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
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](image)
NR-PM to rBC ratio: Radiative impact of internal mixing

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

UK suburban winter
- 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 (SO₄ and NO₃).

Alex Lee et al., 2015 - U. Toronto
Measure rBC Carbon Cluster Ions

Denuded Ethylene Flame Soot

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

- 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

- Neutral density filter
- Coupler Mirror
- Ion Formation Chamber
- Nd:YAG crystal
- Pump laser
- Laser Vaporizer parameters:
  - Laser mode
  - Laser alignment
  - Laser power

Diagram showing the components and their arrangement.
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

Need to optimize vertical position
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 \textit{L}ens transmission
- \( E_B \) = Incomplete vaporization due to particle \textit{B}ounce
- \( E_S \) = Particle beam divergence due to particle \textit{S}hape (and size)

\( E_L \approx 1 \) for \( d_{va} = 70-700 \text{ nm} \)
\( E_B \approx 0.5 \) 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”

\[
C_s = \frac{1}{CE_s \cdot RIE_s \cdot mIE_{NO3} \cdot Q \sum_i I_{s,i}}
\]
Laser Vaporizer Collection Efficiency

\[ CE_{Laser} = E_L \cdot E_B \cdot E_S \]

- \( E_L \): Aerodynamic Lens transmission
- \( E_B \): Incomplete vaporization
- \( E_S \): Particle beam divergence due to particle shape (and size)

\( E_L \approx 1 \) 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

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

Mass concentration of species “s”
### SP-AMS CE’s Vaporizer-dependent

<table>
<thead>
<tr>
<th>Vaporizer</th>
<th>Measured Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tungsten</td>
<td>NR-PM * $E_B$</td>
</tr>
<tr>
<td>Laser</td>
<td>(rBC + R-PM$^\dagger$ + NR-PM$^\dagger$) * $E_S$</td>
</tr>
<tr>
<td>Laser and Tungsten</td>
<td>(rBC + R-PM$^\dagger$ + NR-PM$^\dagger$) * $E_S$ + (NR-PM - NR-PM$^\dagger$ * $E_S$) * $E_B$</td>
</tr>
</tbody>
</table>

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]

$^\dagger$ = Particulate Material on rBC particles as measured 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:

<table>
<thead>
<tr>
<th>#</th>
<th>Observation</th>
<th>Effects</th>
<th>Issue</th>
<th>Vaporizer(s)</th>
<th>Level of Understanding</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Large NR-PM Laser ON/OFF ratios</td>
<td>NR-PM quantification</td>
<td>Laser misalignment</td>
<td>Dual</td>
<td>middle, and increasing</td>
<td>Includes laser beam hitting tungsten vaporizer or ion formation chamber.</td>
</tr>
<tr>
<td>2</td>
<td>Coating/shape dependent CE</td>
<td>rBC quantification, NR-PM/rBC ratios</td>
<td>Particle beam - laser beam overlap</td>
<td>Laser</td>
<td>middle</td>
<td>Collection efficiency (CE) issue strongly dependent upon alignment and particle morphologies. BWP will help with quantification, though difficult (and slow) measurements.</td>
</tr>
<tr>
<td>3</td>
<td>Laser power drop experiments</td>
<td>rBC quantification, NR-PM/rBC ratios</td>
<td>Incomplete vaporization</td>
<td>Laser</td>
<td>low, increasing</td>
<td>Collection efficiency (CE) issue dependent upon laser power and laser beam width.</td>
</tr>
<tr>
<td>4</td>
<td>Increased sensitivity to NR-PM on rBC particles</td>
<td>NR-PM/rBC ratios, RIE’s for laser vaporizer</td>
<td>Differences between vaporizer sensitivities</td>
<td>Laser</td>
<td>low</td>
<td>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.</td>
</tr>
<tr>
<td>5</td>
<td>Incorrect rBC ion fragmentation</td>
<td>rBC quantification, rBC ion distributions</td>
<td>Cn+ ion interference from Org</td>
<td>Laser</td>
<td>high</td>
<td>Problem for dual vaporizer measurements with significant NR-PM Organics. PMF of rBC ion signals appears to effectively distinguish Cn+ ion sources.</td>
</tr>
<tr>
<td>6</td>
<td>Variations in rBC ion distributions</td>
<td>rBC quantification, rBC ion distributions</td>
<td>Large (mid and fullerene) Cn+ ion observations</td>
<td>Laser</td>
<td>low, increasing</td>
<td>Laser power issue that has yet to be resolved.</td>
</tr>
</tbody>
</table>
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
Laser ON vs OFF - BBOP

Government Flats fire (8/21/2013). SP-AMS plume transect with dual vaporizers (left) and tungsten only (right)
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
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
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
Particle-Laser Beam overlap
Beam Width Probe (Huffmann et al./Salcedo et al.)

[Diagram showing Particle beam, laser, wire, and wire motion]

[Graph showing Transmission vs. wire position (mm) with two lines: rBC signal (narrow_beam) and wide_beam]
Laser and Particle Beam Widths

- Particle beam widths: DOS coated Regal black ~ pure DOS particles
- Laser beam width ($\sigma$) is $\leq \sim 0.1$ mm
- Use BWP for CE determination in future
Incomplete vaporization and laser power

- Laser Power Drop experiments show a strong laser power and particle-laser beam overlap dependence
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
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
$C_n^+$ ion interference

Laser vaporizer only

Regal black

Flame 3

Fortner et al., 2015
Resistively heated tungsten vaporizer only
Refractory black carbon (rBC)

Laser vaporizer only

Tungsten vaporizer only

Dual vaporizers

PMF deconvolution
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!