Towards a reference material for soot/LAC measurement: Evaluation of candidates with electron microscopy, SP2 and TOA

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Acknowledgments

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Motivation

• Strongly light-absorbing carbon (LAC)/soot an important player in climate change, air quality, health effects and visibility

• LAC measurements often operationally-defined
  – Thermal-optical methods can produce 2x different results

• Lack of reference material impeding progress on understanding method biases
LAC reference material: requirements

• Known composition and density
• Well-characterized shape
  – Helps correctly identify mass of particles selected through a DMA
• Physical characteristics similar to LAC
  – Refractory
  – Optical properties
• Manufacturing:
  – Reproducible size distribution, easily obtained
  – Size-controlled (monodisperse) production
• Usability:
  – Stable over extended periods of time
  – Dispensable (easily mixes with water)
• Previous work: Black Carbon Steering Committee
  – http://www.geo.unizh.ch/phys/bc/
  – n-hexane soot
  – Wood and grass chars
Candidates

• Glassy carbon
  – Alfa Aesar©, Tokai©

• Fullerene soot
  – Alfa Aesar©

• Acheson Aquadag©

• Graphitized thermal soot (GTS)
  – Moscow State University

• Diffusion flame-generated (“Magic”) soot
  – Lawrence Berkeley National Laboratory
GTS composition: ~100% EC
Identifying LAC with the SP2

Narrowband

Broadband incandescence

Schematic from Moteki & Kondo (2007)
Reference materials and combustion (magic) soot behave similarly in the SP2.
Magic soot

Untreated soot*

Soot, oxidized and exposed to water

normal

compacted

Soot-like aggregates, spherules and agglomerated spherules

Alfa glassy carbon

Tokai GC: solubilized & air-blown

Fullerene soot: 400 & 110 nm

Aquadag (contaminated?)
Graphitized thermal soot (GTS)

Popovicheva et al. (2008)
Reference material density

- Tokai GC: 1.85 g/cm$^3$
- Alfa GC: 1.42 g/cm$^3$
- Fullerene soot: ?
- Aquadag: 1 g/cm$^3$? (mobility density)
  - Not specified by manufacturer
- Graphitized thermal soot (GTS): ~2 g/cm$^3$?
  - Assuming density of graphite
- Magic soot: ~1.9 g/cm$^3$?
  - Assuming density of fresh LAC

- **Material density not the same as mobility density**
  - Hard spherical particles are OK (like *individual* glassy carbon particles)
  - Fractal agglomerates may have a different effective density in a DMA due to non-spherical shape factors
Comparing Aquadag, GTS80, magic soot and fullerene soot

Mobility density:

\[ \rho_{GTS80} = 0.72* \rho_{Aquadag} \]
\[ \rho_{magic} = 0.56* \rho_{Aquadag} \]
\[ \rho_{fullerene} = 0.69* \rho_{Aquadag} \]
Fullerene soot and Regal carbon black (BC/Aerodyne Soot Project 2)

\[ \rho_{\text{RegalCB}} = 0.91 \times \rho_{\text{Aquadag}} \]

Measured soot masses \( \sim 0.4 \) to \( 3.4 \) fg-LAC
Organic-coated GTS: Soot standard?

GTS80 + 4.88% 1,2,4-benzene tricarboxylic acid
Summary

- Magic soot and GTS are ~100% EC
  - GTS can be coated with organic matter as a “soot” proxy
- All materials behave like LAC in the SP2
- Glassy carbon and GTS have spherical/spheroidal shape
  - Good for DMA size selection (mass is known)
  - Fullerene soot, Aquadag, magic soot are more fractal, so DMA-selected mass not certain
- Aquadag behaves nicely in DMA, over a wide range of mobility diameters (0.5 – 100 fg)
- Need to confirm mobility density of fullerene soot, GTS, magic soot and Aquadag
  - DMA/SP2 response differentiated only by mobility density
- Need to test optical properties of most materials
  - Previously, tests have shown discrepancies between PSAP and PASS absorption for GTS
  - GTS microstructure similar to graphite, so optical properties could be similar to graphite
  - Magic soot is freshly-generated LAC
Do the candidates meet our requirements?

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<tr>
<th>Requirement</th>
<th>Alfa GC</th>
<th>Tokai GC</th>
<th>Fullerene soot</th>
<th>Aquadag</th>
<th>GTS</th>
<th>Magic soot</th>
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Good; + further testing needed; nt: not tested
Extra slides follow
Calibration of SP2 using Aquadag and fullerene soot

BC mass = (0.01925 ± 0.00043) * PkHt1 - (0.69 ± 0.41)

r = 0.9987
Production of Elemental Carbon Reference Material

Thermal soot by gas pyrolysis

- Cleaning from
  - organic coverage,
  - inorganics, ash.
- Production of well-graphitized structure,
  perfect chemically uniform surface.
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<th>Sample</th>
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Alfa fullerene soot: soot-like aggregates

DMA @ 400 nm

DMA @ 110 nm
Tokai glassy carbon: spherules and agglomerates

Tokai 200 nm

Tokai 200 nm, not solubilized
Alfa glassy carbon: single spheres and agglomerates
Acheson Aquadag: more aggregates like soot, but contaminated sample?
Measurement Instrumentation

- Single Particle Soot Photometer (SP2)
  -- Individual particle mass measurement
- Thermal/Optical
  -- elemental carbon/organic carbon
- Photoacoustic
  -- *in-situ* particulate light absorption converted to mass
- Filter collection (aethelometer, PSAP, MAAP)
  -- light absorption converted to mass