Development of Techniques for the Calibration of Real-Time Black Carbon Mass Concentration Instruments

Kevin Thomson, Fengshan Liu, Greg Smallwood
National Research Council Canada, Measurement Science and Standards

Matthew Dickau, Tyler Johnson, Jason Olfert
University of Alberta, Mechanical Engineering

2015 CCQM Particulate Workshop, Paris
What is Black Carbon?

“Black Carbon is a distinct type of carbonaceous material that is formed primarily in flames, is directly emitted to the atmosphere, and has a unique combination of physical properties”

- strongly absorbs visible light
- is refractory with a vaporization temperature near 4000 K
- exists as an aggregate of small spheres
- is insoluble in water and common organic solvents

Relative Effect of Black Carbon on Climate

Components of radiative forcing for principal emissions

- **Some GHGs**
  - CO₂
  - CH₄
  - O₃(T)
  - H₂O(S)
  - CO₂

- **Black Carbon**
  - Bond et al., "J Geophys Res - Atmospheres, 118 (2013)

Aerosols

- Sulfate (direct)
- Organic carbon (direct)
- Mineral dust
- Cloud albedo effect

Radiative Forcing (W m⁻²)

Intergovernmental Panel on Climate Change (2007)
Many Methods to Measure BC

• Filter based/offline methods
  – gravimetric
  – thermal optical analysis
• Particle counting & mobility
  – condensation particle counters
  – scanning mobility particle sizers
  – differential mobility sizers
• Filter/optical methods
  – smoke number
  – aethalometer
  – multi-angle absorption photometer
• Aerosol/optical/real time methods
Aerosol/Optical/Real-Time BC Measurement

• light absorption/emission
  – absorption/emission proportional to particle volume and mass
  – scale with optical properties (refractive index)
• light extinction
  – extinction is comprised of absorption and total light scattering
  – must isolate absorption from scattering

\[
eBC = \frac{K_{\text{abs},\lambda}}{MAC_{\lambda}} \left[ \frac{\mu g}{m^3} \right]
\]

\[
MAC_{\lambda} = \frac{6\pi E(m_{\lambda})}{\rho_{BC\lambda}} \left[ \frac{m^2}{g} \right]
\]
Some Commercial Optical Instruments for BC Measurement

- Artium LII 300
  - laser induced incandescence
  - BC emission used to determine $K_{abs,\lambda}$

- AVL Micro Soot Sensor (MSS)
  - photo-acoustic
  - proportional to BC absorption, $K_{abs,\lambda}$
Measurement Calibration Issue

Measuring properties with different instruments

- most instruments are proprietary
  - each manufacturer implements a different measurement and calibration principle
- difficult to compare results obtained with different instruments
- a BC aerosol reference material does not exist

Need for a standard calibration method/service

- calibration against an accepted reference method
- calibration over a relevant concentration range
- calibration using a BC source which produces a BC aerosol with known physical and chemical properties
Correlation to elemental carbon (EC) via thermo-optical method (NIOSH 5040)*

BC Mass Concentration Instrument Calibration Service

- calibration service is applicable to any BC mass concentration instrument
- NRC has calibrated over 20 BC mass concentration instruments in the last 2 years
- particular interest from aviation industry so far
- developing interest from other sectors
  - automotive (in particular diesel)
  - ambient BC monitoring and regulation
  - gas turbine electrical power generation
- presently working on how to make this an ISO 17025 compliant calibration
Centrifugal Particle Mass Analyzer/Electrometer Method

NIOSH 5040
• method is well known, but uncertainty is large, traceable a challenge, experiments are very time consuming

Centrifugal Particle Mass Analyzer-Electrometer Method
• novel method to mass-to-charge select particles and then count the charge to determine mass
CPMA/Electrometer Calibration Principal

CPMA/Electrometer Calibration Setup

Inverted Flame Burner → Catalytic Stripper
Production of nVPM with >99% EC

Selection by mass/charge
Uni-Polar Charger → CPMA

Make-up air
HEPA

Charge measurement
Faraday Cup Electrometer
MFC
Pump

Mass measurement
Mass Concentration Instrument to be Calibrated
MFC
Pump

Production of nVPM with >99% EC
Comparison of Mass Instruments to CPMA-Electrometer System

![Comparison graphs showing LIL and MSS measurement against CPMA-Electrometer measurement. Graphs include linear regression equations and R² values.]

- LIL Measurement (µg/m³) vs. CPMA-Electrometer Measurement (µg/m³)
  - SN0343: \( y = 0.9483x - 0.6074 \)
  - SN0340: \( y = 1.1737x - 4.0544 \)
  - \( R^2 = 0.9987 \)

- MSS Measurement (µg/m³) vs. CPMA-Electrometer Measurement (µg/m³)
  - SN0273: \( y = 0.9621x - 0.0100 \)
  - SN1187: \( y = 1.0625x - 0.8692 \)
  - \( R^2 = 0.9972 \) and \( R^2 = 0.9992 \)
CPMA-electrometer system is a viable option for calibration of aerosol mass concentration instruments

- CPMA-electrometer measurements are highly linearly correlated with both types of mass instruments
- lower uncertainty, averaging 5.2% (k=2), and much quicker than NIOSH 5040 method
- CPMA resolution and presence or absence of a charge neutralizer do not appear to affect the measurements
- lower concentrations more readily achieved than filter based methods

Thank you

Dr. Kevin Thomson
Program Leader, Measurement Science for Emerging Technologies
phone: 613-991-0868
e-mail: kevin.thomson@nrc-cnrc.gc.ca
web: www.nrc-cnrc.gc.ca
Thank you

Dr. Kevin Thomson
Program Leader, Measurement Science for Emerging Technologies

phone: 613-991-0868
e-mail: kevin.thomson@nrc-cnrc.gc.ca
web: www.nrc-cnrc.gc.ca
Measurements With and Without a Charge Neutralizer Before the Mass Instrument

- charge on particles appears to have minimal effect on measurements made by mass instruments
Measurements at Different CPMA Resolutions

- CPMA resolution setting appears to have minimal effect on measurements made by mass instruments
Measurement on a NIOSH 5040 EC Calibrated Mass Instrument – Repeatability

CPMA-Electrometer method

- excellent linearity
- slopes within +/-5% of reported values on NIOSH 5040 EC calibrated instrument for all three repeats
- error bars represent 95% confidence intervals (k=2)
Sources of Uncertainty and System Improvement

Uncertainty averaged 8.6% (k=2), as low as 5.2% (k=2) for some measurements

- flow rate measurement
- CPMA set point from voltage and rotational speed measurement
- CPMA resolution
- Largest source of uncertainty was noise and offset in current measurement

System improvements

- modification to unipolar charger to reduce particle loss
- improvements to Faraday cage electrometer to reduce noise and drift in electrometer readings
Measurement on a NIOSH 5040 EC Calibrated Mass Instrument

CPMA-Electrometer method

- concentration range extended to 500 µg/m³
- average uncertainty reduced to 5.2% (k=2)
- error bars represent 95% confidence intervals (k=2)
Thermal Optical Analysis Principal

Filter Acquisition

BC Aerosol

Organic Carbon Analysis

He $\rightarrow$ $C_xH_y$

Elemental Carbon Analysis

He + $O_2$ $\rightarrow$ $CO_2$
Example SAE AIR6241 Calibration Result (AVL MSS)

\[ y = 1.0603x \]

\[ R^2 = 0.9995 \]