SP-AMS
Introduction and Updates

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Thanks especially to Leah, Tim, Ed, Bill, Wade
Soot Particle-AMS

AMS plus laser vaporizer module

One filament facing upward

Onasch et al, 2012

Slide thanks: Onasch
Laser Vaporizer Detection Scheme

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

Slide thanks: Onasch
Measure refractory species: BC, metals

Denuded Ethylene Flame Soot

Onasch et al, 2015
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

\[ CE = E_L \times E_S \times E_B \]

• 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

\[ CE = E_L \times E_S \times E_B \]

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

\[ RIE_{rBC} = \frac{mI_{E_{rBC}}}{mI_{E_{NO3}}} \]
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
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

Leah says will you say why 200 rather than 300?
Results: Beam Width Probe (BWP)

- 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

Huffman et al 2005

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…

Note: preliminary mass spectra
Switching gears to dual vaporizer only issues
Dual Vaporizer Quantification

- 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
  - RIE differences
    - Ionization efficiency is higher for material vaporized in the laser than on the tungsten surface. Temperature or geometry.

Ambient data from ClearfLo campaign, UK, 2012.
Baffles reduce laser heat load on IC

Avery et al., AS&T 2020
Dual Vaporizer Quantification

- 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 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.

Ambient data from ClearLo campaign, UK, 2012.
Avery et al., AS&T 2020
**Experiment**

- **Atomizer**
- **Dryer**
- **DMA**

**Size select:** 300, 350, or 400 nm

- **Q-AMS**
  - With LS; Bounce=Q-AMS particle counts/CPC,
  - Can’t measure rBC
  - Can’t measure bounce

- **CPC**
  - Laser on/Laser off ratio

- **LToF-SP-AMS**
  - Mixing state: internal mixtures
  - Quantify absorbing, scattering

**Aqueous mixtures of Cab-O-Jet +**
- **NH₄NO₃**
- **(NH₄)₂SO₄**
-**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

\[ CE = \frac{E_L \times E_S}{E_B} \]

- Constant
- Calc. with QAMS
Particles with more rBC bounce more, as expected.
More thinly coated particles have higher Laser On/Laser Off.
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 ©
    • Cab-o-jet 300 ©
Measure rBC Carbon Cluster Ions

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

*Slide thanks: Onasch*
Metal Nanoparticles

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

Slide thanks: Onasch
Model

Laser Vaporizer

9 Org
1 rBC
Laser On
RIE = 2, CE = 1
Org = 18
Lon/Loff = 2

Laser Off
RIE = 1, CE = 1
Org = 9

1 Org
9 rBC
Laser On
RIE = 2, CE = 1
Org = 2
Lon/Loff = 7

Laser Off
RIE = 1, CE = 0.3
Org = 0.3

Tungsten Vaporizer
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.

Average Ratio Total NR-PM Lon/Loff = 1.2
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)
- Ambient Lon > Loff even for small rBC mass fraction
  - 6-8% in ambient here
- This says the difference is a combination of RIE and CE
Intervention: add baffles

- Measure temperature difference $\Delta T_{IC}$ and $\Delta T_V$
  - Added thermocouples to IC and baffle
- Light restriction
- Position restriction
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

Tungsten

Normalized Measured Loading / CPC ratio

Vaporizer Temperature (°C)

- NO$_3$
- NH$_4$
- SO$_4$
- Org (α-pinene ozonolysis SOA)

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 $\text{SO}_4$ and organics changes by 2x

\[ \Delta T_{\text{IC}} = L_{\text{on}} - L_{\text{off}} \]

Perspective: laser camera

Tungsten

Xu et al, 2017, AS&T
0.5% of solids is the biocide
Intervention:

- Add baffles for:
  - Light restriction
  - Position restriction
Recent updates: why is Lon>Loфф?

- 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 diameter

- RIE differences
  - Laser vaporizer efficiency is higher than tungsten efficiency
Results: temperatures

(a) 

(b) 

Radial Distance from Center (mm) 

X Position (mm) 

ΔT_c (°C) 

ΔT_v (°C) 

- No baffle 
- Stack 
- Cylinder 
- Crystal 
- Stack+Cylinder 

Baffle Diameter (mm) 

2.0 2.5 3.0 3.5 4.0
SP-AMS Vaporizer(s)

- Standard vaporizer + laser vaporizer
  - Fundamentally different mechanisms
  - Used in tandem, to what effect?
Implementation considerations: time for temperature change

<table>
<thead>
<tr>
<th>Baffle</th>
<th>Time (s)</th>
</tr>
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<tbody>
<tr>
<td>No Baffle</td>
<td>387</td>
</tr>
<tr>
<td>Cylinder</td>
<td>375</td>
</tr>
<tr>
<td>Crystal</td>
<td>518</td>
</tr>
<tr>
<td>Stack+Crystal</td>
<td>692</td>
</tr>
<tr>
<td>Stack</td>
<td>1007</td>
</tr>
</tbody>
</table>
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
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)
Figure 4. Schematic diagram of particles impacting the standard vaporizer (a and b) and capture vaporizer (c), showing (a) the vaporization, (b) bounce off the surface, and (c) trapped and delayed vaporization. Shading represents idealized vapor plume. Black arrows denote T/C attach points.