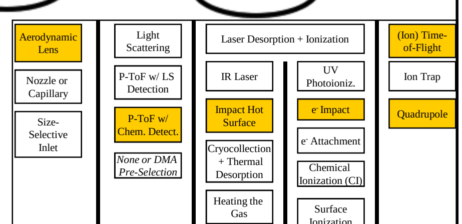
Edmon de Hoffmann and Vincent Stroobant. Mass Spectrometry: Principles and Applications. John Wiley & Sons, 2002.

Type 2A: Aerodyne AMS

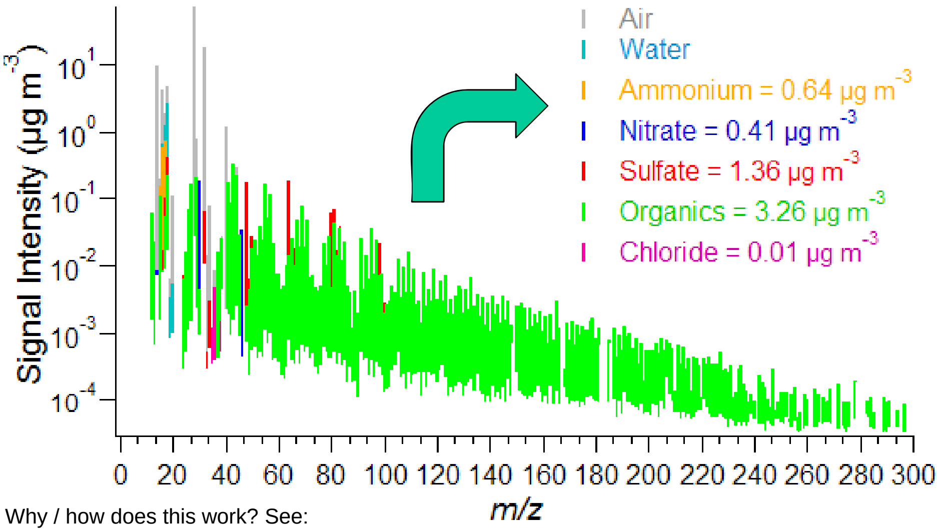


<u>**Key instrument papers**</u>

- Jayne et al., *Aerosol Sci. Technol.* 33, 49-70, 2000.
- Jimenez et al., *J. Geophys. Res.-Atmos.*, 108, 8425, 2003.
- Drewnick et al., *Aerosol Sci. Technol.*, 39, 637-658, 2005.
- DeCarlo et al., *Anal. Chem.*, 78, 8281-8289, 2006.
- Canagaratna et al. *Mass Spec. Rev.*, 26, 185-222, 2007.



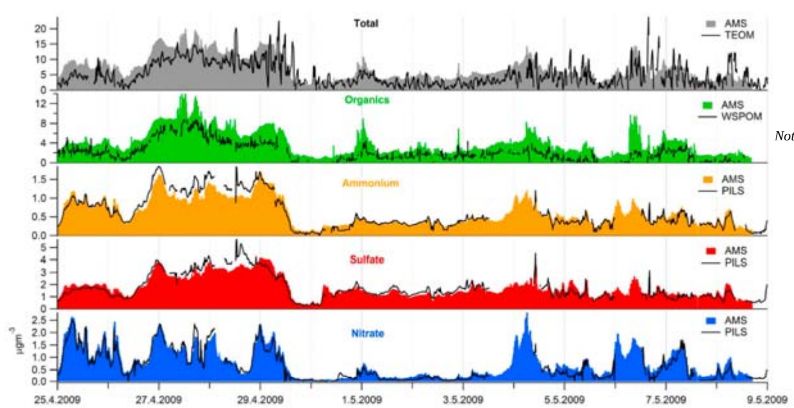
AMS: Ambient Mass Spectrum



Why / how does this work? See:

- Jimenez et al. *J. Geophys. Res.*, 108, 8425, 2003.
- Allan et al., *J. Aerosol Sci.*, 35, 909, 2004.
- Canagaratna et al., *Mass. Spec. Rev*., 26, 185-222, 2007

AMS vs. Other Instruments: Helsinki

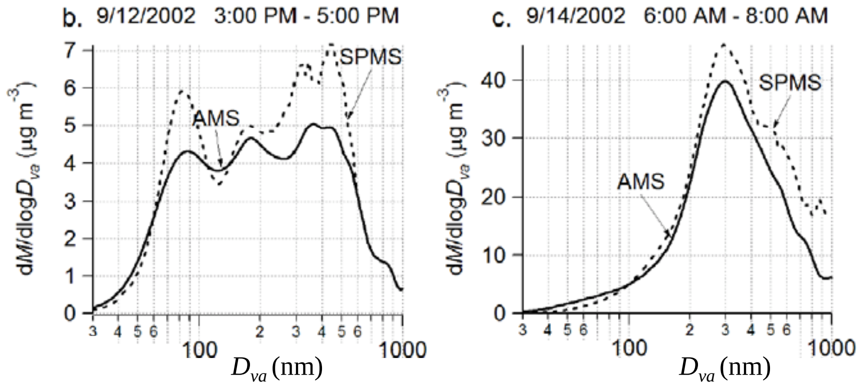


Note OA > WSOA

Fig. 2. Concentrations of major ions and WSPOM (using conversion factor 1.6 to convert WSOC to WSPOM) measured by PILS-TOC-IC and AMS from 25 April to 8 May 2009. PILS-TOC-IC (ions, WSPOM) and TEOM (total mass) results are marked with the black line. AMS results are marked with colors (blue = nitrate, red = sulfate, yellow = ammonium, green = total organics, grey = total mass i.e. sum of ions and organics).

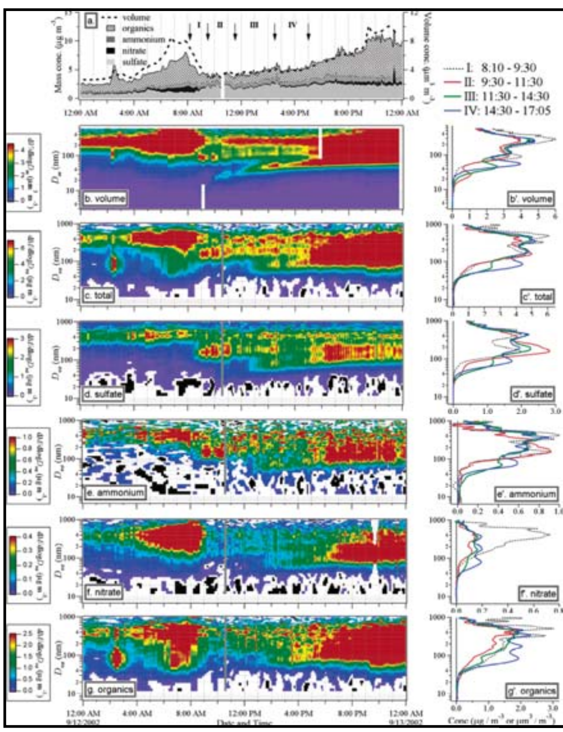
Timonen, H., M. Aurela, S. Carbone, K. Saarnio, S. Saarikoski, T. Makela, M. Kulmala, V.-M. Kerminen, D.R. Worsnop, and R. Hillamo. High Time-resolution Chemical Characterization of the Water-soluble Fraction of Ambient Aerosols with PILS-TOC-IC and AMS. *Atmospheric Measurement Techniques*, 3, 1063-1074, 2010.

AMS: Comparison with SMPS



- Typical level of agreement between AMS and SMPS
- Real differences: effect of shape, refractory particles, size transmission…

Q. Zhang, M.R. Canagaratna, J.T. Jayne, D.R. Worsnop, and J.L. Jimenez. Time and Size-Resolved Chemical Composition of Submicron Particles in Pittsburgh – Implications for Aerosol Sources and Processes. *J. Geophys. Res.*, 110, D07S09, doi:10.1029/2004JD004649, 2005. http://cires.colorado.edu/jimenez/Papers/Pittsburgh_Overview.pdf



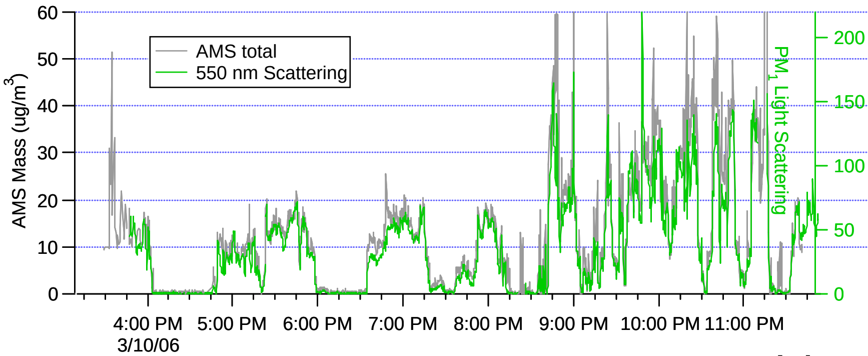
AMS: characterization of coupled size & chemistry @ Pittsburgh Supersite

- Enormous detail on size-resolved composition
- Surprinsingly underutilized

Q. Zhang, C.O. Stanier, M.C. Canagaratna, J.T. Jayne, D.R. Worsnop, S.N. Pandis, and J.L. Jimenez. Insights into the Chemistry of Nucleation Bursts and New Particle Growth Events in Pittsburgh Based on Aerosol Mass Spectrometry. Environmental Science and Technology, 38: 4797-4809, 2004. http://cires.colorado.edu/jimenez/Papers/es035417u_Published.pdf

See Ulbrich et al., Talk 5B3, Tue @ 3:15

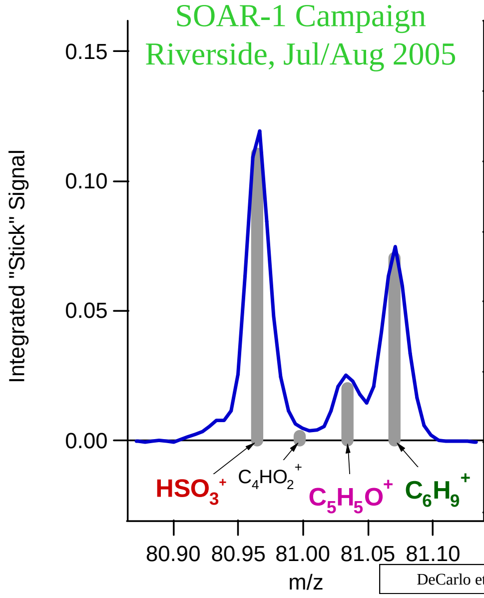
HR-ToF-AMS in C-130 Aircraft

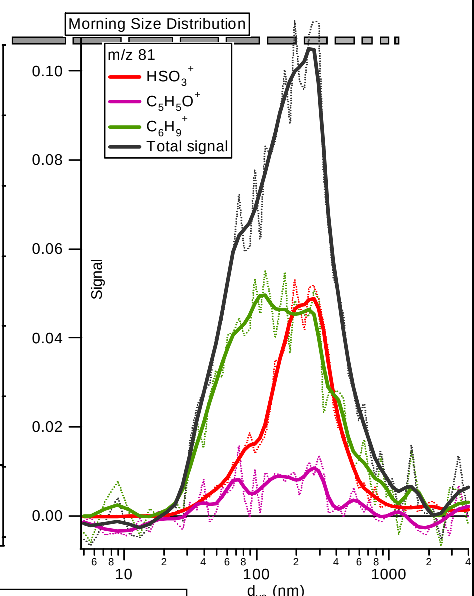


- 3/10/06 MIRAGE Flight
- 15 Second AMS PM_1 mass correlates very well with PM_1 Light Scattering
- Other flights show good correlation as well

DeCarlo et al., *Anal. Chem.* 2006

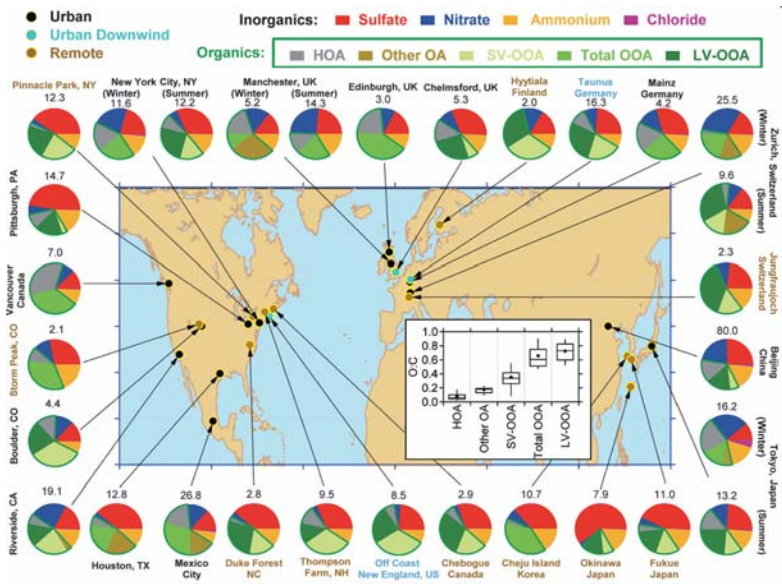
First High Resolution Aerosol Field Data





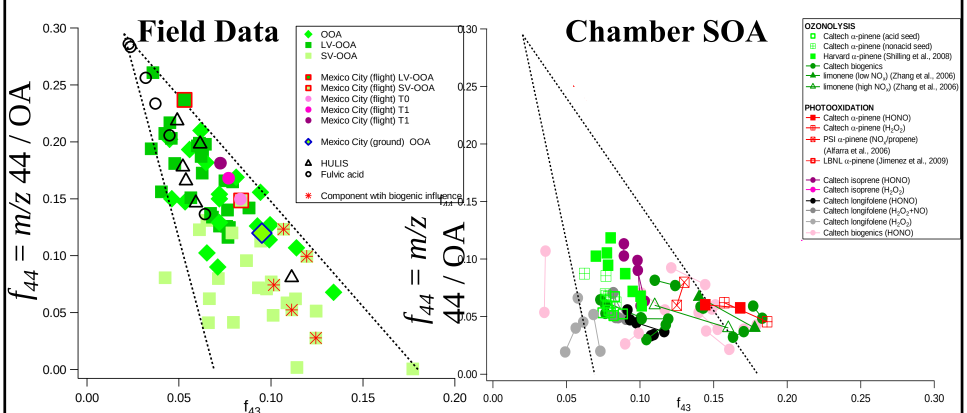
DeCarlo et al., *Anal. Chem.* 2006

AMS: Non-Refractory Composition Worldwide



Jimenez, Canagaratna, Donahue, et al., Science 326, 1525 (2009)

AMS: Field vs. Lab Comparisons



f_{43} = *m/z* 43 / OA f_{43} = *m/z* 43 / OA

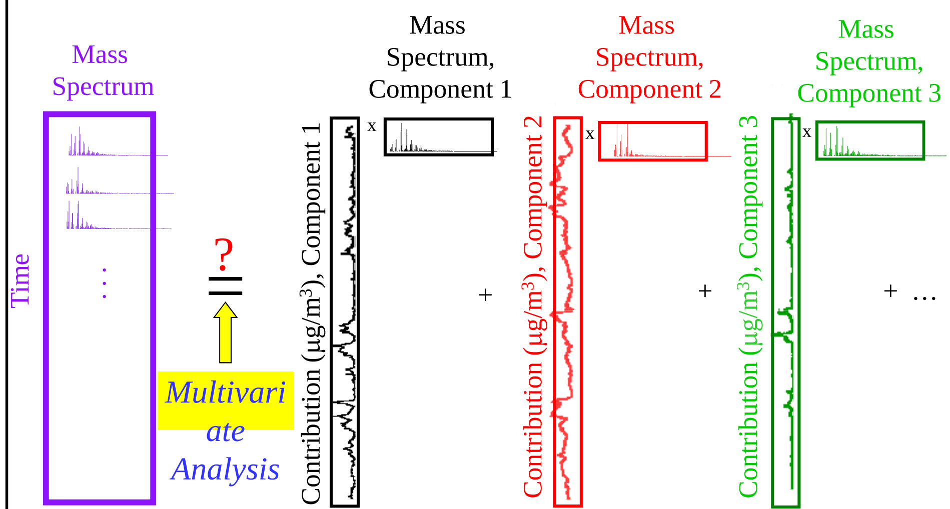
- Not enough OH exposure?
  - < 6 x 10^7 molec cm^{-3} hr (chamber) vs 5 x 10^8 (atmosphere)

Ng, Canagaratna, Zhang, Jimenez, et al., Atmos. Chem. Phys. 10, 4625-4641

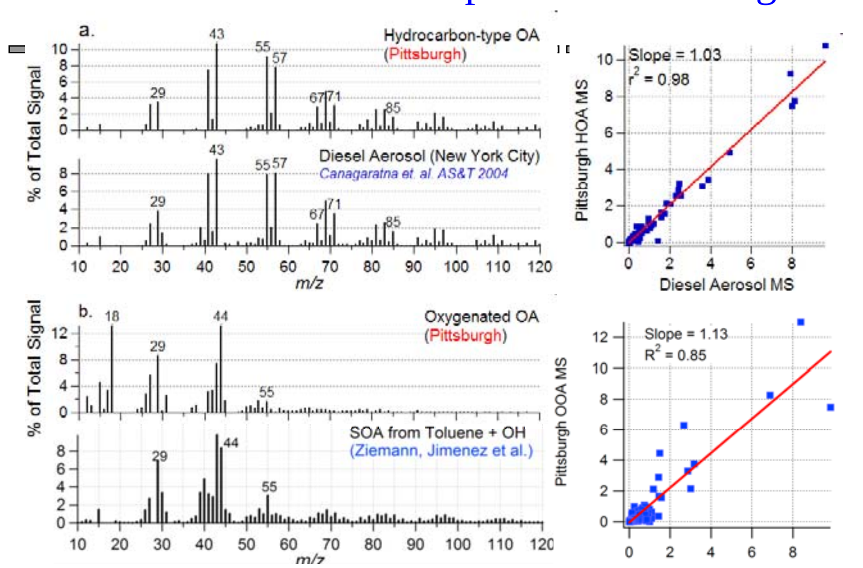
Determine OA Components: Factor Analysis

$$ms_{mixture} = c_a \cdot ms_a + c_b \cdot ms_b + c_c \cdot ms_c + \ldots$$

$$ORG = C \times MS + E$$



HOA and OOA Mass Spectra in Pittsburgh

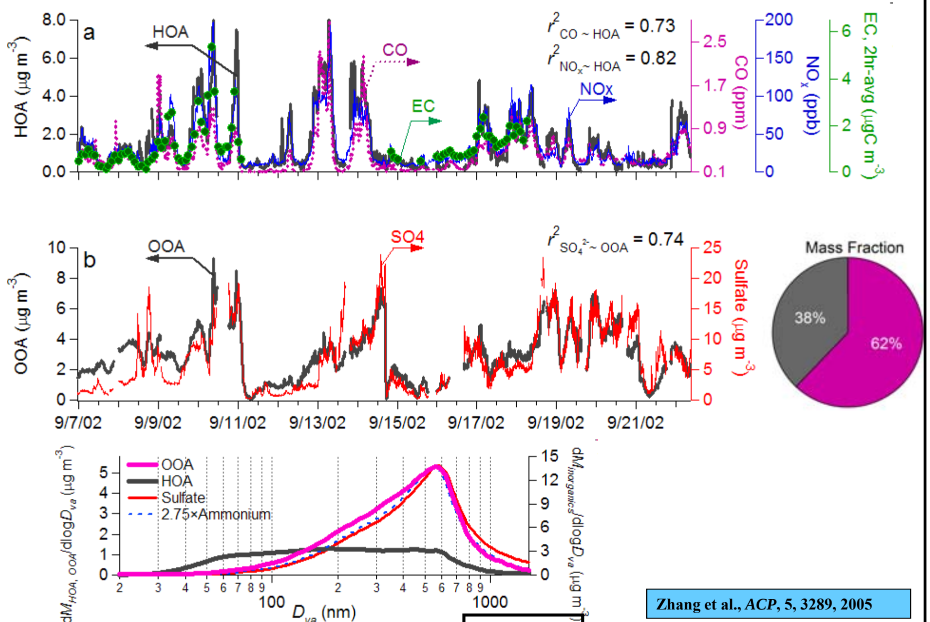


Components ≠ Individual Sources

Multiple sources may have similar MS

Zhang et al., *ES&T*, 2005.

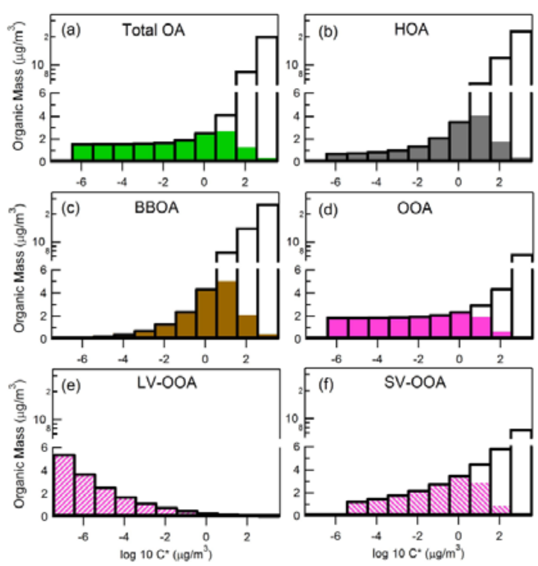
Results: HOA and OOA



Zhang et al., *ACP*, 5, 3289, 2005

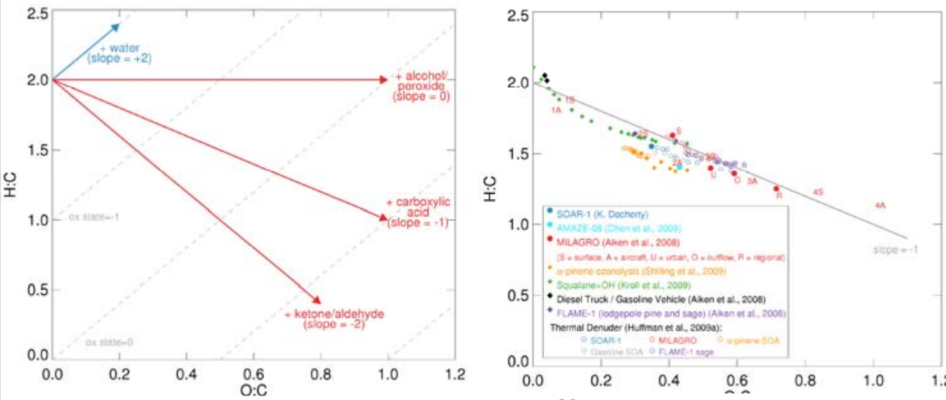
AMS: volatility of Types of OA

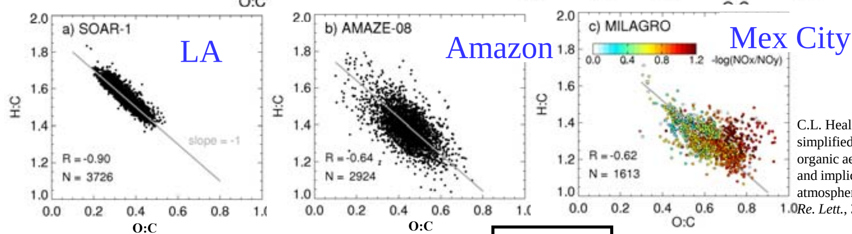
- Hyphenated experiments: thermal-denuder + AMS
- POA is definitely semivolatile
- LV-OOA appears to be non-volatile (solid?)



C.D. Cappa and J.L. Jimenez. Quantitative Estimates of the Volatility of Ambient Organic Aerosol. Atmospheric Chemistry and Physics, 10, 5409-5424, doi:10.5194/acp-10-5409-2010, 2010.

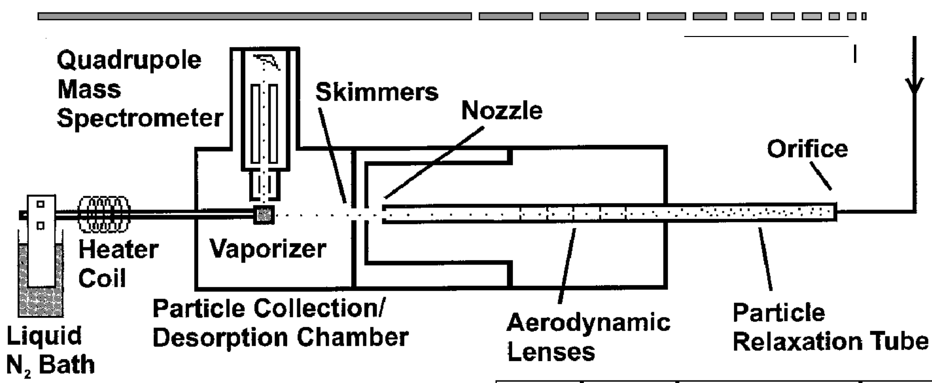
AMS: Elemental Analysis & Van Krevelen Diagrams



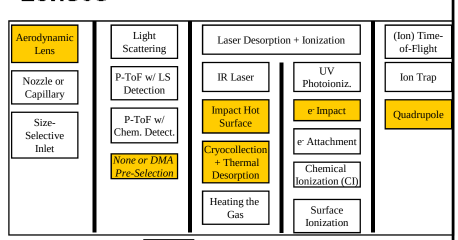


C.L. Heald, et al. A simplified description of organic aerosol composition and implications for atmospheric aging. *Geophy. Re. Lett.*, 37, L08803, 2010.

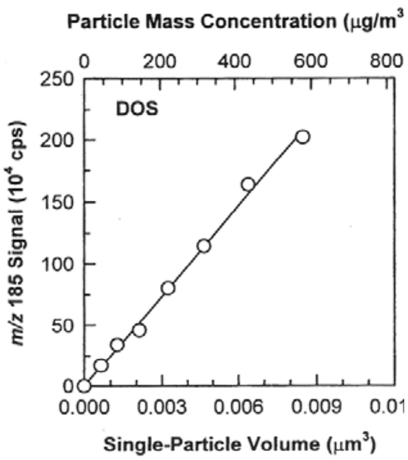
Type 2A: TDPBMS (Ziemann *et al.*)

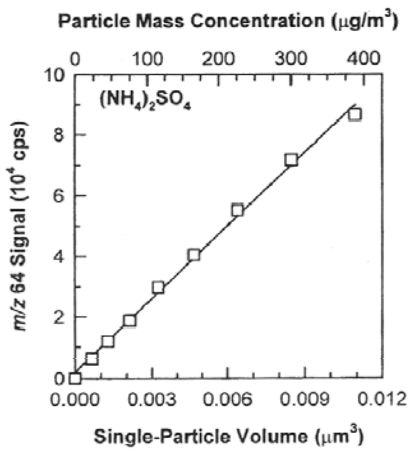


Herbert J. Tobias and Paul J. Ziemann. Compound Identification in Organic Aerosols Using Temperature-Programmed Thermal Desorption Particle Beam Mass Spectrometry. Anal. Chem.1999, 71, 3428-3435.



Type 2A: TDPBMS: 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).

Type 2A: TDPBMS: Volatility + MS

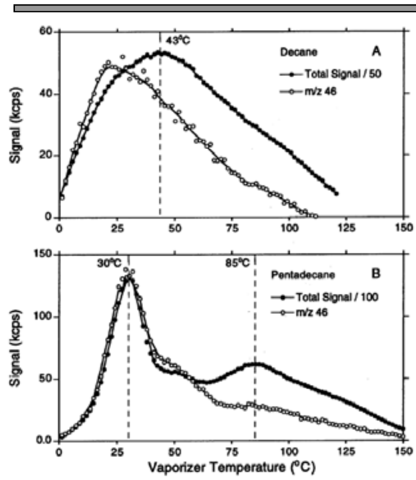


FIGURE 3. Thermal desorption profiles of SOA formed from reactions of (A) decane and (B) pentadecane with OH radicals in the presence of NO_x. Total signal was divided by the factor shown in the legend.

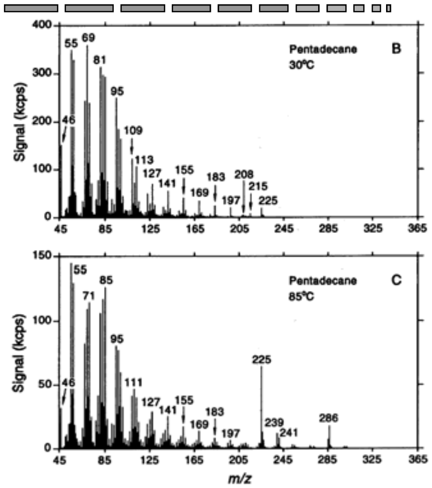
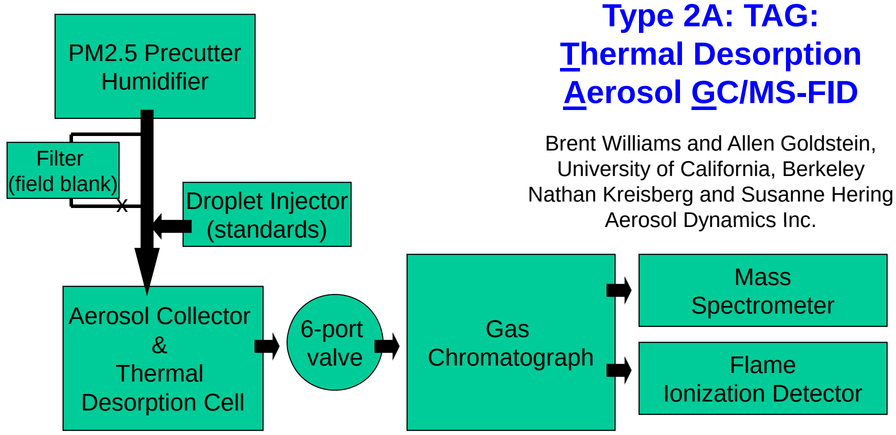


FIGURE 4. TPTD mass spectra of SOA formed from reactions of (A) decane and (B, C) pentadecane with OH radicals in the presence of NO_x. Temperatures correspond to peaks in desorption profiles at which mass spectra were obtained.

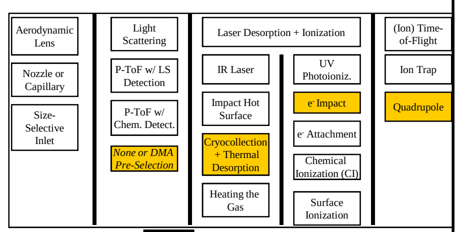
Y.B. Lim and P.J. Ziemann, Products and Mechanism of Secondary Organic Aerosol Formation from Reactions of n-Alkanes with OH Radicals in the Presence of Nox. *Environ. Sci. Technol.* 2005, 39, 9229-9236

Type 2A: TAG: Thermal Desorption Aerosol GC/MS-FID

Brent Williams and Allen Goldstein,
University of California, Berkeley
Nathan Kreisberg and Susanne Hering
Aerosol Dynamics Inc.



Semi-continuous, in-situ measurement: One-hour time resolution



Type 2A: TAG: Ambient Data

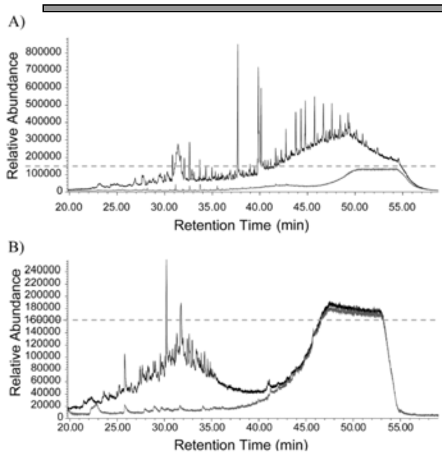


FIG. 7. A comparison between (a) an urban organic aerosol sample, 0.4 m^3 of air collected in Berkeley, CA, and (b) a remote organic aerosol sample, 0.25 m^3 of air collected at Chebogue Point, Nova Scotia. The overlapping chromatograms, present in lower abundance and displayed in light gray, are field blanks through a Teflon filter. The dotted gray line represents equivalent detector signal. The rise in background signal after 40 minutes on all chromatograms is a result of typical column bleed.

- Some compounds identified
- Most of the mass is "UCM": unidentified complex mixture
  - Investigating derivatization and 2D chromatography
- Large changes between urban and rural/remote location

B.J. Williams, A.H. Goldstein, N.M. Kreisberg, and S.V. Hering. An In-Situ Instrument for Speciated Organic Composition of Atmospheric Aerosols: Thermal Desorption Aerosol GC/MS-FID (TAG). *Aerosol Science and Technology*, 40:627–638, 2006.

Type 2A: 2D-TAG

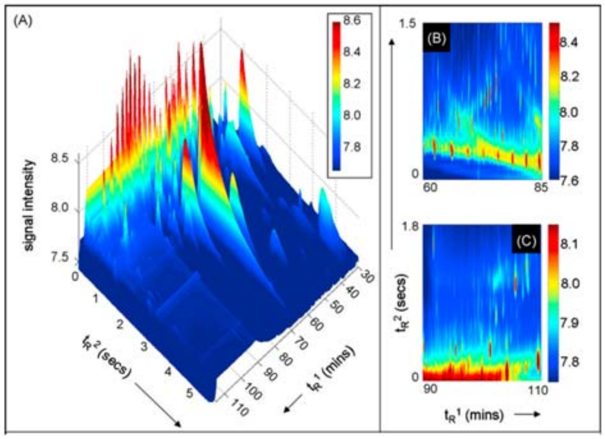


Fig. 7. 2D-TAG chromatogram of a 90 min ambient air sample collected in Berkeley, CA on 25 February 2007 (panel A). Enlargements of two regions (labeled B and C) are also shown in the right panel to illustrate the good peak shapes and observable banding structure indicative of compound classes.

A.H. Goldstein, D.R. Worton, B.J. Williams, S.V. Hering, N.M. Kreisberg, O. Panic, T. Gorecki. Thermal desorption comprehensive two-dimensional gas chromatography for in-situ measurements of organic aerosols. *Journal of Chromatography A*, 1186 (2008) 340–347.

Type 2B: TD + Soft Ionization

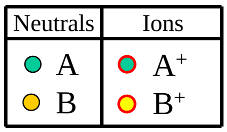
- Aerosol Chemical Ionization MS (A-CIMS): U. Georgia, G. Smith *et al.*
- Thermal Desorption Chemical Ionization MS (TDCIMS): NCAR, J. Smith *et al.*

- A New Chemical Ionization Mass Spectrometry Method for the Online Analysis of Organic Aerosols. John D. Hearn and Geoffrey D. Smith, *Anal. Chem.*, 76, 2820-2826, 2004.
- http://www.chem.uga.edu/gsmith
- Thermal Desorption Chemical Ionization Mass Spectrometer for Ultrafine Particle Chemical Composition, D. Voisin, J. N. Smith, H. Sakurai, P. H. McMurry, and F. L. Eisele, *Aerosol Sci. Technol.*, 37, 471-475, 2003.
- http://www.acd.ucar.edu/~jimsmith/POP

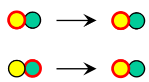
Ion-Molecule Reactions

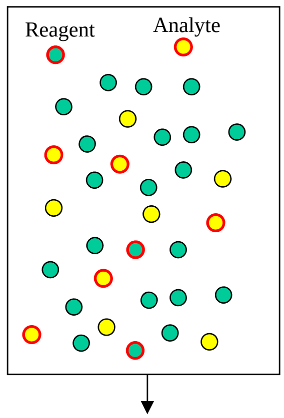
Limit 1: High local Pressure => many collisions

Limit 2: Very Low Local Pressure: no collisions

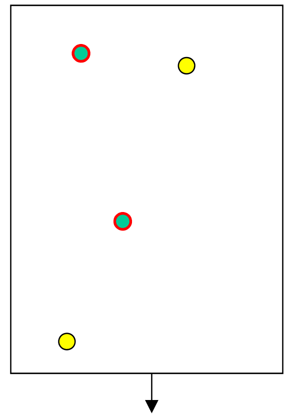


$IP_A > IP_B$





Extensive Chemical Ionization



No CI

Efficiency of Ion-Molecule Reactions

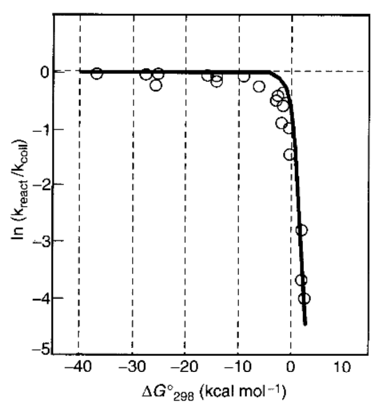


Figure 1.38
The natural logarithm of the number of reactions per collision ratio indicates that the proton transfer is almost 100% efficient when the process is exergonic. When it becomes endergonic, the efficiency drops sharply. (Reproduced (modified) from Ref. 77 with permission)

- Approx. every collision leads to chemical ionization, if $\Delta G^0 < 0$

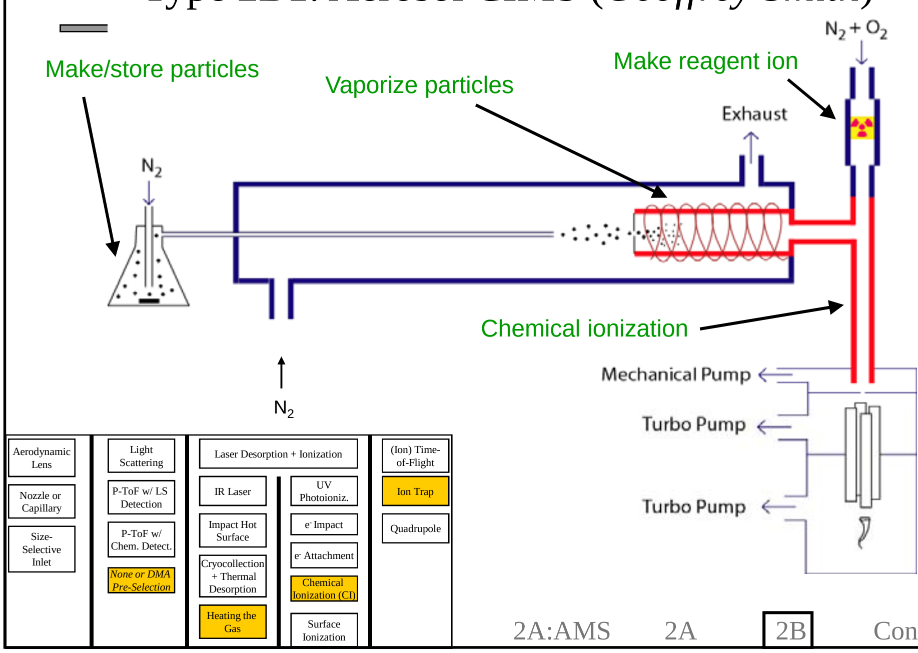
Edmon de Hoffmann and Vincent Stroobant. Mass Spectrometry: Principles and Applications. John Wiley & Sons, 2002.

Ionization: Chemical

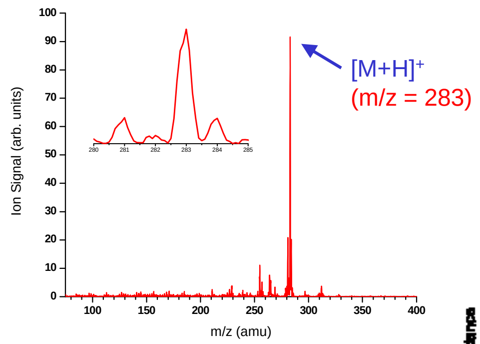
- Electron transfer: $M + I^- \rightarrow M^- + I$
- Proton transfer: $M + H_3O^+ \rightarrow (M{+}H)^+ + H_2O$
- Adduct formation: $M + CF_3O^- \rightarrow (M{+}\ CF_3O)^-$

- Need Collisions!
  - λ < 0.1 mm (P > 1 mbar)
  - Sometimes at 1 atm (APCI)

Type 2B1: Aerosol CIMS (*Geoffrey Smith*)



Low Fragmentation with Chemical Ionization

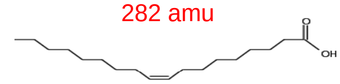


Chemical Ionization using $H^+(H_2O)_2$

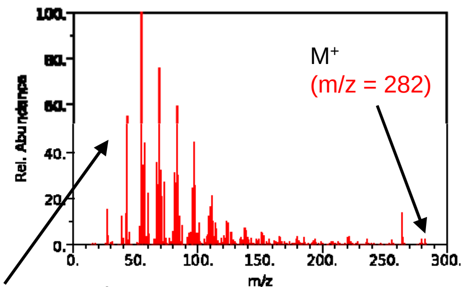
Low degree of fragmentation aids in:

- identification
- quantification

Oleic acid
282 amu



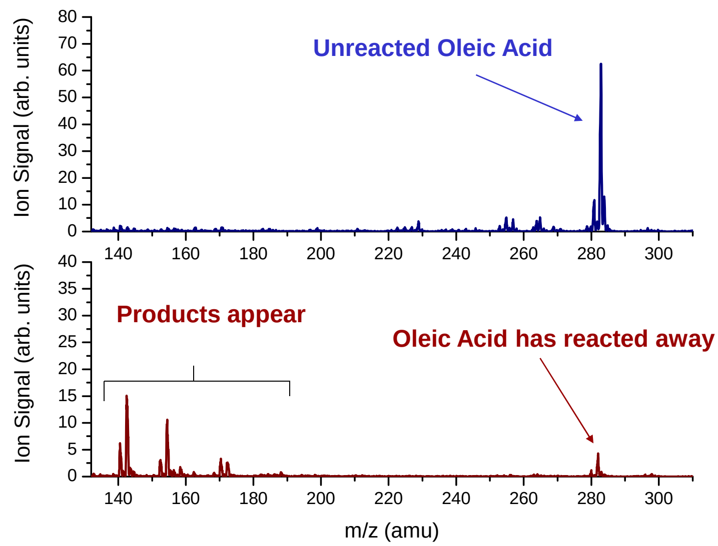
Electron Impact (EI) Ionization



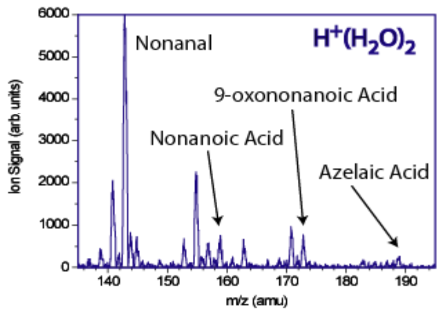
Large degree of fragmentation

From: NIST Chemistry WebBook

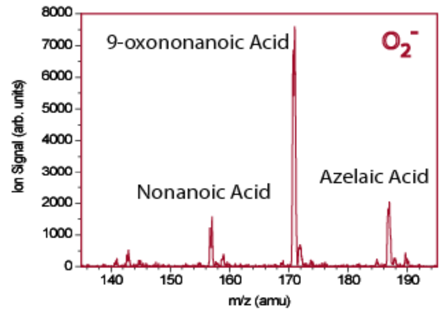
Mass Spectra of Reacted Particles



Use of different CI reagent ions



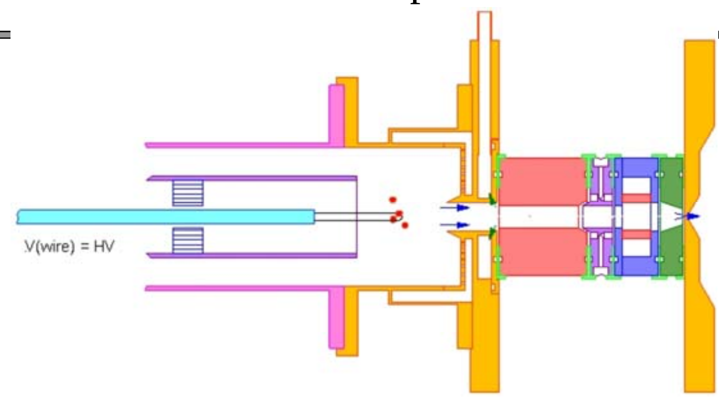
Proton transfer



Negative CI with O_2^-

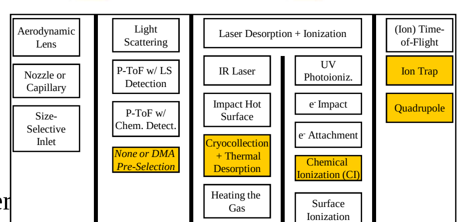
Hearn & Smith, "Kinetics and Product Studies for Ozonolysis Reactions of Organic Particles Using Aerosol CIMS, *J. Phys. Chem. A*, 108, 10019-10029 (2004).

TDCIMS: Step 1 – Particle Collection

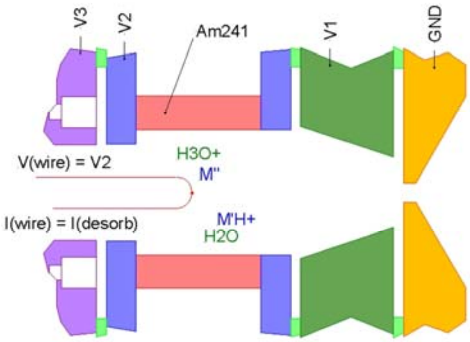


Animation courtesy of Jim Smith, NCAR
http://www.acd.ucar.edu/~jimsmith/POP

- Sample air with charged particles
- Collection filament is biased at 4 KV
- Particles cross flow to collect on filament
- After a few min., wire is inserted in ionizer



TDCIMS: Step 2 – Sample Desorption and Analysis



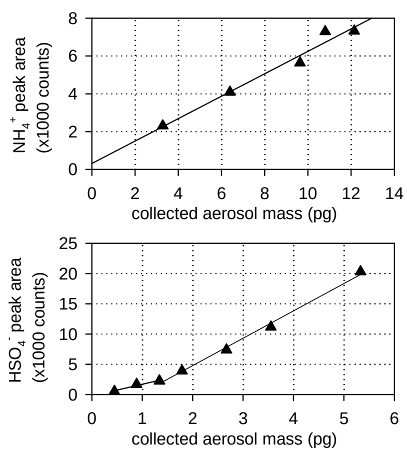
- Wire momentarily heated at temperatures up to 300 °C to desorb sample
- Neutral compounds are ionized using chemical ionization, e.g.: $H_3O^+ + NH_3 \rightarrow NH_4^+ + H_2O$
- Reagent ions are created by α particles emitted from the source, generating mostly H_3O^+, O_2^- and CO_3^-
- Ionized analyte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

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

TD-CIMS: Quantification

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

Instrument response as a function of collected mass



Voisin et al., Aerosol Sci. Technol., 37(6): 471-475, 2003.

TDCIMS: Ambient Sampling

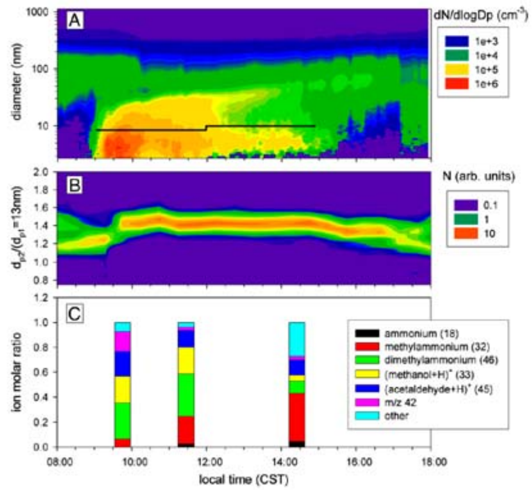


Fig. 2. Analysis of a new particle formation event commencing at 9:00 on March 21, 2006, in Tecamac, Mexico. (*A*) Particle size distribution intensity plot. Black lines mark the particle sizes that are analyzed by the TDCIMS. (*B*) Hygroscopic growth factors obtained at 90% RH for 13 nm ambient particles. (*C*) TDCIMS positive ion molecular composition for the diameters indicated in (*A*). Individual bar lengths correspond to the ion molar ratio, defined as the ratio of the average ion abundance for each compound to the total average ion abundance, and their width indicates sampling time. Average uncertainty for each species measurement is ±25%; refer to *Materials and Methods* for an uncertainty analysis.

J.N. Smith, K.C. Barsanti, H.R. Friedli, M. Ehn, M. Kulmala, D.R. Collins, J.H. Scheckman, B.J. Williams, and P.H. McMurry. Observations of aminium salts in atmospheric nanoparticles and possible climatic implications. *Proc. Nat. Acad. Sci. USA*, 107, 6634-6639, 2010.

Part 3:
The Future

My Take on Near Future of Aerosol MS

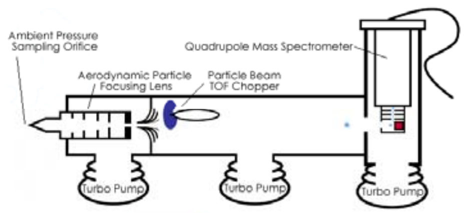
- New techniques will continue to be developed
  - Specialized for problems that the commercial instruments don't do well
- Components
  - Inlets: aerodynamic lenses dominate, slowly going supermicron
  - Practical soft ionization finally coming online
  - EI and LDI will remain very important
- Uses of Aerosol MS
  - *Research* tool
    - Commonplace, e.g. at least one in each field study site / airplane…
    - Advanced users/developers vs. basic users
  - Specialization on what different techniques do well, e.g.:
    - LDI for ice nucleation, low number density situation
    - AMS and soft ionization for organic aerosols
    - NAMS and TDCIMS for nanoparticles
  - Rapidly expanding into advanced monitoring (ACSM)
  - A few more commercial options soon (e.g. soft ionization)

Additional References

- Special issues on mass spectrometry of aerosols
  - *Aerosol Science and Technology*, 33(1-2), July/Aug. 2000.
  - *International Journal of Mass Spectrometry*, 258(1-3), Dec. 2006
- Other review papers, first two good historical reviews:
  - David T. Suess and Kimberly A. Prather (1999). Mass Spectrometry of Aerosols. *Chem. Rev.* 99, 3007-3035.
  - 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 Spec. Rev.*, 19, 248-274.
  - 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.
  - Nash, D.G., Baer, T., Johnston, M.V. Aerosol mass spectrometry: An introductory review. *Int. J. Mass Spec*. 258, 2-12, 2006.
- All AMS papers: http://cires.colorado.edu/jimenez/ams.html
- List of Single Particle MS papers: http://mae.ucdavis.edu/wexler/spa_refs.html

http://cires.colorado.edu/jimenez/ams.html

Aerosol Mass Spectrometry Web Page



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

This page is maintained by Jose-Luis Jimenez. Email me at jose.jimenez@colorado.edu if you have any questions, corrections, and/or items that you would like me to add here. Information on aerosol mass spectrometry groups (with either custom or commercial instruments) that are not listed here is especially appreciated.

1. Introduction
2. Information on All Types of Real-Time Aerosol Mass Spectrometers
   - 2.1- Type 1: Laser Vaporization
     - 2.1.1- Type 1A: Laser Desorption-Ionization (LDI)
     - 2.1.2- Type 1B: Two Laser Systems
     - 2.1.2- Type 1C: Laser Vaporization + Chemical Ionization
   - 2.2- Type 2: Thermal Vaporization
     - 2.2.1- Type 2A: Thermal Vaporization + Electron Impact Ionization

- My Aerosol MS web page
  - Repository of information & links
  - Slightly out of date *(send me updates!)*

3.4- Resources for Aerodyne AMS Users

Acknowledgements

- Deborah Gross
- Jochen Schreiner
- Paul Ziemann
- Brent Williams
- Geoffrey Smith
- Jim Smith
- Joe Petrucci
- Ann Middlebrook
- Qi Zhang
- John Jayne
- Doug Worsnop
- Manjula Canagaratna
- James Allan
- Frank Drewnick
- Many AMS Users
- *My mass spec. students & my group at Colorado*

Funding that keeps us going: