Soot Particle-AMS

or

Laser Vaporizer-AMS

Aerodyne Research, Inc.
et al.
# Research Group | Instrument | Status
---|---|---
1 Aerodyne Research, Inc. | SP module | Delivered
2 Aerodyne Research, Inc. | SP module | Delivered
3 University of Manchester | SP module | Delivered
4 University of Toronto | SP-AMS | Delivered
5 Lund University, Sweden | SP module | Delivered
6 ETH, Switzerland | SP module | Delivered
7 FMI Helsinki | SP module | Delivered
8 NASA Langley | SP-AMS | Delivered
9 Drexel University | SP-AMS | Delivered
10 Aarhus University/Denmark | SP-AMS | Delivered
11 Environment Canada | SP-AMS | Delivered
12 Massachusetts Institute of Technology | SP module | Delivered
13 University of Eastern Finland, Kuopio | SP module | Delivered
14 Carnegie Mellon University | SP module (HR-AMS upgrade) | Delivered
15 NIUST/Handix | SP-AMS | Delivered
16 Environment Canada | SP-AMS | Ordered
SP-AMS Papers

<table>
<thead>
<tr>
<th>#</th>
<th>SP-AMS papers</th>
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</table>
Outline

• SP-AMS hardware
• Nomenclature
• Quantification
  – Collection Efficiencies
  – Sensitivities
SP-AMS hardware

• SP Module
  – New vaporizer to AMS
  – New ionization chamber configuration
  – Three potential vaporizer configurations

• ADQ and ePTOF upgrades
Laser Vaporizer Module

Onasch et al. (AS&T 2012)
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
Suggested Modifications

• Pump and intracavity lasers are class IV lasers. All class IV lasers need to be fully enclosed with interlocks that shut down the lasers when the enclosures are opened.
  – Following up with James Allan about how they modified their instrument
• Need computer logged laser diagnostics
  – Ideally, this might be USB connection to laser electronics box to control laser and obtain pump and intracavity laser intensities and Nd:YAG crystal temperatures
  – Access to CCD camera during operations and logging of the CCD camera output
    • Currently, can log CCD camera data, but very complicated, too much data is saved, and we have not successfully done this...
• Do all Laser electronics have the laser ON/OFF capabilities?
  • Need labeling and a description of how this works (Amewu)
• It is not currently clear how useful the photo-diode laser detector is or how it is being used
  • Appears to be location sensitive, especially compared with thermal-based laser intensity monitors and even the camera
• Micrometers on laser adjustment knobs: laser tuning adjustment knobs are fine, but without a micrometer like setup, there is no good method for adjusting and returning the same tunings...
Laser Vaporizer Detection Scheme

The laser is not the vaporizer, the absorbing particles are the vaporizer!!
Ambient Mass Spectrum

- **Black Carbon**
  - 86% C1-C5
- **Organic**
  - 4% C32-C70
- **Nitrate**
  - 10% C6-C31

**C_{32}^+**

**C_{60}^+**
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
Quantification

• Collection Efficiencies
  – Tungsten Vaporizer
  – Laser Vaporizer

• Sensitivities
  – Refractory black carbon (rBC) [Laser]
  – Non-Refractory PM [Laser and Tungsten]
Tungsten Vaporizer Collection Efficiency

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

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

- \( E_L \approx 1 \) for \( d_{va} = 70-700 \) 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

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

\( E_L \) = Aerodynamic Lens transmission
\( E_B \) = Incomplete vaporization **
\( E_S \) = Particle beam divergence due to particle Shape (and size)

\( E_L \sim 1 \) 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 Laser Vaporizer
→ Beam width probe measurement

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

<table>
<thead>
<tr>
<th>Vaporizer</th>
<th>Measured Species</th>
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<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
Measuring $CE_{\text{Laser}} = E_S$

Beam Width Probe (BWP)

Huffman et al. 2005

Willis et al., 2014
Laser and Particle Beam Widths

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

Salcedo et al., 2007

Willis et al., 2014
CE vs PBW

- $CE_{\text{Laser}} \sim E_S$ is a strong function of Particle Beam Width
- BWP will help make SP-AMS measurements independent
BES coating experiments

University of Toronto – Abbatt lab

Willis, Lee et al., 2014
$CE_{Laser}$ as function of $R_{BC}$

$rBC$

$R_{Org/RB} = \frac{m_{Org}}{m_{RB}}$

Willis et al., 2014
- Observe similar $R_{BC}$-dependent CE for rBC in field
- Not expected to be same, as NR-PM in ambient is likely significantly different than liquid BES

Massoli et al., 2014
SP-AMS Sensitivities

• rBC
  – Refractory carbon ion distribution dependent?
  – Black carbon particle type dependent?

• NR-PM
  – Vaporizer dependent?
Refractory Carbon Ion Spectra

- Different rBC particle types generate different refractory carbon ion distributions
- Fullerene ions are detected where expected and not otherwise
- All rBC particle types exhibit low carbon ion signal ($C_1^+ - C_5^+$)

Onasch et al., 2014
$C_1^{+-}-C_5^{+-}$ vs HRBC
HRBC calibration plot
• Regal black and fullerene soot appear to agree reasonably well
• Aquadag is significantly lower ($E_S < 1$ ?)
• Suggests low carbon ($C_1^+ - C_5^+$) be used for quantification
Laser-induced ion generation

- Fullerene ions generated in laser (with electron beam off)
- Larger ions generated more easily
$C_1^+ - C_3^+$ Ratios

- Need more work to verify quantification of rBC for various particle types

### Table

<table>
<thead>
<tr>
<th>Aerosol</th>
<th>Abbreviation</th>
<th>Mobility Diameter [nm]</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAST Black</td>
<td>CBK</td>
<td>125, 200, 305</td>
<td>Jan 26</td>
</tr>
<tr>
<td>CAST Brown</td>
<td>CBW</td>
<td>125, 200, 305</td>
<td>Jan 27</td>
</tr>
<tr>
<td>Spark-generated particles</td>
<td>GFG</td>
<td>125, 200, 305, 500</td>
<td>Jan 30</td>
</tr>
<tr>
<td>Regal Black</td>
<td>RB</td>
<td>125, 200, 305, 500</td>
<td>Jan 31</td>
</tr>
<tr>
<td>Fullerene-Enriched Soot</td>
<td>FS</td>
<td>125, 200, 305, 500</td>
<td>Feb 1</td>
</tr>
<tr>
<td>Thermodenued CBW</td>
<td>CBWTD</td>
<td>125, 200, 305</td>
<td>Feb 2</td>
</tr>
<tr>
<td>Aircraft gas-turbine</td>
<td>TU</td>
<td>Polydisperse (mode 25)</td>
<td>Apr 30</td>
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</table>

Corbin et al., 2014
Emissions Measurements

- Distinct combustion sources generate different SP-AMS refractory carbon ion mass spectra (both in terms of carbon ion distributions and $C_1^+/C_3^+$ ratios)
- Potential to provide insights into ambient particulate sources

Caldecott Tunnel *Dallmann et al., 2014*

FLAME3 *McMeeking et al., JGR 2009*
Is the SP-AMS NR-PM measurement sensitivity vaporizer dependent?
$CE_{\text{Laser}}$ as function of $R_{BC}$

- Laser and Tungsten vaporizers
- Correlated CE’s for rBC and NR-PM
- NR-PM sensitivity is rather large

$rBC$

NR-PM (BES)

Willis et al., 2014
Laser OFF/ON ambient results

- Increase in signal with laser ON for Org components related to BC particles

Lee et al., 2014
Effects on relative coat-core measurements

- SP-AMS measures composition down to at least 5% rBC by mass (i.e., small core, large coating) once corrected
- Uncorrected relative results appear decent, but more work needs to be done to verify

- $f_{BC}$ measurements up to 50% low
- $R_{BC}$ measurements up to 2X high

Willis et al., 2014 – U Toronto
Summary

- **Hardware**: Working to optimize ionization chamber configurations.
- **Nomenclature**: Corbin et al. have set SP-AMS terminology based on vaporization temperature (instrument and particle specific) and laser-light absorbing (particle specific) properties.
- **Collection efficiency**: Willis et al. have shown that $E_s$ dominates SP-AMS CE, which can be quantified with BWP measurements.
- **Sensitivity (rBC)**: Low carbon ($C_1^+ – C_5^+$) ion signals are likely best for quantification. Working on assessing rBC quantification for different BC particle types (i.e., Sensitivity vs CE). Refractory carbon ion distributions appear to be related to BC chemical composition (i.e., graphitization).
- **Sensitivity (NR-PM)**: NR-PM mIE from laser vaporizer appears to be greater than NR-PM mIE from tungsten vaporizer; working on quantifying.

SP-AMS technology is rapidly maturing and opening new avenues for studying absorbing, refractory particles.