Measuring the chemical composition of soot containing particles

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ICCPA August 2008

Need for new soot particle instruments

- Black carbon (BC) particles
  - Absorb light efficiently, contributing to radiative forcing
  - Significant anthropogenic sources
- BC particles typically coated in the atmosphere
  - Primary combustion products
  - Secondary organic and inorganic condensates
  - Compositions and fate of BC containing particles are not well known
- Need new instruments capable of measuring the refractory and non-refractory mass, size and composition of soot containing particles

Instrument concept

- SP2 + AMS => SP2-AMS

  SP2: Single Particle Soot Photometer
  (Droplet Measurement Technologies)

  - little information on absorbed compounds, particle chemistry

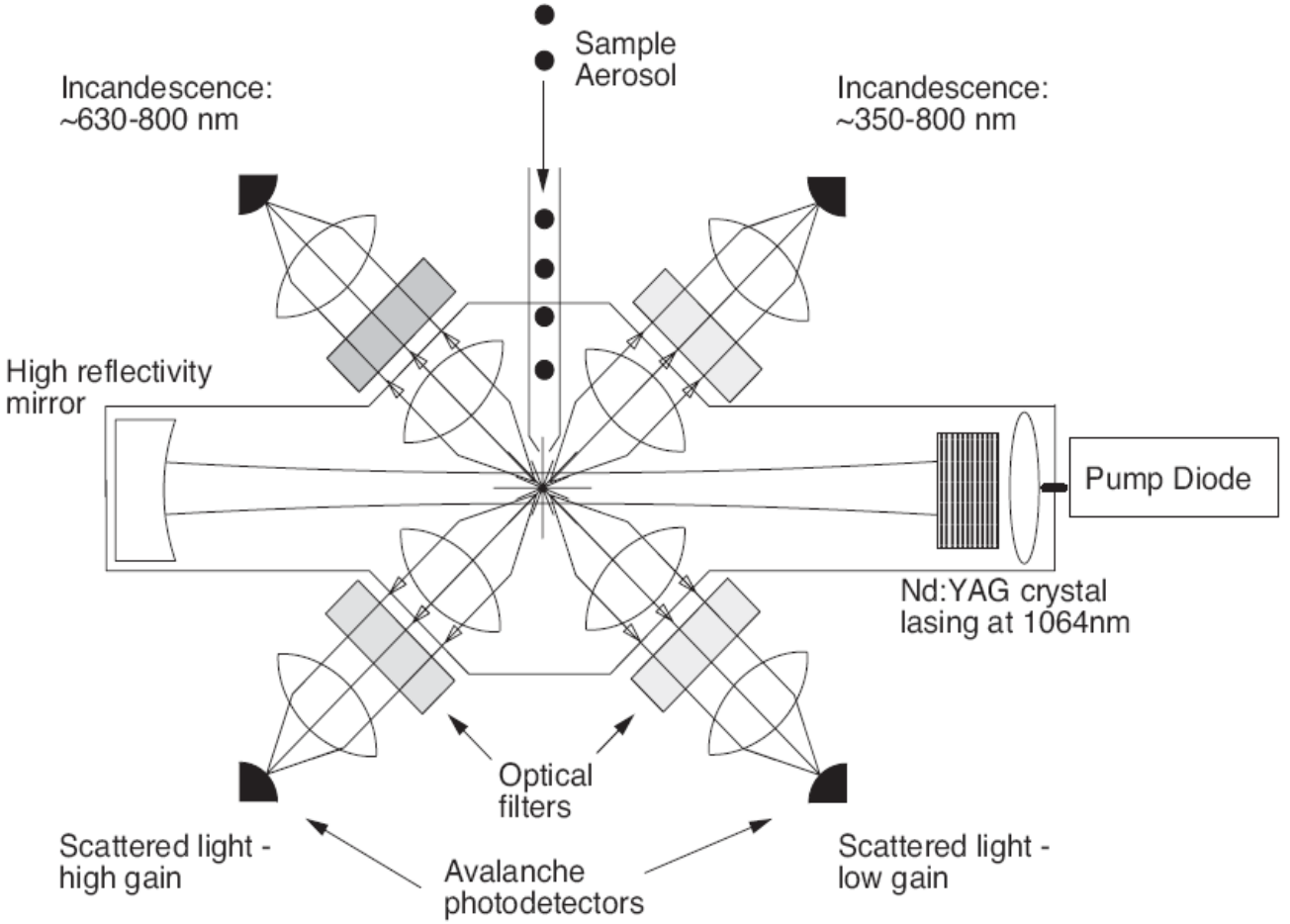
  AMS: Aerosol Mass Spectrometer
  (Aerodyne Research, Inc.)

  - Lack of sensitivity to refractory particles (i.e. black carbon soot)

- SP2-AMS: new combined instrument
  - Intracavity laser vaporization of the coatings and refractory cores of absorbing (λ = 1 μm) particles
  - Electron impact ionization
  - Measures both the non-refractory components of the coatings (e.g. organics, sulfates, nitrates, etc.) and the refractory carbon cores (i.e. black carbon) via Time-of-Flight mass spectrometry

SP2 (Single Particle Soot Photometer)

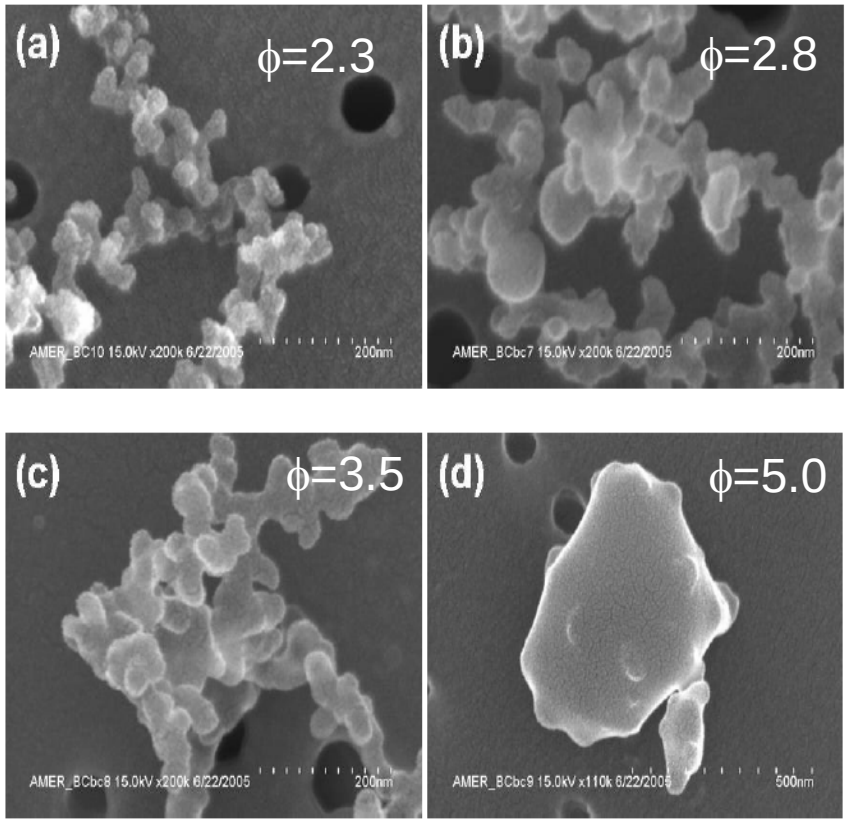
developed by DMT (Droplet Measurement Technologies)



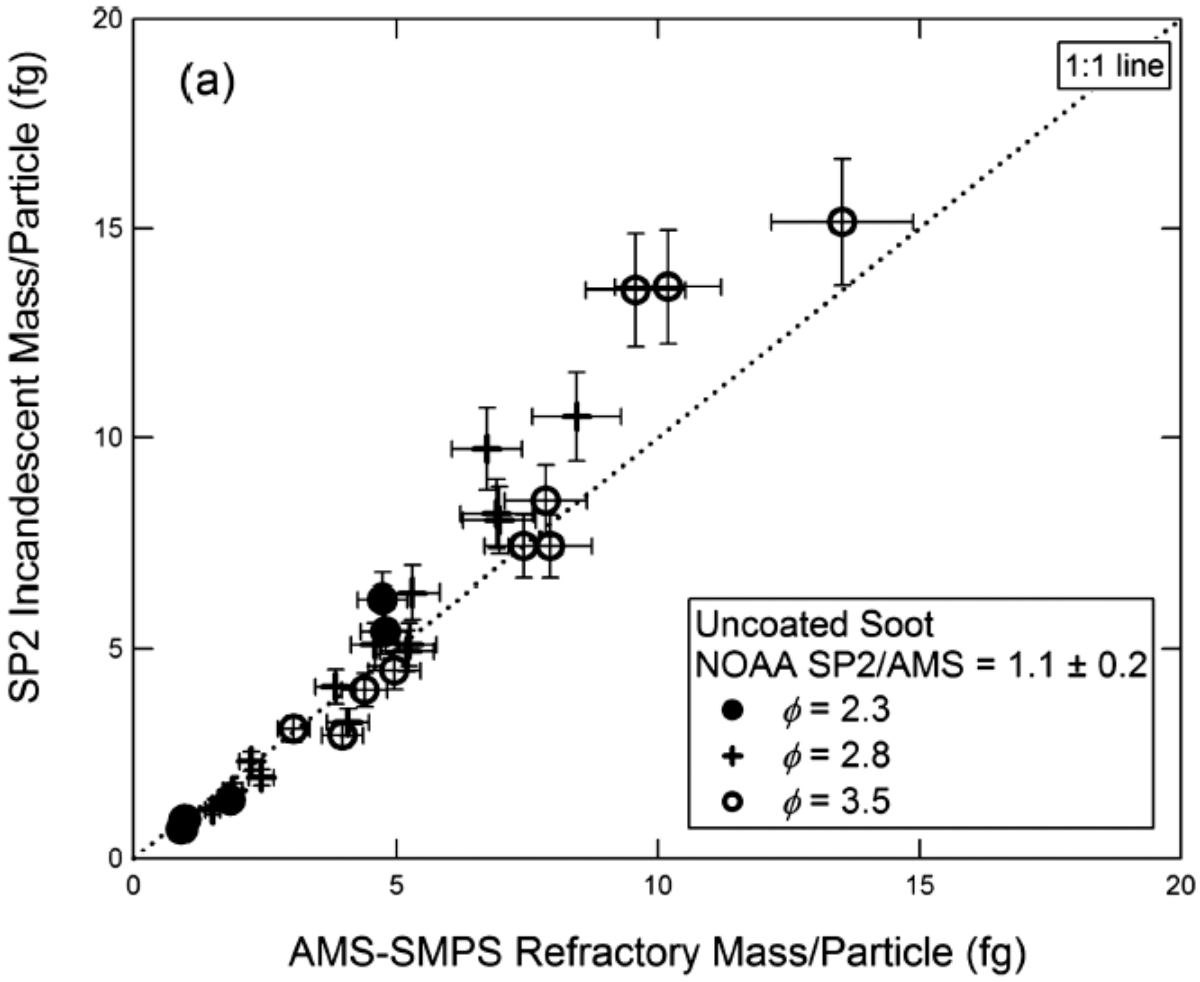
- Measures incandescence from absorbing refractory components of particles (e.g. black carbon, metals, etc.)
- Measures scattered light from absorbing particles as the particles (coatings and core) evaporate

Schwarz et. al., 2006; Gao et al. 2007

SP2 Calibration



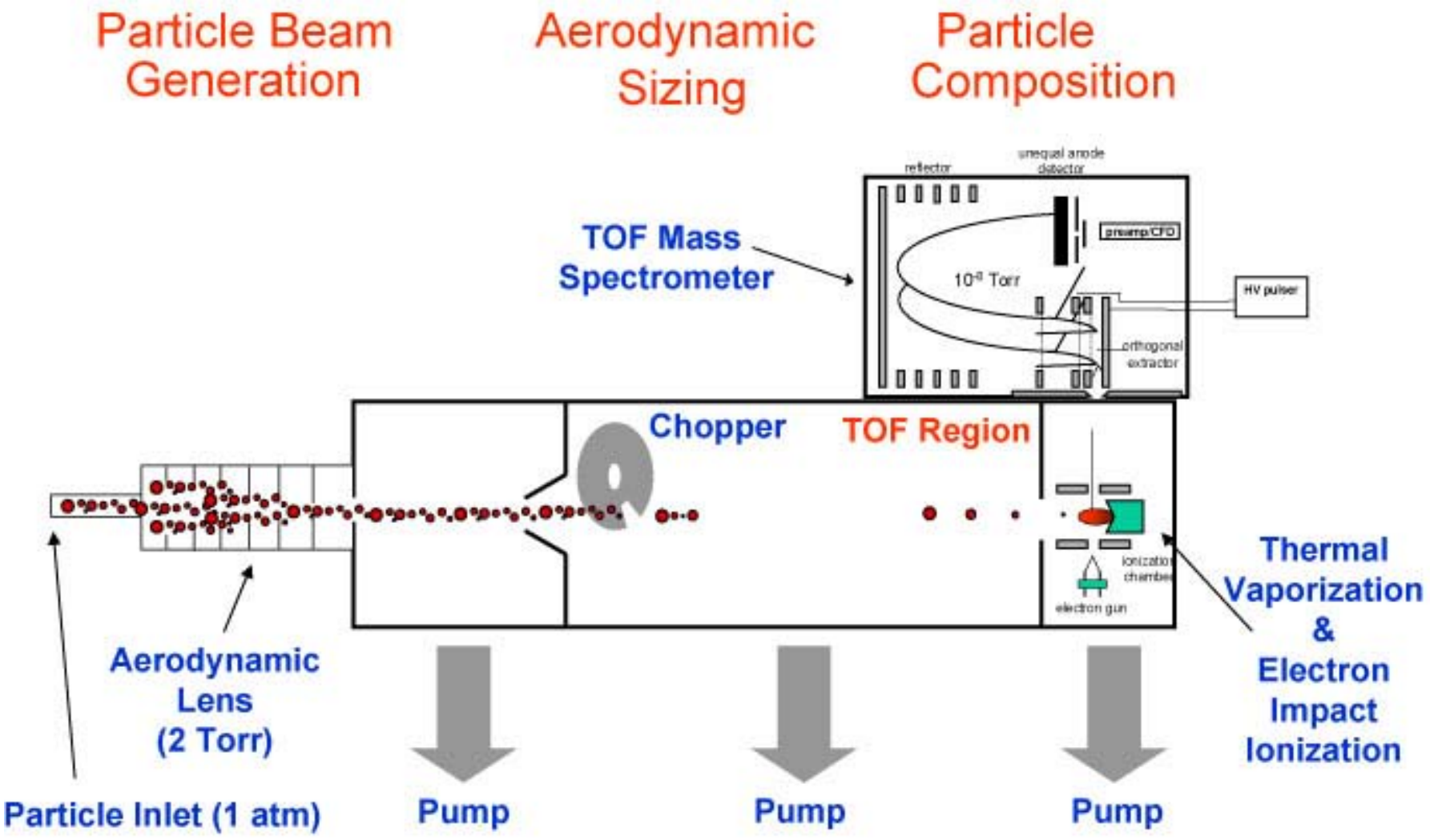
ϕ: fuel equivalent ratio



SP2 incandescence is proportional to black carbon mass
- independent of morphology and coating

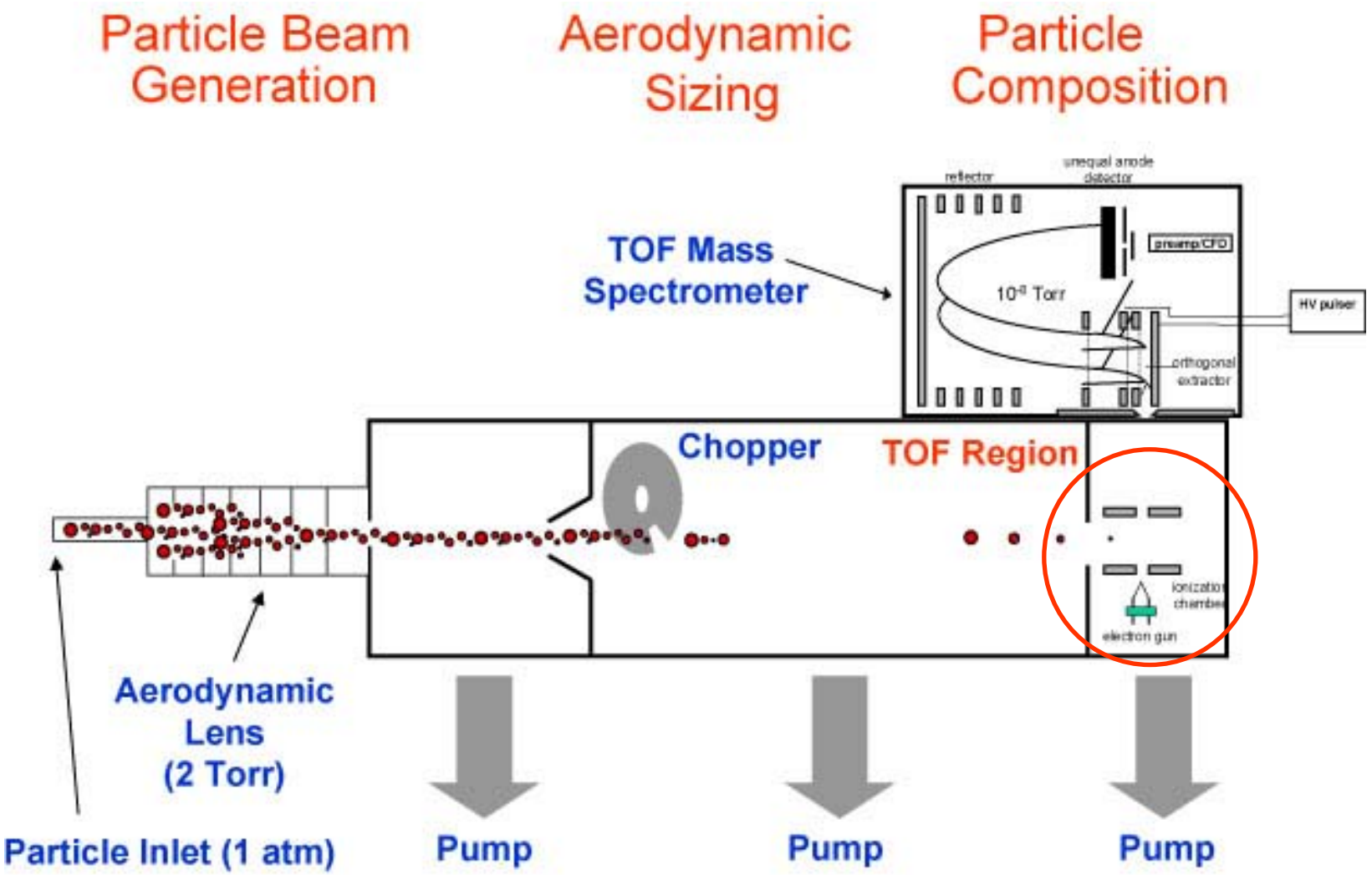
Slowik et. al., 2007

AMS Schematic



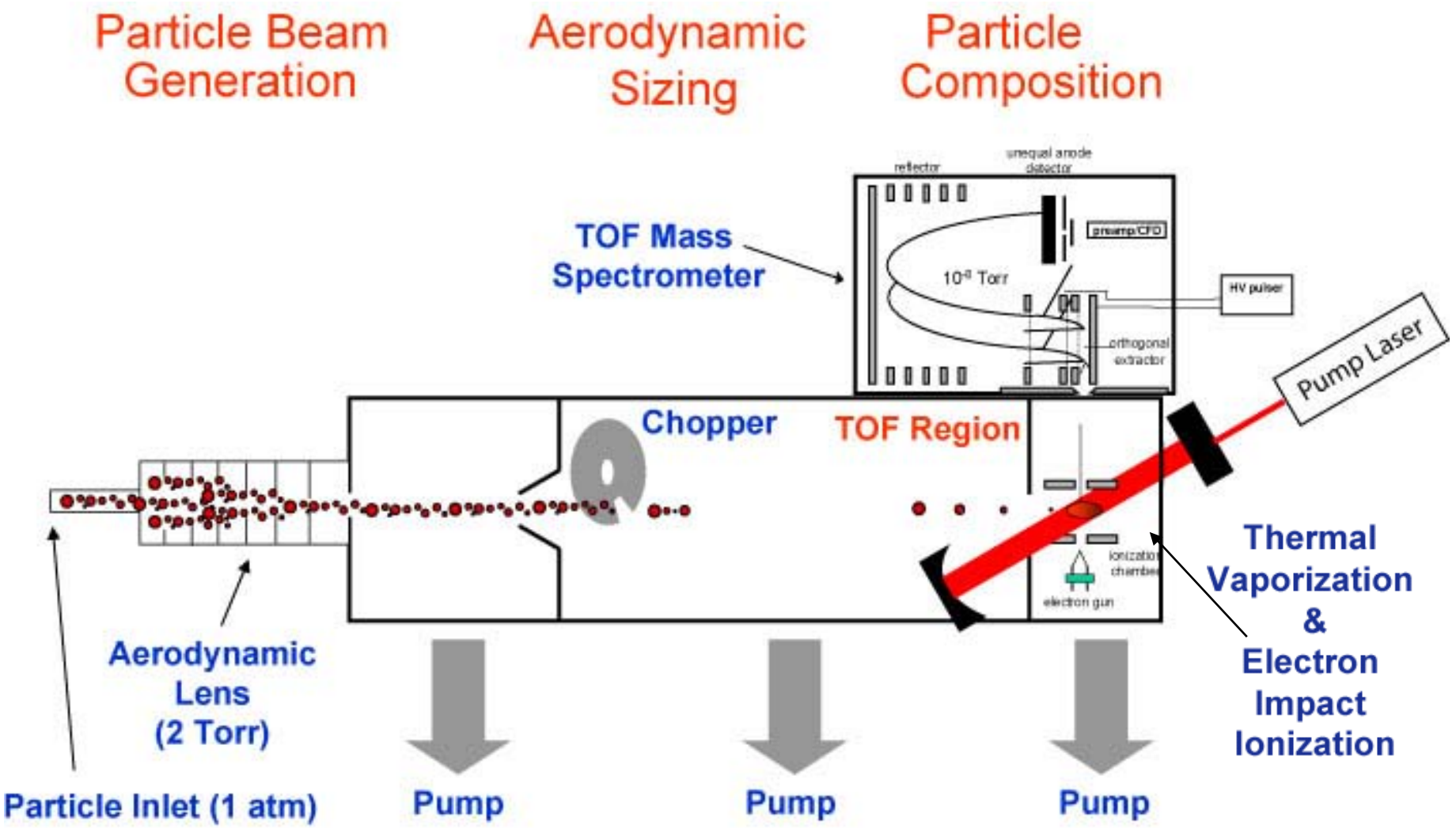
- Measures non-refractory aerosol chemical composition and mass
- Insensitive to refractory aerosol (e.g. black carbon)

How to build a SP2-AMS



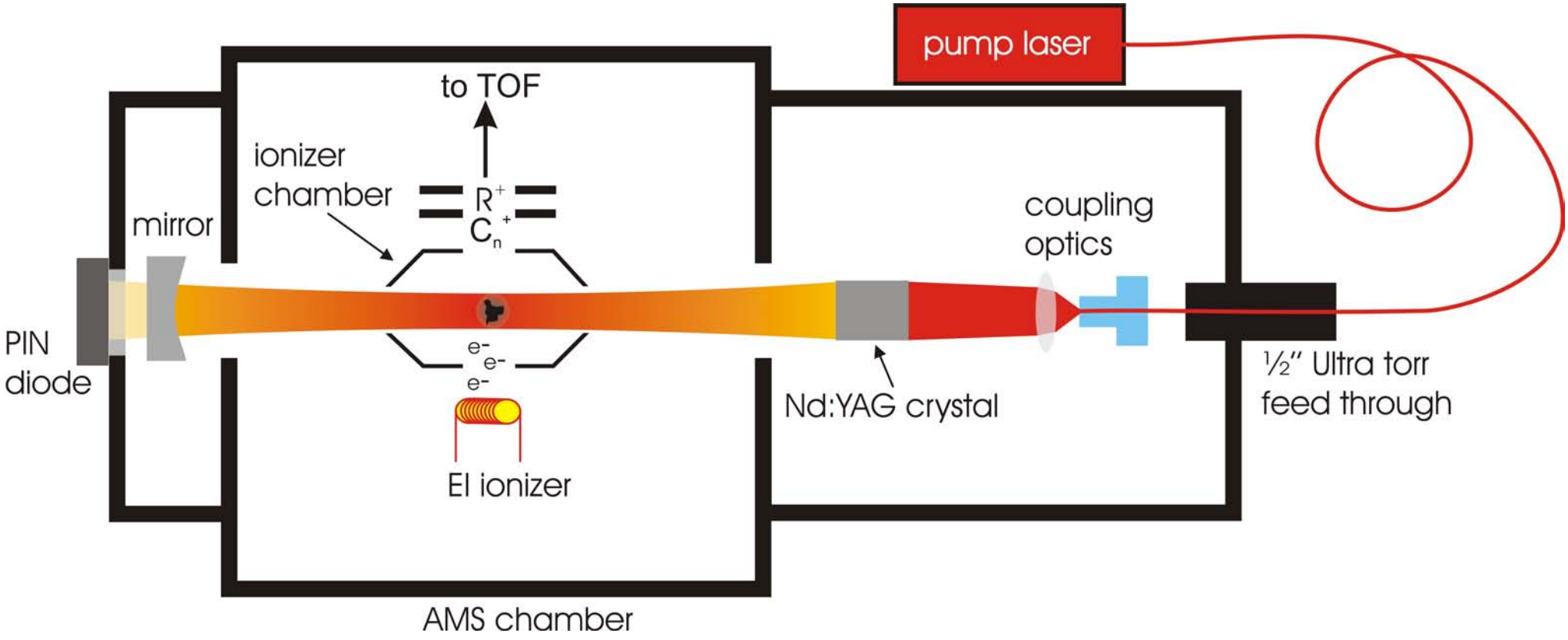
- Remove vaporizer

SP2-AMS schematic



- Install SP2 module

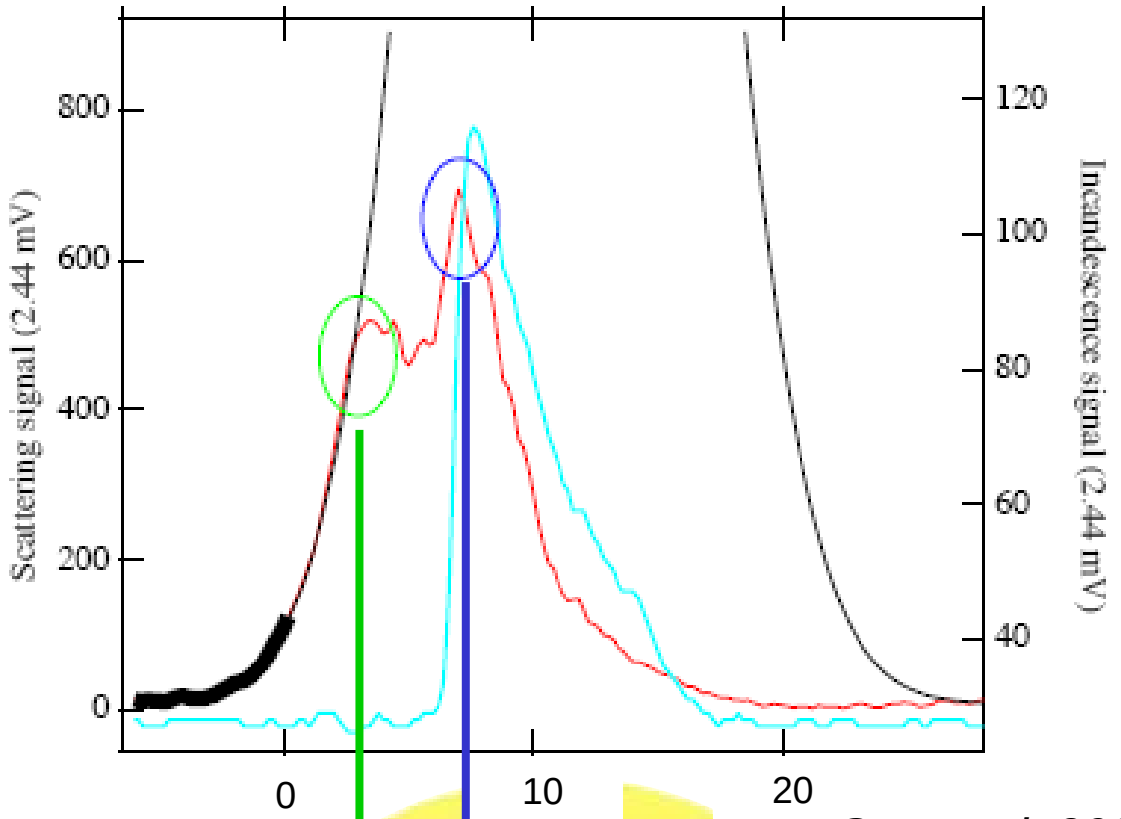
Schematic of the SP2-AMS module



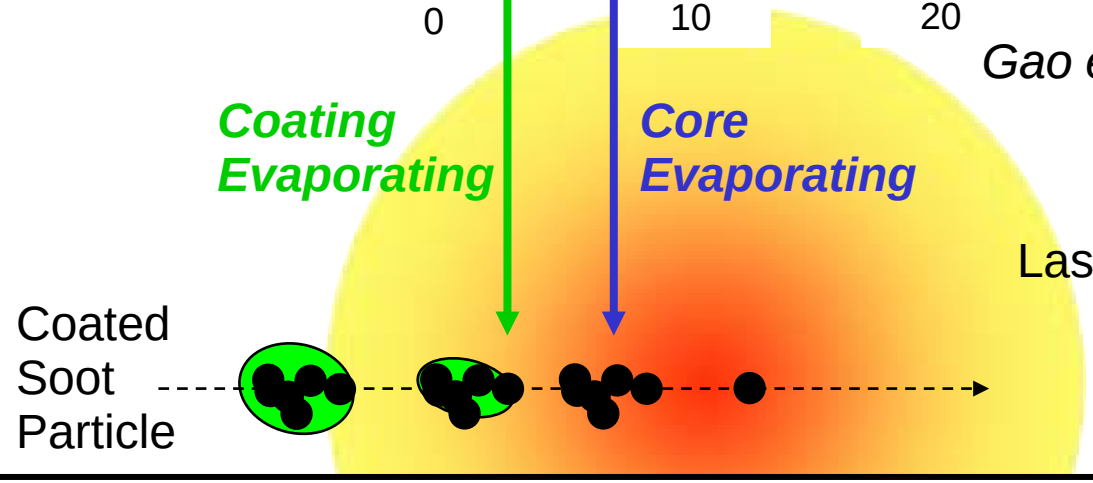
- Absorbing particles (coating and core) vaporize in laser
- Vapor is ionized by electron impact ionization
- Detection of the ions by Time-of-Flight mass spectrometry
- Readily installed in any exiting AMS instrument

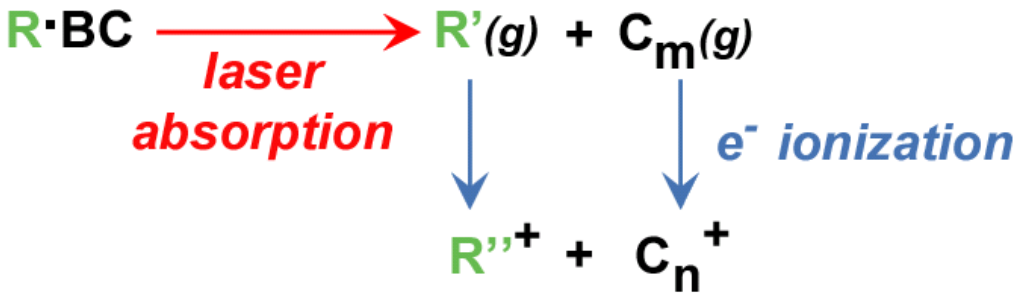
Transit of Soot Particles Across Laser Beam

- 5-20 microsecond evaporation time
- Coatings evaporate first at relatively low temperatures (<600°C) potentially dependent upon vapor pressures
- Core evaporates last at high temperature (>1000°C) under SP2-like incandescence conditions
- Coating and core material ionized and detected with mass spectrometry

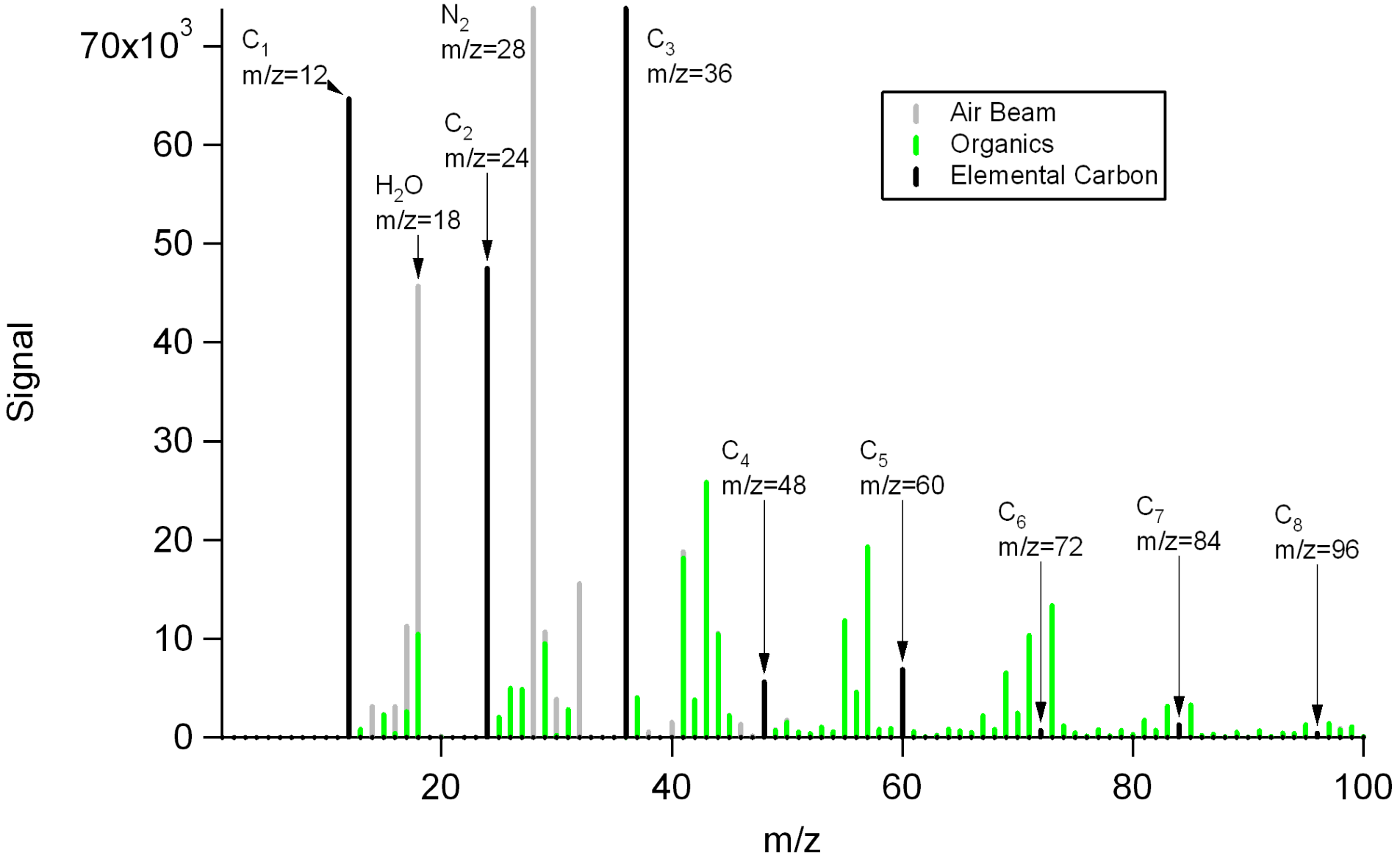


Gao et al. 2007



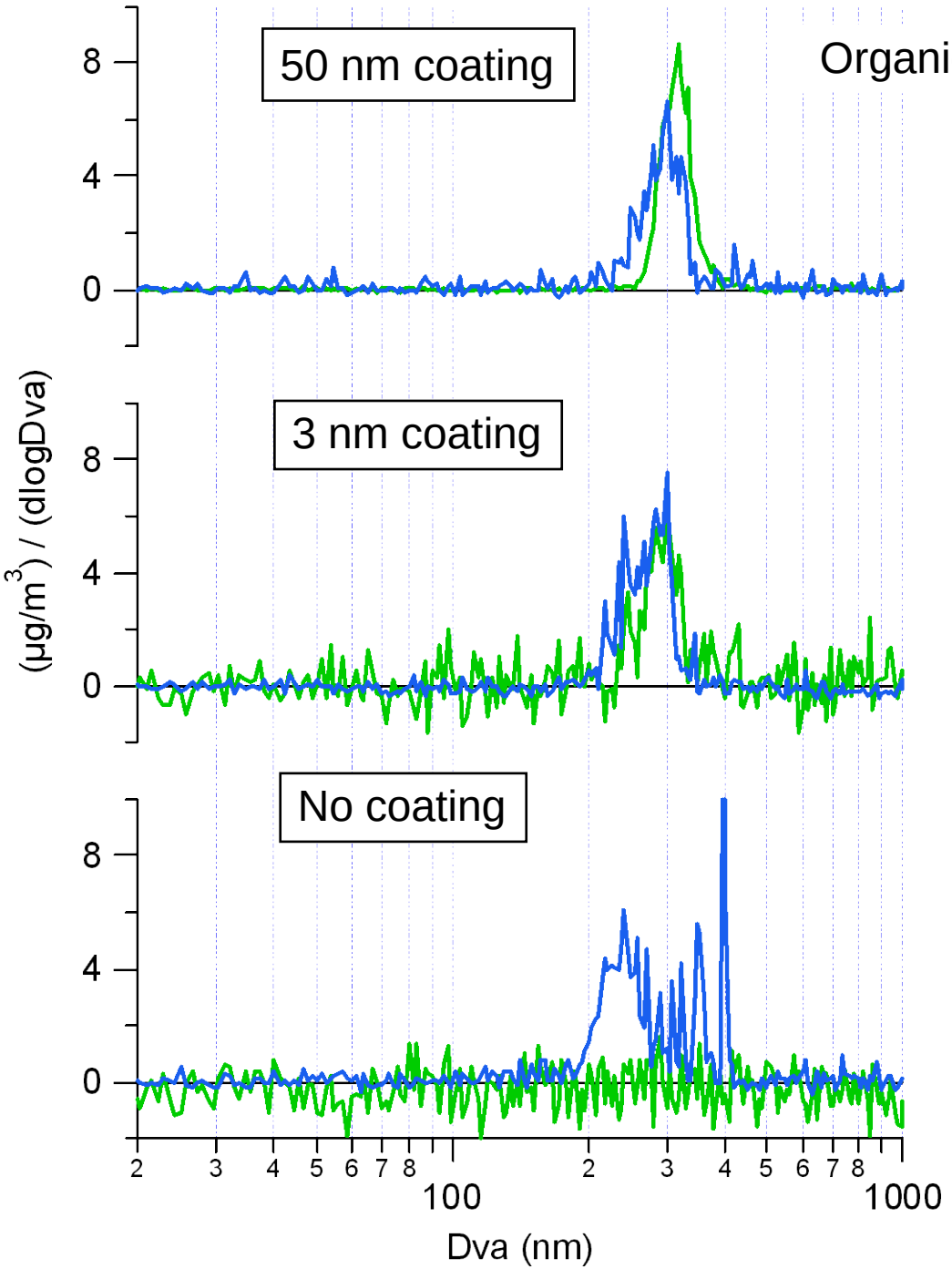


Oil Lamp Soot Particles



Obtain chemical information on elemental carbon clusters and organic compounds coating the soot cores

Size Distributions for uncoated and coated particles

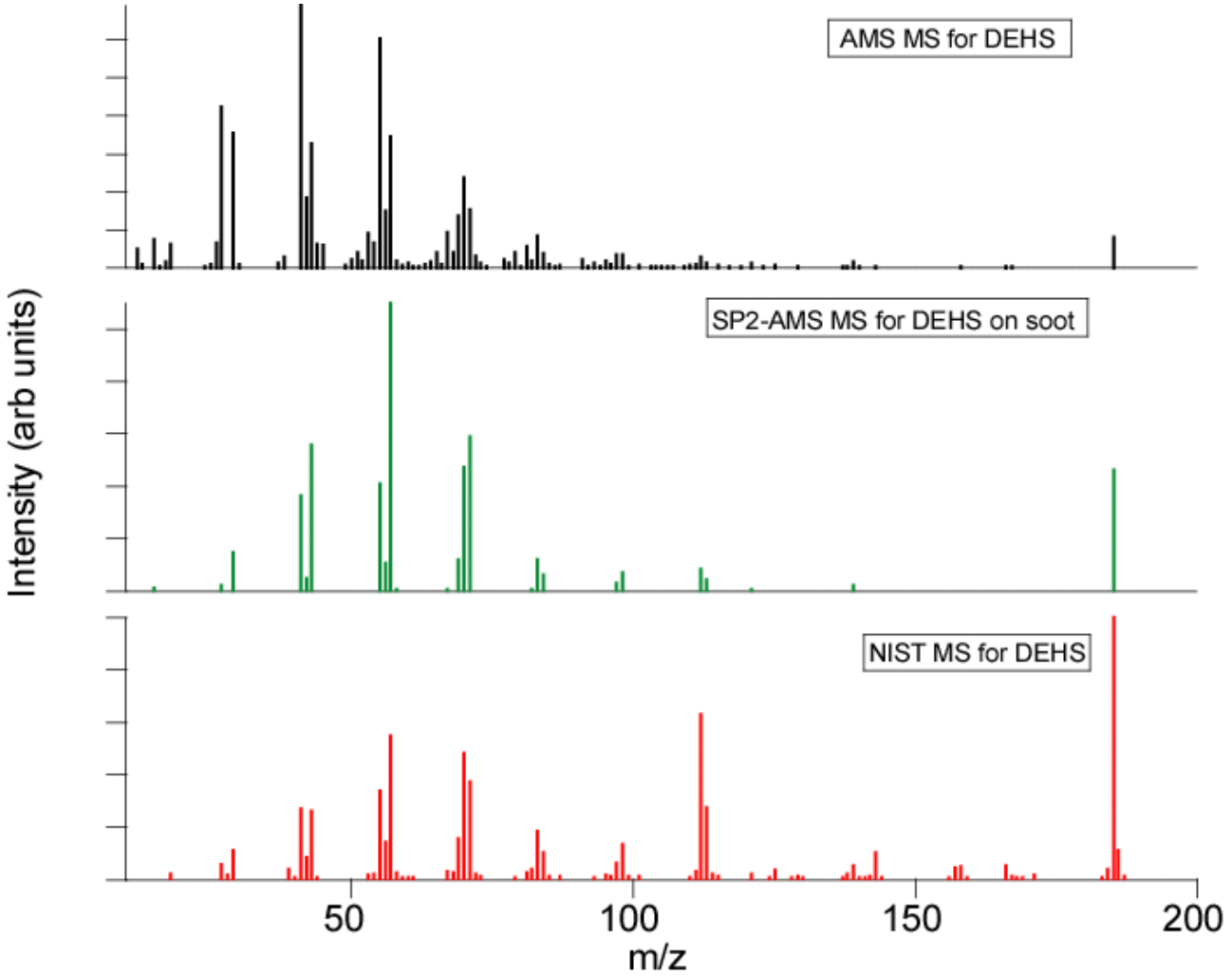


225 nm Glassy Carbon Spheres uncoated and coated with DEHS oil

Carbon Signal
Organic Signal

- Obtain chemical mass distribution information for both carbon and organic signals
- PTOF show size and particle mass signals increasing with particle coatings

Coating Signals: DEHS Mass Spectra



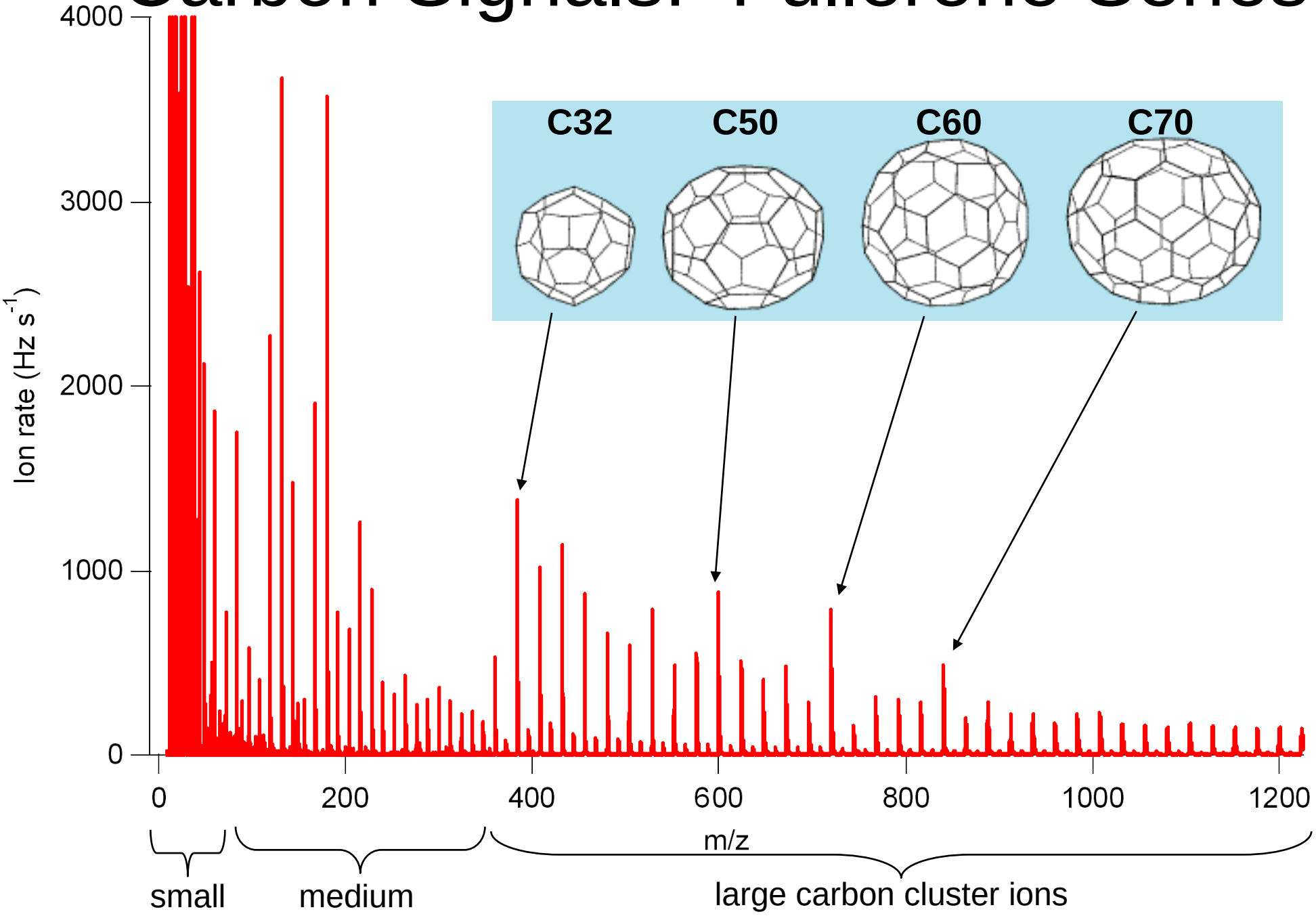
Vaporized from 600°C vaporizer

Vaporized from laser-heated soot particles

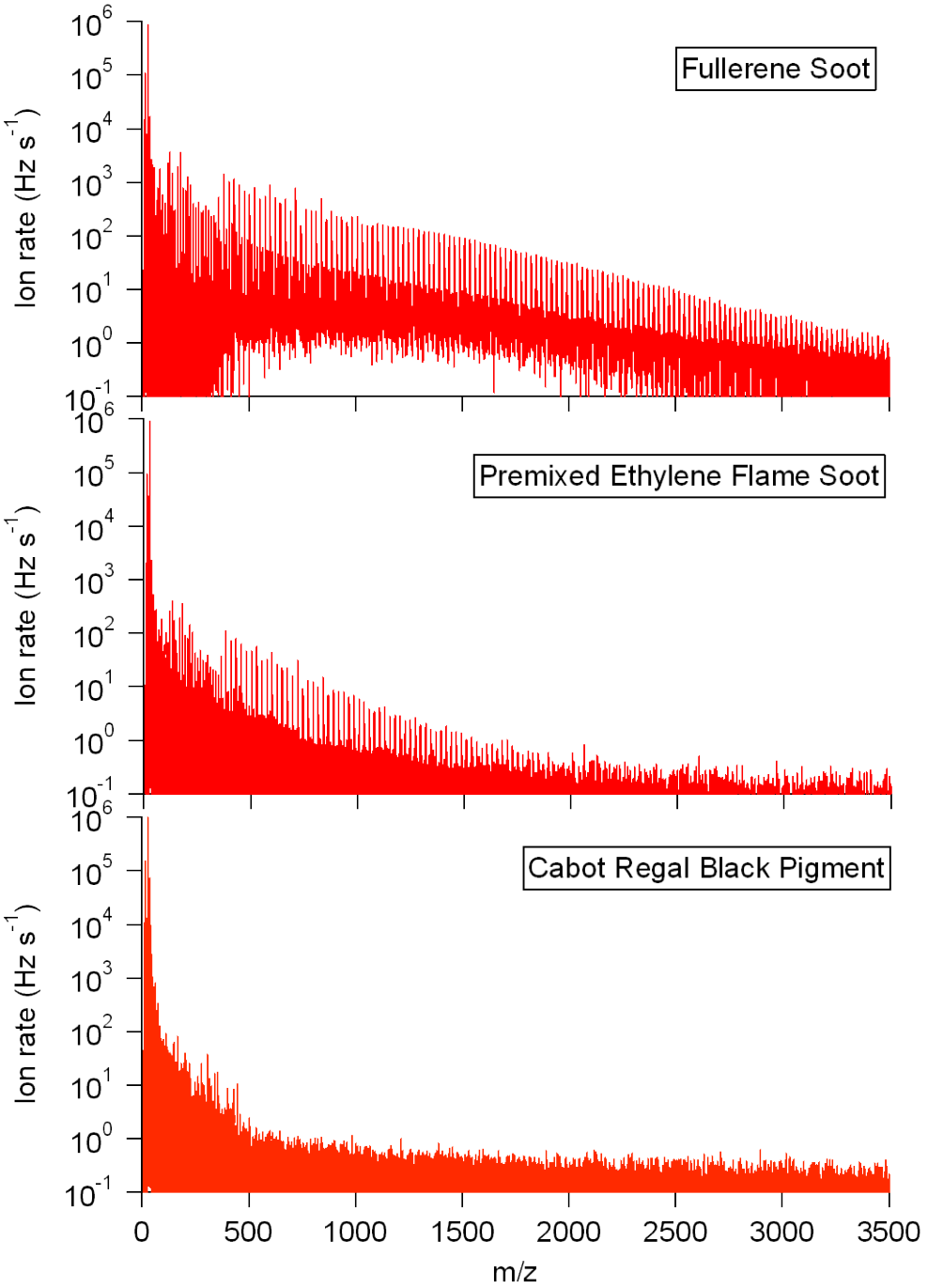
NIST database

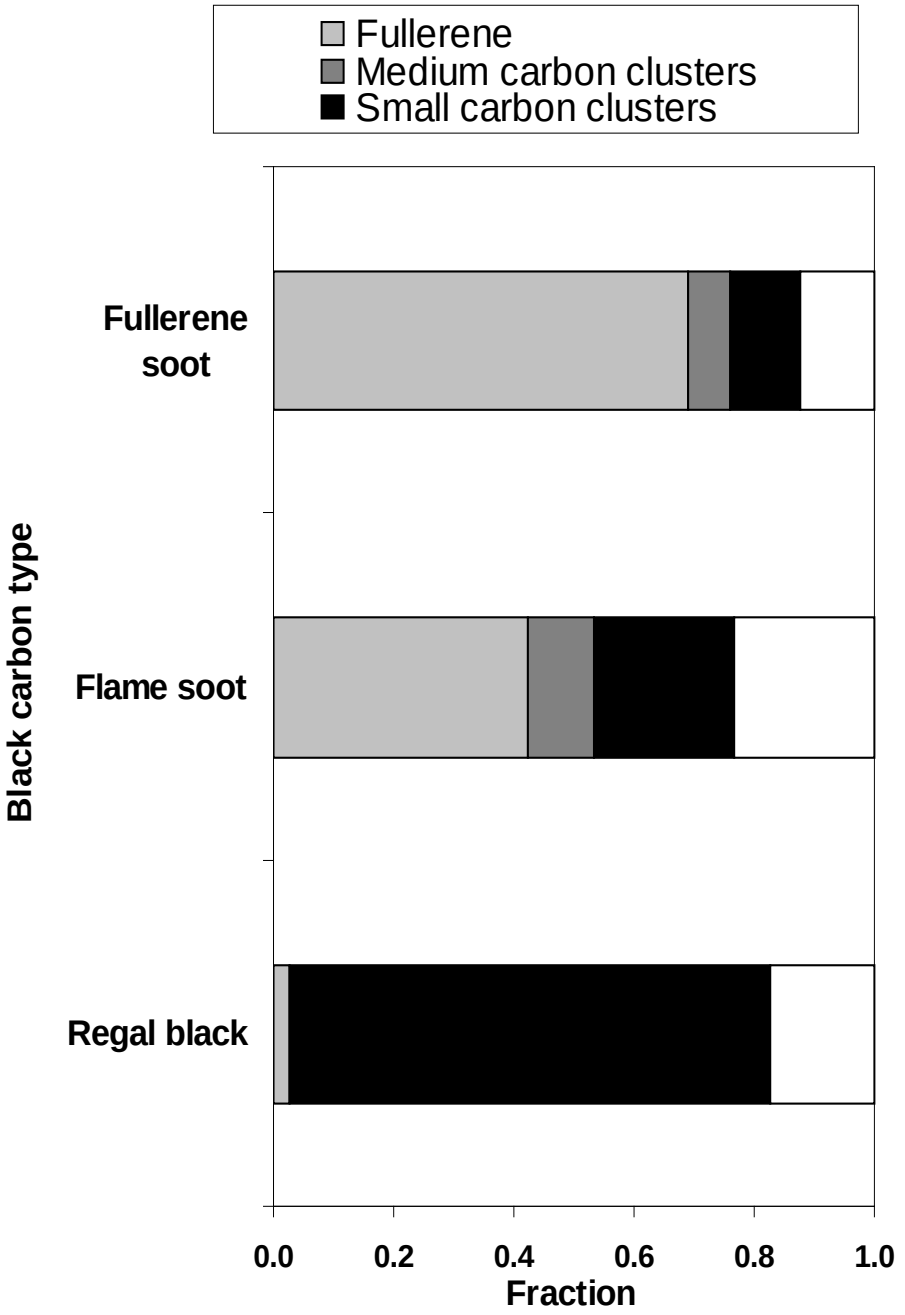
- Less fragmentation in SP2-AMS than in AMS
- Large parent ion signal and fragmentation pattern more similar to NIST data base spectrum
- Most of the coating material evaporates at temperatures < 600°C

Carbon Signals: Fullerene Series

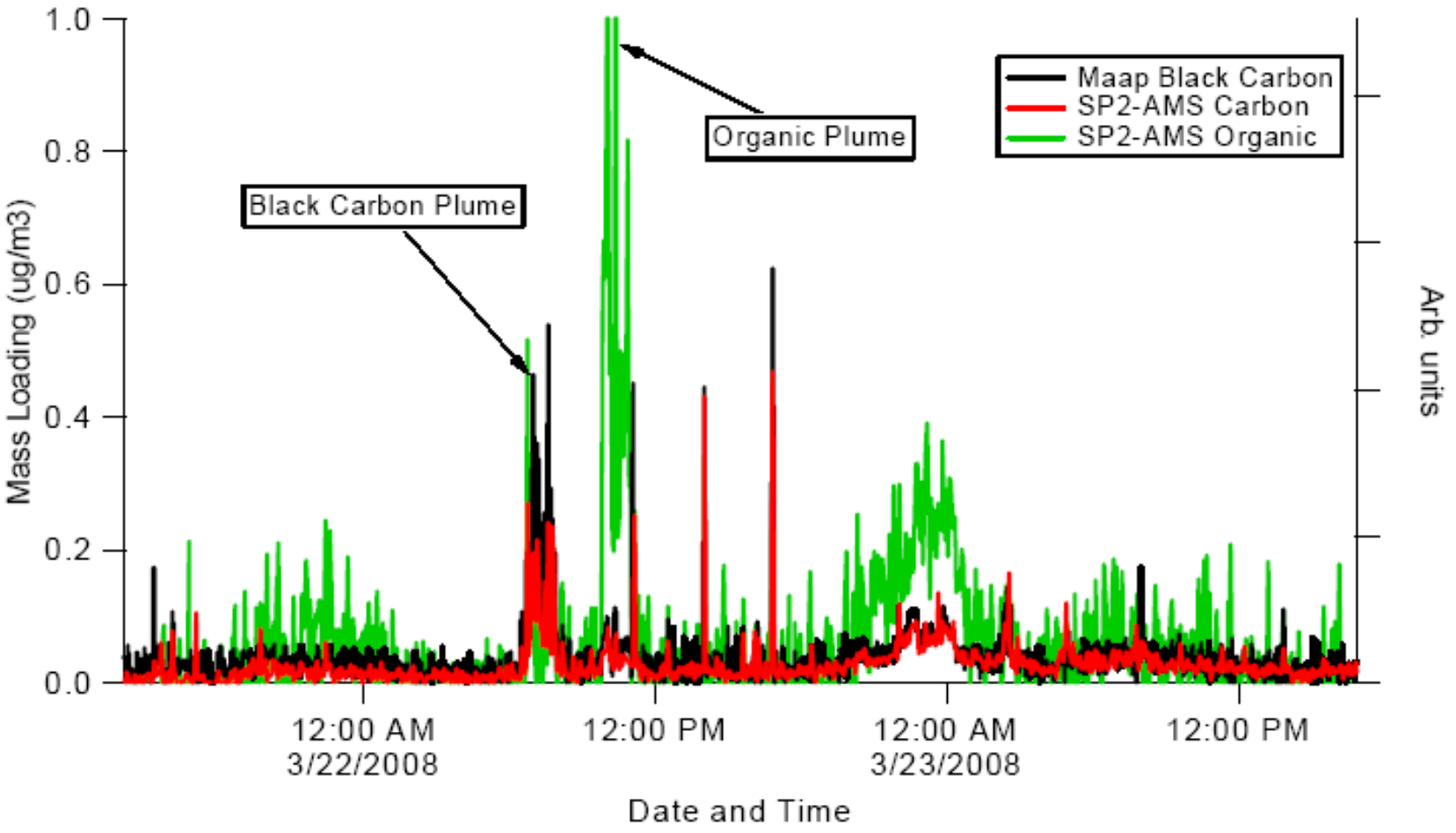


‘Black Carbon’ Chemical Composition

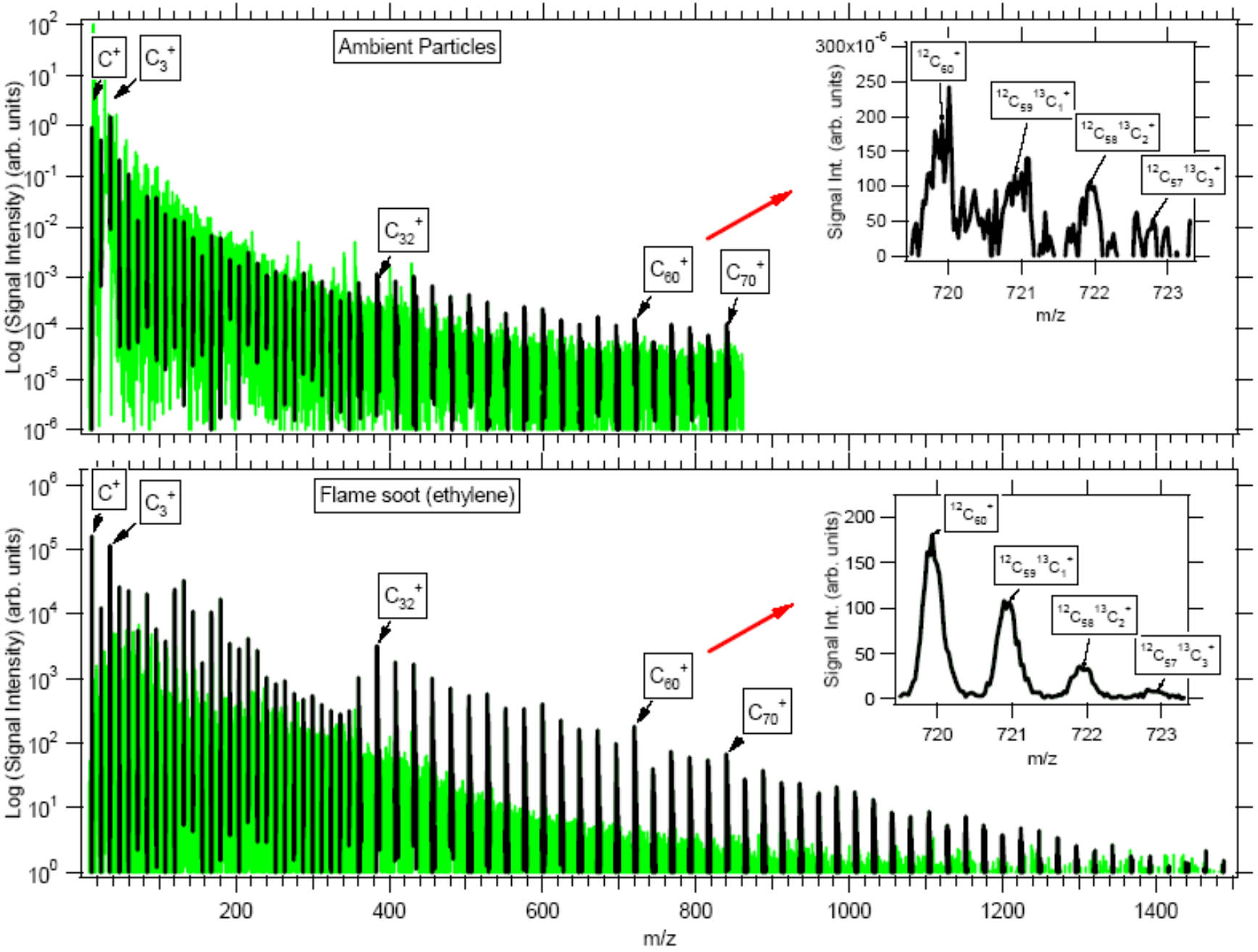




Ambient Measurements



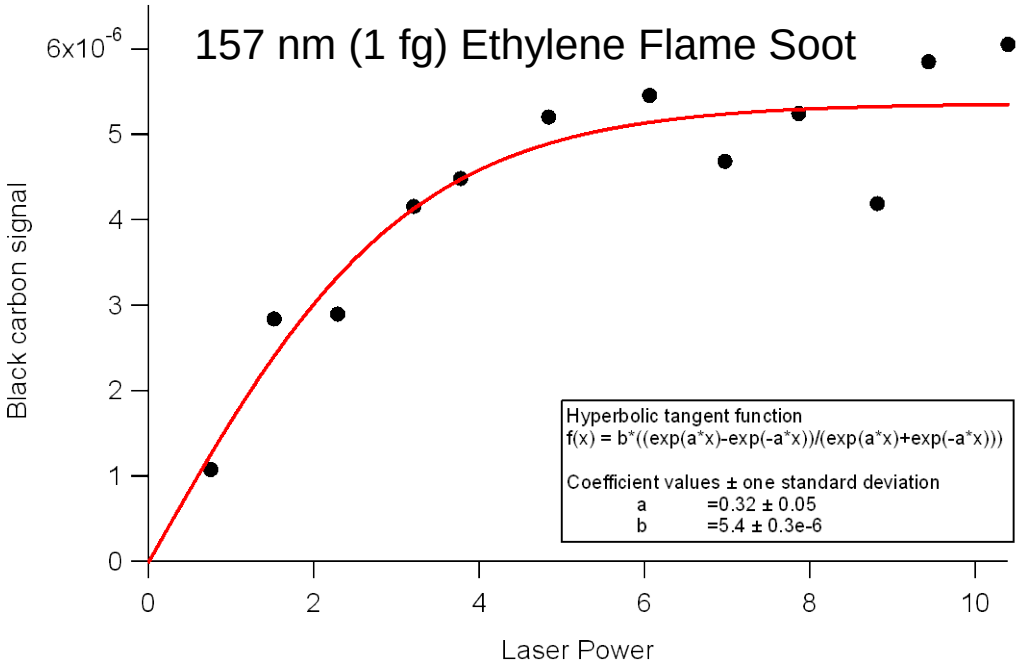
Ambient aerosol particles sampled by the SP2-AMS (red=carbon, green=organics, left axis) and the MAAP (black, right axis) in Chestnut Hill, MA.



SP2-AMS mass spectra for ambient particles (top panel) and for soot from an ethylene flame (bottom panel). Carbon clusters are shown in black and are spaced 12 m/z apart for m/z < 360 and 24 m/z apart for m/z >360. The inset shows the carbon isotopes for the C_{60} cluster.

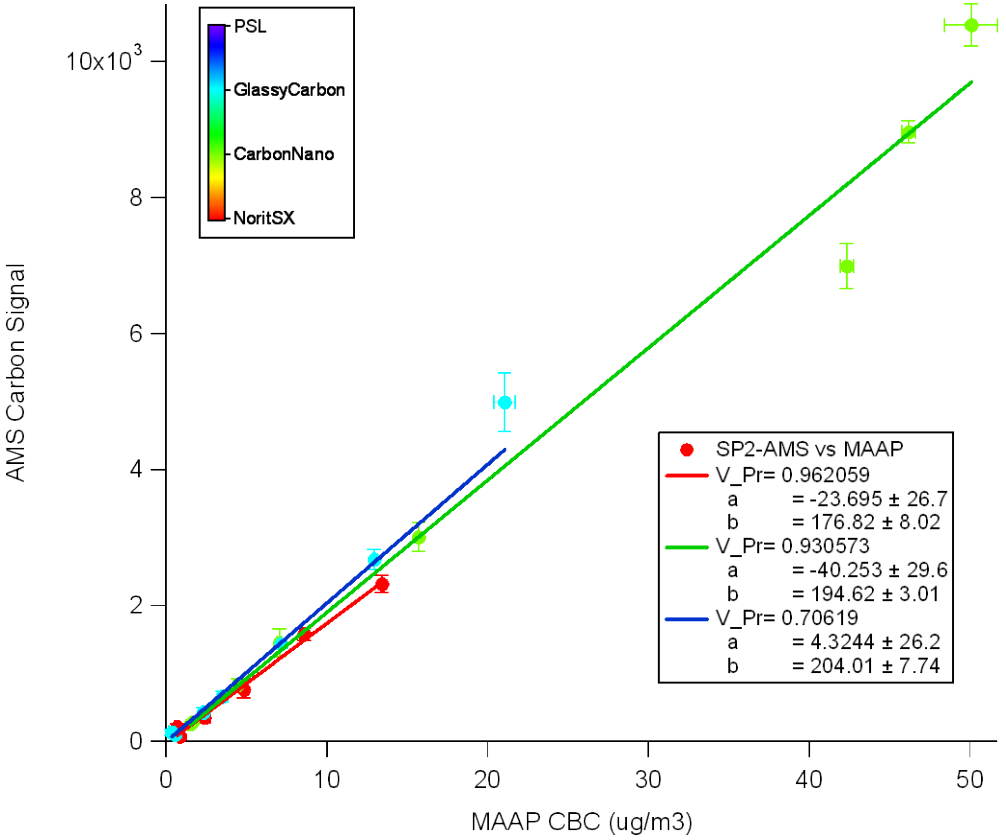
Quantification and Detection Limits

Carbon Signal vs Laser Power



- SP2 instruments operate at laser powers of ~2
- Higher laser powers required in SP2AMS due to faster particle velocities

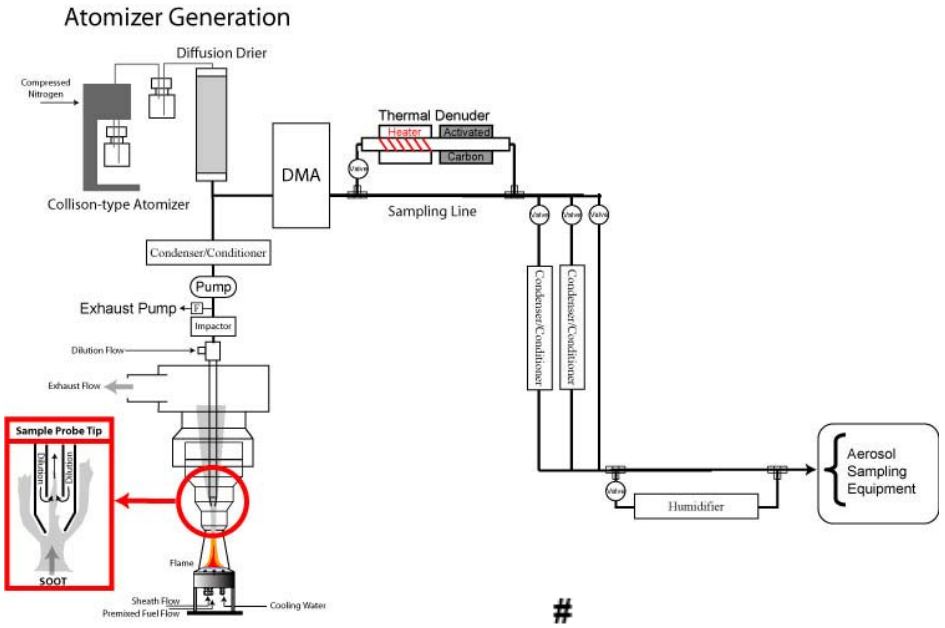
Carbon Signal vs MAAP CBC



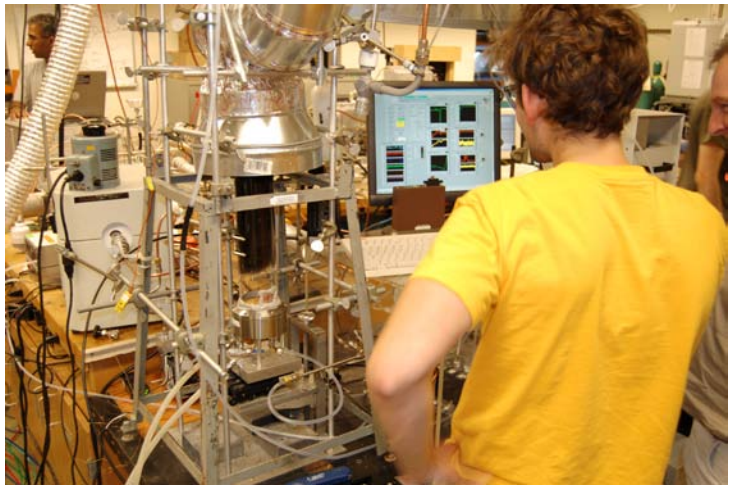
- Total carbon signal is constant for different monodisperse soot particles

Soot Project 2

(July 7-25, 2008)



Sooting Flame



- Twenty-six scientists operating 19 instruments (9 mass-based, 8 optically-based and 2 filter samples) and representing 12 institutions participated in the project

#	Highlights
1	Particle shape determination as a function of fuel-to-air ratio and collapse observed due to coatings
2	Characterization of several new instruments currently under development
3	Characterization of the physical and chemical properties of various types of black carbon particles (including incandescence, fullerene content, surface-bound PAH, etc.)
4	Mass specific absorption measurements as a function of fuel-to-air ratio and carbon particle type
5	Optical absorption enhancement measurements as a function of coatings
6	Wavelength-dependent measurements of absorption, scattering, and extinction as a function of fuel-to-air ratio, particle coating, and relative humidity

Summary

- SP2AMS: Successfully adapted SP2 module into AMS
  - Separate volatilization and ionization mechanisms
  - Only sensitive to absorbing particles (soot or metals)
  - Chemical and size information obtain for elemental carbon cores and non-refractory organic coatings
- Measure of organic coating mass and size
  - Shows less fragmentation than standard AMS spectra
- Measure of particulate elemental carbon mass and size
  - Provides chemical information on ‘black carbon’ particles
  - Linear correlation between MAAP absorption and carbon cluster ion signals from SP2-AMS for several different types of soot particles
  - Fully vaporizes 160 nm (~1 fg) soot particles under higher laser powers
- Quantification studies have been carried out and are being analyzed
  - Boston College – Aerodyne Soot Project 2

Department of Energy (DOE) SBIR