SP-AMS
Introduction and Updates

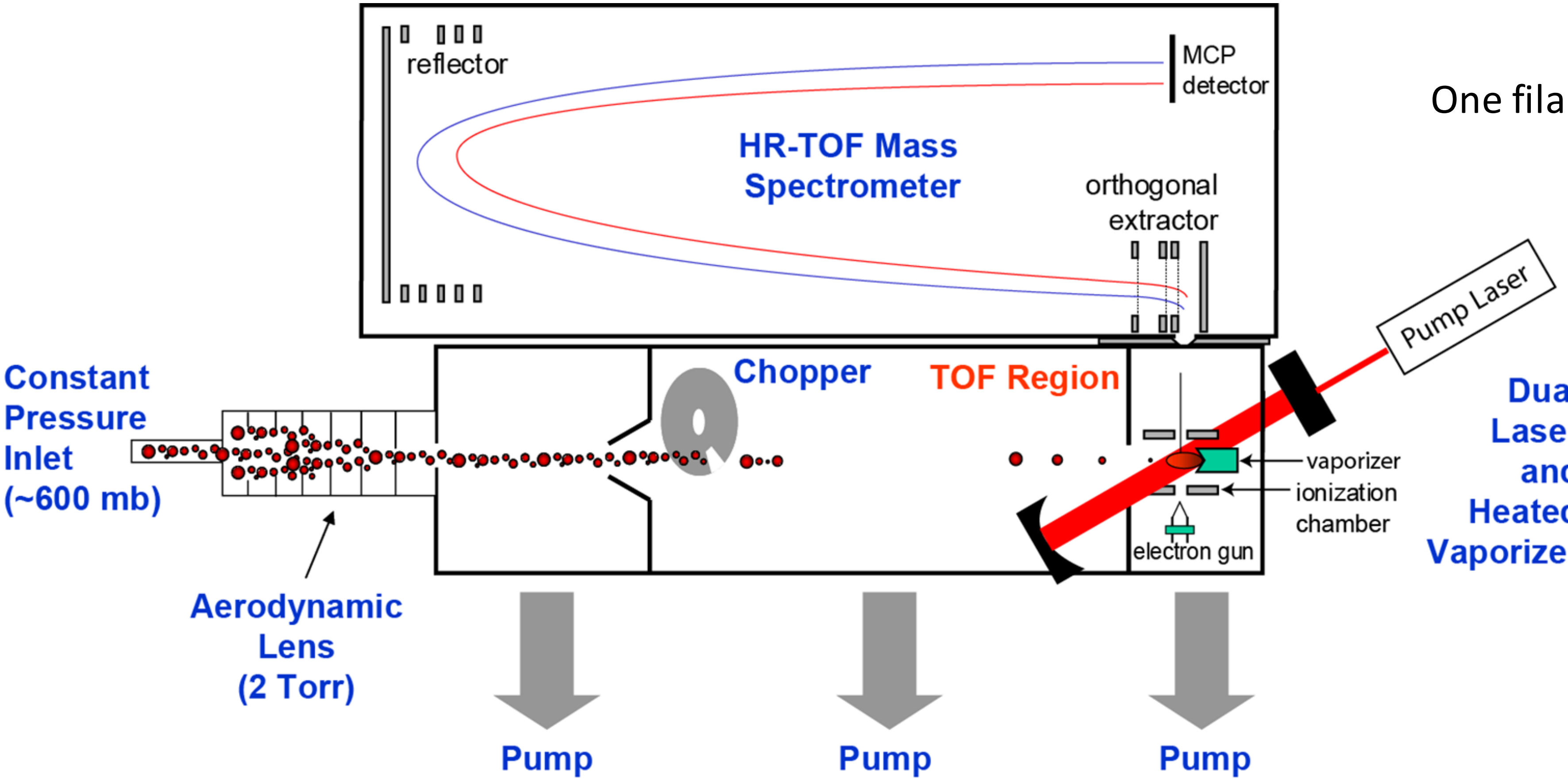
Anita Avery

AMS Virtual Users Meeting

January 20, 2021

Thanks especially to Leah, Tim, Ed, Bill, Wade

Soot Particle-AMS



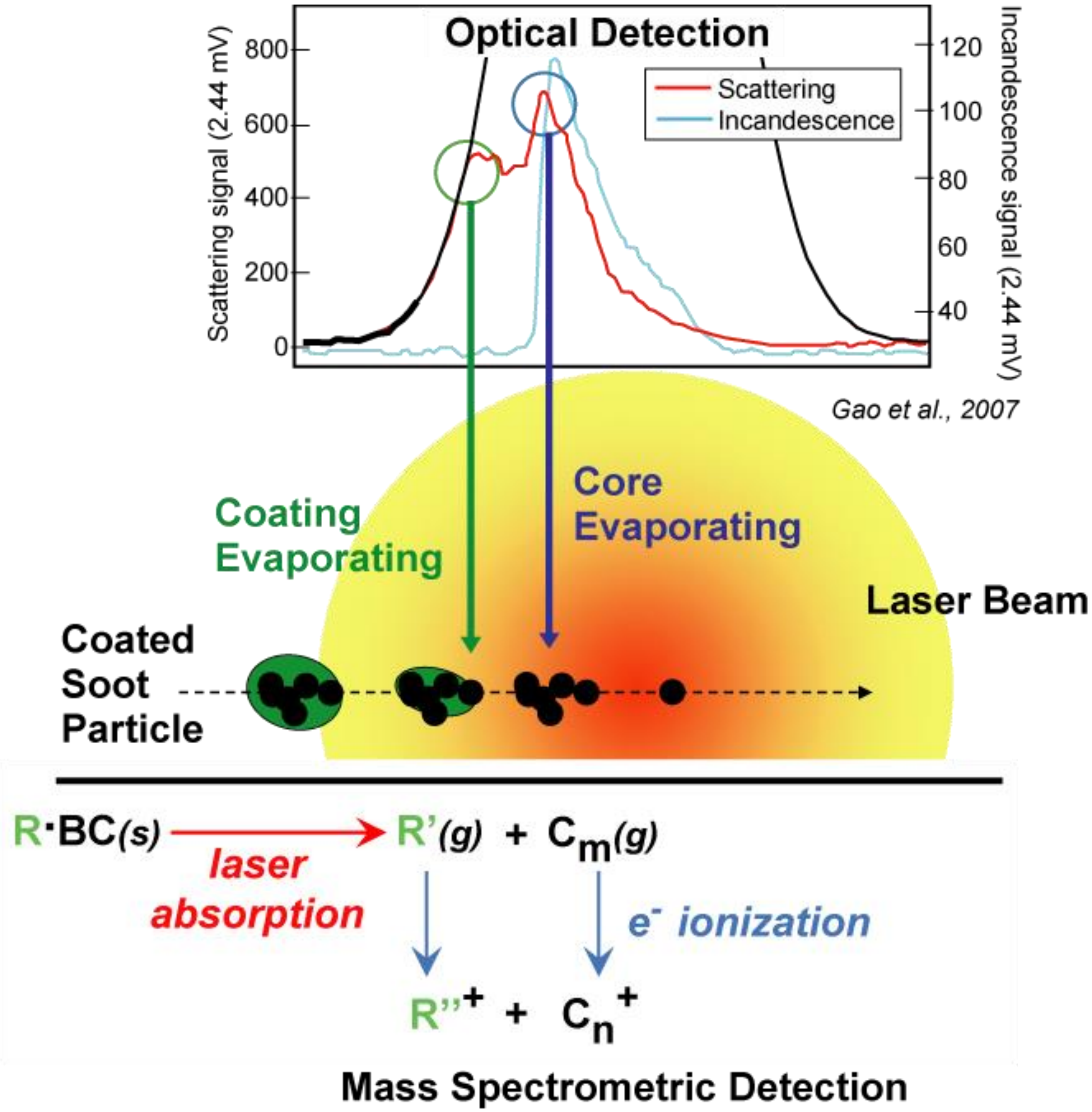
One filament facing upward

Dual Laser and Heated Vaporizer

Onasch et al, 2012

Slide thanks: Onasch

AMS plus laser vaporizer module

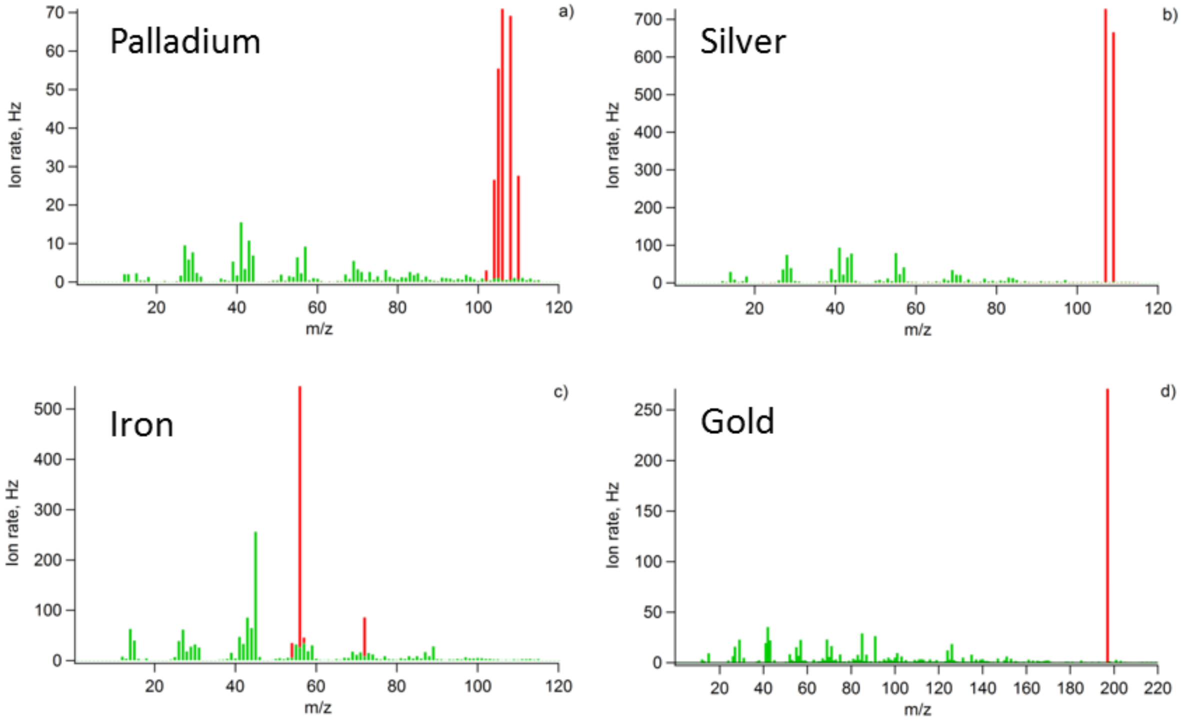


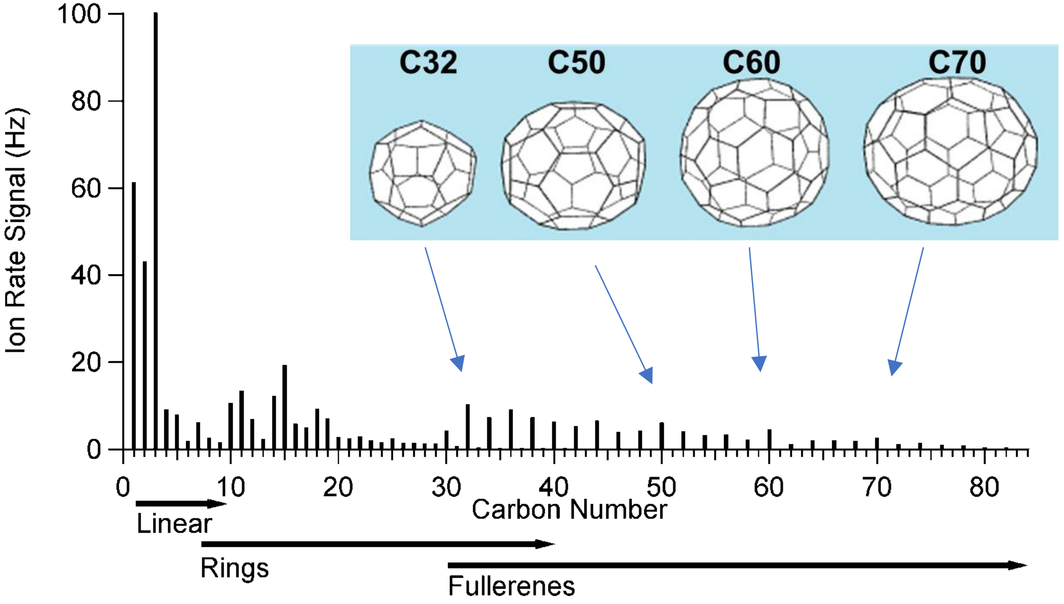
Laser Vaporizer Detection Scheme

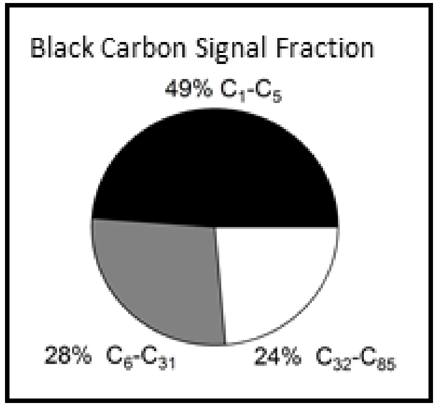
The laser is not the vaporizer, the absorbing particles are the vaporizer!!

Slide thanks: Onasch

Measure refractory species: BC, metals

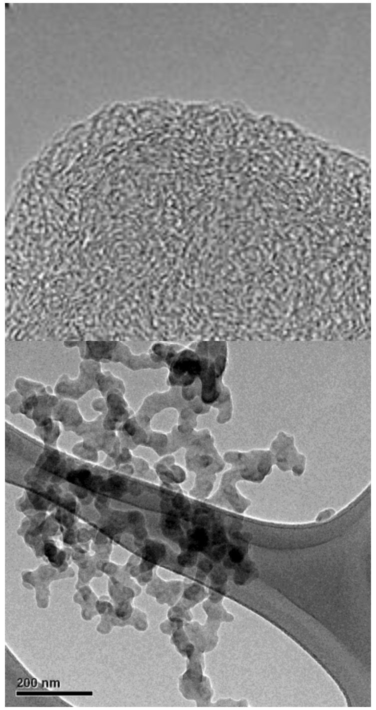






Onasch et al, 2015

Denuded Ethylene Flame Soot



Slide thanks: Onasch

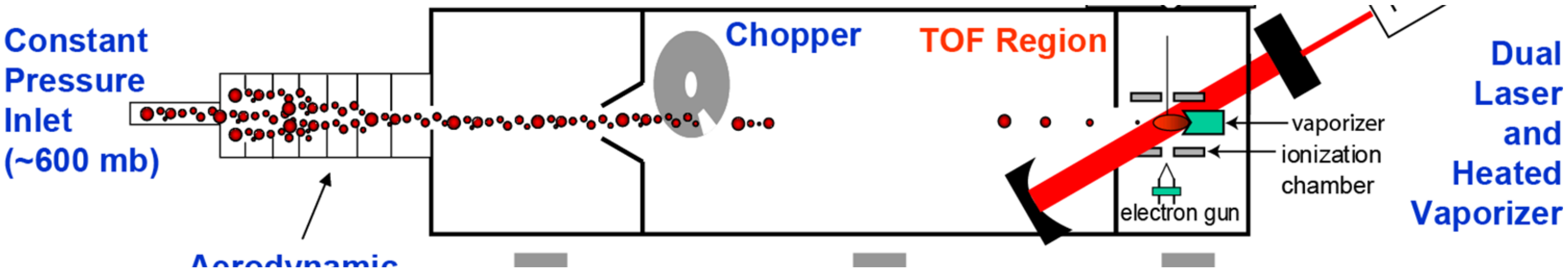
Modes of Operation

- Laser only (recommended!)
  - Laser-only = rBC+Coating
  - Remove Tungsten Vaporizer (TV), don't just turn it off!
  - Still need to be aligned with particle beam inside of ion chamber

$$CE = E_L \times \underline{E_S} \times \cancel{E_B}$$

- Dual-Vaporizer
  - Switching between laser on and laser off (Lon and Loff) allows to do all at once!
    - Loff=NR-PM, Lon=NR-PM + rBC+Coating
    - …with a load of assumptions
  - Both E_S and E_B are <1

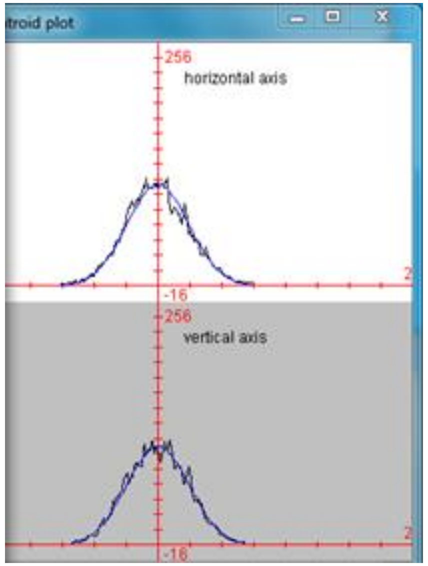
$$CE = E_L \times \underline{E_S} \times \underline{E_B}$$



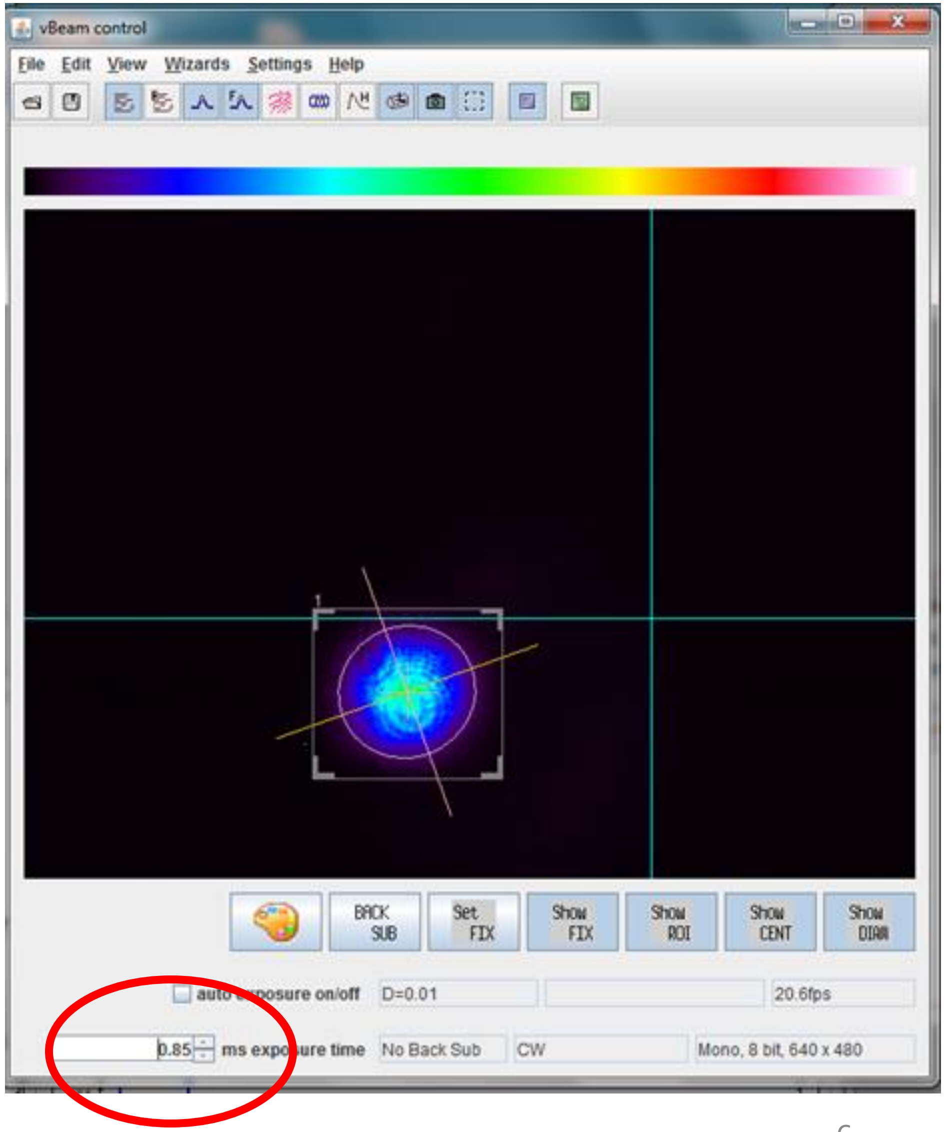
TV ~ 4mm, Laser ~ 1mm

SP-AMS set up

- Lens alignment: center the particle beam in the ion chamber (use TV)
- Optimize intracavity lasing
  - Clear gaussian at ~ 1ms exposure
- Center the laser on the particle beam in the vertical
  - While generating 300nm rBC, view in m/z cal window, “Time series” tab, m/z 36
  - Move laser with 3x/side coupler mounts
  - Optimize m/z 36 signal by moving laser
- Avoid horizontal extremes in alignment
  - Your instrument may be centered or look low (like here)



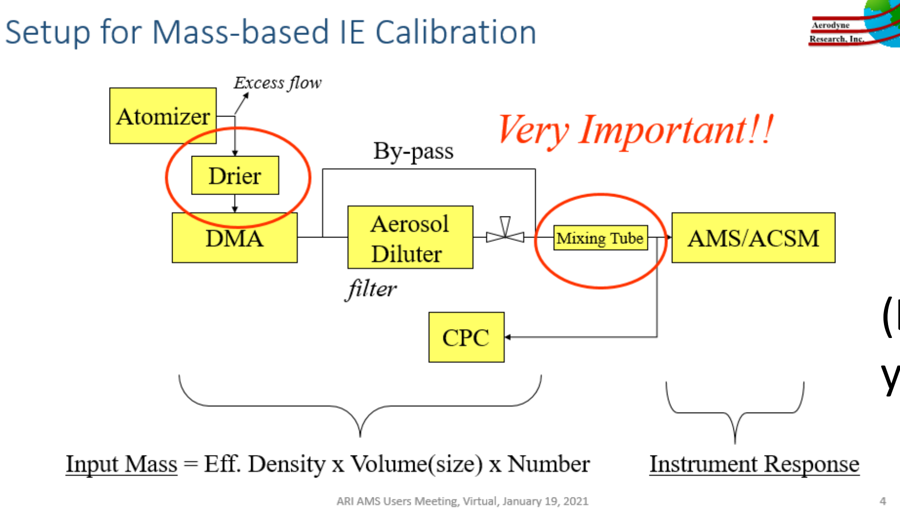
Lost laser beam? Use “HeNe alignment” procedure (see Knowledge Base)



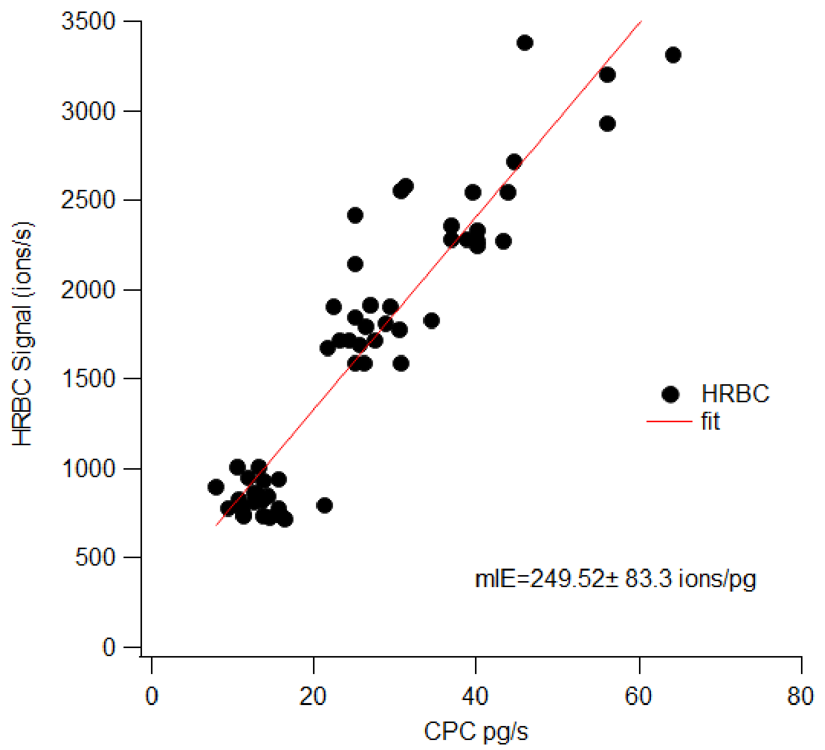
SP-AMS calibration

- Generate 300nm rBC
  - Regal Black: may need to use sonicator to keep in suspension
  - Changing soon to Cabojet – keep an eye out – its much easier to use
- Use diluter to adjust mass loading
  - Avoid high solution concentrations that produce doubly charged particles (check with ptof)
- Default RIE =0.2
  - Possible with good laser strength and alignment with particle beam

$$RIE_{rBC} = \frac{mIE_{rBC}}{mIE_{NO3}}$$

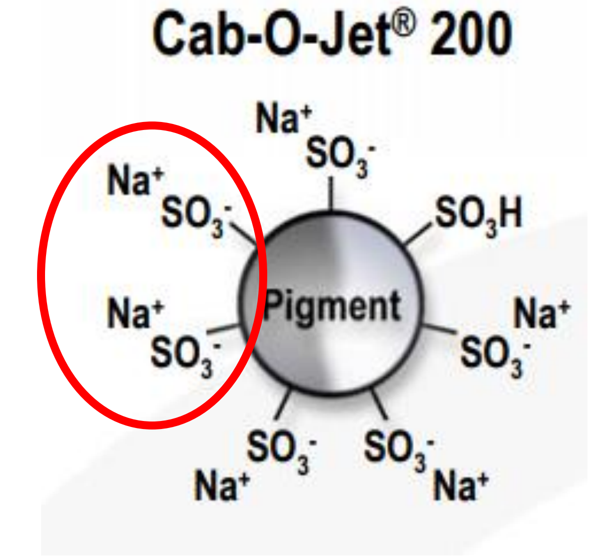


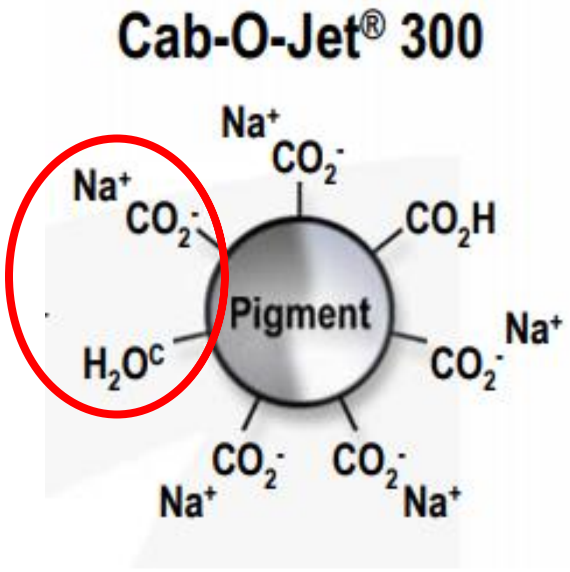
(Leah's talk yesterday)

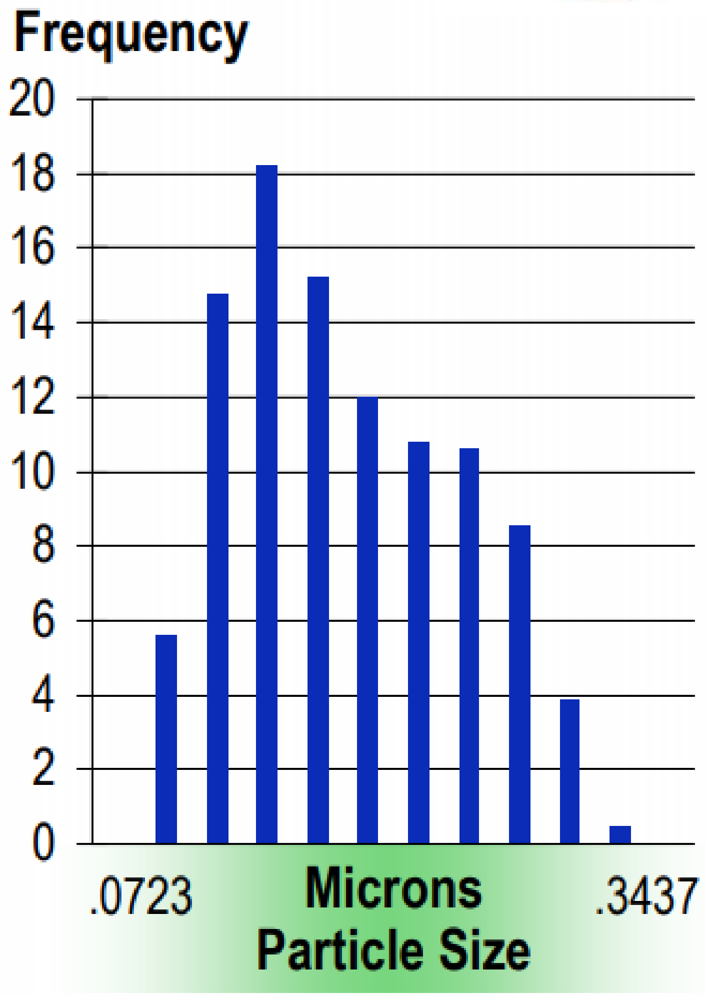


What is Cab-O-Jet?

- Inkjet Pigment from Cabot
  - “Pigment” = BC
- Surface modified for consistent jet from printer head and properties on paper
- “Colloidally stable” so no change in particle size or shape over time
- Particles < 150nm
  - Cabo 300 = 130nm
- Stabilizing groups attached to pigment surfaces
- NIST Standard BC for photoacoustic instruments





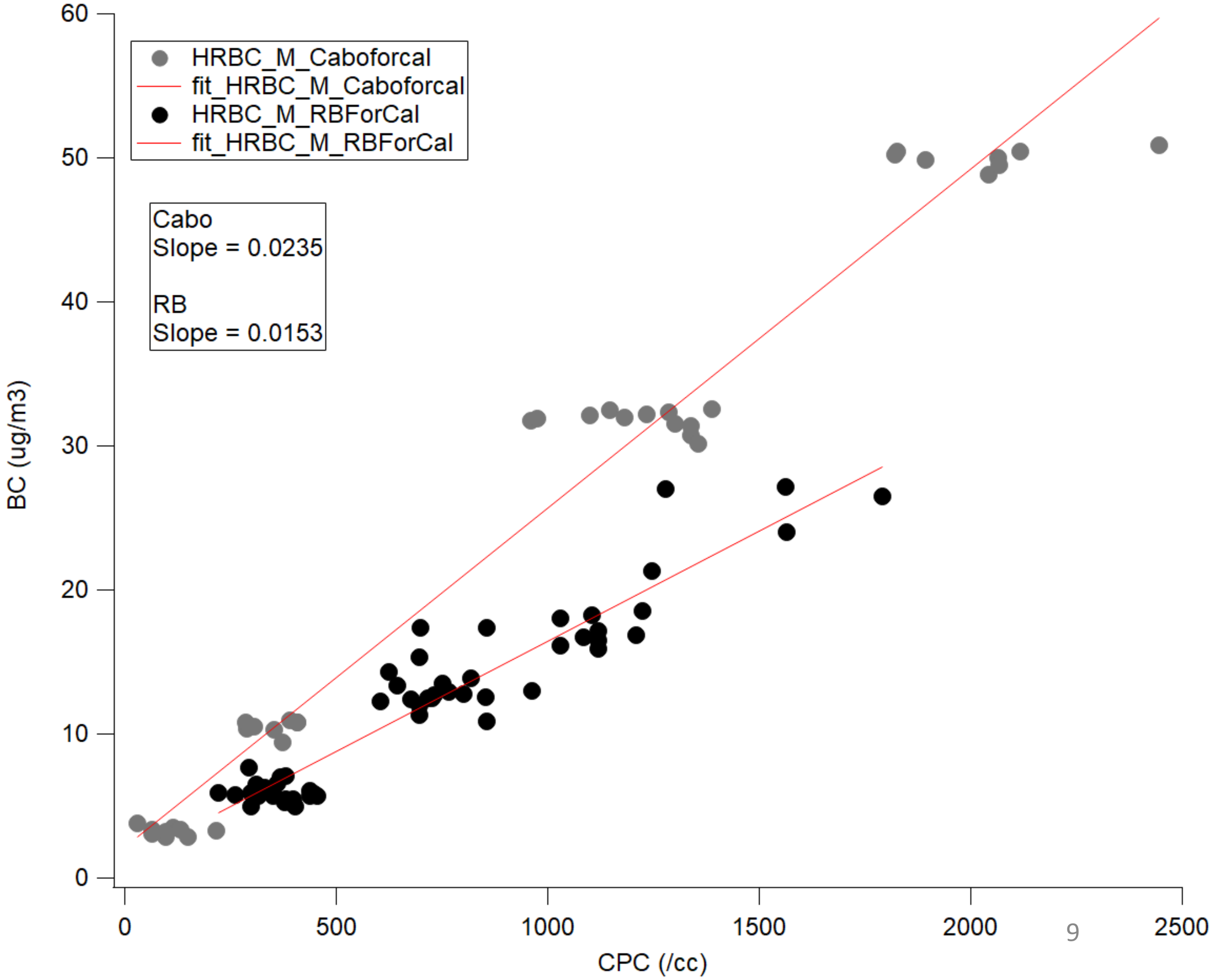


Source: nanoparticles.org/pdf/Kowalski.pdf

Leah says will you say why 200 rather than 300?

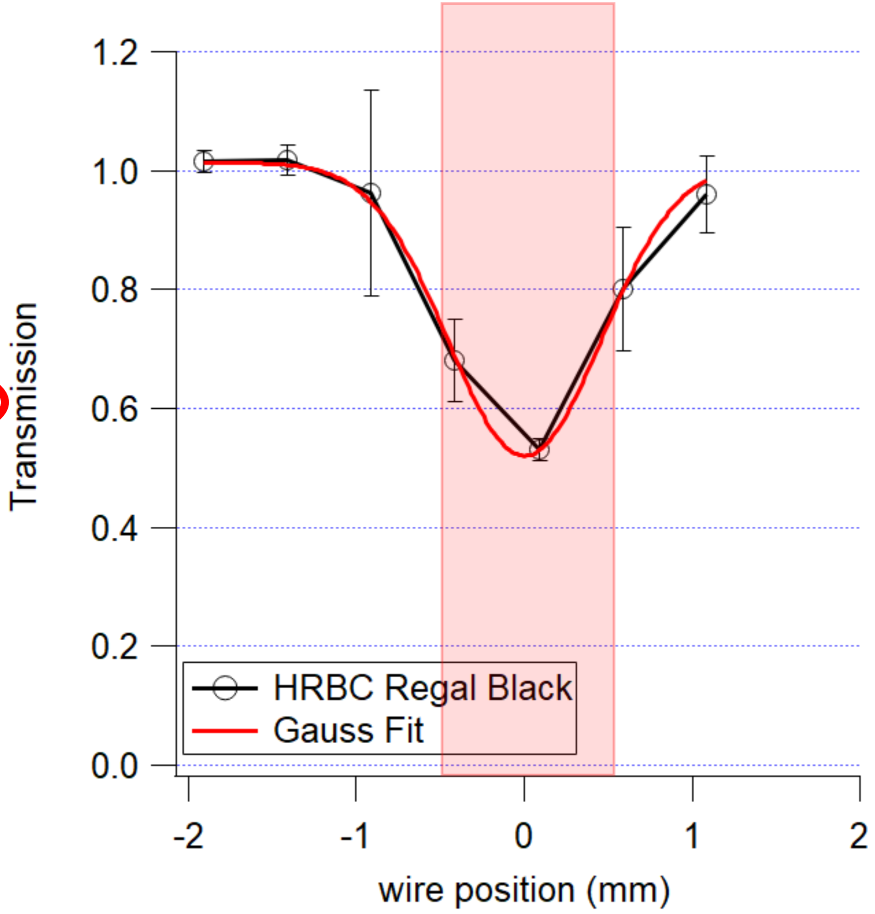
First step: Sensitivity of Cab-O-Jet 200

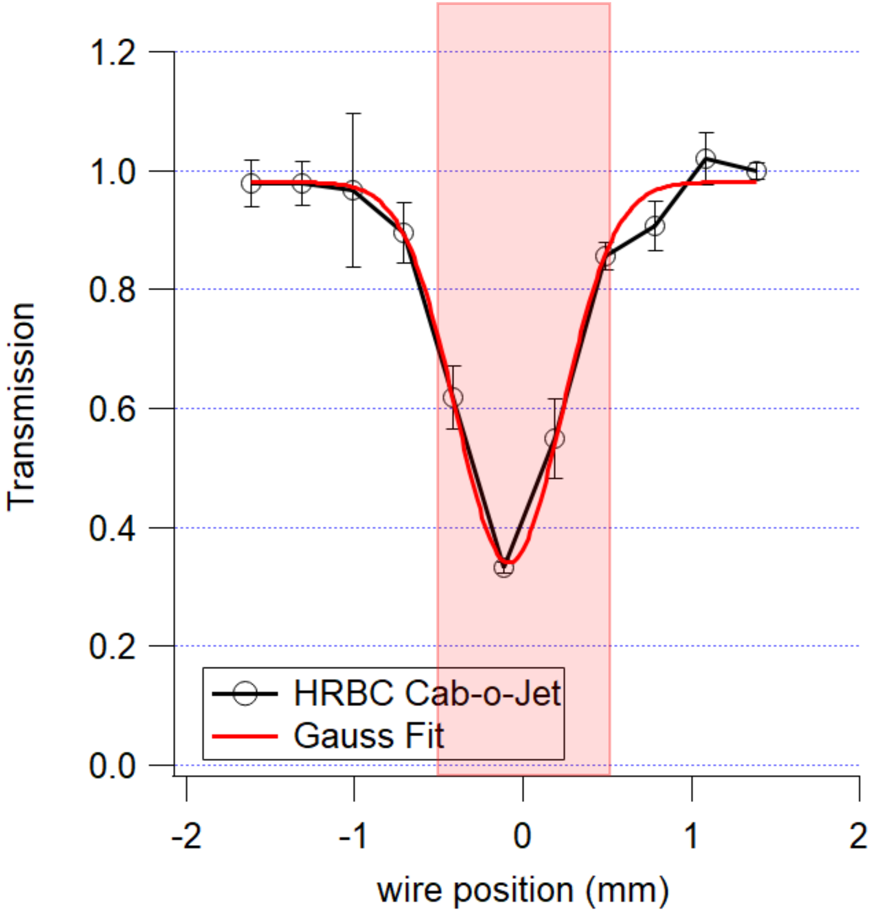
- Atomized, DMA-selected 300nm
- Nominally 50% higher sensitivity for HRBC
- Why is this?
  - Physical properties:
    - Fractal vs Spherical
  - Chemical properties:
    - Cx mass spectrum
    - Non-Cx mass spectrum



Results: Beam Width Probe (BWP) *Huffman et al 2005*

- BWP: vertical wire walks across beam at discrete points to understand particle beam
- Cab-O-Jet
  - Much better focused
  - Smaller whiskers since atomization is more consistent
- This difference explains nominal difference in sensitivity – more accurate to ambient with coating



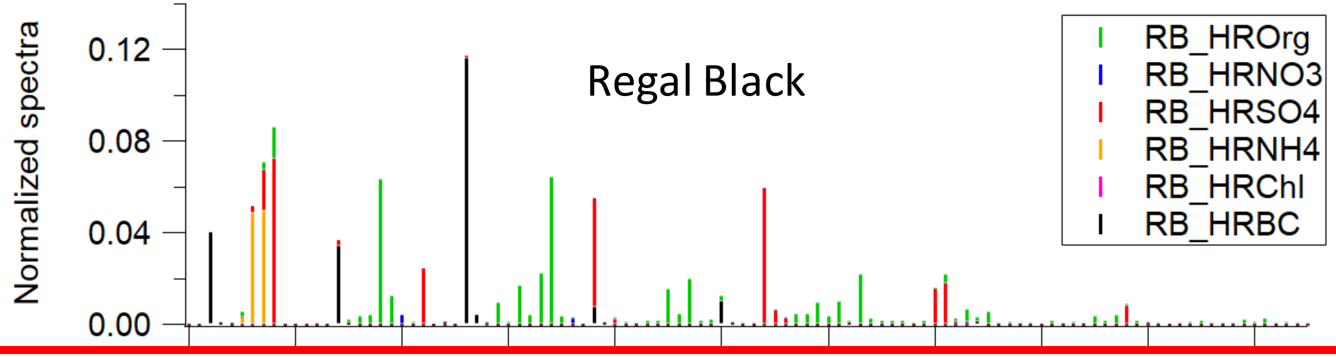


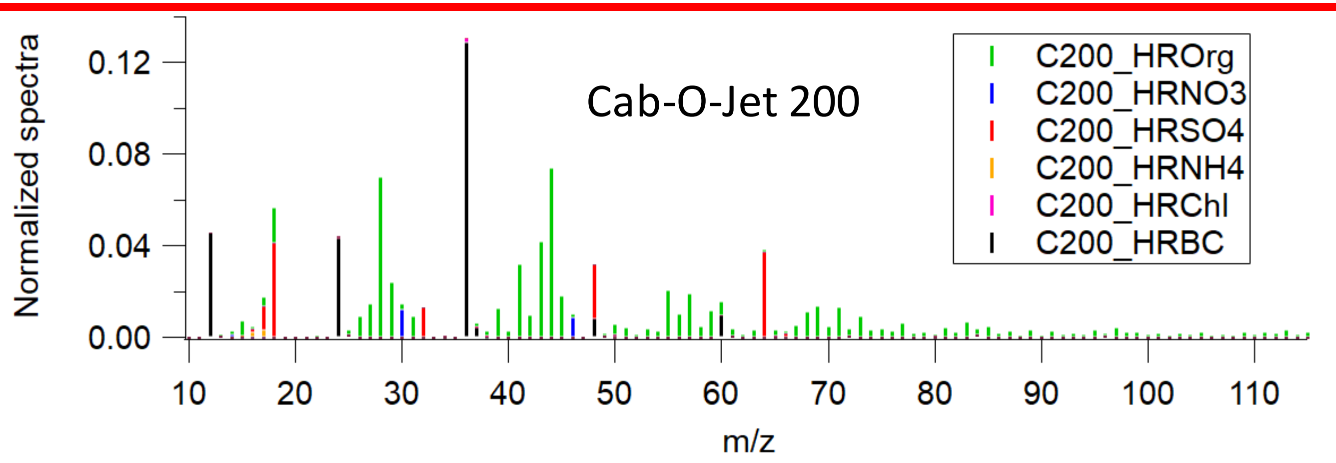
Laser is ~ 1mm wide, 0.5 mm probe used here

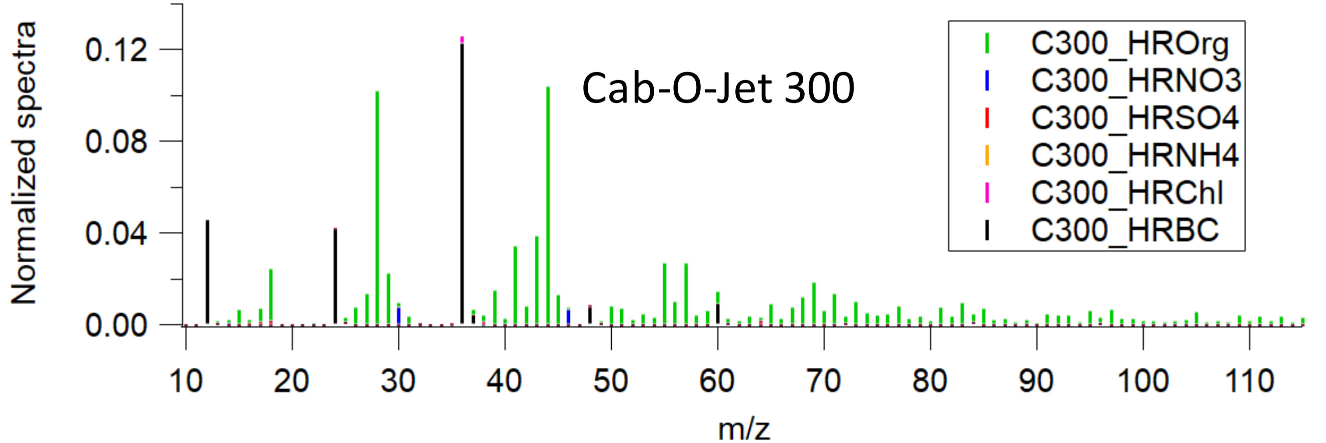
Cabo MS

- Well-described RB MS
  - $C_3 > C_1 > C_2$
  - C_1 here is lower because of poor fitting for LToF at m/z <20
- RIE not applied in MS: rBC is ~ 4x higher!
- Cab-O-Jet 200 and Cab-O-Jet 300 have non-rBC according to stabilizing groups
- This small amount of non-rBC complicates analysis of next section…

NOT different HRBC composition from Regal Black



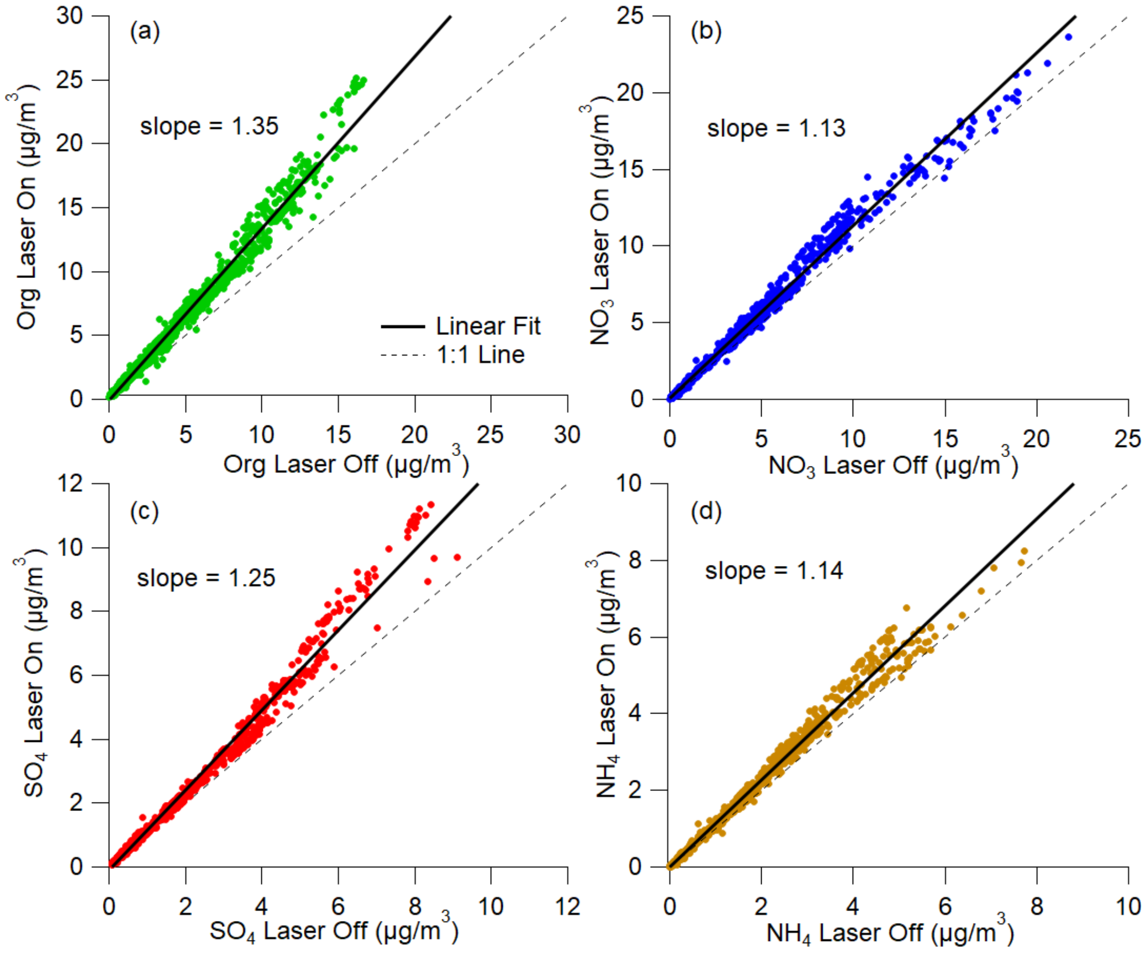




Note: preliminary mass spectra

Switching gears to dual vaporizer only issues

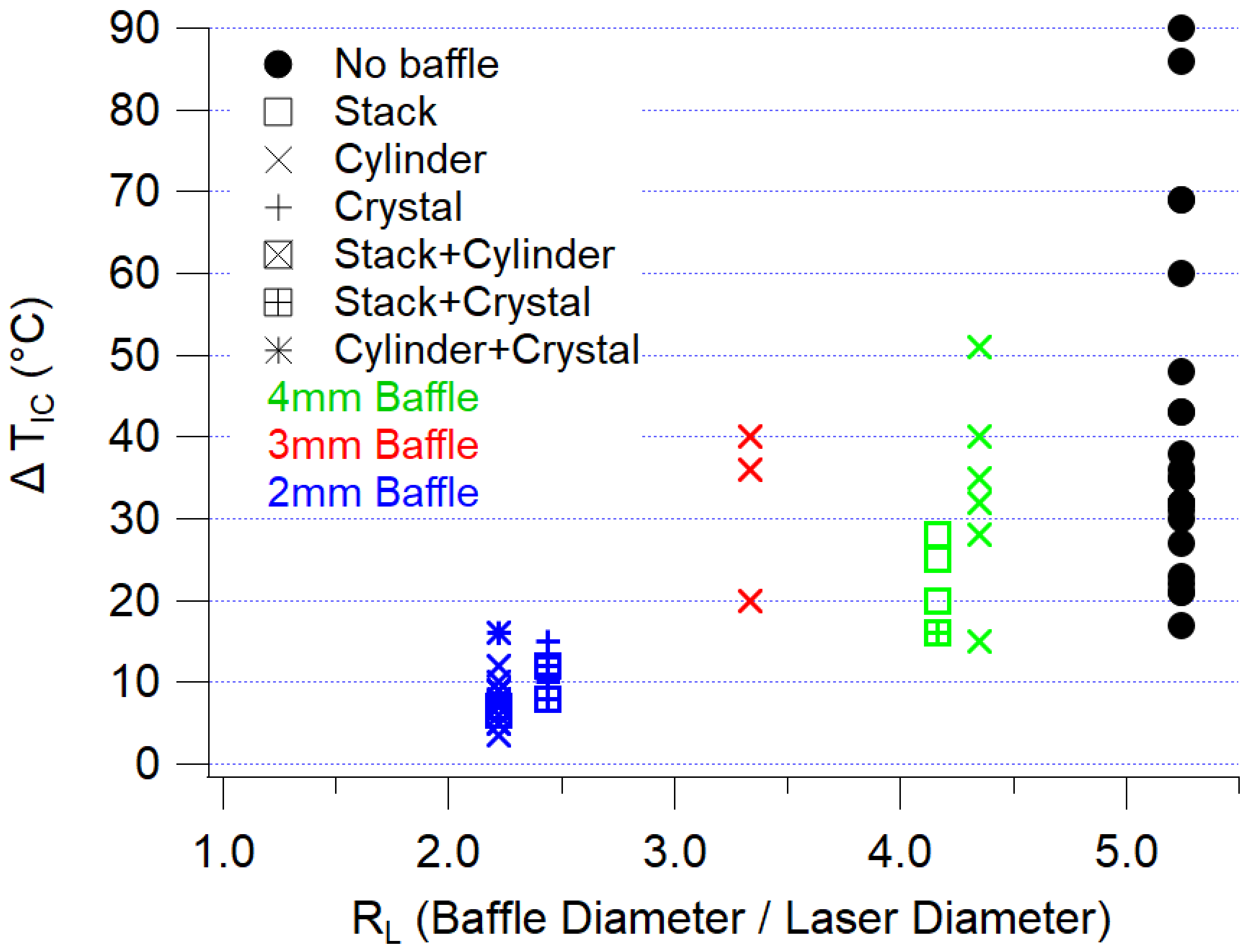
Dual Vaporizer Quantification

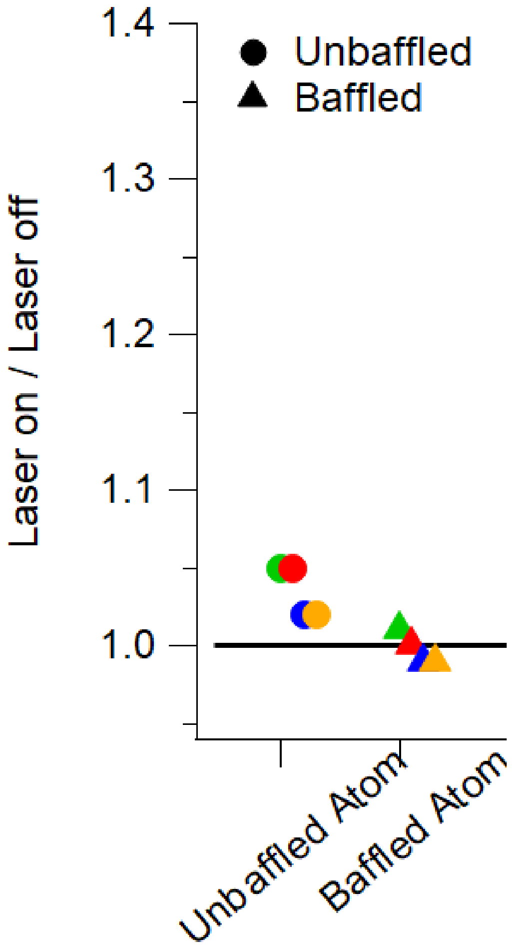


Ambient data from ClearfLo campaign, UK, 2012.

- Laser on > Laser off for ambient particles
- Possible Explanations
  - Heat load on ion chamber (IC) changes with laser state
    - NR-PM species bounce and are vaporized on IC (Cross et al 2007), which is hotter while laser on.
  - CE differences
    - Coating vaporized by rBC in laser will not be detected by tungsten
    - Laser diameter < tungsten diameter
  - RIE differences
    - Ionization efficiency is higher for material vaporized in the laser than on the tungsten surface. Temperature or geometry.

Baffles reduce laser heat load on IC

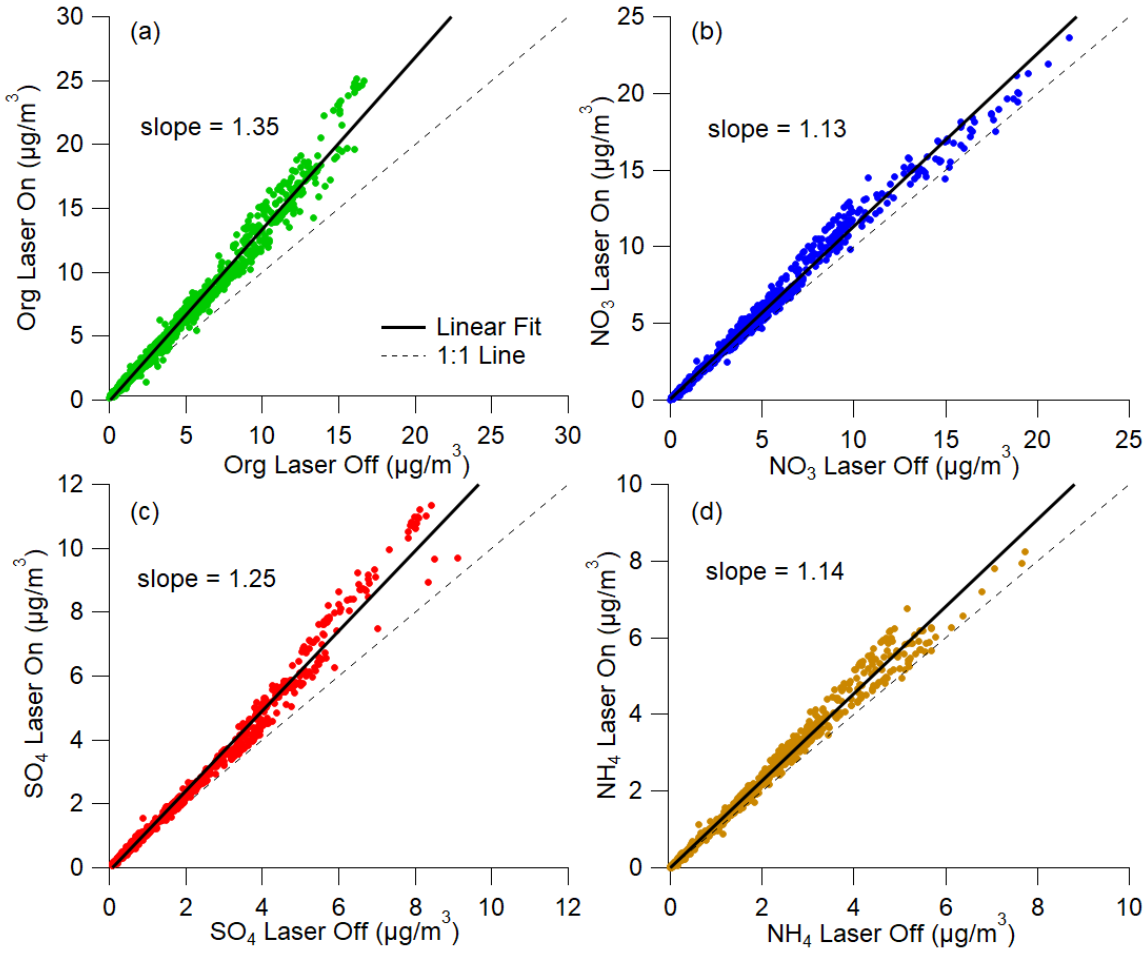




Baffles added to new instruments

Avery et al., AS&T 2020

Dual Vaporizer Quantification



Ambient data from ClearfLo campaign, UK, 2012.

Avery et al., AS&T 2020

- Laser on > Laser off for ambient particles
- Explanations
  - Heat load on ion chamber (IC) changes with laser state
    - NR-PM species bounce and are vaporized on IC (Cross et al 2007), which is hotter while laser on. Minor effect!
  - CE differences
    - Coating vapori… rBC in laser will not be … by tungsten
    - Laser … < tungsten d…
  - P… …ences
    - …ionization efficiency is higher for material vaporized in the laser than on the tungsten surface. Temperature or geometry.

Let's investigate this

Experiment

Size select: 300, 350, or 400 nm

Atomizer — Dryer — DMA

Q-AMS — With LS; Bounce=Q-AMS particle counts/CPC,

CPC

Can't measure rBC

Can't measure bounce

LToF-SP-AMS — Laser on/Laser off ratio

SP2 — Mixing state: internal mixtures
Quantify absorbing, scattering

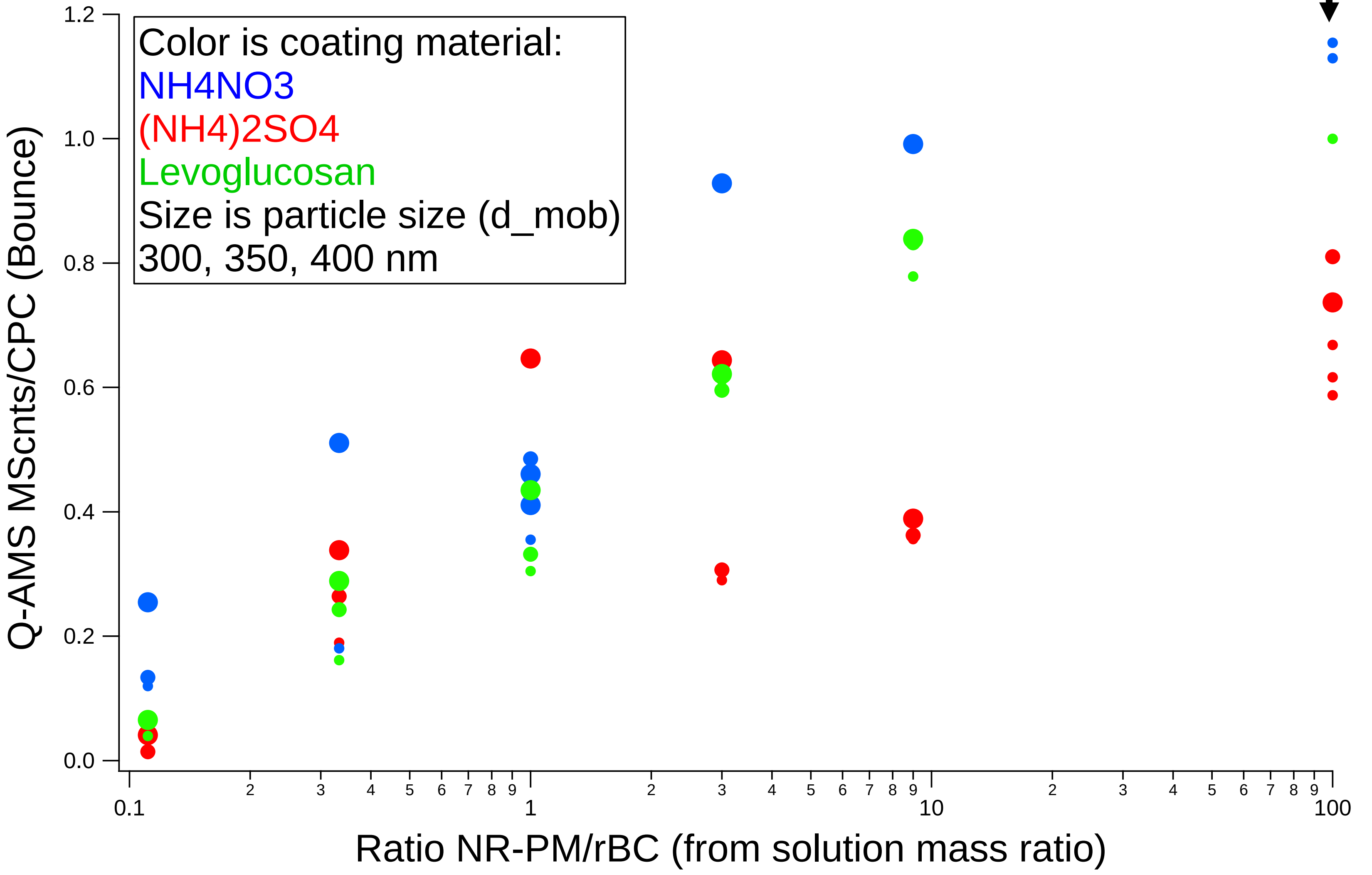
- Aqueous mixtures of Cab-O-Jet +
  - NH_4NO_3
  - $(NH_4)_2SO_4$
  - Levoglucosan
- Various ratios by mass
  - 9:1, 3:1, 1:1, 1:3, 1:9
  - HUGE range of bounce by ratio and chemical, changes between laser on and off
- Need to control for all CE terms: lens transmission, beam divergence, bounce
  - Lens transmission won't change, DMA controls for beam

$$CE = \underbrace{E_L \times E_S}_{\text{Constant}} \times E_B$$

Calc. with QAMS

Q-AMS Bounce

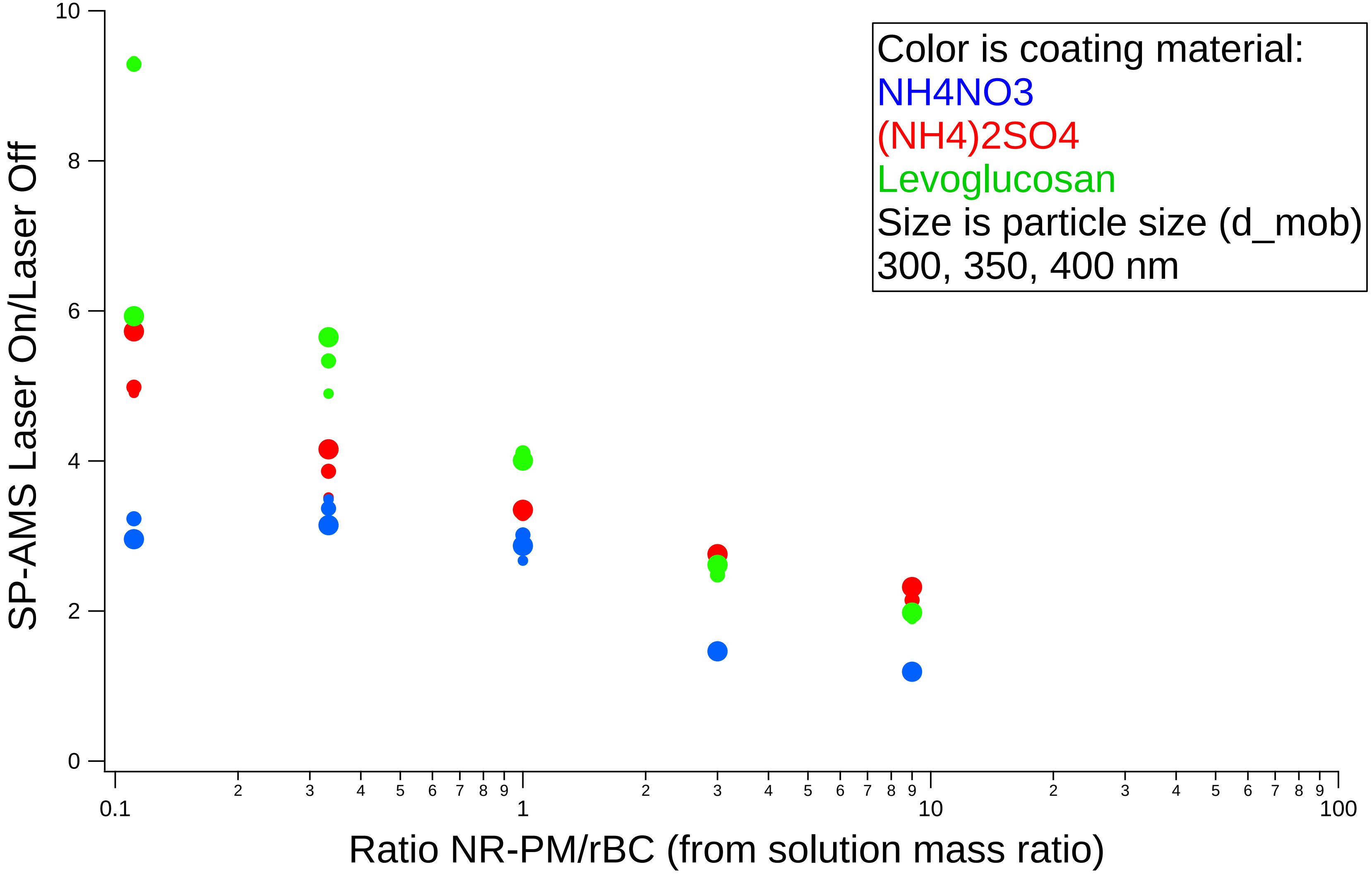
Pure compound



Particles with more rBC bounce more, as expected.

Preliminary

SP-AMS Laser on / Laser off



More thinly coated particles have higher Laser On/Laser Off.

Preliminary

Summary/ Recommendations

- Baffles
  - Effective in reducing heat from stray light, but only 5% difference in Lon/Loff ratio (Avery et al., 2020, AS&T)
  - Installed on new instruments, separate baffle for existing instruments
- Effective strategies for dual mode:
  - Keep laser horizontally centered
  - Sample > 1 run between switching
  - Switch no faster than ~ 5 min
- Switch to Cab-o-jet coming soon!

rBC + Coating

- Explanation for why Lon > Loff
  - Laser and tungsten vaporizers have CE that varies differently with coating thickness.
  - Laser and tungsten vaporizers have different RIE.
- Can we extract information on NR-PM associated with rBC from alternating Lon and Loff?
  - Coating thickness? Maybe too many variables.
  - Composition of coating? Maybe from PMF because MS slightly different between vaporizers due to different temperatures of vaporization.

Thanks!

Questions?

Update II Conclusions

- Cabojet is easier to use
- Cabojet appears more sensitive, but this is probably just more accurate since the laser is seeing a higher % of input BC

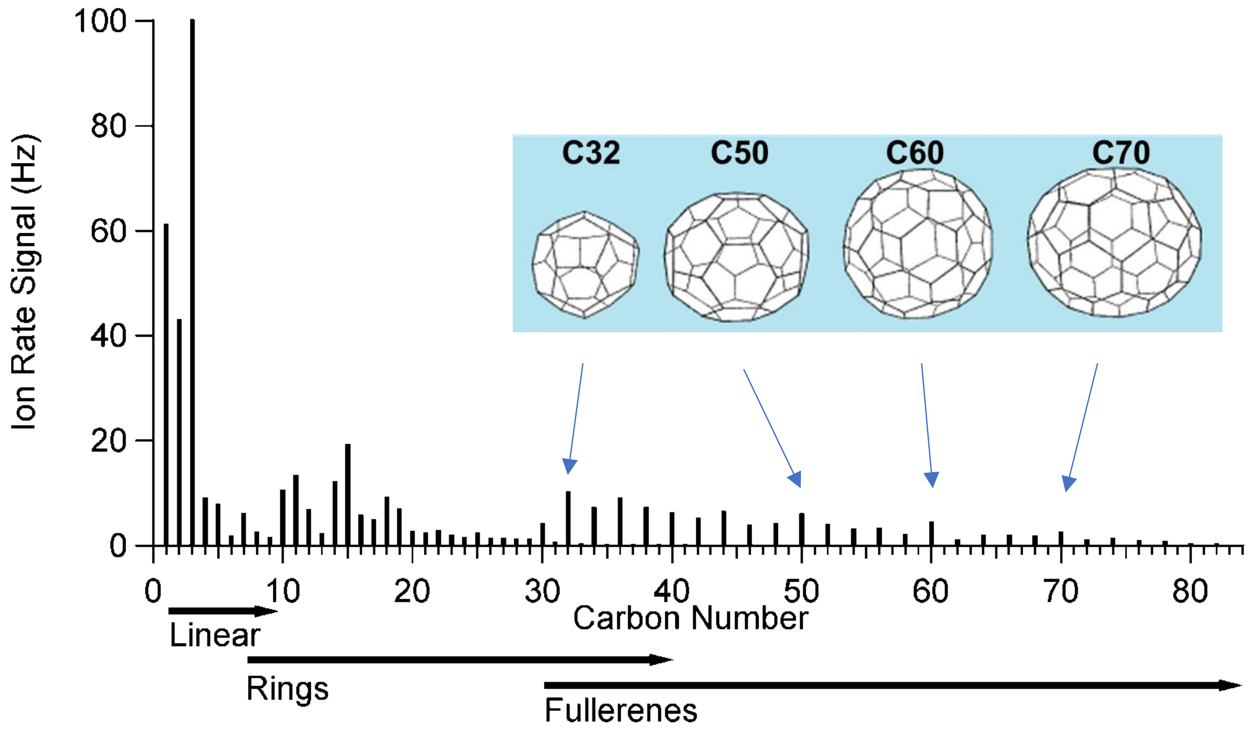
- Next steps
  - Quantitate differences between BWP and sensitivity
  - More detailed chemistry characterization

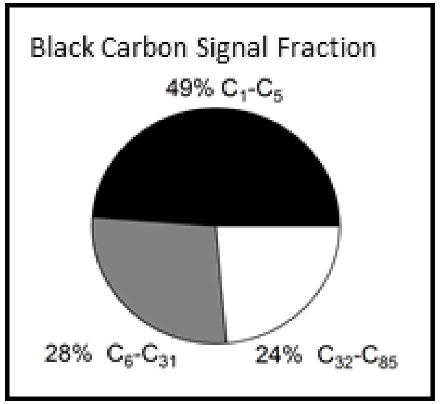
- Atomizing Regal Black is not easy
  - Gets everywhere – hard to clean
  - Suspension, not solution (must sonicate, etc.)
  - Wide particle beam

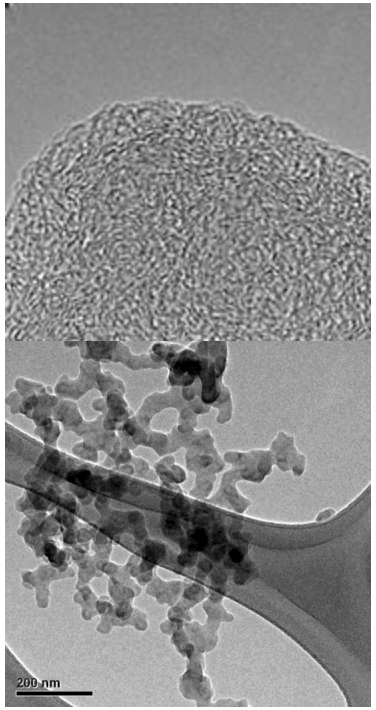
- This work:
  - Describe chemical and physical characteristics of regal black
  - Investigate other calibrants:
    - Cab-o-jet 200 ©

Measure rBC Carbon Cluster Ions

Denuded Ethylene Flame Soot





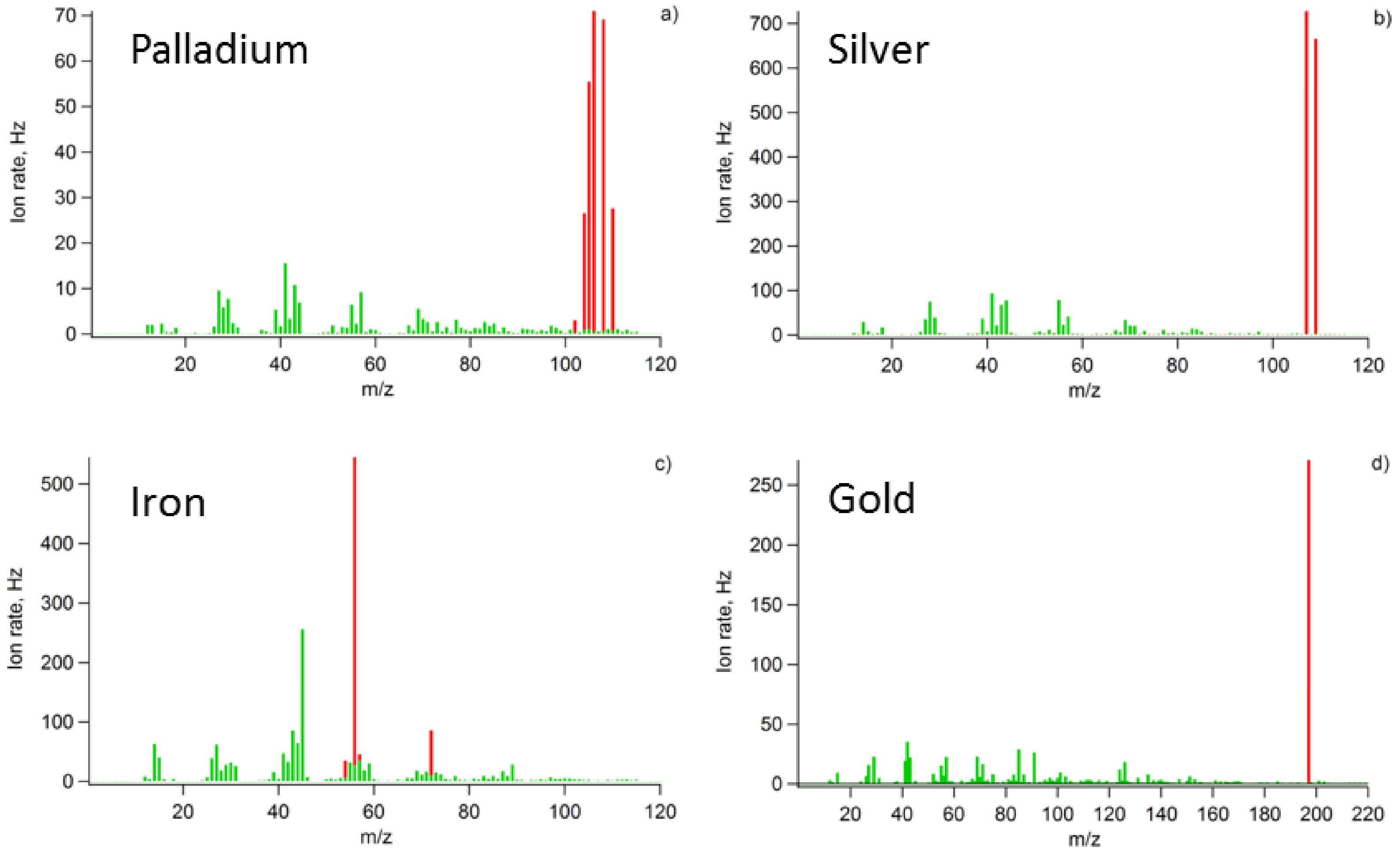


- Are refractory carbon ion distributions associated with underlying carbon structures?

Slide thanks: Onasch

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

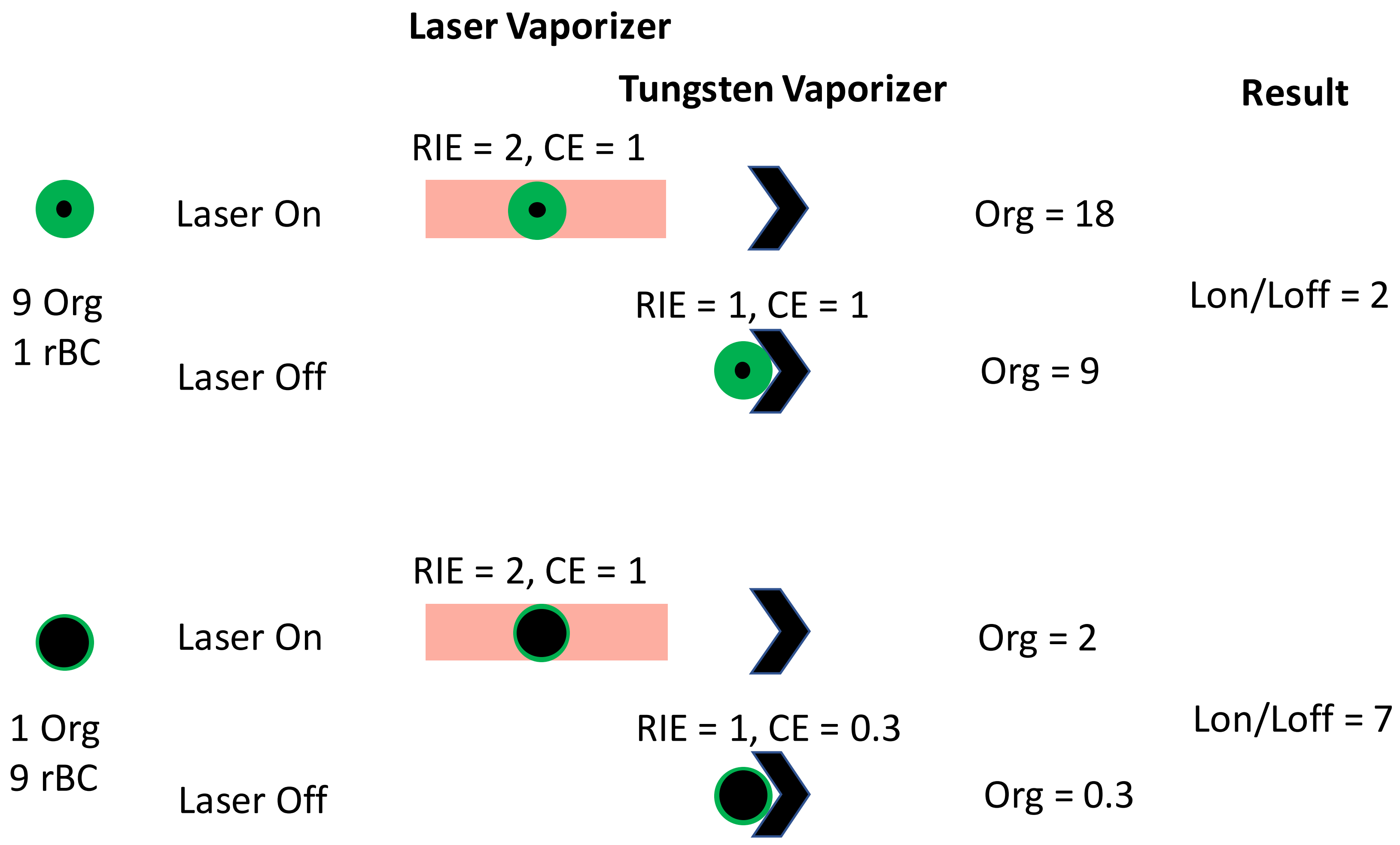
Metal Nanoparticles



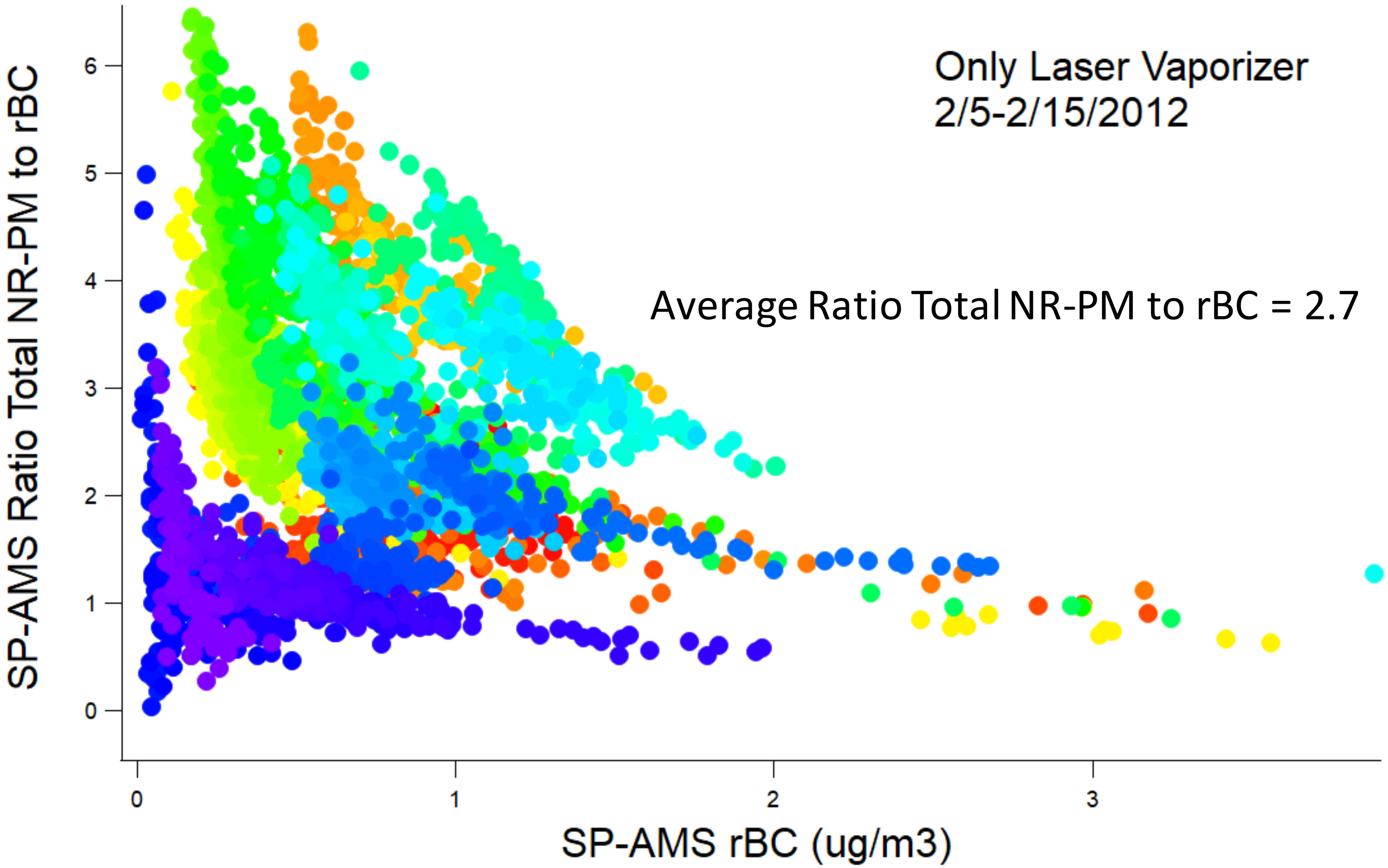
- Metal Nanoparticle detection, identification, and quantification of purity and total mass

Slide thanks: Onasch

Model

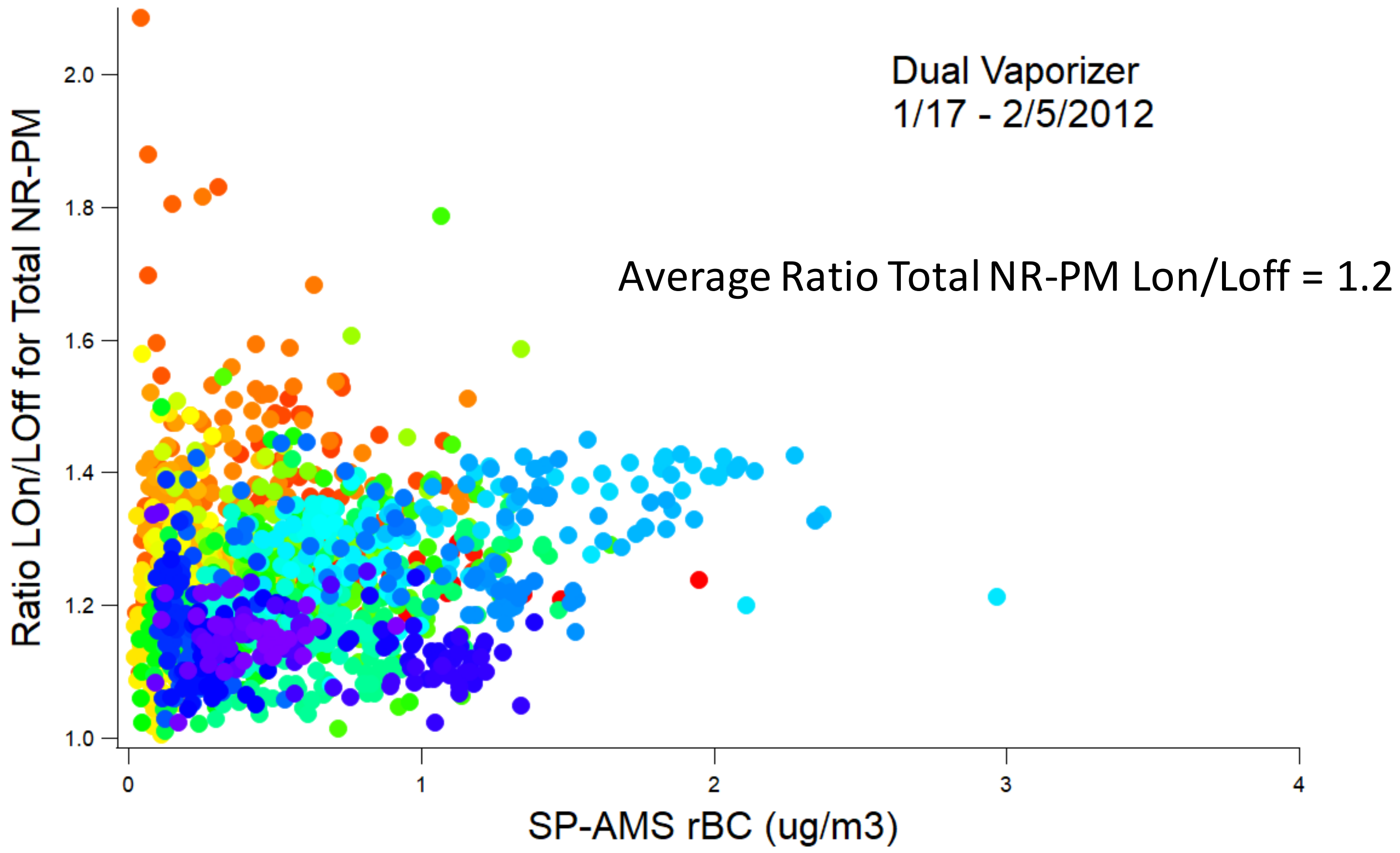

Laser Vaporizer
Tungsten Vaporizer
Result
RIE = 2, CE = 1
Laser On
Org = 18
9 Org
1 rBC
Lon/Loff = 2
RIE = 1, CE = 1
Laser Off
Org = 9
RIE = 2, CE = 1
Laser On
Org = 2
1 Org
9 rBC
Lon/Loff = 7
RIE = 1, CE = 0.3
Laser Off
Org = 0.3

Laser Only



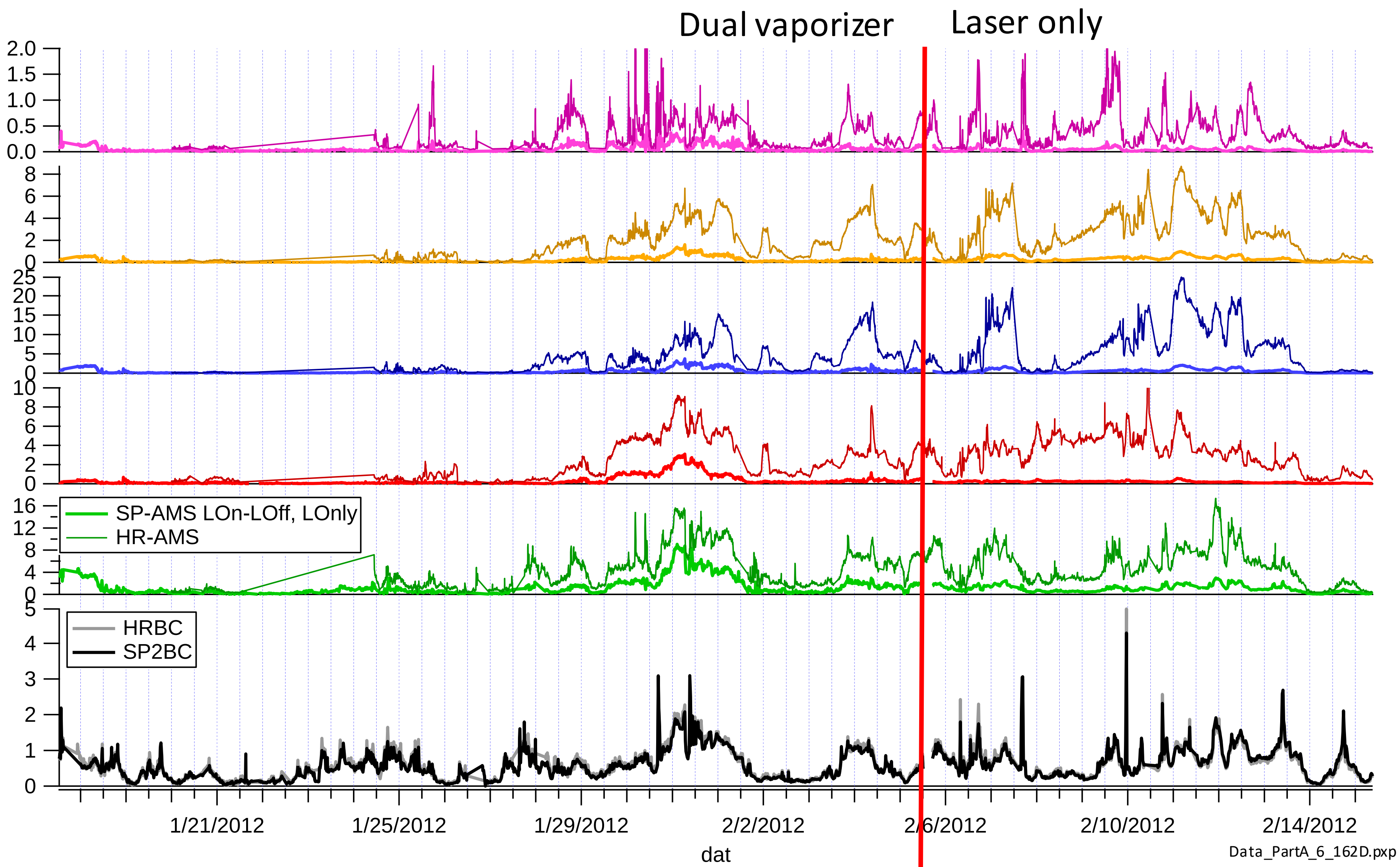
Detecting only rBC and associated NR-PM. Higher rBC mass loading associated with thinner coatings.

Ratio Lon/Loff for Total NR-PM



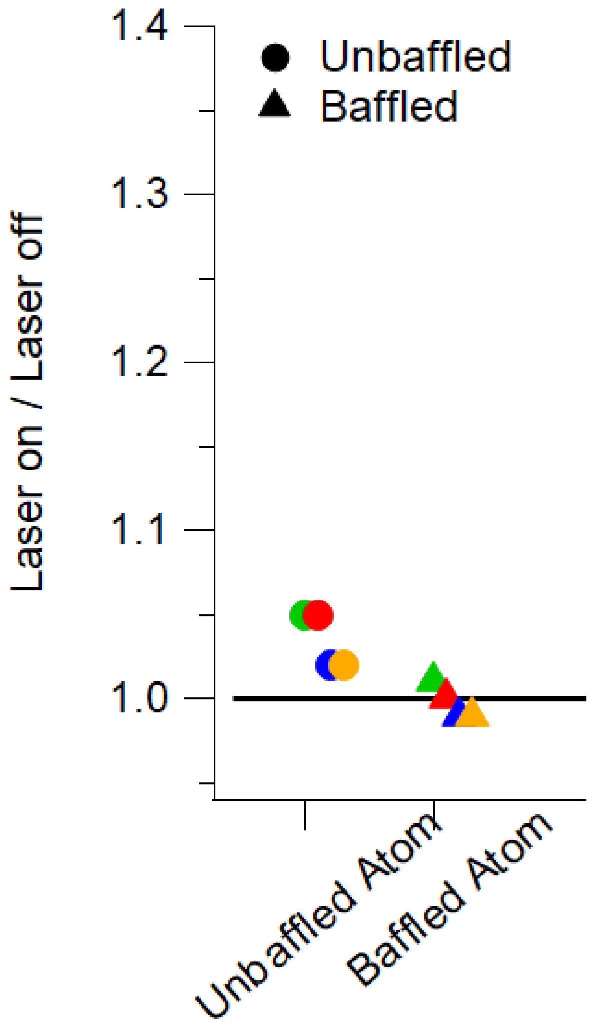
- Maybe trend of higher ratio with higher rBC (~thinner coatings).
- Average Total NR-PM to rBC = 2.7 suggests Lon/Loff ~ 2.
- But not all ambient particles contain rBC.

Detling, UK 2012



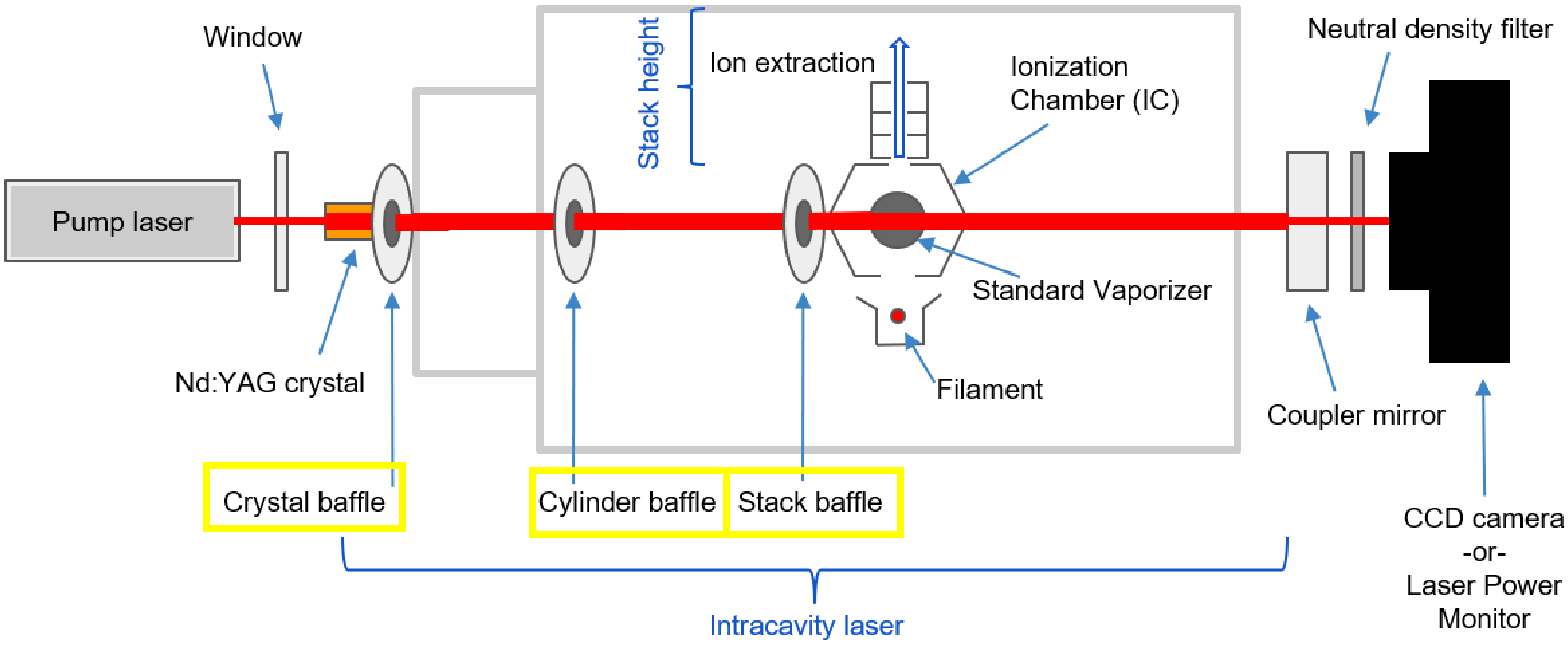
The effect of baffles on Lon/Loff

- Is real, but minimal (~ 5%)
  - Could be higher if laser is not aligned in center (hitting tungsten vaporizer or IC directly)



Intervention: add baffles

- Measure temperature difference ΔT_{IC} and ΔT_V
  - Added thermocouples to IC and baffle
- Light restriction
- Position restriction

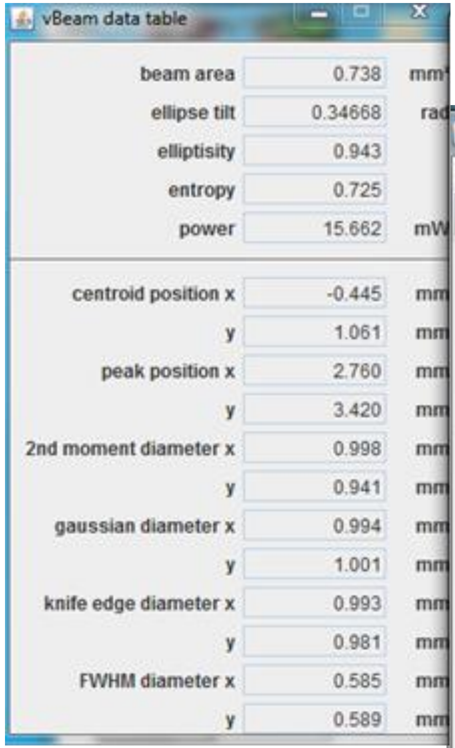


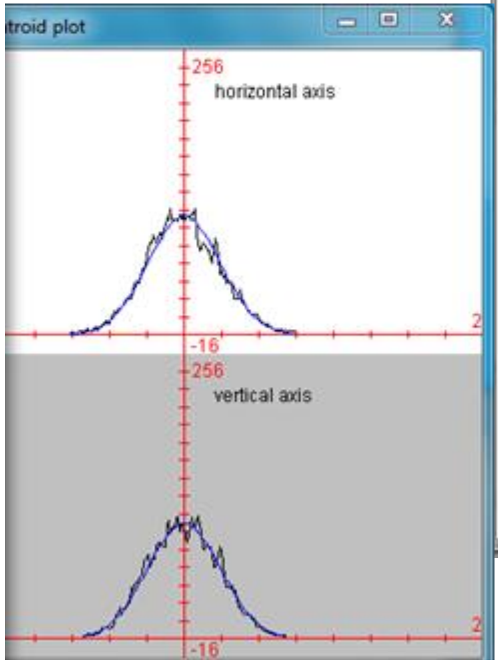
(not to scale)

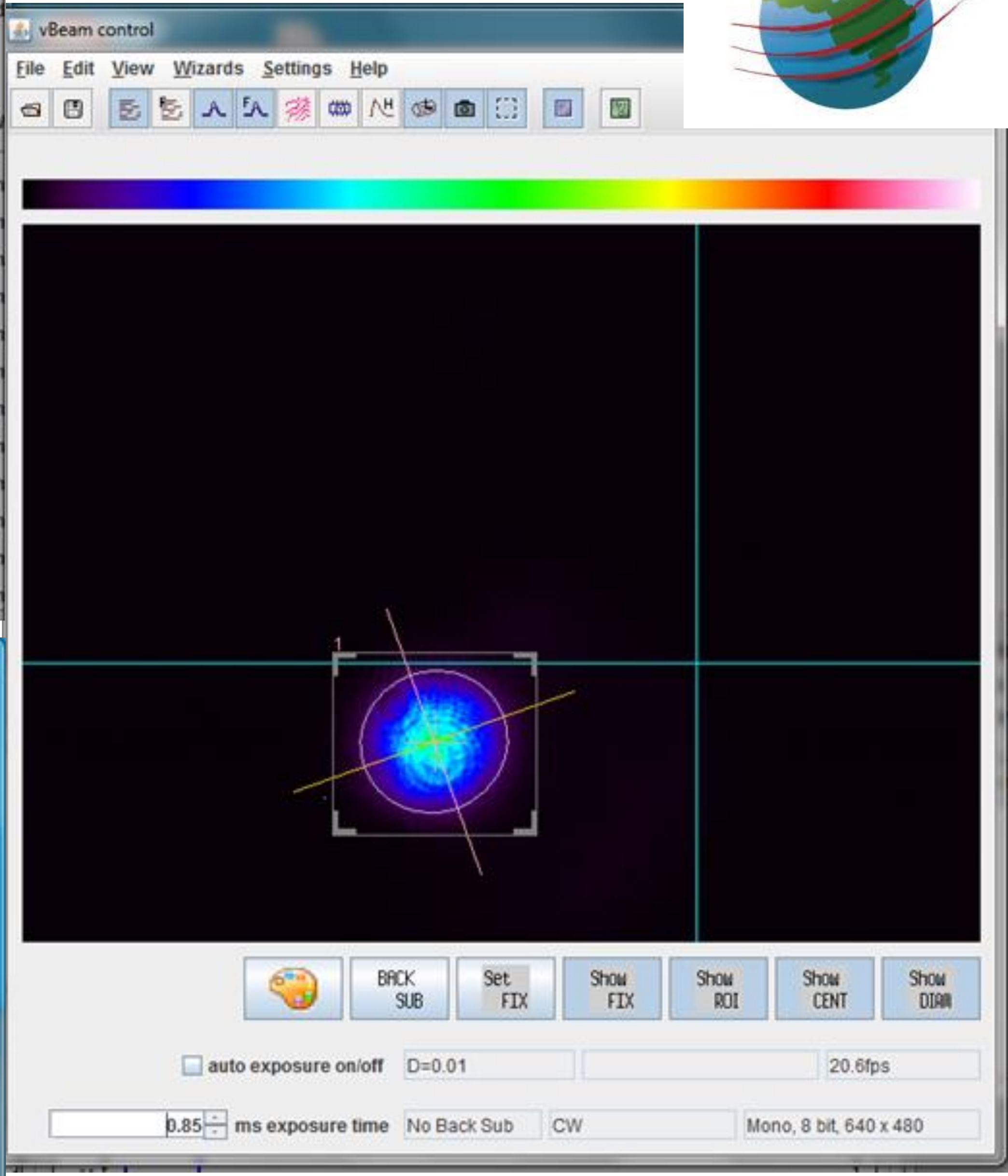
Perspective: particle beam

Camera perspective and general alignment

- Camera position is inverted relative to physical
  - Tungsten vaporizer left (avoid hitting!), filament above
- Laser alignment (after initial las)
  - Align with particle beam, maximize power, circular shape
  - Note power and position



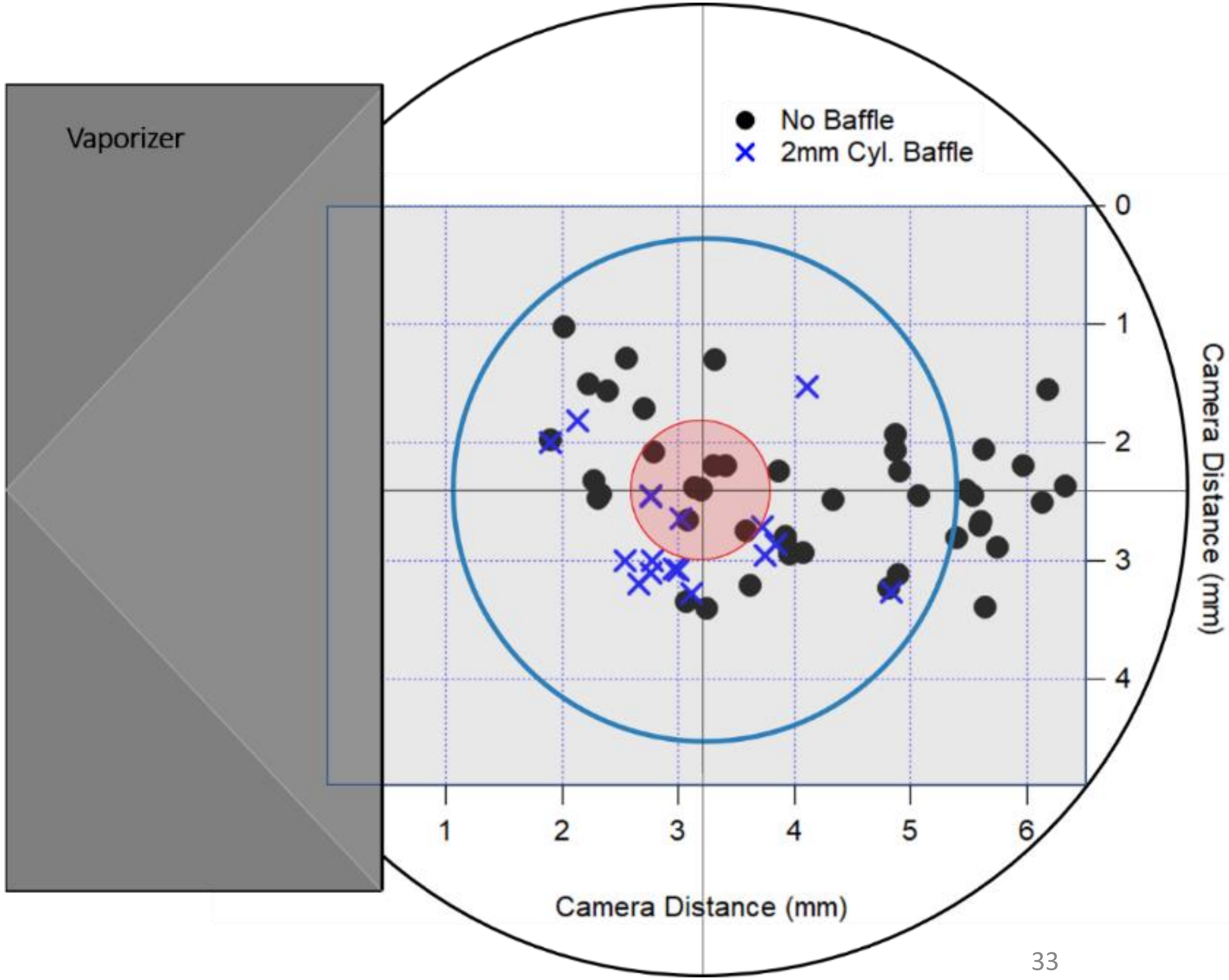




How does this relate to physical space???

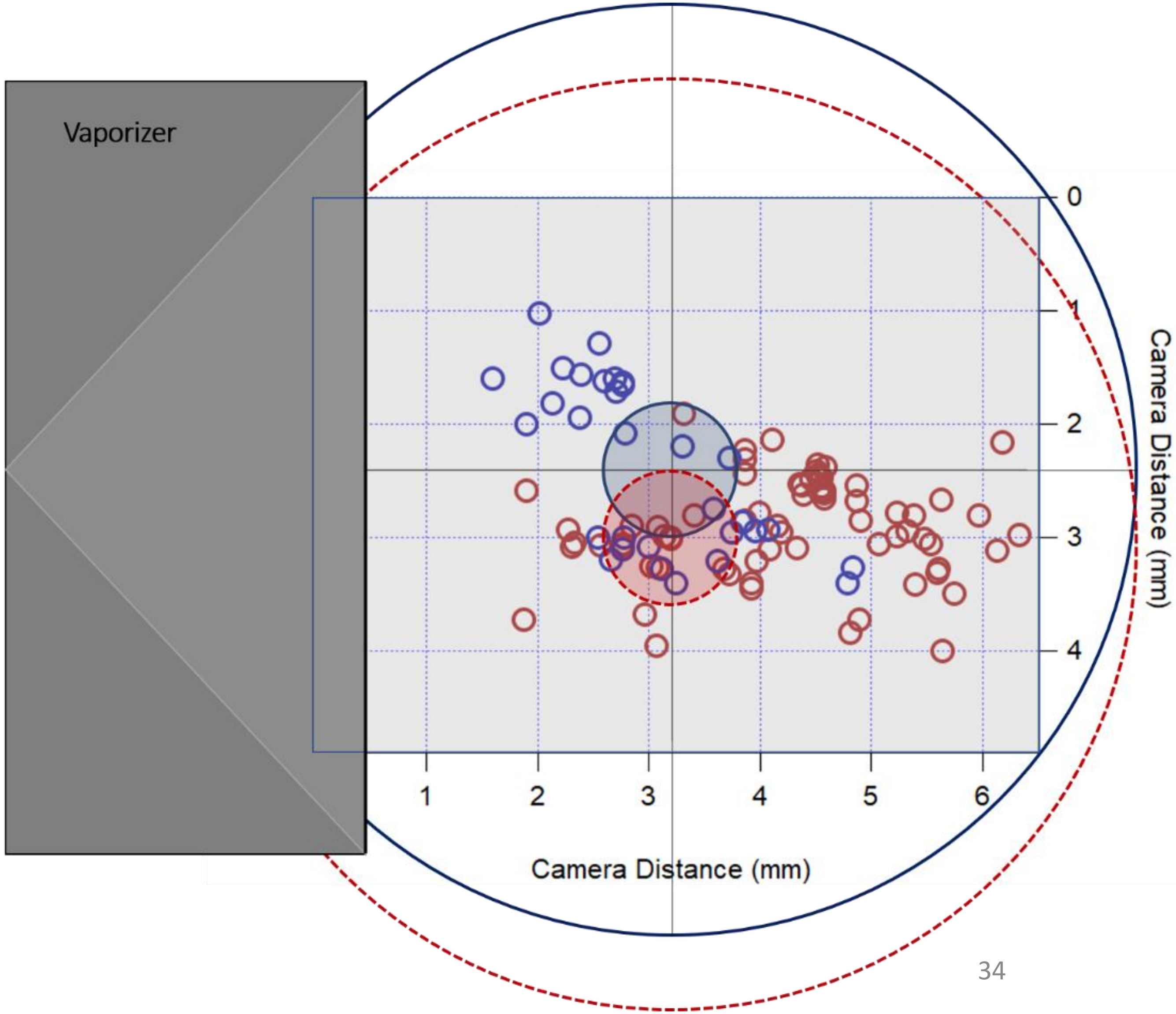
Camera perspective: Position Restriction

- Hole in the IC (black circle) is larger than the coordinates of the camera
- Projected diameter of the 2mm cylinder baffle (blue circle) is smaller and restricts the possible laser positions.
- Horizontal position restricted by need to overlap with particle beam



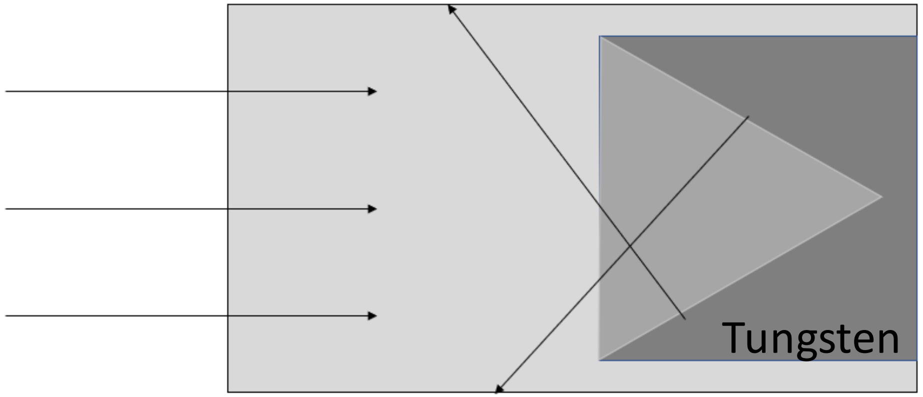
Aside: Stack height effect on position

- Lens stack height *may* be off by 0.015” (0.4mm)
  - Incorrect stack heights (Red points) look misaligned compared with correct stack height (blue points)
  - This difference further constricts laser position preventing usability of cylinder baffles



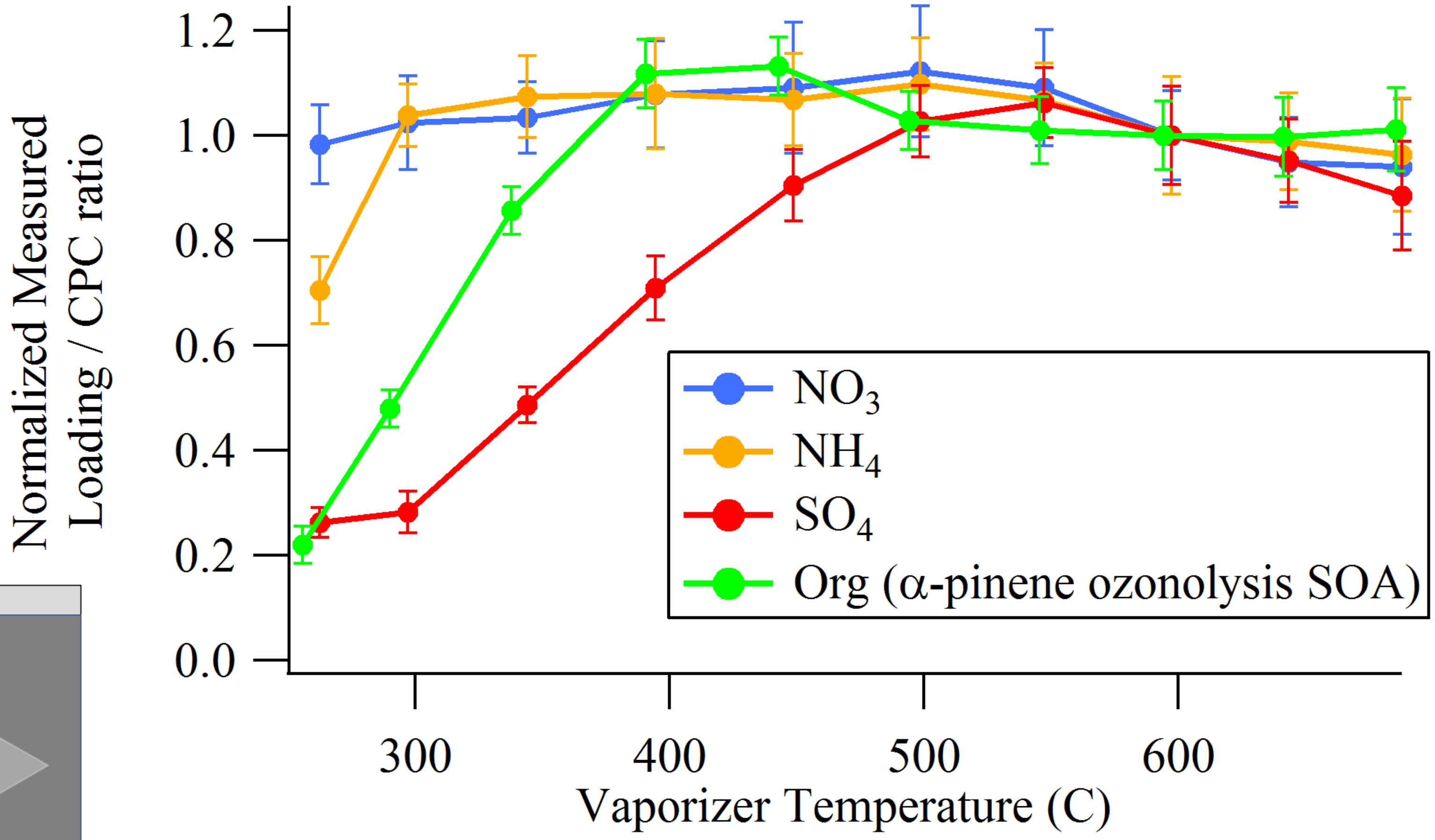
Why Ion Chamber Temperature?

- Bounced particles land on ion chamber
  - How warm is that?
  - Why does that matter?



Perspective: laser camera

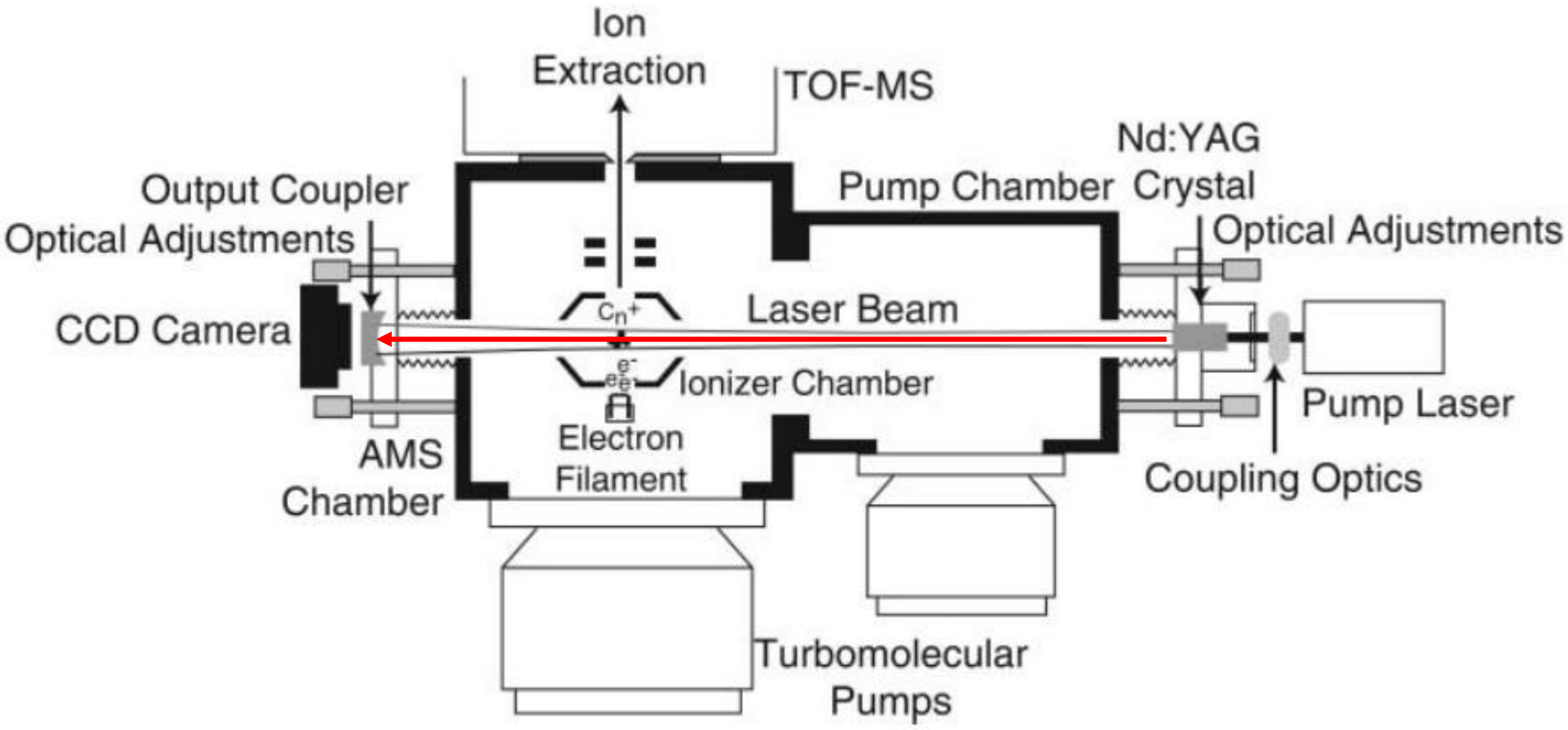
Ion Chamber



Xu et al, 2017, AS&T

Update 1: Dual vaporizer quantification

- Laser-only = rBC+Coating
  - **Remove** tungsten
  - Still recommended, but not discussed further
- Dual vaporizer = NR+rBC+Coating
  - Subtract Laser off from Laser on to get coating
  - Note hole in Ion chamber
  - Each vaporizer has separate CE and RIE

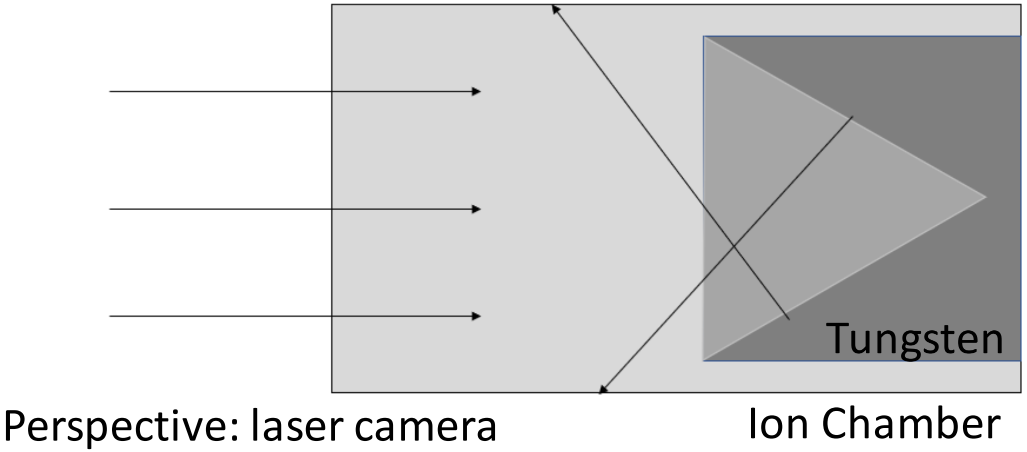


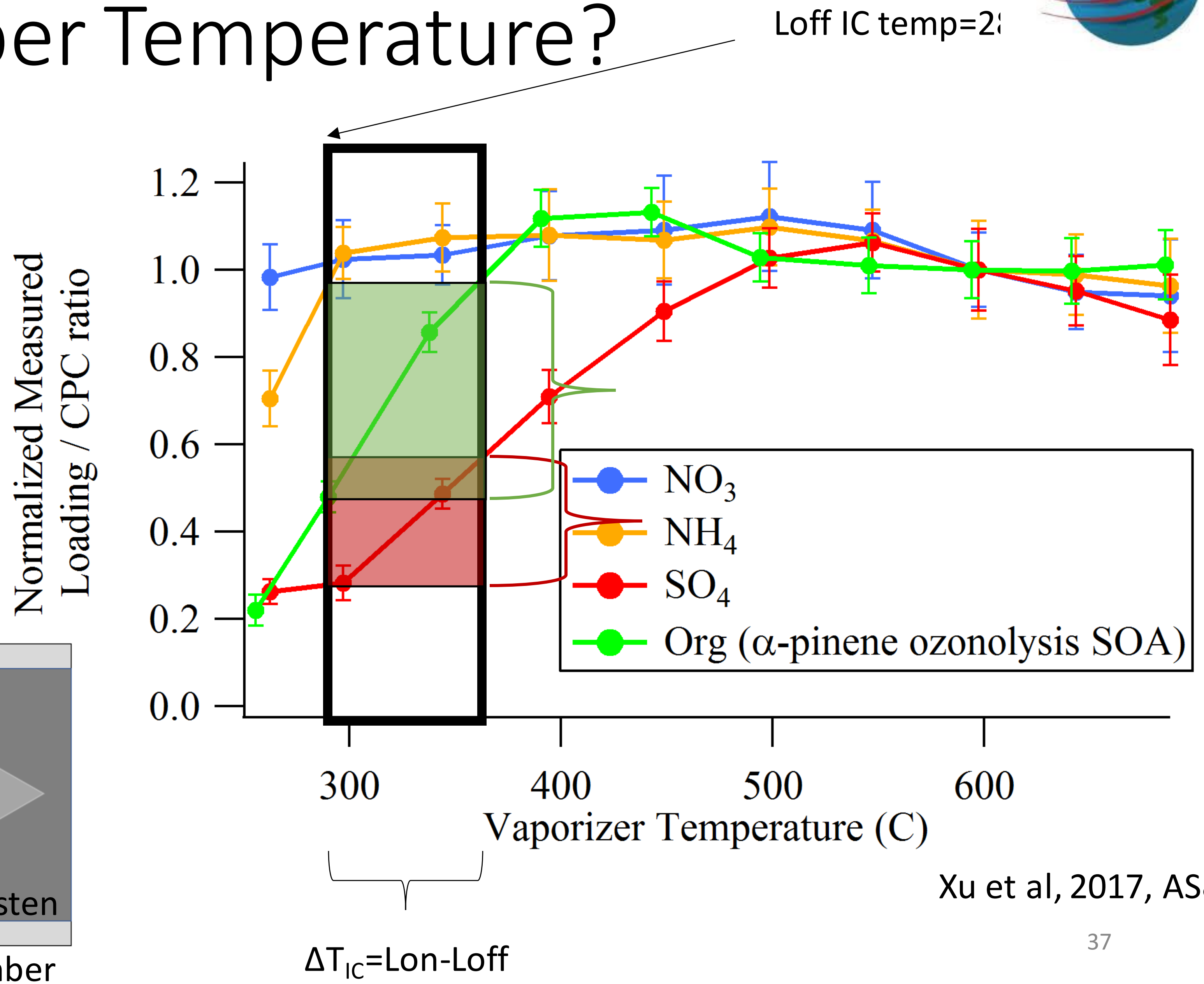
Perspective: tungsten vaporizer

Onasch et al, 2012

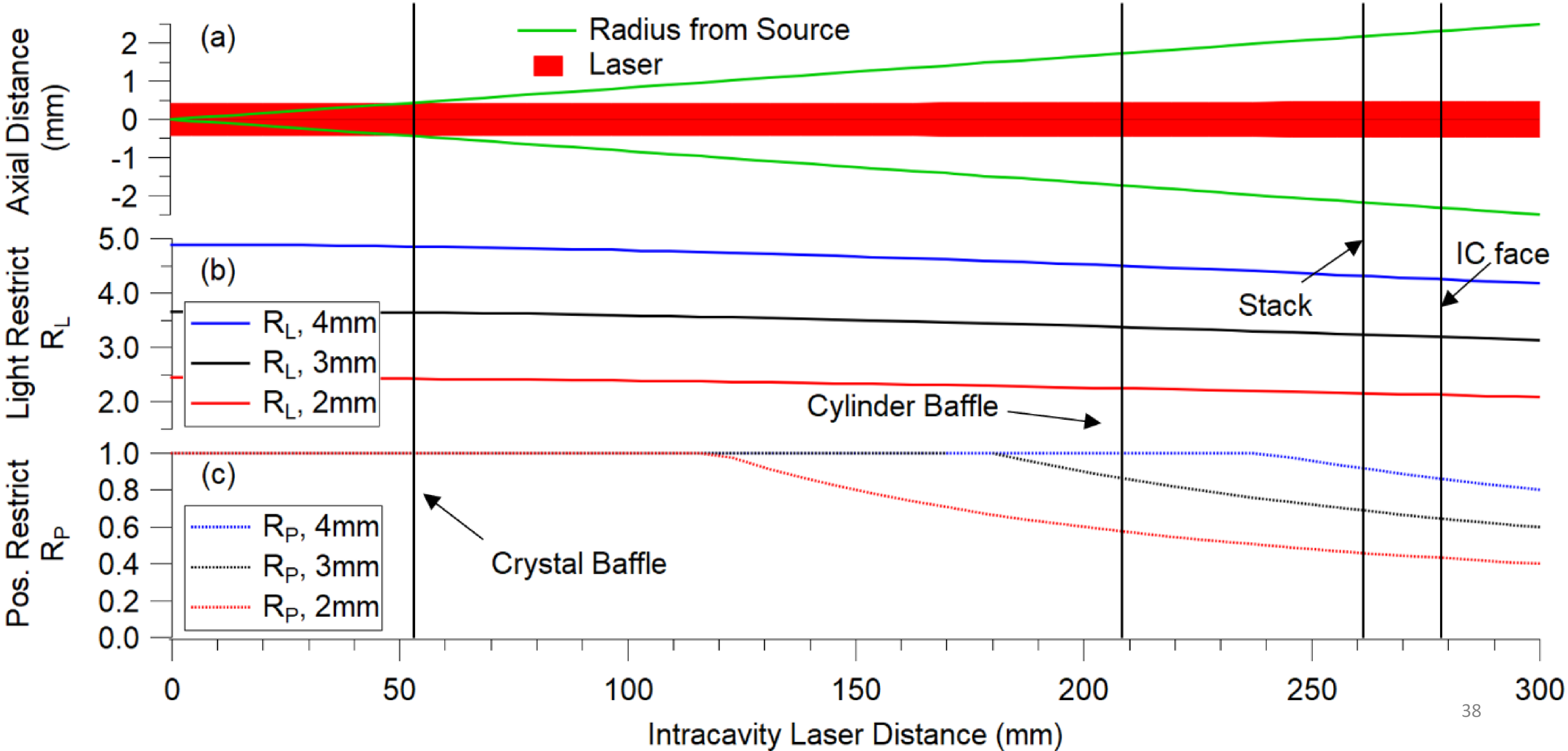
Why Ion Chamber Temperature?

- Bounced particles land on ion chamber
- Over the range of ion chamber temps:
  - Sensitivity to SO_4 and organics changes by 2x

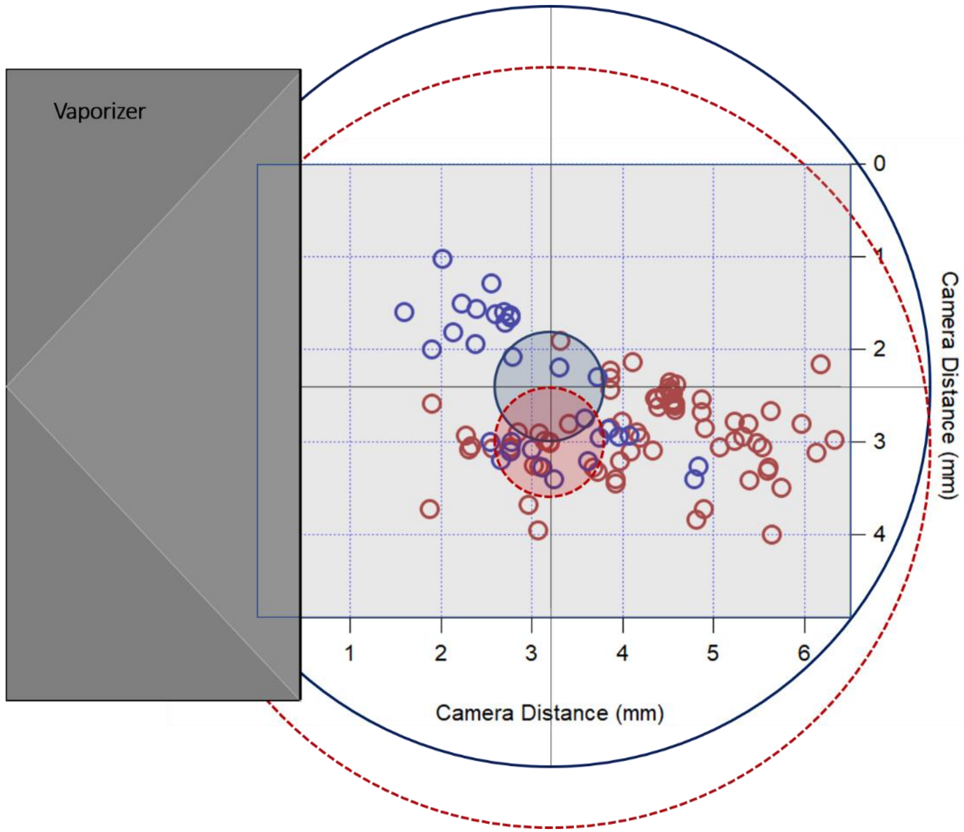




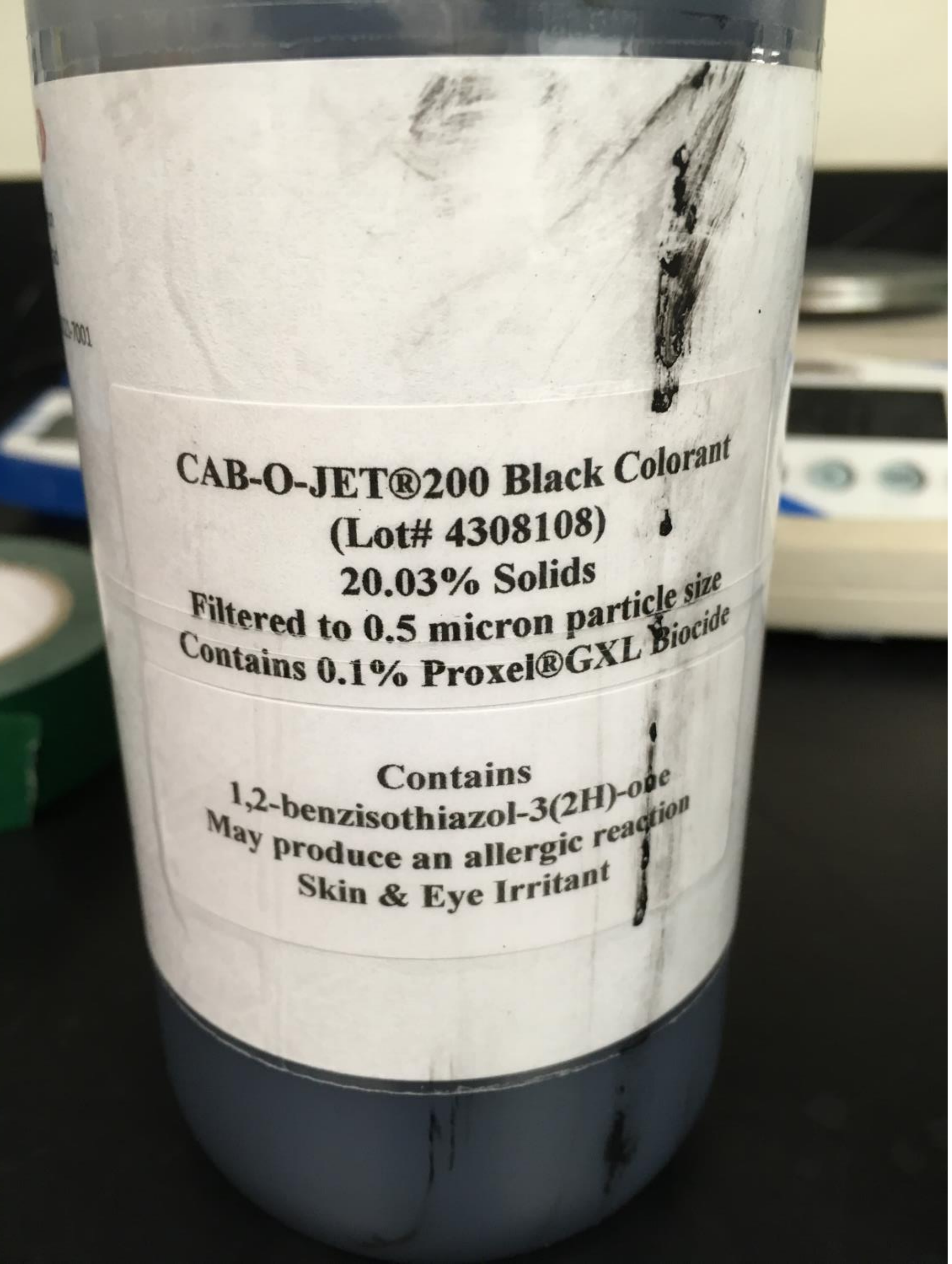
Xu et al, 2017, AS&T

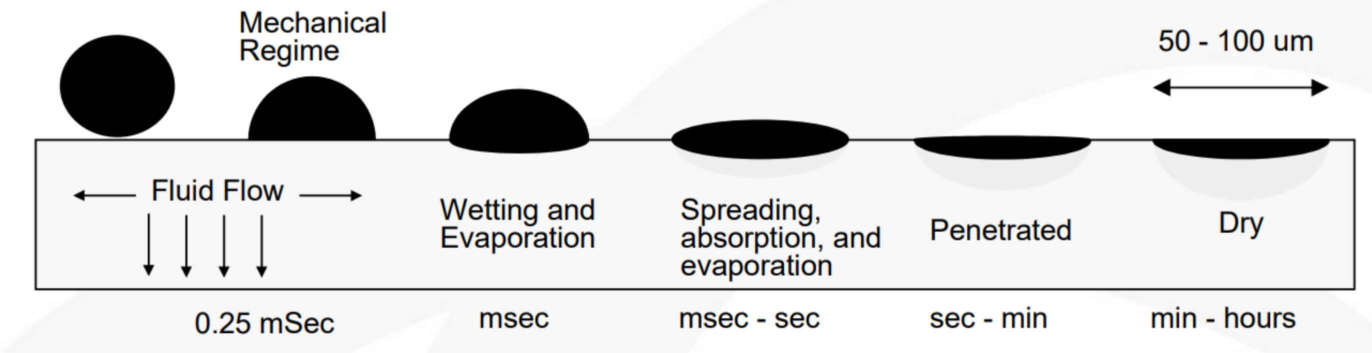


(a)
Radius from Source
Laser
Axial Distance (mm)
(b)
Light Restrict R_L
R_L, 4mm
R_L, 3mm
R_L, 2mm
Stack
IC face
Cylinder Baffle
(c)
Pos. Restrict R_P
R_P, 4mm
R_P, 3mm
R_P, 2mm
Crystal Baffle
Intracavity Laser Distance (mm)

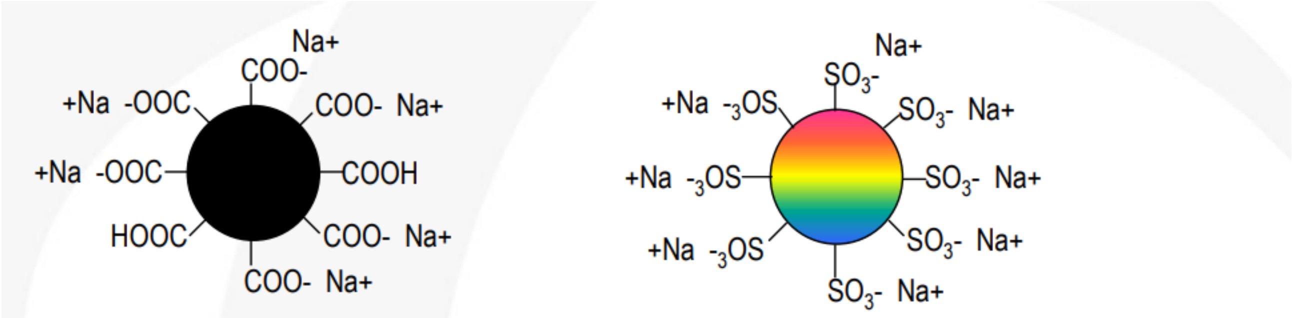


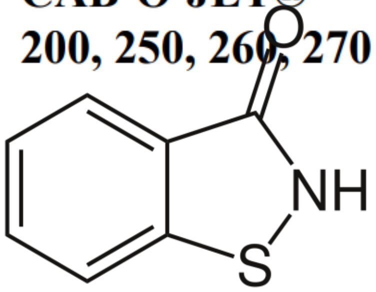
Vaporizer
0
1
2
3
4
Camera Distance (mm)
1
2
3
4
5
6
Camera Distance (mm)





0.5% of solids is the biocide

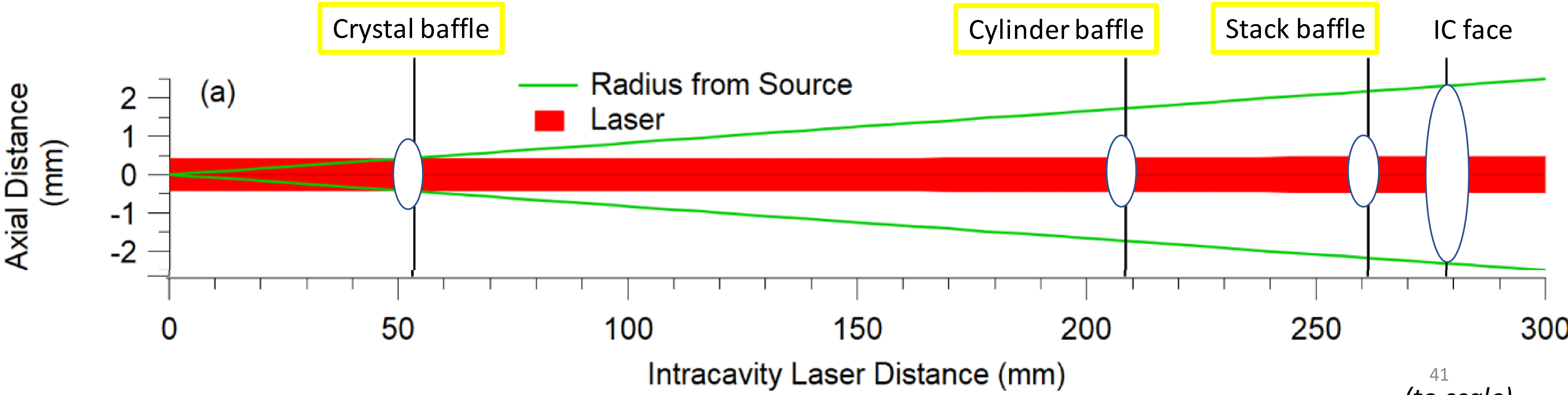




CABOT

Intervention:

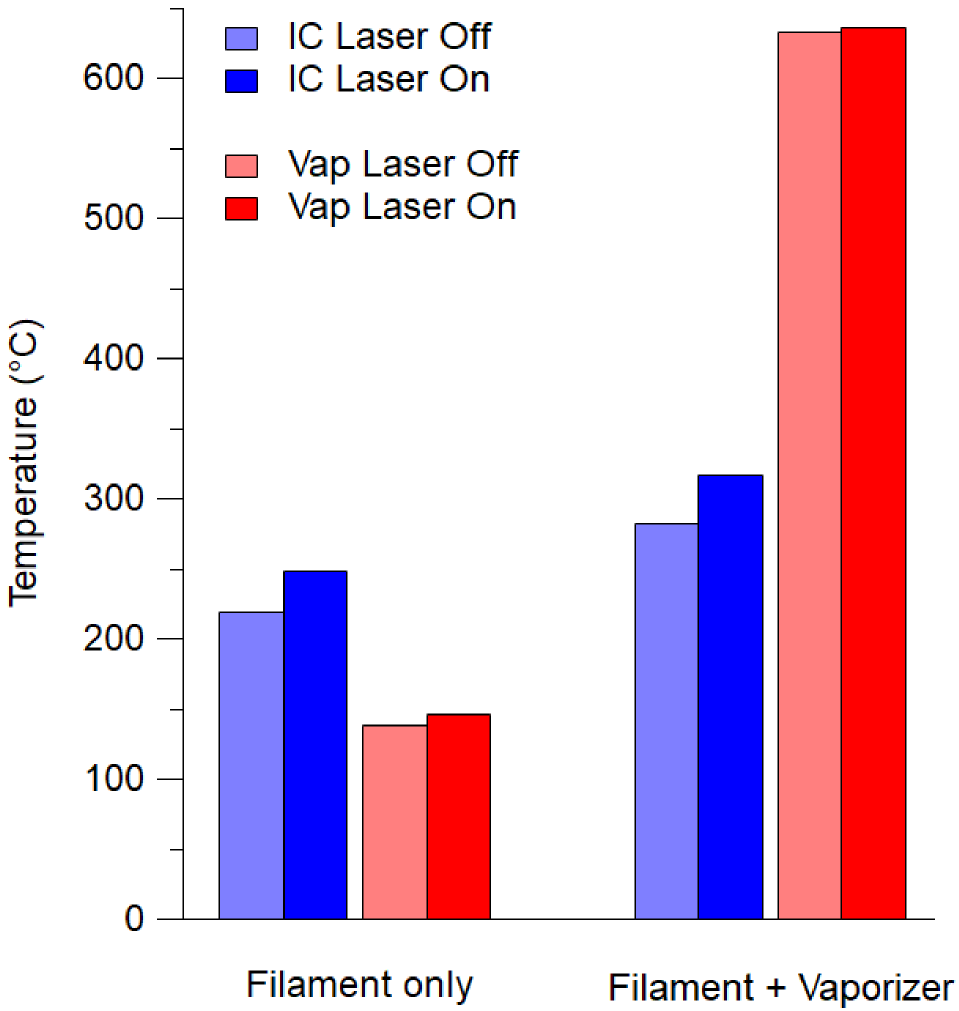
- Add baffles for:
  - Light restriction
  - Position restriction



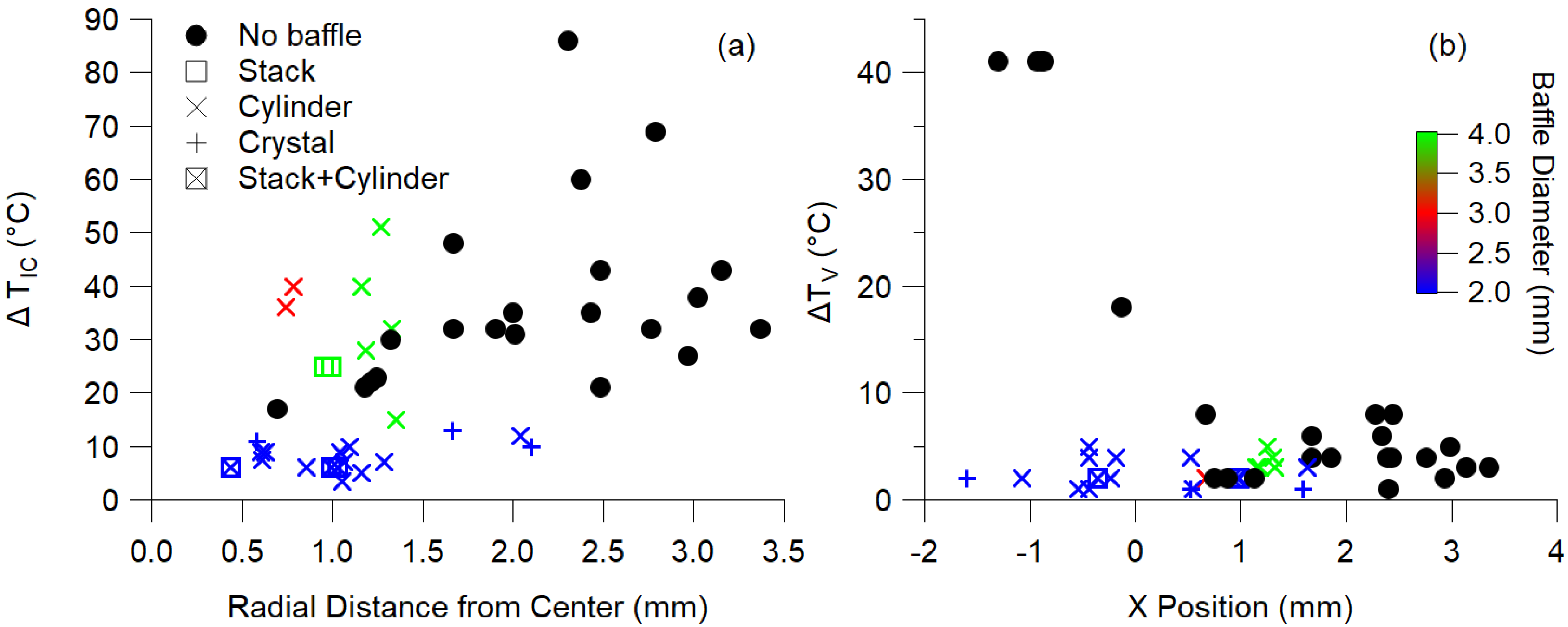
(to scale)

Recent updates: why is Lon>Loff?

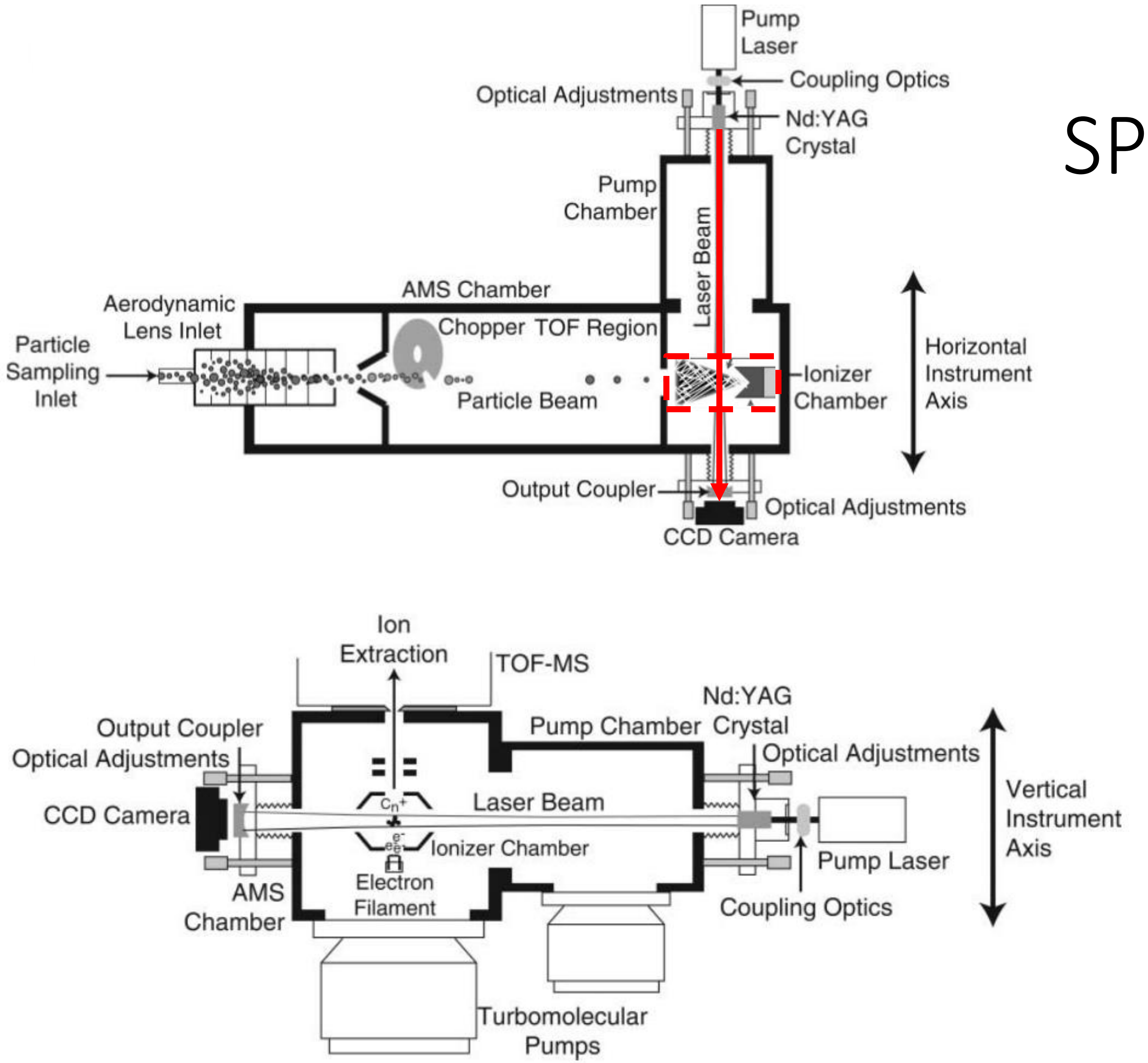
- Temperature differences
  - NR species bounce and are detected on ion chamber, which is hotter while laser on
- CE differences
  - Coating vaporized by rBC in laser will not be detected by tungsten
  - Laser diameter < tungsten diamter
- RIE differences
  - Laser vaporizer efficiency is higher than tungsten efficiency



Results: temperatures

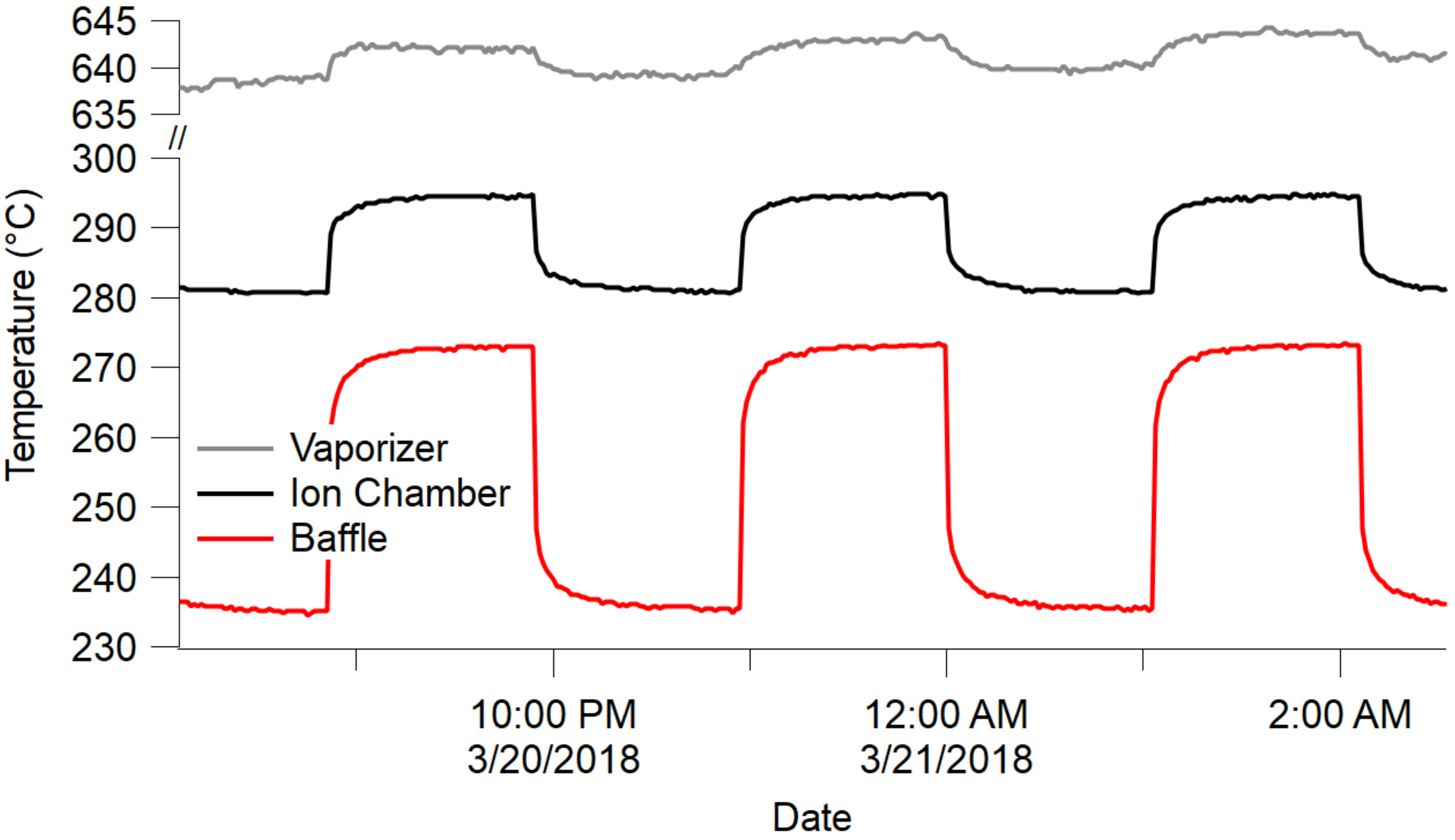


SP-AMS Vaporizer(s)



- Standard vaporizer + laser vaporizer
  - Fundamentally different mechanisms
  - Used in tandem, to what effect?

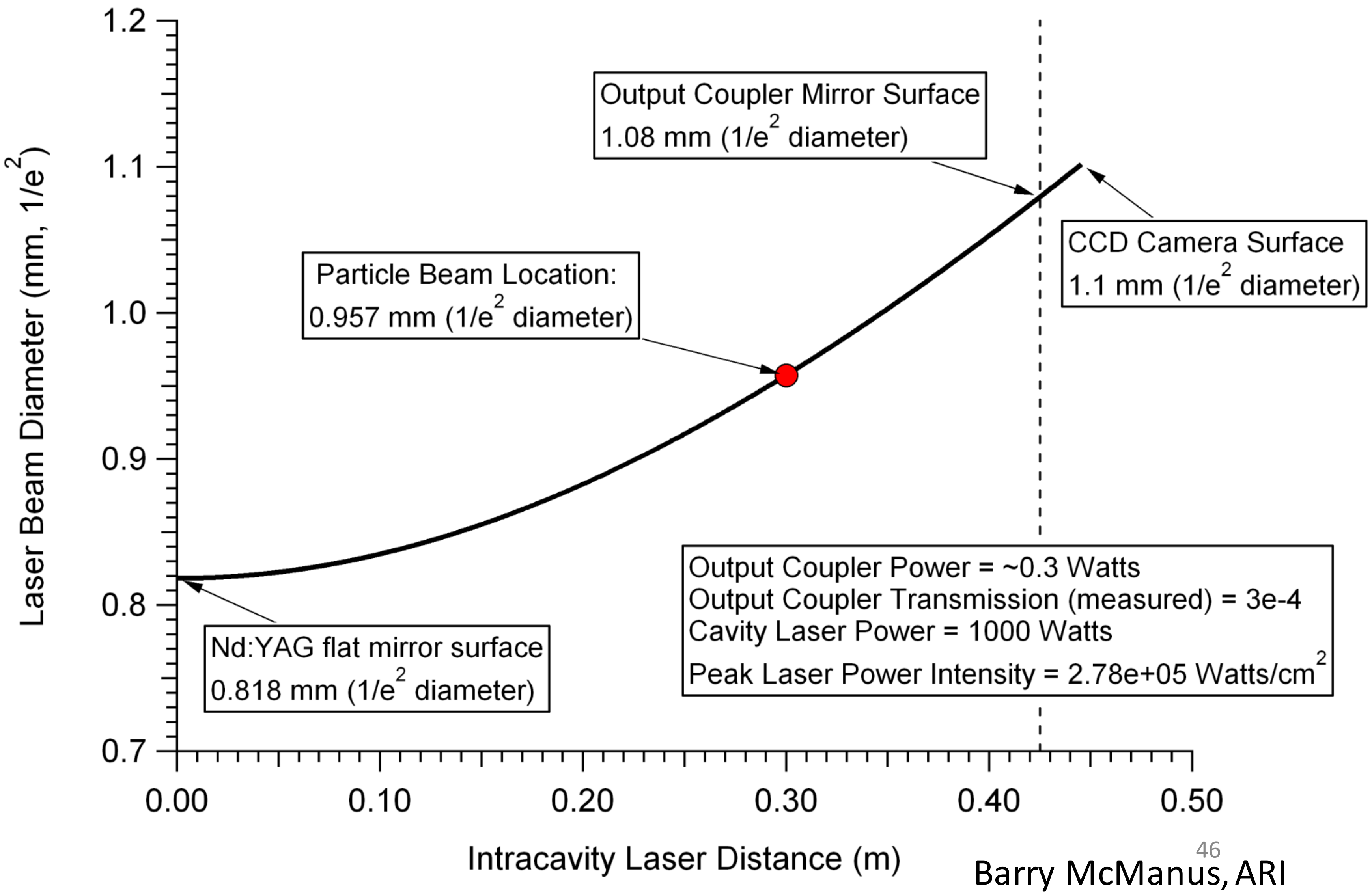
Implementation considerations: time for temperature change



Baffle	Time (s)
No Baffle	387
Cylinder	375
Crystal	518
Stack+Crystal	692
Stack	1007

Laser specifics and intervention

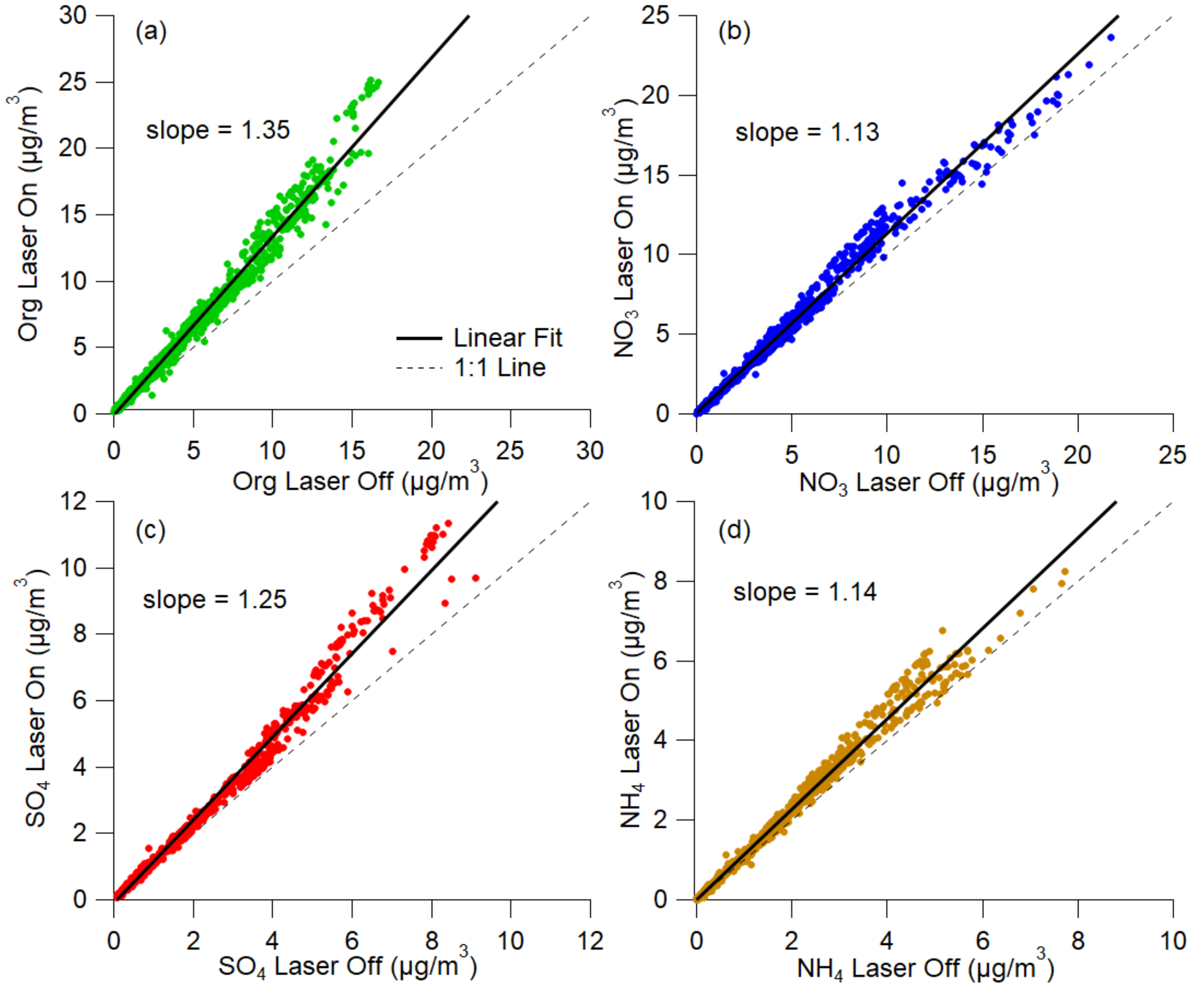
- Laser is ~ 1mm, but wings of heating are wide
- Laser diameter < ion chamber space so moveable in space
- Add baffles at various points along the air beam
    - 3 points, multiple diameters
    - Limit lasing position
    - Limit heating



Barry McManus, ARI

Recent Updates Part 1: why is Lon>Loff?

- Dual-Vaporizer Theory
  - Tungsten-only = NR
  - Laser-only = rBC+Coating
  - Together= NR+R+Coating
  - Switching allows to do all at once!
    - Subtract NR from Total to get coating
    - Mostly organics, source/age dependent
- Observations
  - Laser ON/Laser OFF >1, more than expected for coating only
    - Species-dependent



Data from Detling, UK (Leah Williams

Mendeley Desktop

File Edit View Go Tools Help

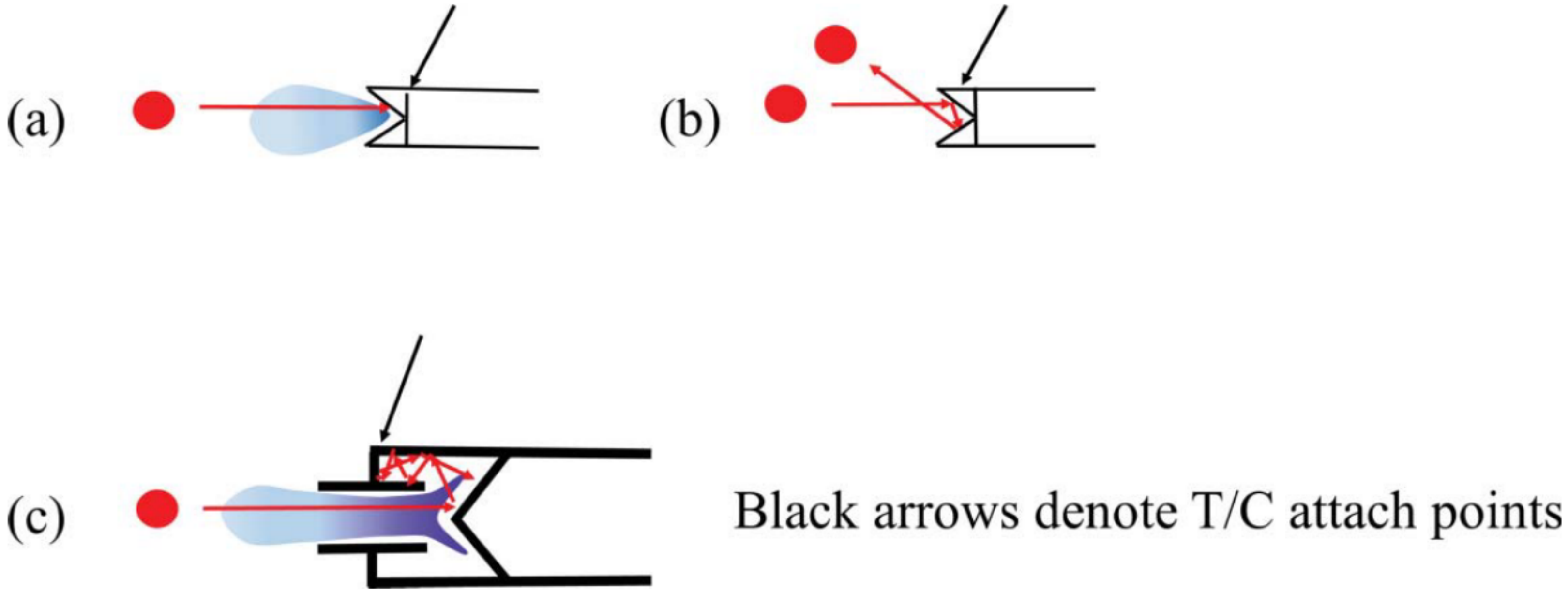
Select Pan Note Highlight Color Zoom Zoom To Fit Fullscreen Sync Help

capture vaporizer

Anita

My Library | Relating aerosol mass ... | Adsorption of Phthalat... | The National Human A... | Evaluation of the new ... | Laboratory characteriz...

Showing match 25 of 25 Previous Next



re 4. Schematic diagram of particles impacting the standard vaporizer (a and b) and capture vaporizer (c), showing (a) f
n, (b) bounce off the surface, and (c) trapped and delayed vaporization. Shading represents idealized vapor plume. Black

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Details Notes Contents

Type: Journal Article

Laboratory characterization of an aerosol chemical speciation monitor with PM2.5 measurement capability

Authors: W. Xu, P. Croteau, L. Williams et al.

View research catalog entry for this paper

Journal: *Aerosol Science and Technology*

Year: 2017

Volume: 51

Issue: 1

Pages: 69-83

Abstract:

The Aerodyne Aerosol Chemical Speciation Monitor (ACSM) is well suited for measuring non-refractory particulate matter up to approximately 1.0 mm in aerodynamic diameter (NR-sub-PM 1). However, for larger particles the detection efficiency is limited by losses in the sampling inlet system and through the standard aerodynamic focusing lens. In addition, larger particles have reduced collection efficiency due to particle bounce at the vaporizer. These factors have limited the NR-sub-PM 1 ACSM from meeting PM 2.5 (particulate matter with aerodynamic diameter smaller than 2.5 mm) monitoring standards. To overcome these limitations, we have redesigned the sampling inlet, the aerodynamic lens, and particle vaporizer. Both the new lens and vaporizer are tested in the lab using a quadruple aerosol mass spectrometer (QAMS) system ...

Tags:

Author Keywords:

Citation Key:

ISI:000394660100006

Type of Work:

article

URL:

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Catalog IDs

ArXiv ID:

DOI: 10.1080/02786826.2016.1241859