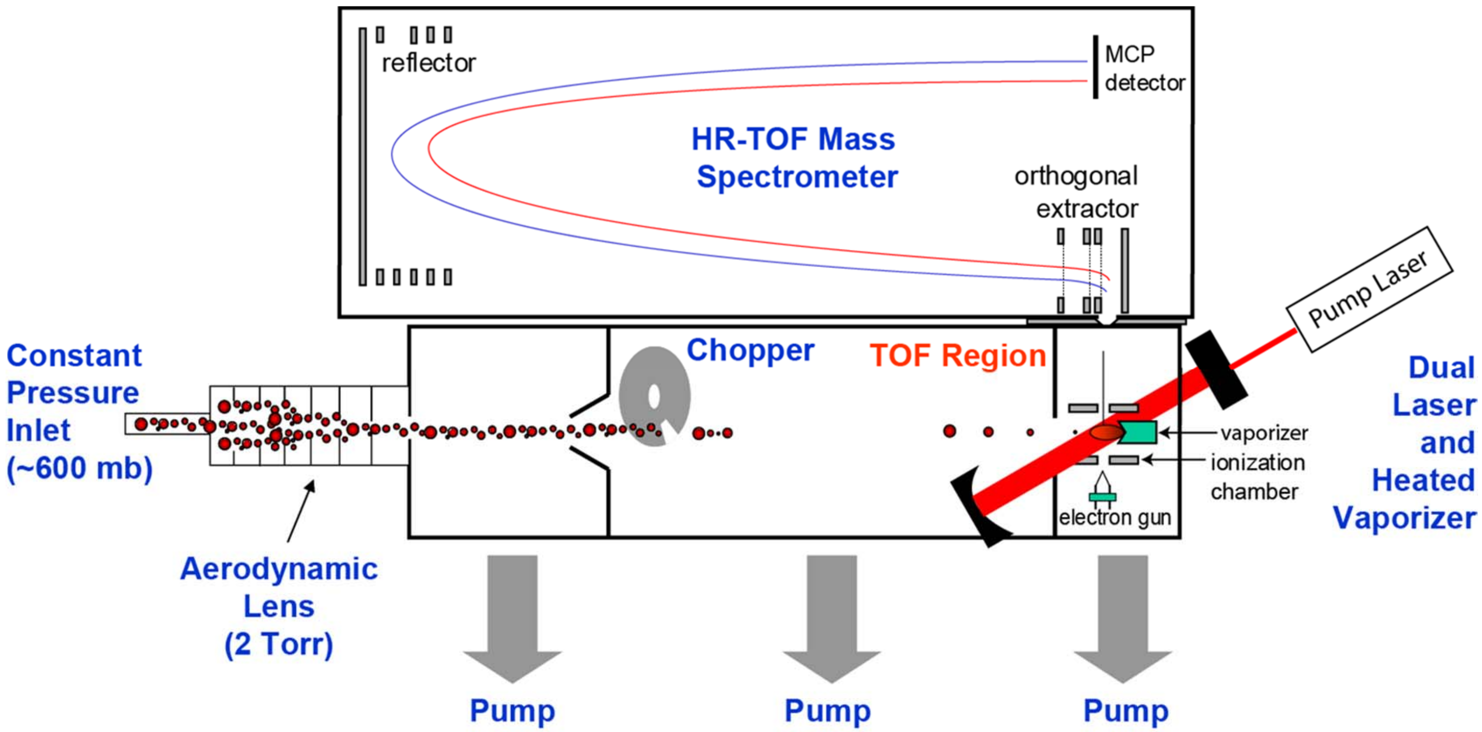
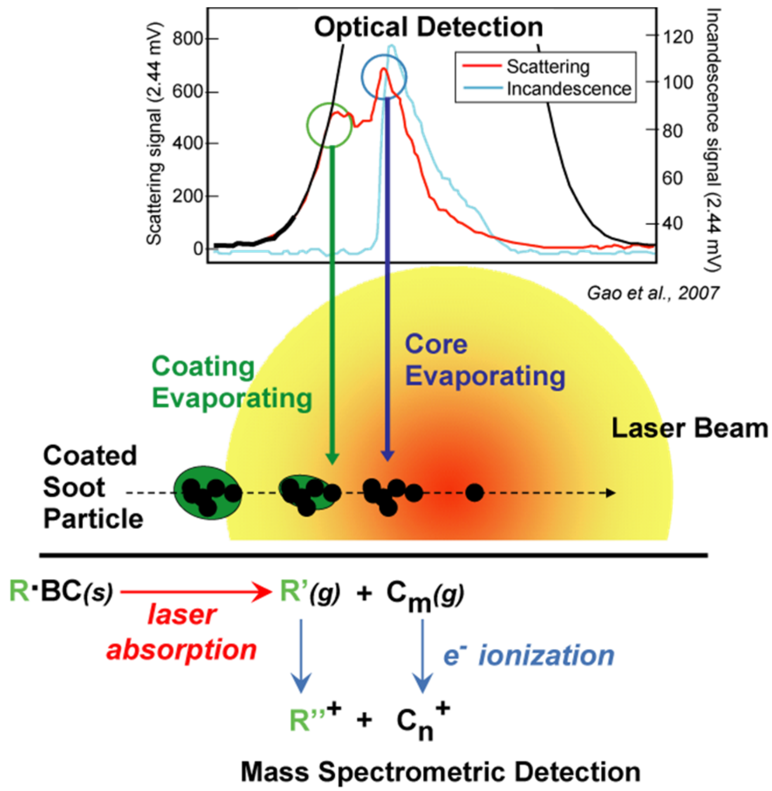
Soot Particle-AMS



AMS plus laser vaporizer module

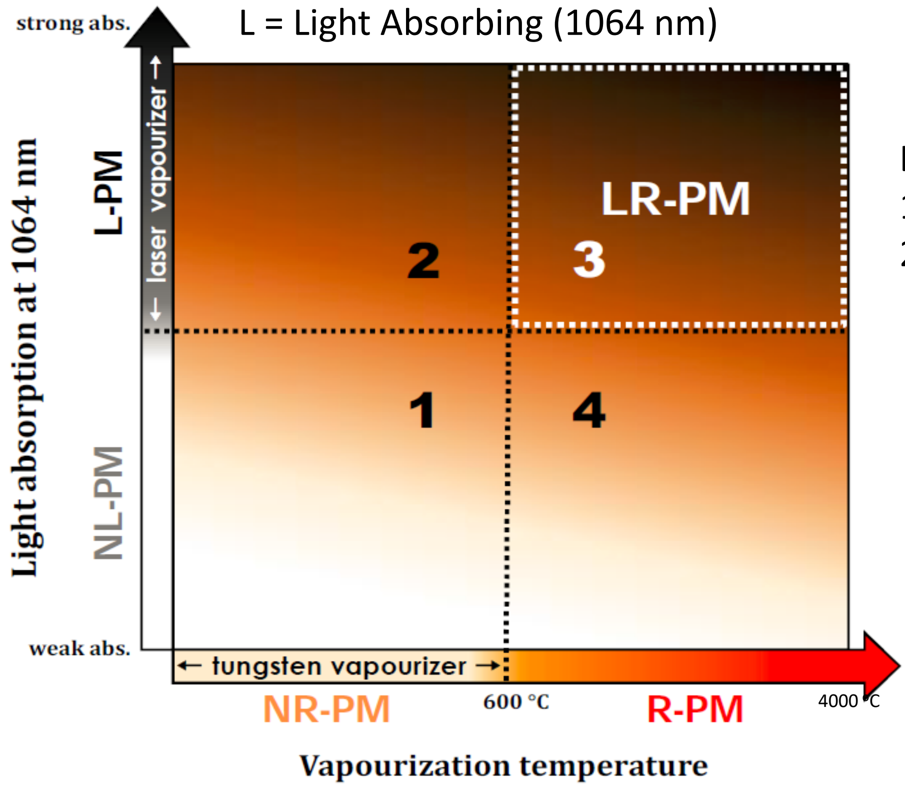
Laser Vaporizer Detection Scheme



The laser is not the vaporizer, the absorbing particles are the vaporizer!!

Nomenclature

PM = Particulate Matter
NR = Non-Refractory
R = Refractory
L = Light Absorbing (1064 nm)



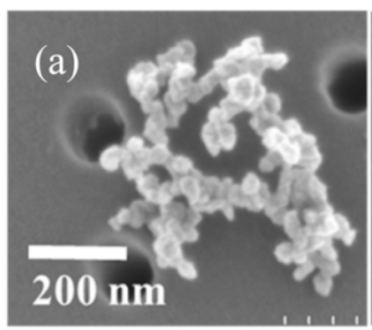
LR-PM:
1. Refractory Black Carbon (rBC)
2. Metals

Corbin et al., 2014 - ETH

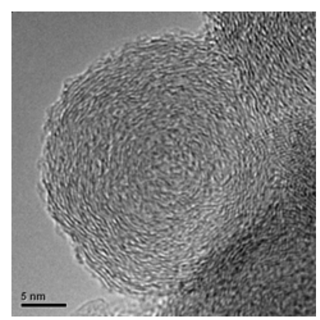
SP-AMS Applications

Atmospheric Refractory Black Carbon (rBC)

- A product of incomplete combustion
- Resistant to heat (i.e., Refractory)
- Highly absorbing (i.e., Black)
- *Almost* elemental carbon (i.e., Carbon)
- Also known as “soot”, “black carbon”, “elemental carbon”…



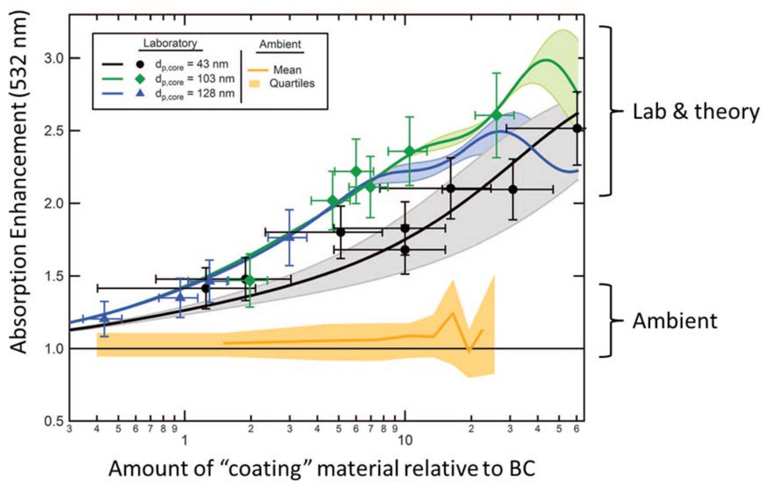
aggregate of *spherules*



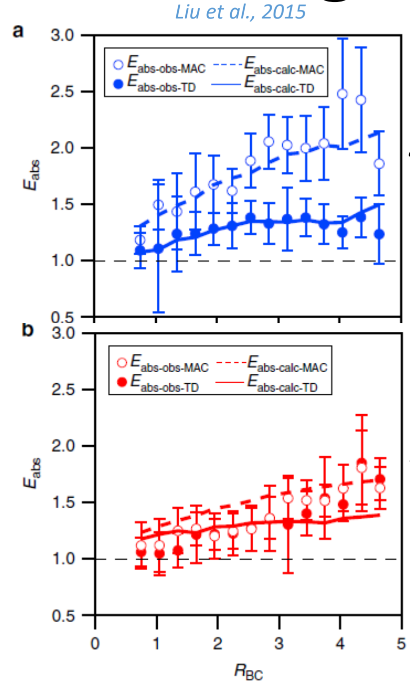
NR-PM to rBC ratio:
Radiative impact of internal mixing

Cappa et al., 2012

532 nm



Liu et al., 2015



405 nm

781 nm

<u>California urban summer</u>

- Mainly urban (traffic, etc.) sources with little/no biofuels
- Measurements lower than shell-core Mie theory

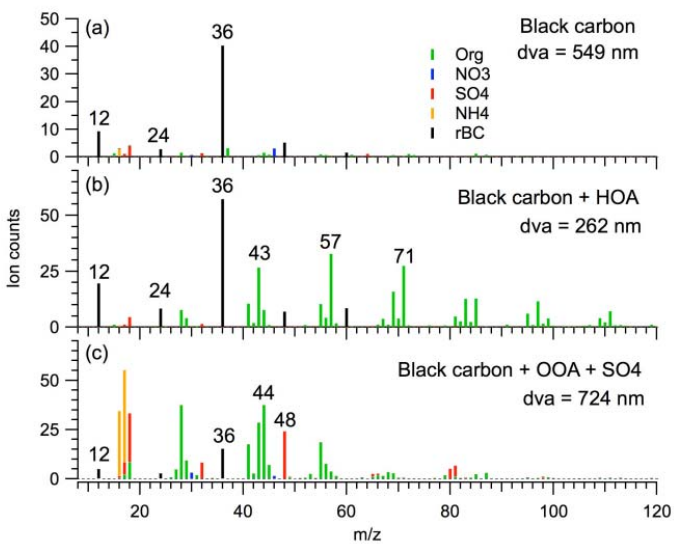
<u>UK suburban winter</u>

- Mixed sources including solid fuel burning
- Measurements match shell-core Mie theory

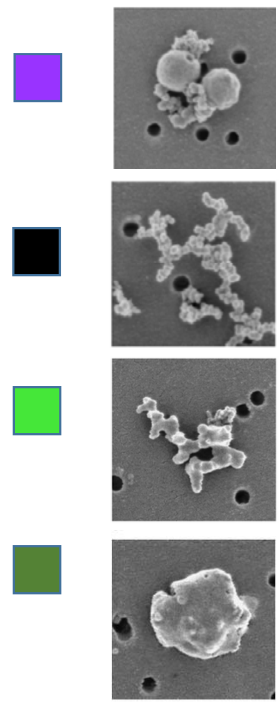
rBC Particle mixing state

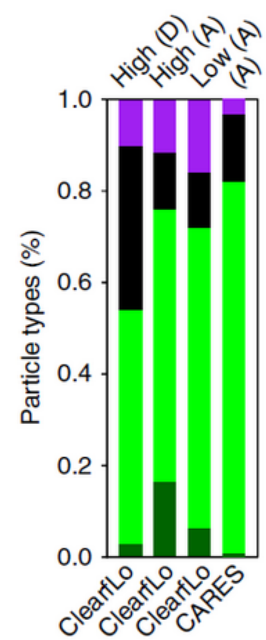
- In urban and rural environments, BC is found internally mixed to varying extents with organics (POA and SOA) and inorganics (SO_4 and NO_3).

??



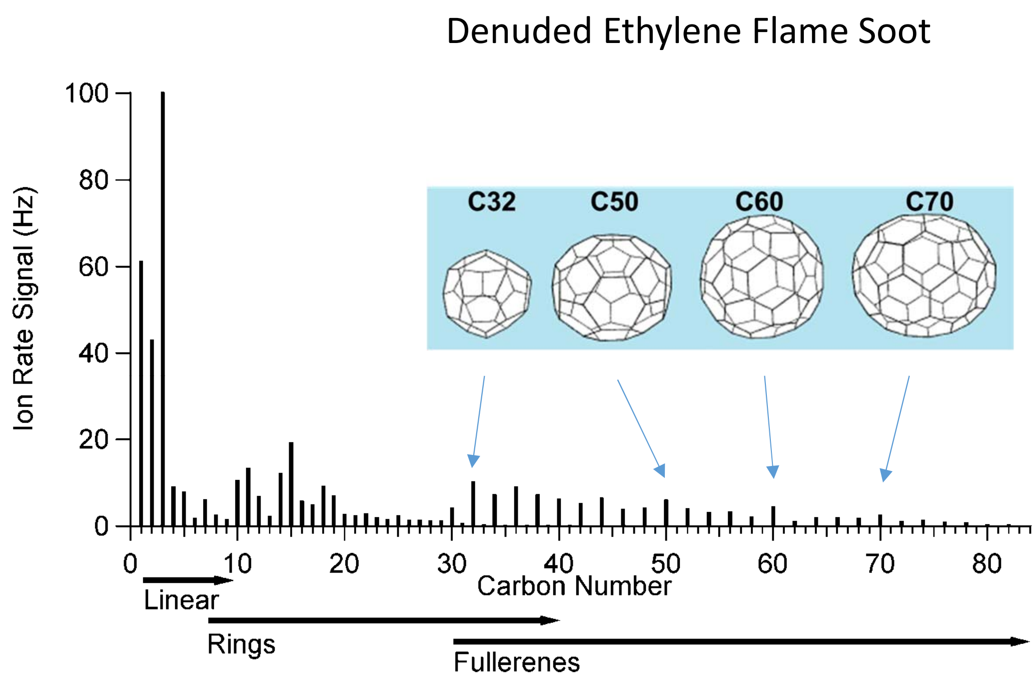
Alex Lee et al., 2015 - U. Toronto

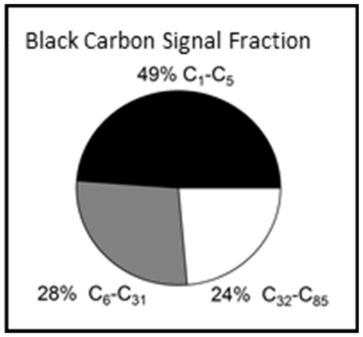


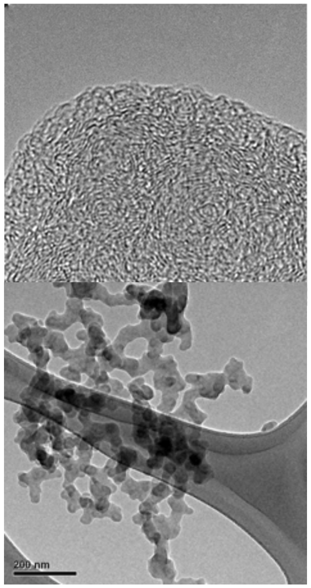


Liu et al., 2015 - Mich. Tech. Univ.

Measure rBC Carbon Cluster Ions



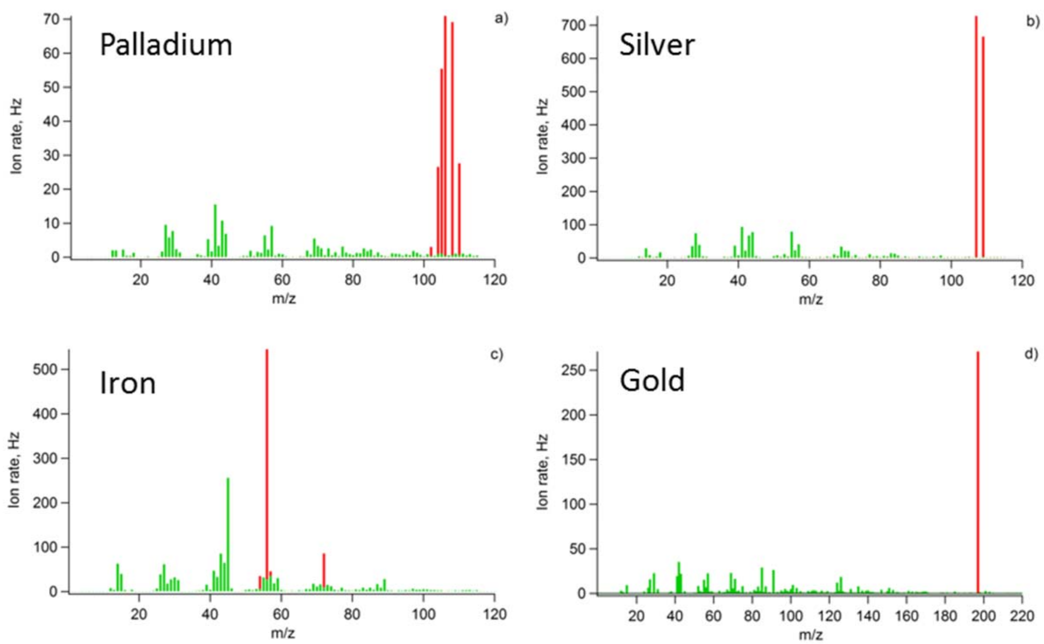




- Are refractory carbon ion distributions associated with underlying carbon structures?

Nilsson, Eriksson, Pagels, et al., 2014 – Lund
Carbone, et al., 2015 - Helsinki

Metal Nanoparticles

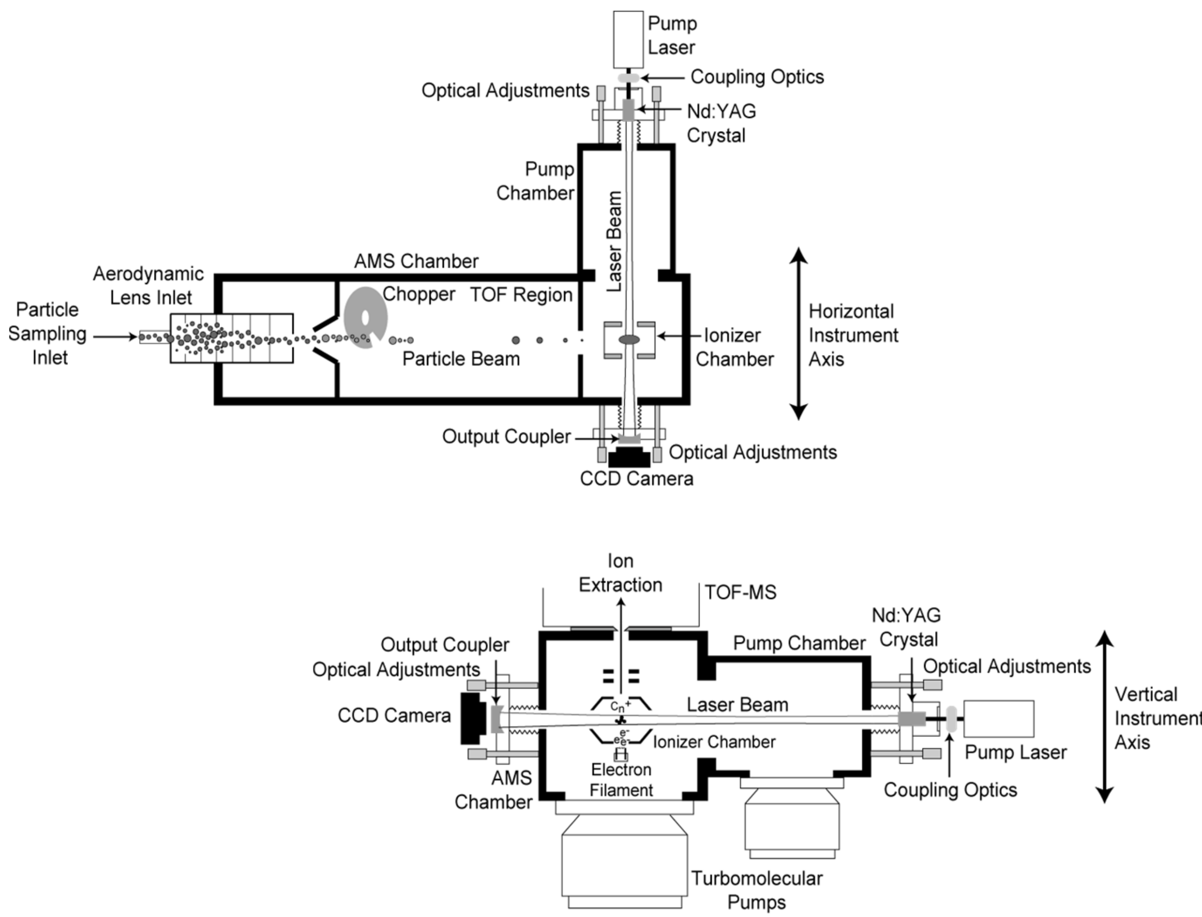


LR-PM

- Metal Nanoparticle detection, identification, and quantification of purity and total mass

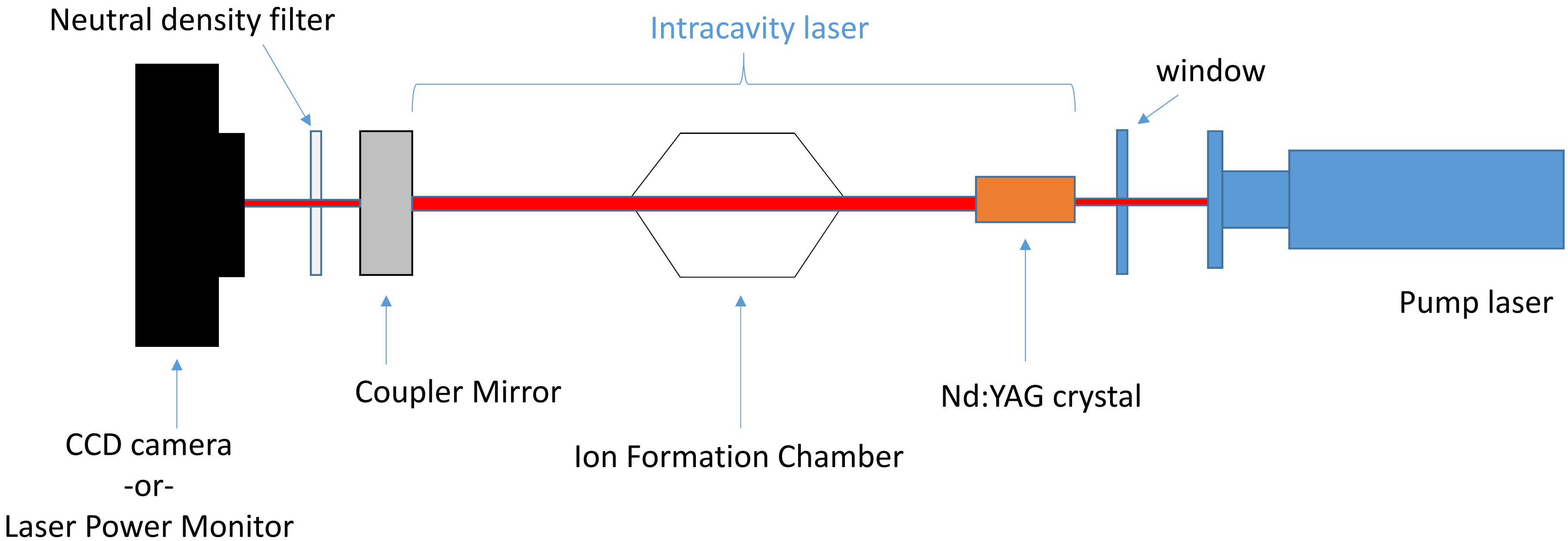
SP-AMS hardware

Laser Vaporizer Module



Onasch et al. (AS&T 2012)

SP-AMS laser vaporizer components



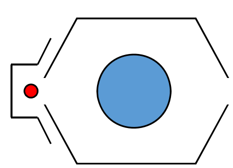
Laser Vaporizer parameters:

- Laser mode
- Laser alignment
- Laser power

Ionizer Configurations

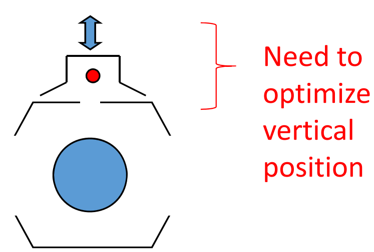
HR-AMS (Tungsten vaporizer)

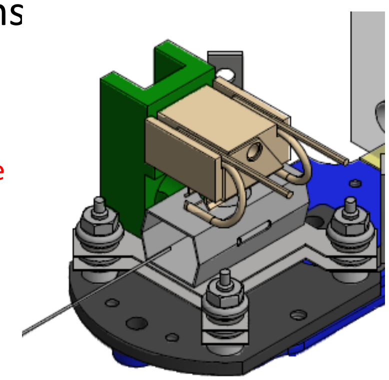
- Filaments on sides of ion chamber
- Filament position is mechanically set
- Filament wire is typically well positioned with respect to well formed slits in ion chamber walls
- Narrow or Wide chamber widths



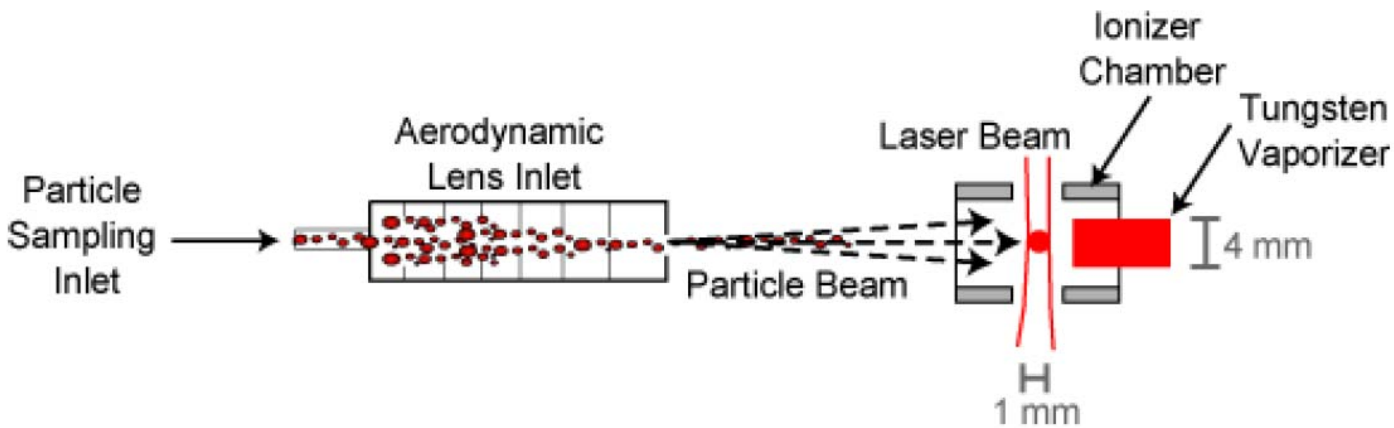
SP-AMS (Laser Vaporizer)

- Filament is on bottom of ion chamber
- Filament position is moveable (vert & horz)
- Filament slit width and breadth may vary due to custom procedure
- Large holes in sides to accommodate laser beam
- Narrow or Wide chamber widths



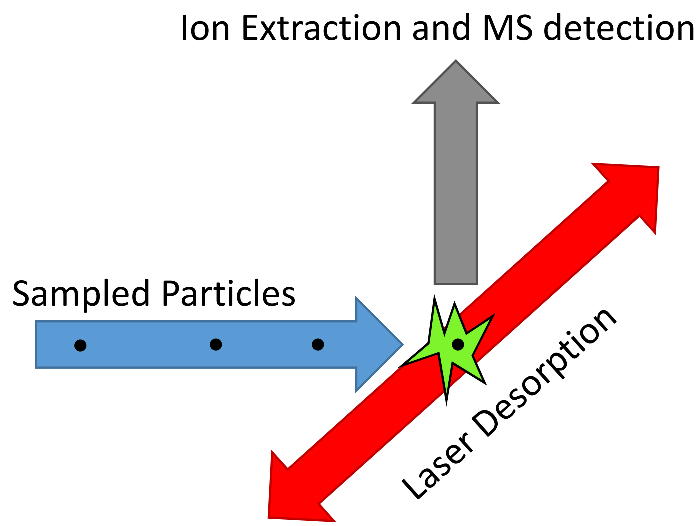


Vaporizer Configurations



1. Tungsten Vaporizer (HR-AMS)
2. Laser Vaporizer
3. Laser + Tungsten Vaporizers

SP-AMS Orthogonal Detection Axes



- Characterization of particle-laser interaction region:
  - Vertical Particle Beam Walk
  - Horizontal/Vertical Beam Width Probe
  - Laser Beam Walk

SP-AMS Quantification

Tungsten Vaporizer Collection Efficiency

$$CE = E_L \cdot E_B \cdot E_S$$

E_L = Aerodynamic ***L***ens transmission
E_B = Incomplete vaporization due to particle ***B***ounce
E_S = Particle beam divergence due to particle ***S***hape (and size)

E_L ~ 1 for d_{va} = 70-700 nm
E_B ~ 0.5 due to solid/refractory particle bounce
E_S = 1 as particle beam width < tungsten vaporizer width

***E_B* governs the overall CE for Tungsten Vaporizer**

Mass concentration of species "s"

$$C_s = \frac{1}{CE_s \cdot RIE_s \cdot mIE_{NO_3} \cdot Q} \sum_i I_{s,i}$$

Laser Vaporizer Collection Efficiency

$$CE_{Laser} = E_L \cdot E_B \cdot E_S$$

E_L = Aerodynamic ***L***ens transmission
E_B = Incomplete vaporization **
E_S = Particle beam divergence due to particle ***S***hape (and size)

$E_L \sim 1$ for d_{va} = 70-700 nm
$E_B \leq 1$ due inefficient energy absorption/transfer issues **
$E_S < 1$ as particle beam width < laser vaporizer width

E_S governs the overall CE for rBC and NR-PM (laser only)
→ Beam width probe measurement
E_B complicates rBC (R_{BC}) measurements

Mass concentration of species “s”

$$C_s = \frac{1}{CE_s \cdot RIE_s \cdot mIE_{NO_3} \cdot Q} \sum_i I_{s,i}$$

SP-AMS CE's Vaporizer-dependent

Vaporizer	**Measured Species**
Tungsten	NR-PM * E_B
Laser	(rBC + R-PM‡ + NR-PM‡) * E_S
Laser and Tungsten	(rBC + R-PM‡ + NR-PM‡) * E_S + (NR-PM - NR-PM‡ * E_S) * E_B

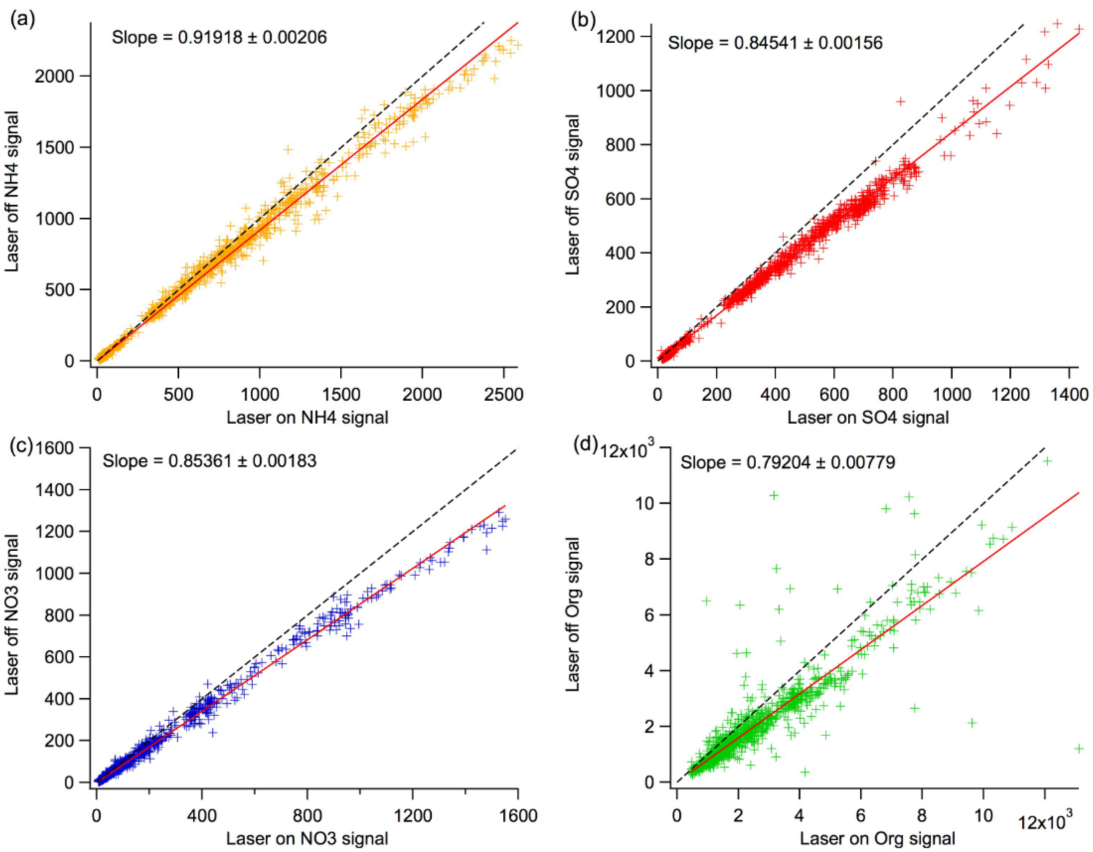
NR-PM = Nonrefractory Particulate Material measured by a standard AMS [*Jimenez et al., 2003*]
R-PM = Refractory Particulate Material measured by the SP-AMS (see text for details)
rBC = Refractory black carbon measured by the SP-AMS (and SP2) [*Schwarz et al., 2006*]
‡ = Particulate Material on rBC particles as mesaured by the SP-AMS (see text for details)
E_B = Particle bounce related Collection Efficiency of the AMS
E_S = Size and shape related Collection Efficiency of the SP-AMS

Summary of quantification issues:

#	Observation	Effects	Issue	Vaporizer(s)	Level of Understanding	Comments
1	Large NR-PM Laser ON/OFF ratios	NR-PM quantification	Laser misalignment	Dual	middle, and increasing	Includes laser beam hitting tungsten vaporizer or ion formation chamber.
2	Coating/shape dependent CE	rBC quantification, NR-PM/rBC ratios	Particle beam - laser beam overlap	Laser	middle	Collection efficiency (CE) issue strongly dependent upon alignment and particle morphologies. **BWP** will help with quantification, though difficult (and slow) measurements.
3	Laser power drop experiments	rBC quantification, NR-PM/rBC ratios	Incomplete vaporization	Laser	low, increasing	Collection efficiency (CE) issue dependent upon laser power and laser beam width.
4	Increased sensitivity to NR-PM on rBC particles	NR-PM/rBC ratios, RIE's for laser vaporizer	Differences between vaporizer sensitivities	Laser	low	mIE sensitivity issue likely due to vaporization temperatures of molecules and subsent velocities in ion formation chamber. Difficult mIE measurements for NR-PM from laser vaporizer. Laser vaporizer RIE's need verification (or determination). Not well characterized to date.
5	Incorrect rBC ion fragmentation	rBC quantification, rBC ion distributions	Cn+ ion interference from Org	Laser	high	Problem for dual vaporizer measurements with significant NR-PM Organics. PMF of rBC ion signals appears to effectively distinguish Cn+ ion sources.
6	Variations in rBC ion distributions	rBC quantification, rBC ion distributions	Large (mid and fullerene) Cn+ ion observations	Laser	low, increasing	Laser power issue that has yet to be resolved.

ISSUE #1

Laser OFF vs ON - Toronto

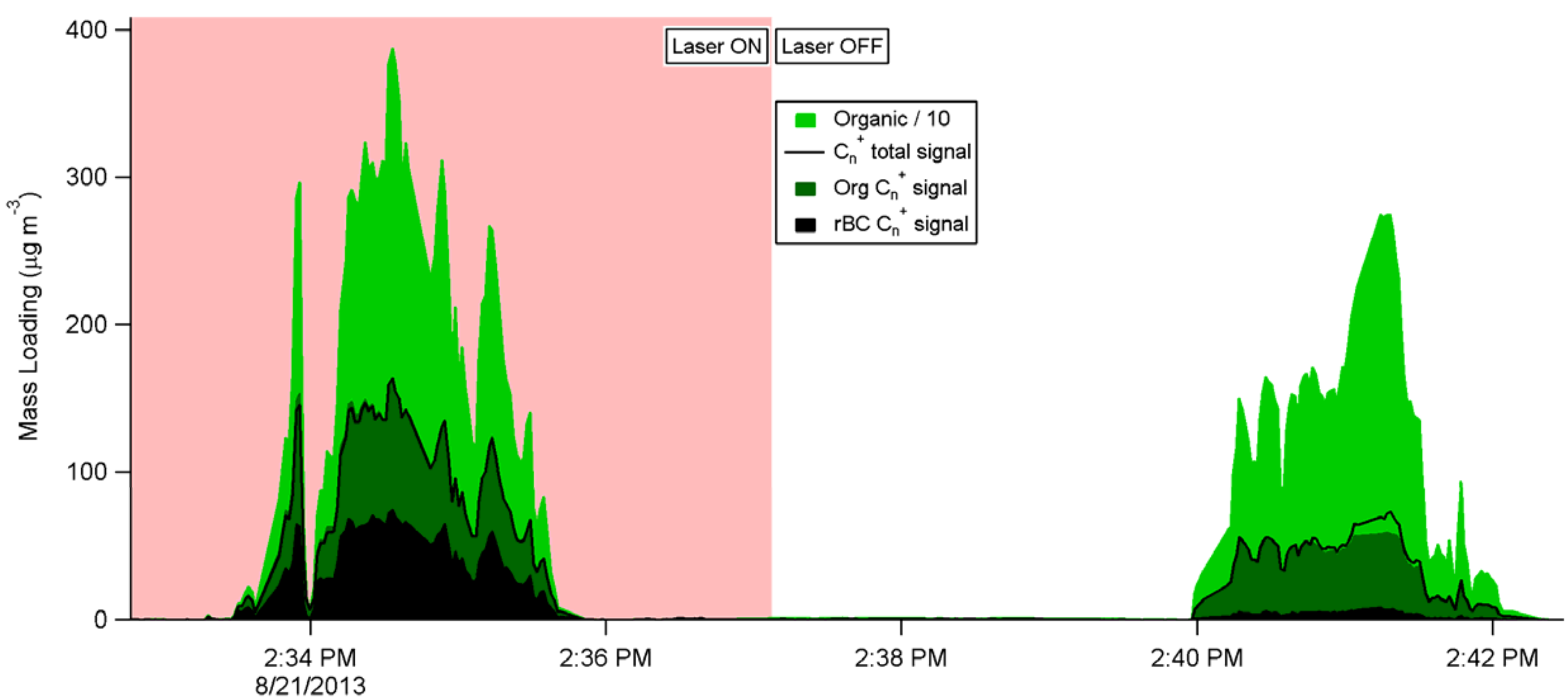


Alex Lee et al., 2015

- Laser ON NR-PM > Laser OFF NR-PM
- Largest effects on organics and HOA signals, lesser on inorganics

ISSUE #1

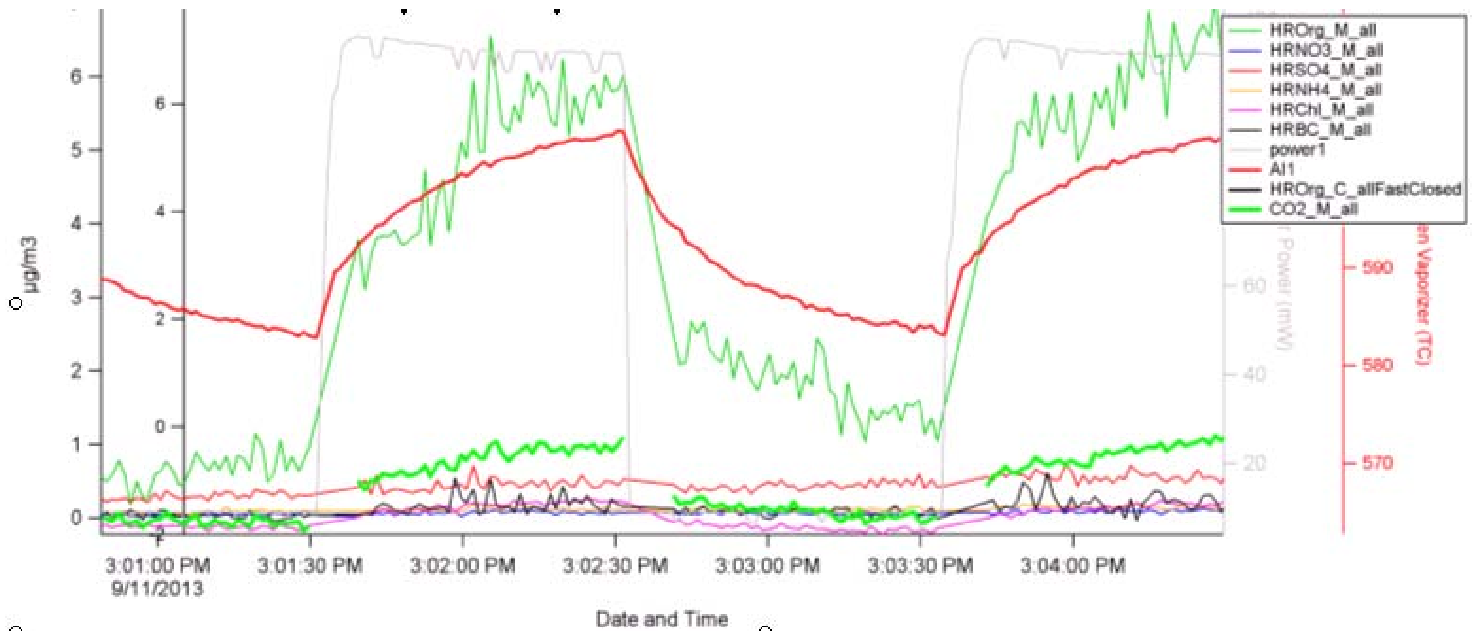
Laser ON vs OFF - BBOP



Government Flats fire (8/21/2013). SP-AMS plume transect with dual vaporizers (left) and tungsten only (right)

ISSUE #1

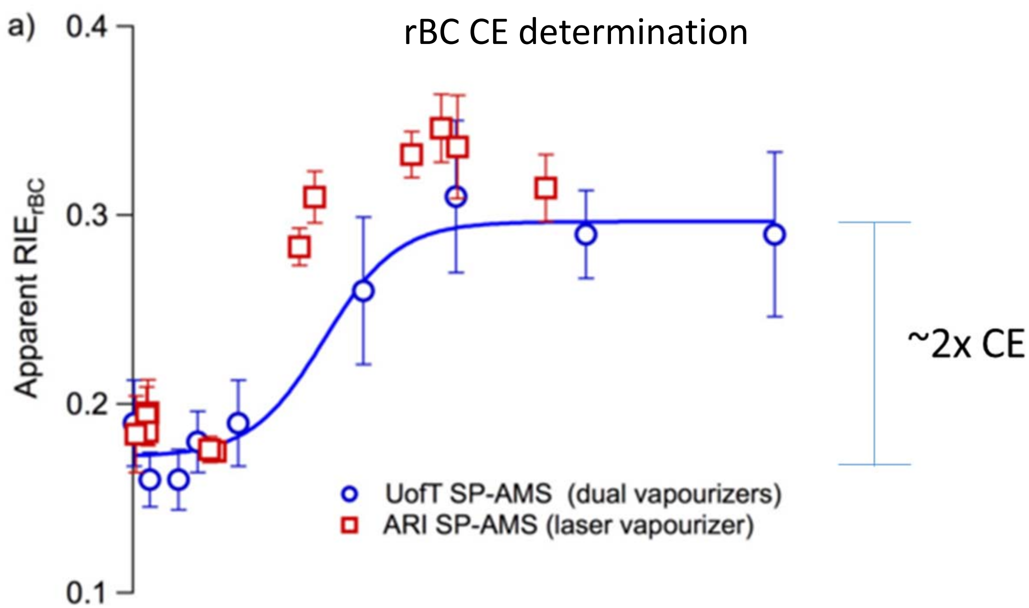
Laser ON/OFF time dependence..



- Laser on causes > 30oC changes in the tungsten vaporizer
- Significantly affects the DIFF HROrg signal due to changing background conditions that do not subtract out correctly

ISSUE #2

Collection Efficiency - rBC

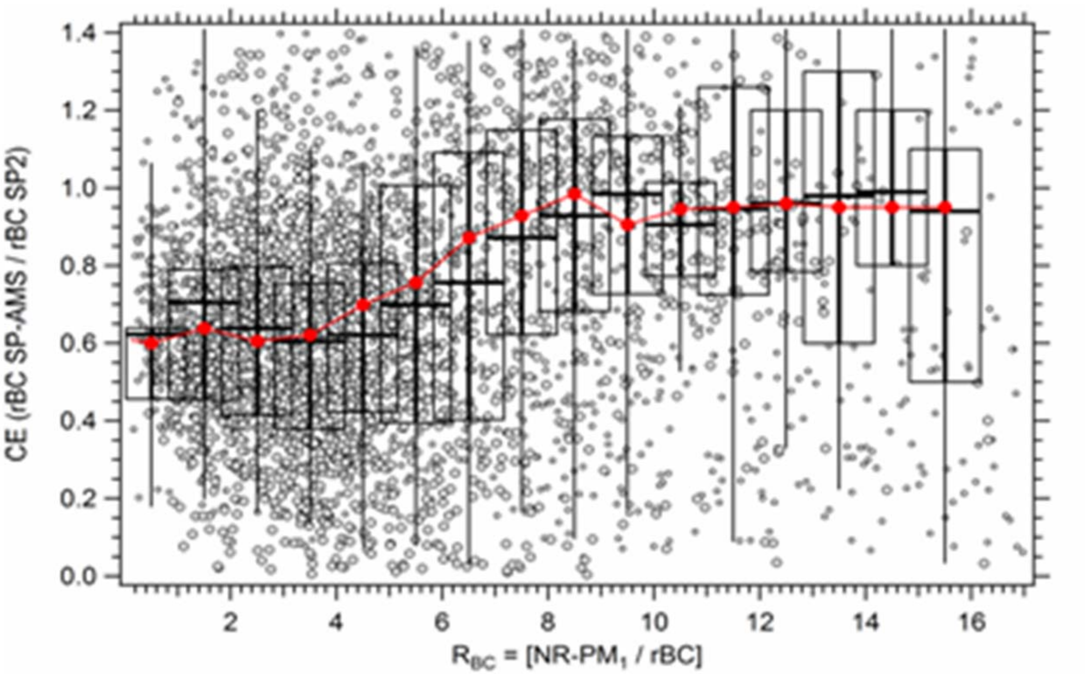


- Coated Regal black particles with DOS to make spherical
- With thicker coatings, RIE_rBC increased as the particle beam narrowed down closer to laser beam width
- Dual laser/tungsten vaporizer setup

Willis et al., 2014 AMT

ISSUE #2

Ambient rBC CE observations



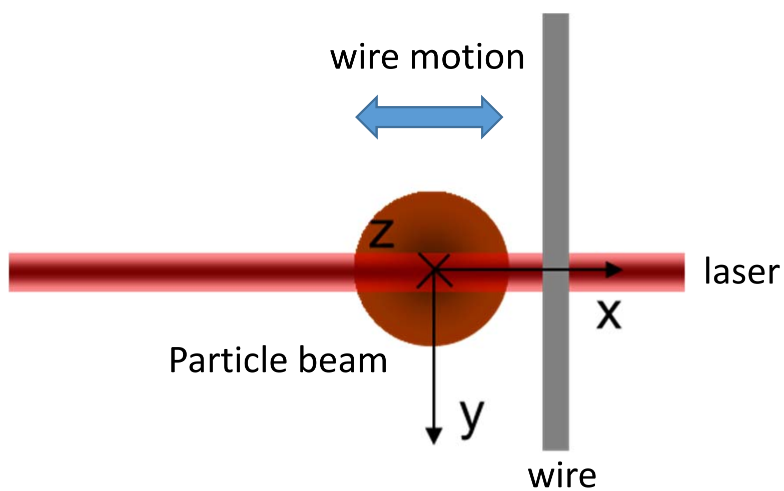
- Observed similar increase in CE for rBC mass loadings (compared to SP2) for ambient measurements
- Complicated by low signals and varying size distributions

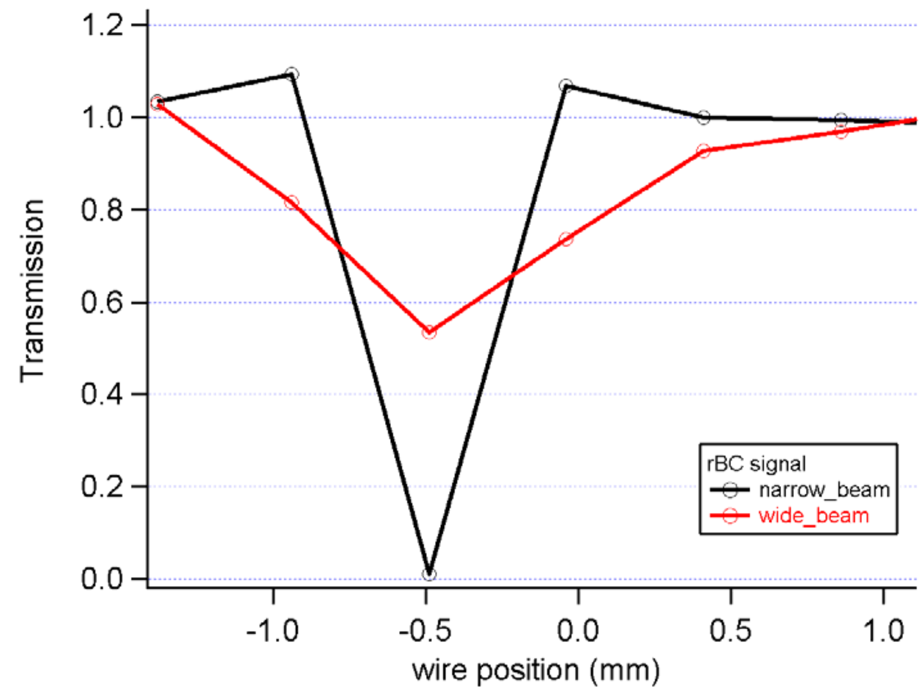
Massoli et al., 2015 JGR

ISSUE #2

Particle-Laser Beam overlap

Beam Width Probe (Huffmann et al./Salcedo et al.)

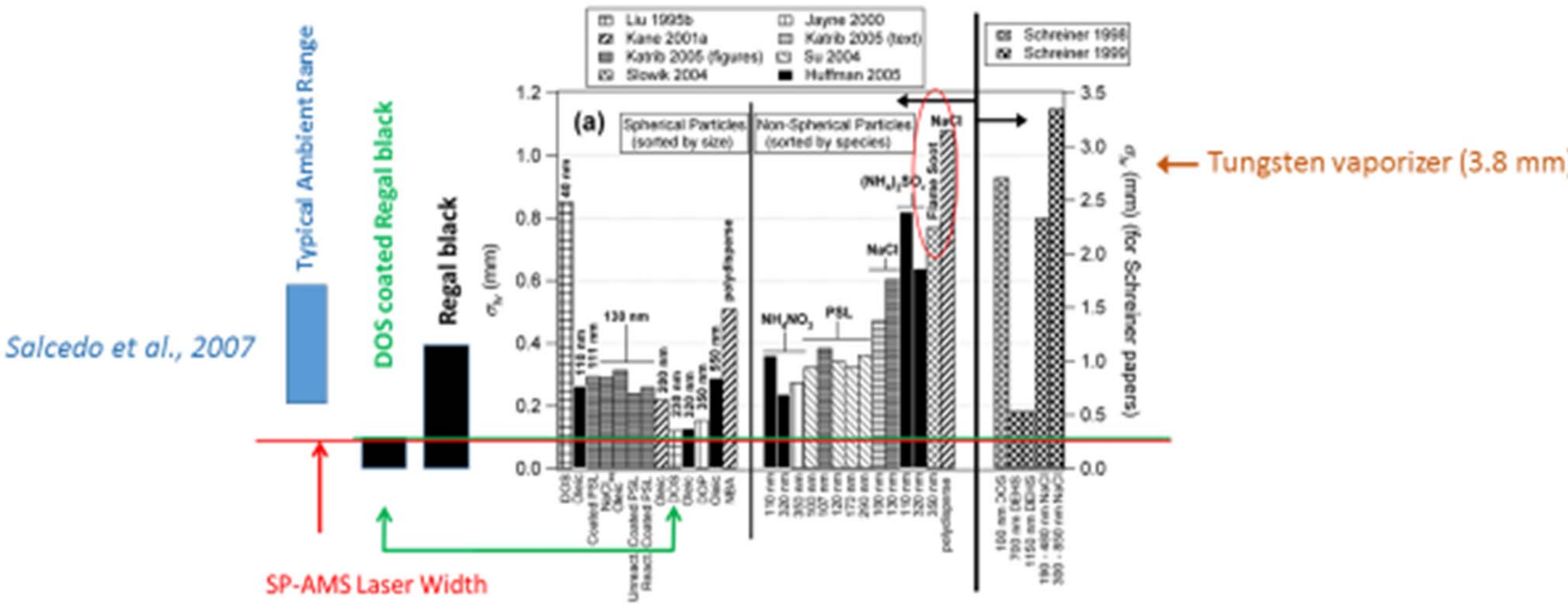




ISSUE #2

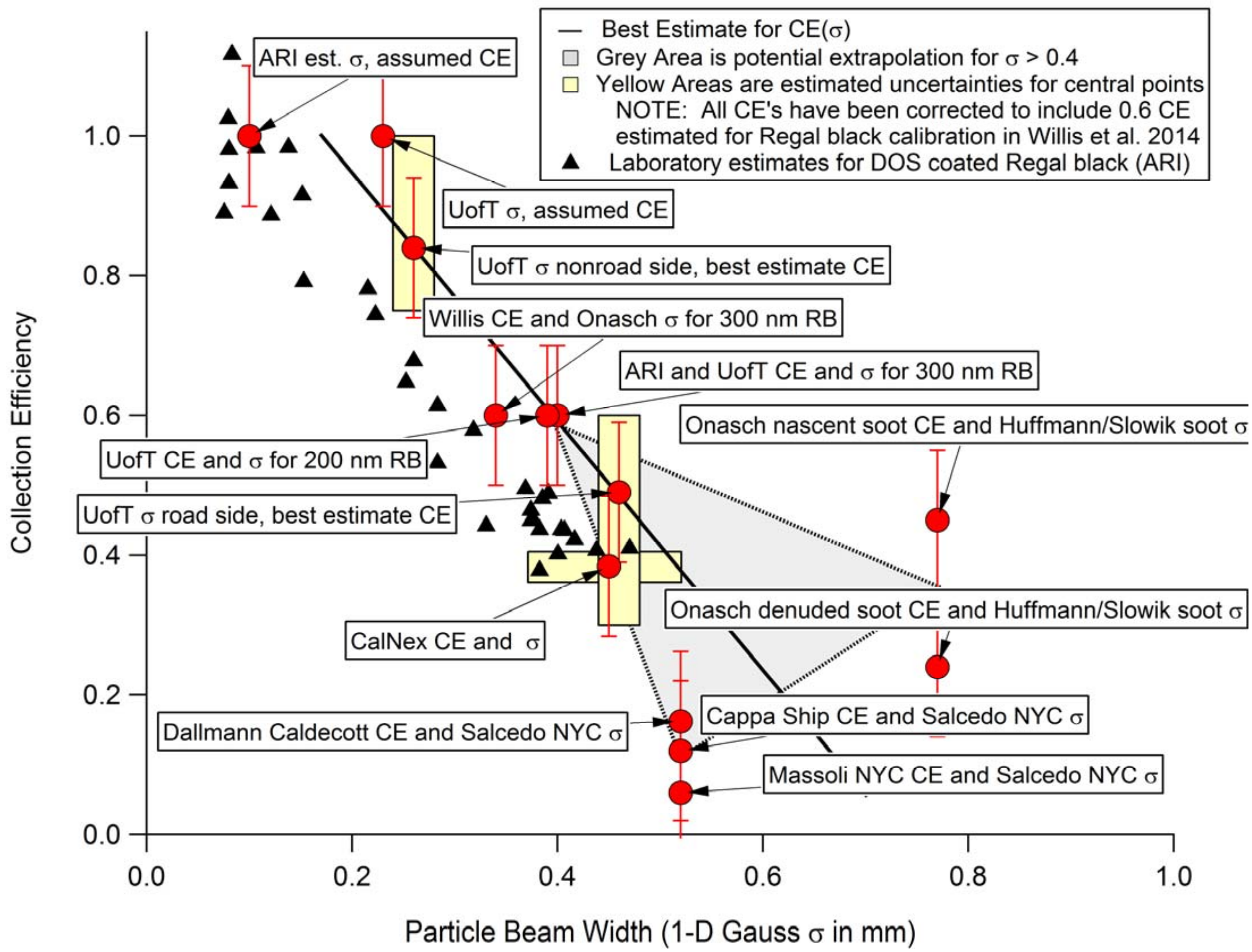
Willis et al., 2014 – U Toronto

Laser and Particle Beam Widths



- Particle beam widths: DOS coated Regal black ~ pure DOS particles
- Laser beam width (σ) is ≤ ~ 0.1 mm
- Use BWP for CE determination in future

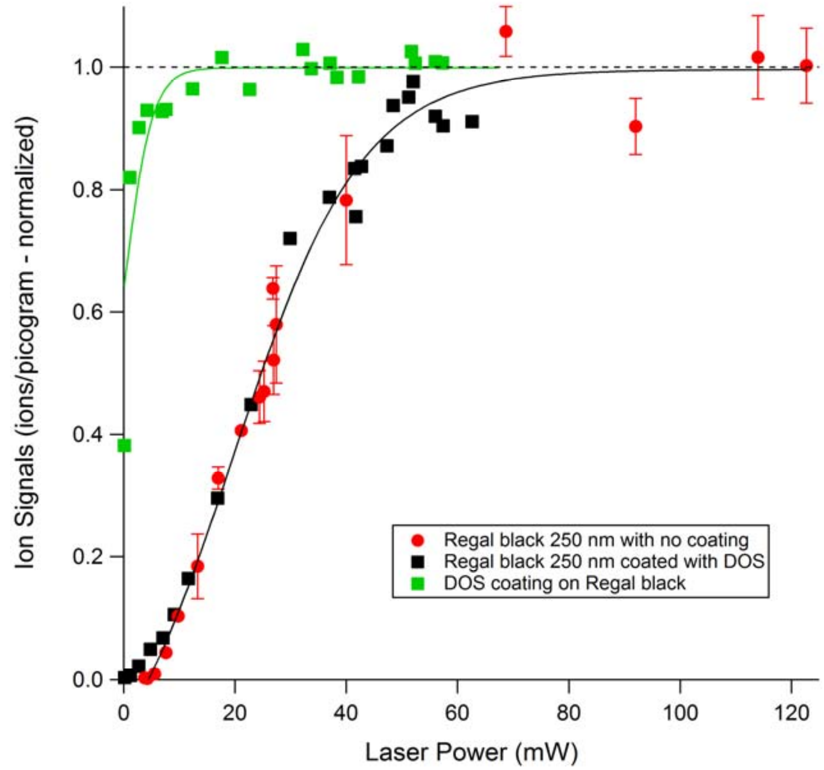
ISSUE #2



Best Estimate for CE(σ)
Grey Area is potential extrapolation for σ > 0.4
Yellow Areas are estimated uncertainties for central points
NOTE: All CE's have been corrected to include 0.6 CE estimated for Regal black calibration in Willis et al. 2014
Laboratory estimates for DOS coated Regal black (ARI)
ARI est. σ, assumed CE
UofT σ, assumed CE
UofT σ nonroad side, best estimate CE
Willis CE and Onasch σ for 300 nm RB
ARI and UofT CE and σ for 300 nm RB
Onasch nascent soot CE and Huffmann/Slowik soot σ
UofT CE and σ for 200 nm RB
UofT σ road side, best estimate CE
Onasch denuded soot CE and Huffmann/Slowik soot σ
CalNex CE and σ
Cappa Ship CE and Salcedo NYC σ
Dallmann Caldecott CE and Salcedo NYC σ
Massoli NYC CE and Salcedo NYC σ
Collection Efficiency
Particle Beam Width (1-D Gauss σ in mm)
0.0
0.2
0.4
0.6
0.8
1.0

ISSUE #3

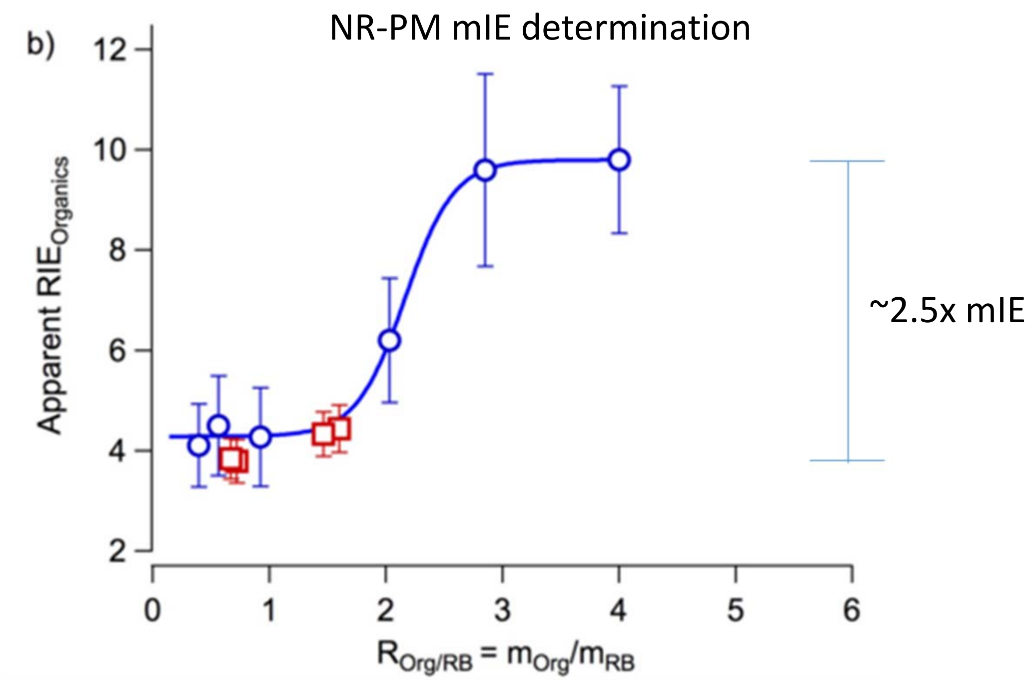
Incomplete vaporization and laser power



- Laser Power Drop experiments show a strong laser power and particle-laser beam overlap dependence

ISSUE #4

NR-PM on rBC Collection Efficiency

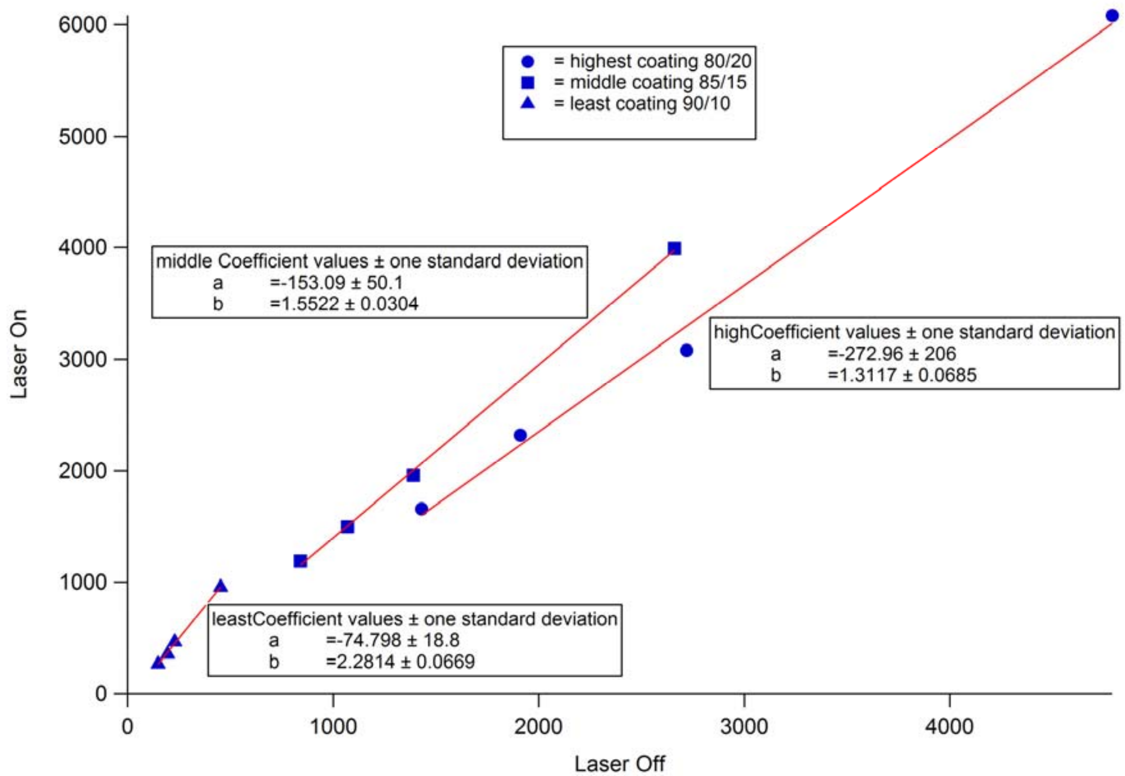


- Coated Regal black particles with DOS to make spherical
- With thicker coatings, RIE_rBC increased as the particle beam narrowed down closer to laser beam width
- Dual laser/tungsten vaporizer setup
- *Both* rBC and Org ion signals increased
- NR-PM mIE for DOS appears to be ~2.5x larger from laser vaporizer than from tungsten vaporizer

Willis et al., 2014 AMT

ISSUE #4

AN coated BC with vaporizer and laser



- Dual vaporizers
- Atomize solution of Regal black and ammonium nitrate
- Large [AN] likely produce significant number of particles without Regal black
- Small [AN] likely produce Regal black particles with thin coatings of AN
- Apparent mIE for AN on laser vaporizer is ~2.3x tungsten vaporizer (laser OFF)

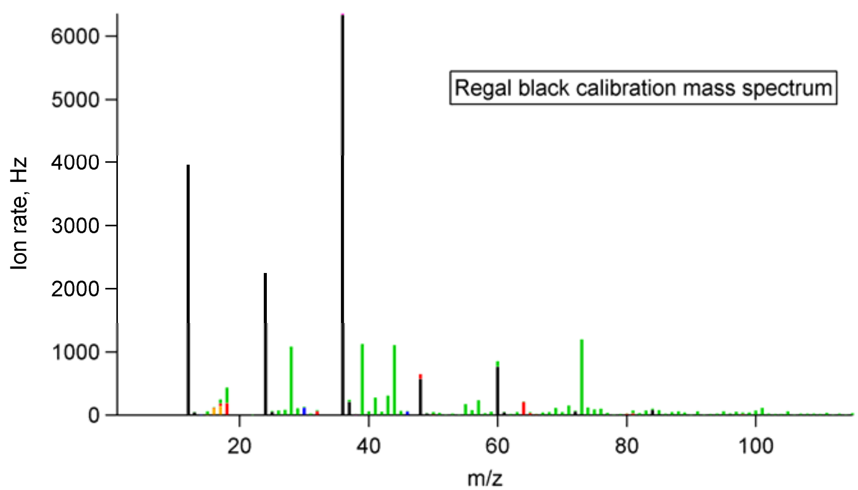
Carbone et al., 2015 AMTD; Fortner lab experiments

ISSUE #5

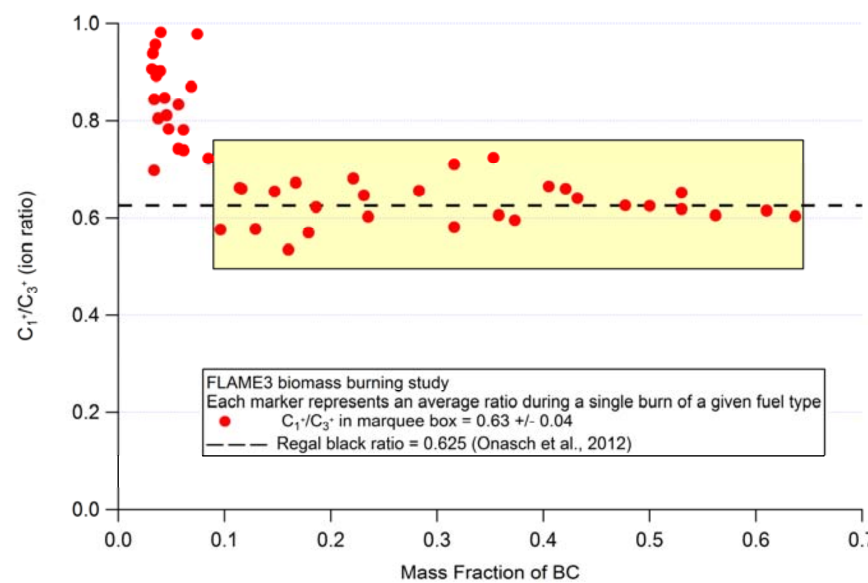
C_n^+ ion interference

Laser vaporizer only

Regal black



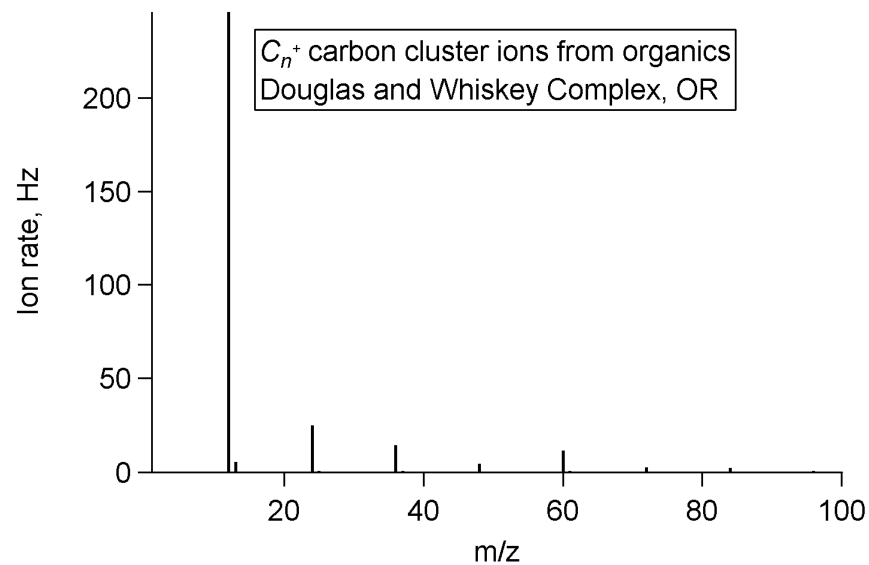
Flame 3

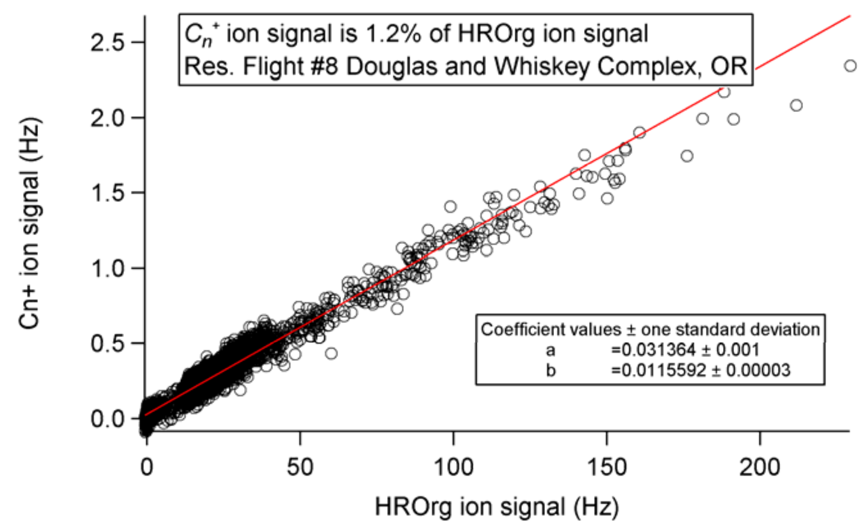


Fortner et al., 2015

ISSUE #5

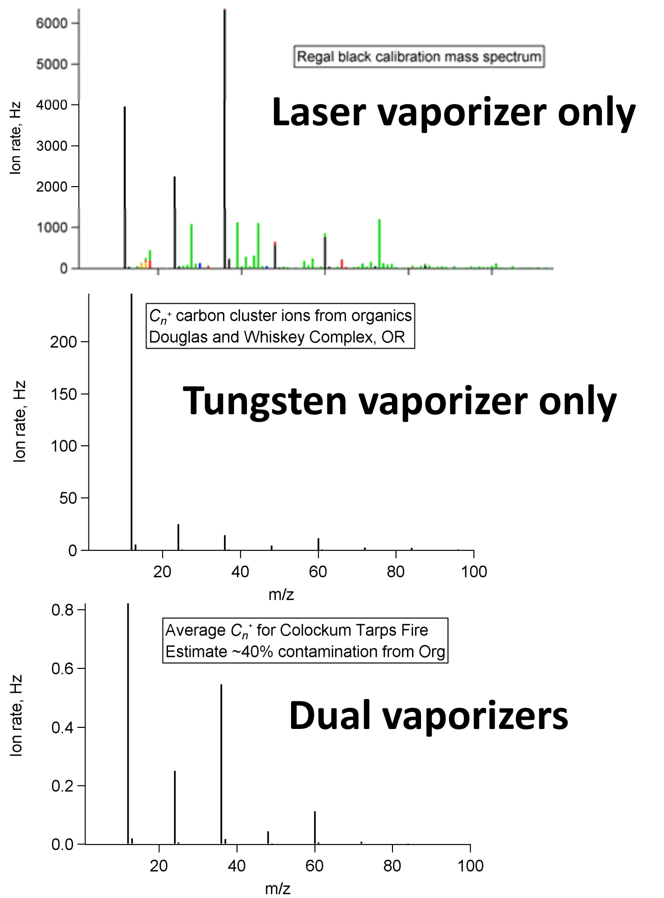
Resistively heated tungsten vaporizer only

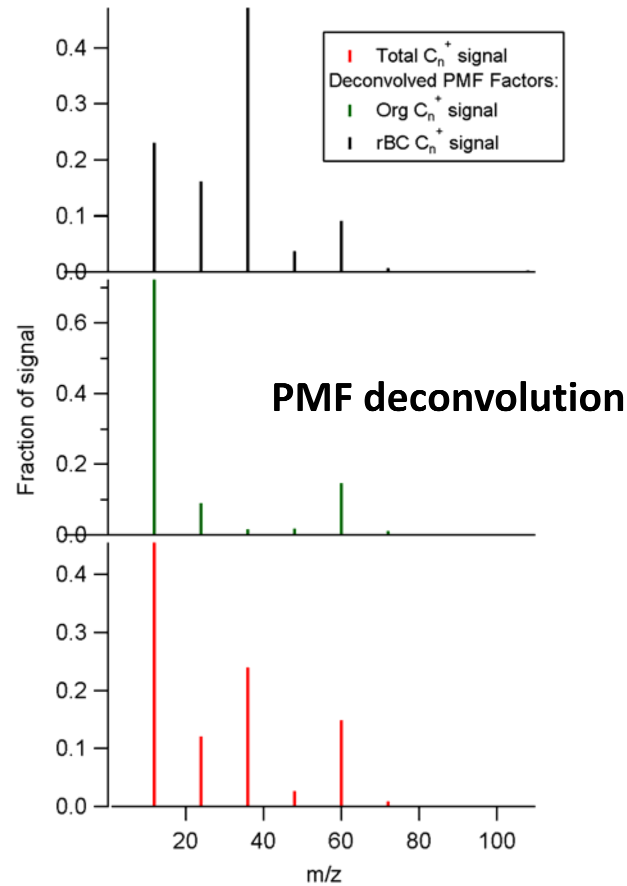




ISSUE #5

Refractory black carbon (rBC)





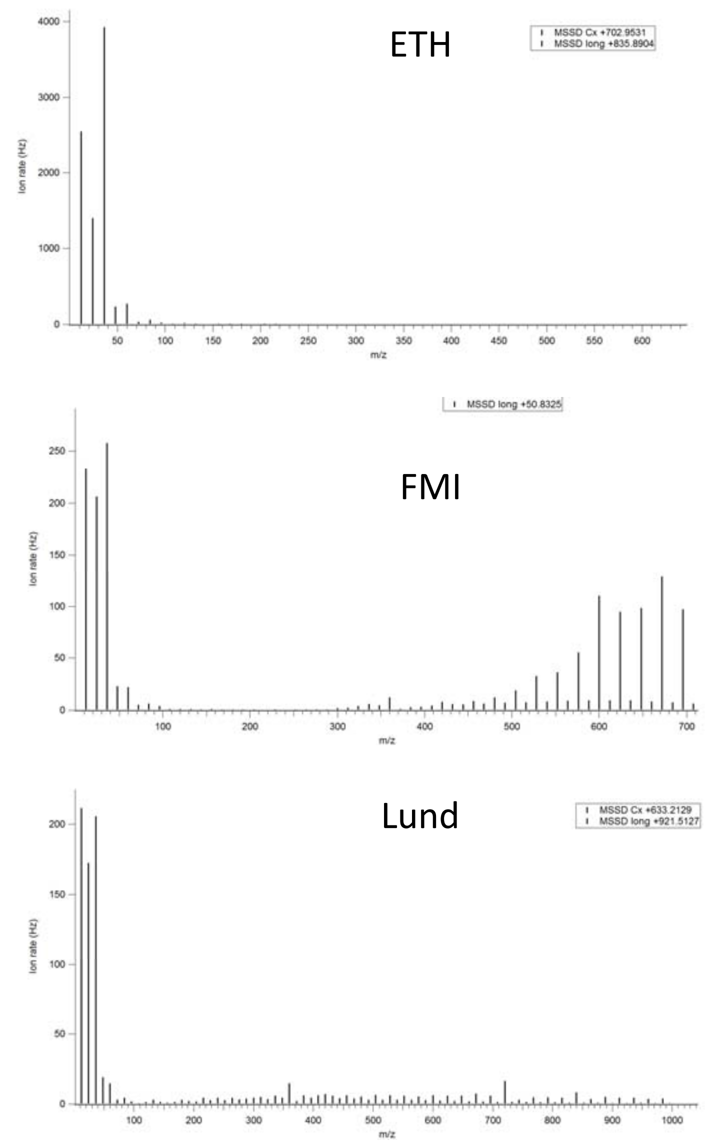
ISSUE #5

rBC ion distributions

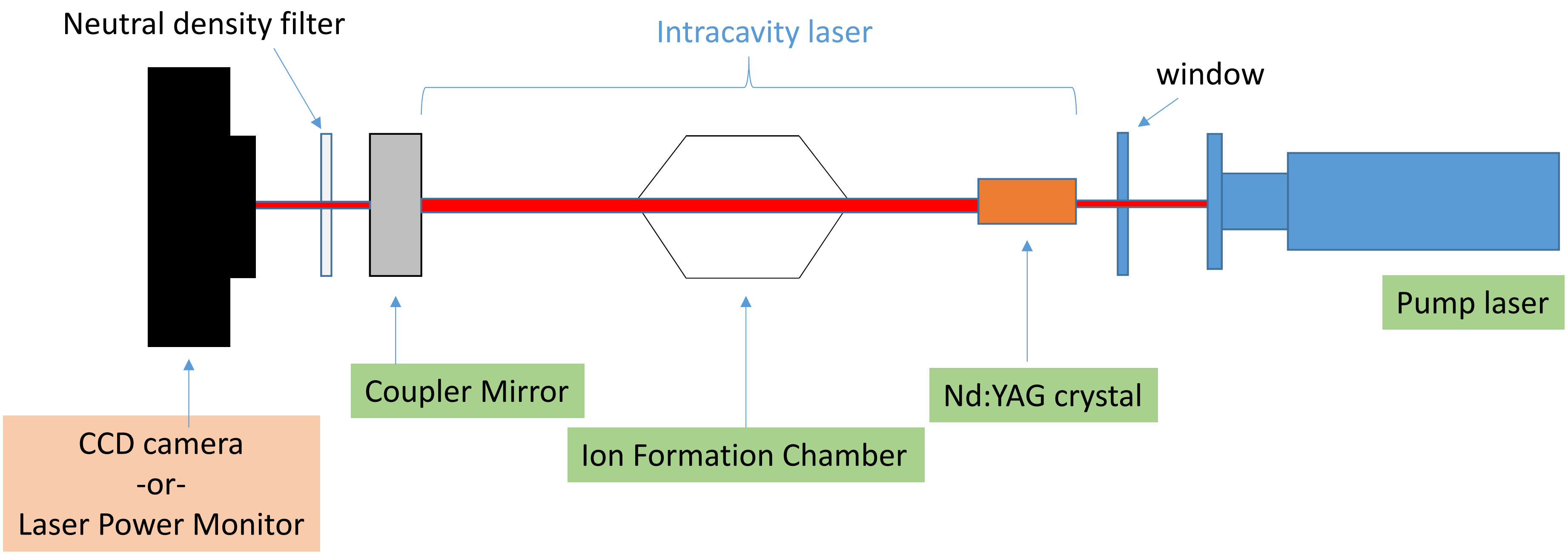
Experiment #51
(ETH sample fullerene soot)

Amewu Mensah et al.

- Three independent SP-AMS instruments sampling the same fullerene soot sample showing different carbon ion distributions!



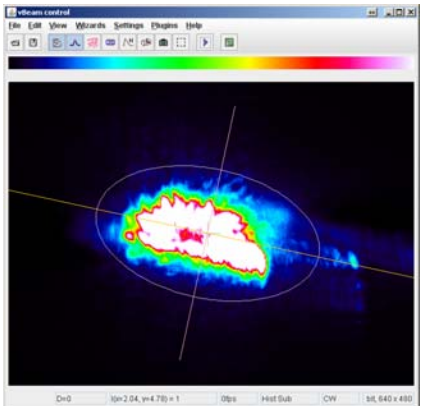
SP-AMS laser vaporizer components

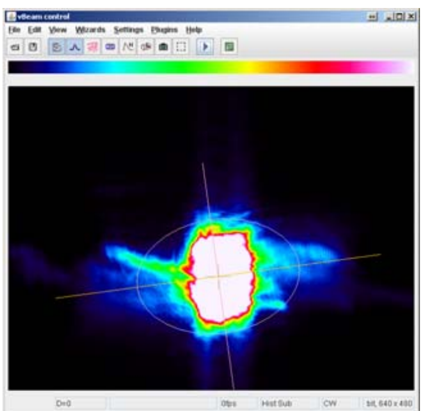


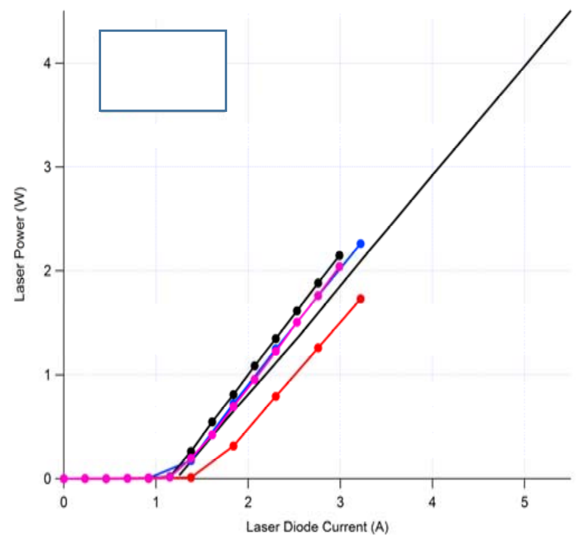
Laser vaporizer important parameters:

- Laser mode
- Laser alignment
- Laser power

Pump laser beam quality and power

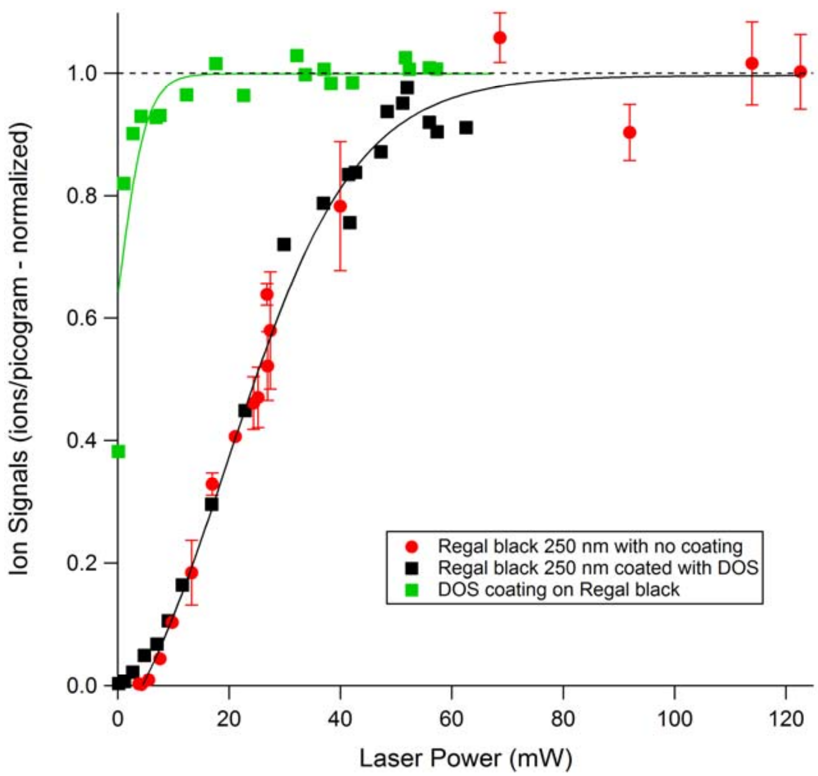






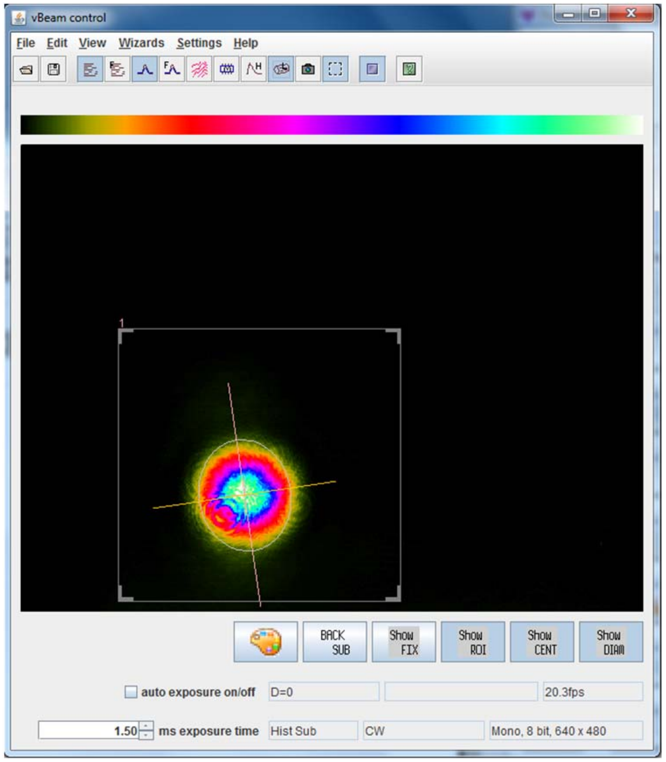
- Variations in pump laser beam profile and power can directly affect how readily the intracavity laser vaporizer can be reproducibly aligned

Intracavity laser power



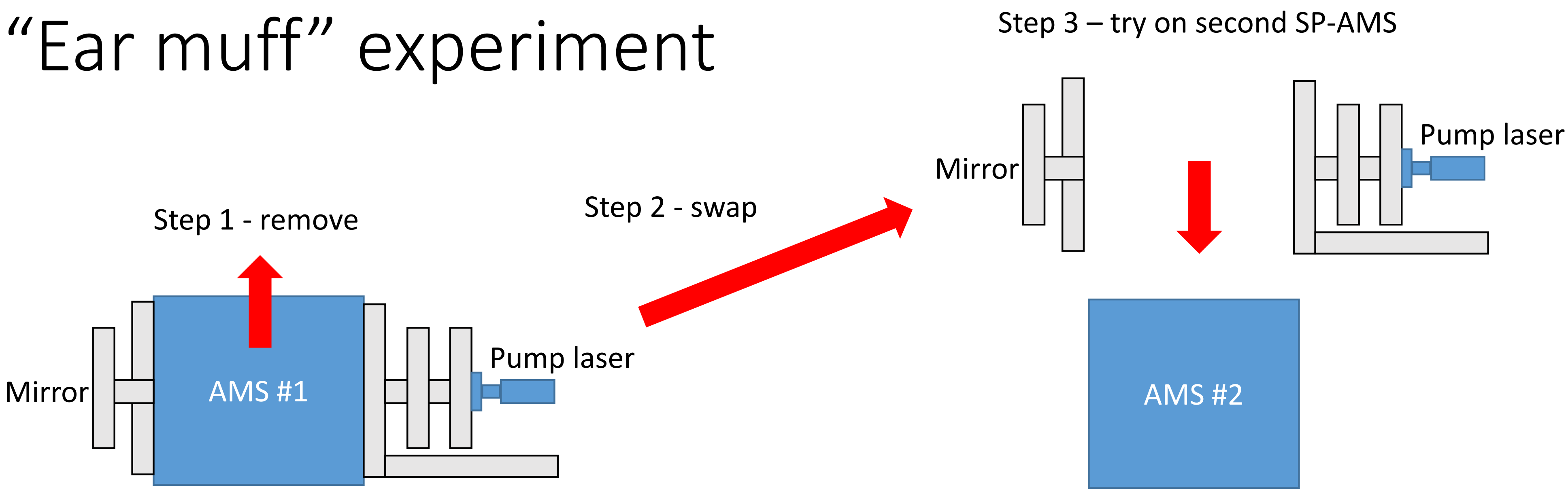
- Laser power measurements really need a laser power monitor to measure the leaked light
- Currently highly variable
- Pump laser quality matters
- Requires laser power drop experiments to test mIE_rBC

Laser mode and alignment



- Need TEM00 mode (for robust replication) as shown here
- Align the laser beam to the CENTER of the camera window (as ignored here)
- Trust the machining…

“Ear muff” experiment



- Can successfully move full intracavity laser system from one SP-AMS to another with only minor tweaks necessary for laser vaporizer setup
- Interpretation that we can trust the machining measurements/alignments of the SP-AMS

Summary

- SP-AMS hardware = laser vaporizer inside HR-AMS
  - Provides refractory PM detection (chemical, mass, and size information)
  - Three vaporizer configurations (laser only, tungsten vaporizer only, dual vaporizers)
  - Single particle detection
- SP-AMS technique finding applications in ambient measurements, source (combustion) characterization, laboratory measurements, metal nanoparticles, and single particle detection
- SP-AMS quantification is progressing through systematic studies of laser vaporizer parameters
  - Needs more users working on these topics!