Greg Smallwood, Kevin Thomson, Fengshan Liu, Dan Clavel
National Research Council Canada, Ottawa, Ontario, K1A 0R6, Canada

Matthew Dickau, Tyler Johnson, Jason Olfert
University of Alberta, Edmonton, Alberta, T6G 2G8, Canada

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Calibration of Black Carbon Real-Time Mass Instruments: Development and Status

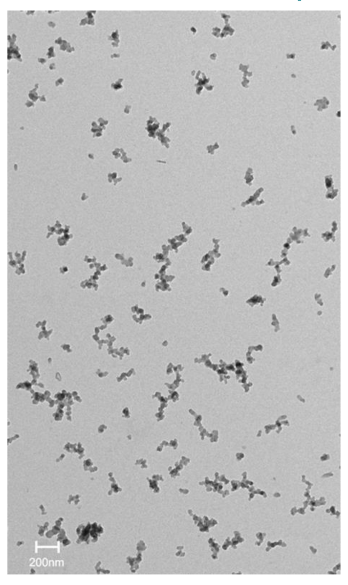
OVERVIEW

- Black Carbon (BC) is a known health hazard and a critical climate forcer. Recent studies implicate BC as the second-most important climate-forcing agent after carbon dioxide.
- BC is recognized by Climate and Clean Air Coalition (CCAC) as a significant short lived climate pollutant.
- As such, reliable measurement of BC emissions from sources and in the environment is required.
- Real-time mass concentration measurement instruments, including those based on photo-acoustic principles or laser-induced incandescence principles, have been demonstrated many times to have excellent linearity and correlation with BC concentration.
- These instruments often demonstrate biases when engaged in comparisons, likely due to differences between the initial calibration and the instrument response to BC. There is a potential benefit in terms of improved measurement accuracy when instruments are calibrated against an absolute reference for black carbon.

1960's 1980's 2000's

BACKGROUND

- The International Civil Aviation Organization (ICAO) Committee on Aviation Environmental Protection (CAEP) have requested SAE E-31, the Aircraft Exhaust Emissions Measurement Committee, to developing new standards and recommended practices for the measurement of nonvolatile particulate matter (nvPM) mass and number concentration in real time.
- nvPM emissions from aircraft engines are predominantly 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*"[1]



- 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

1. Bond et al., "Bounding the role of black carbon in the climate system: A scientific assessment,"Journal of Geophysical Research – Atmospheres, 118, (2013)

- BC is the most light-absorbing nano-aerosol
- BC absorbs 680x more energy by mass than CO_2
- BC is a key contributor to global warming
- BC effects are stronger in sensitive regions, faster ice and snow melt in the Arctic
- BC mitigation could rapidly slow the rate of climate change, by up to 40% within 20 years

METROLOGY ISSUES

- Traceability
  - many instruments offer no opportunity for traceability
  - filter-based mass can be traceable
    - issues with sensitivity (mass of particulate vs. mass of filter)
    - issues with filter artifacts
      - gaseous adsorption, fibre loss, less than 100% removal efficiency
    - issues with size cutoff
      - impactors and cyclones do not cut sharply at threshold (i.e. PM2.5)
  - number concentration can be made traceable (sort of)
- Reliability and Repeatability
  - difficult to establish
- Uncertainty
  - large uncertainties (can be order of magnitude in number, factor of 2 in mass)
- Reference Materials
  - airborne particulate RMs don't exist
- Representativeness
  - all ex-situ methods suffer from sampling issues
    - how representative is the sample at the measurement location of the airborne particulates?
      - losses, agglomeration, evaporation/condensation
- Measuring properties with different methods
  - most instruments are proprietary
    - each manufacturer implements a different measurement principle
  - difficult to intercompare results obtained with different instruments
  - examples
    - size
      - mobility diameter, aerodynamic diameter, geometric diameter, radius of gyration
    - black carbon mass
      - directly measured, or inferred from optical absorption, extinction, or emission measurements
- Measuring specific properties with a myriad of interferences
  - selectivity
    - how does one measure properties of one component of PM when many others are present?
  - sensitivity
    - atmospheric concentrations are often very low (<1 μg/m3)
  - gas composition
    - can be highly variable
    - can influence measurement
  - morphology
    - spherical particles vs. fractal aggregates
  - single particle vs. ensemble measurements
  - variations over time, elevation, temperature, humidity, sunlight, etc.

METHODS

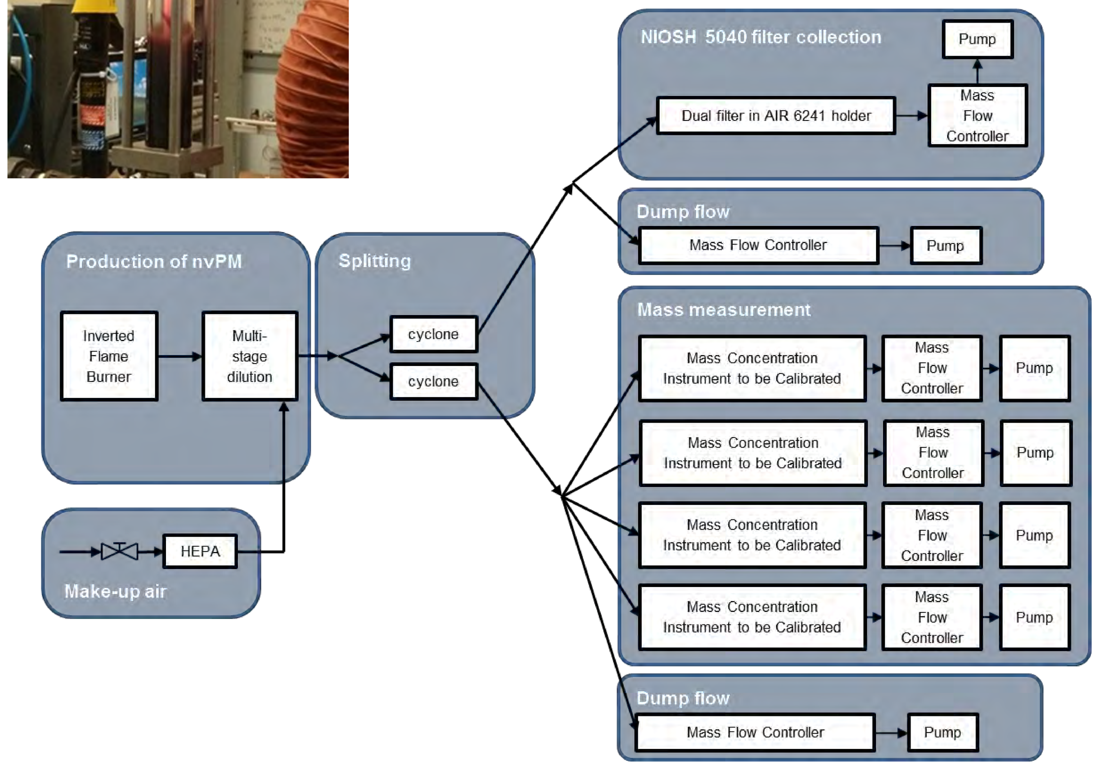
- Two approaches for the calibration of real-time BC mass concentration instruments are presented.
- In both cases, the source is a stable black carbon aerosol source, an inverted flame burner producing a soot aerosol with over 95% elemental carbon (EC).
- The output of this BC source is sampled, passed through a one micron cyclone to remove particles shed from the walls, and split into multiple streams.
- In the first calibration method, the particulate stream is sampled with quartz filter collection, and then analyzed using a thermal/optical method to assess the EC and organic carbon (OC) masses following the NIOSH 5040 standard.
- The second calibration method involves the use of a centrifugal particle mass analyzer (CPMA) in conjunction with an aerosol electrometer to measure the mass concentration of a charged aerosol in real time.

THERMO-OPTICAL METHOD (NIOSH 5040)[2]

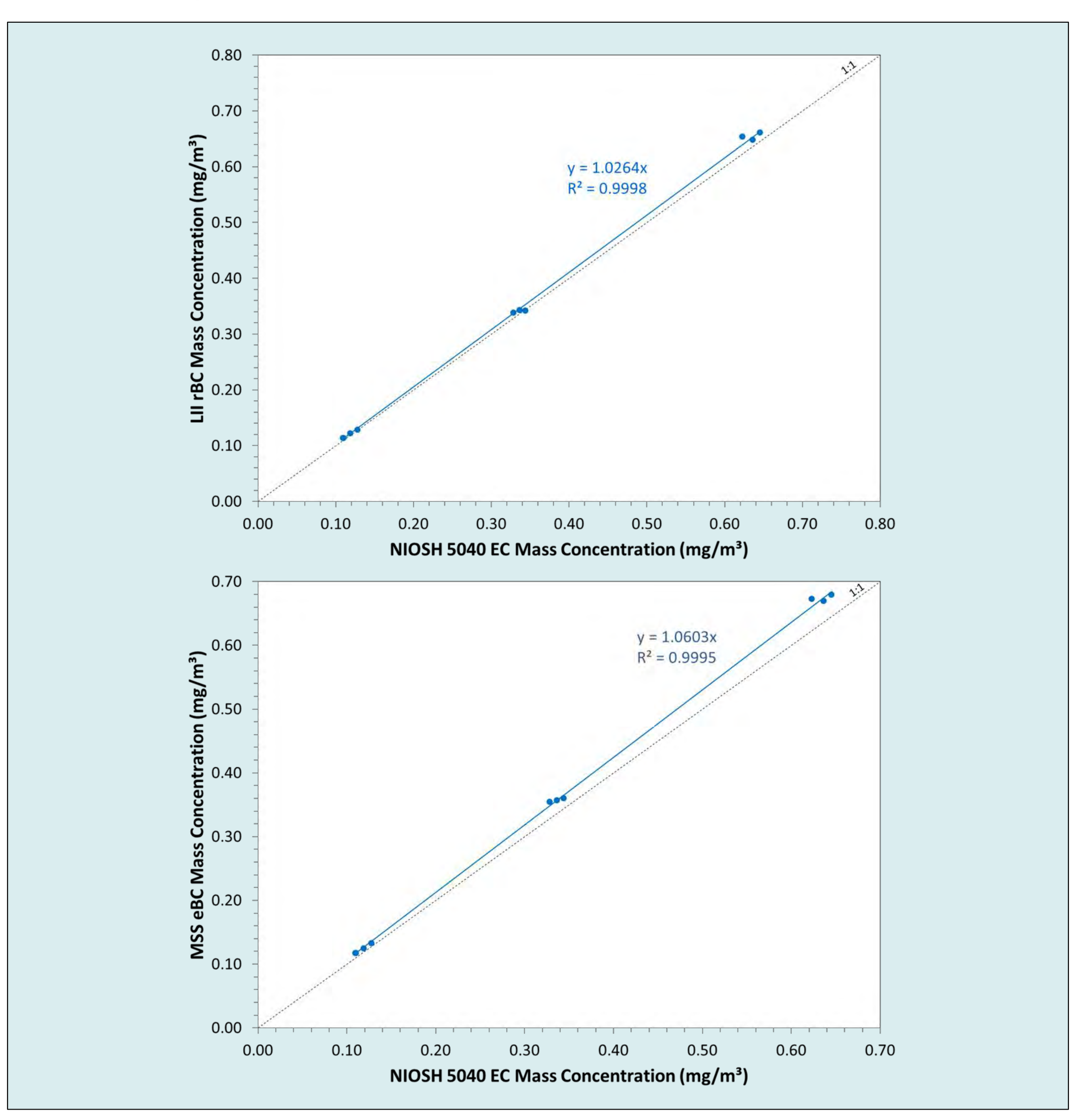
2. SAE AIR6241, "Procedure for the Continuous Sampling and Measurement of Non-Volatile Particle Emissions from Aircraft Turbine Engines," (2013)

- Correlation to EC collected on quartz filters

- Layout
  - 1.0 μm cyclones at 25 SLPM
  - SAE AIR6241 compliant splitters
  - equal length (2.0 m) heated conductive 3/8" tubing from splitters to all measurement devices
  - everything from inlet to first splitter to measurement devices heated to 60 C
  - two stage filter collection in SAE AIR6241 compliant housing
  - inverted flame burner with >95% elemental carbon (EC) PM content



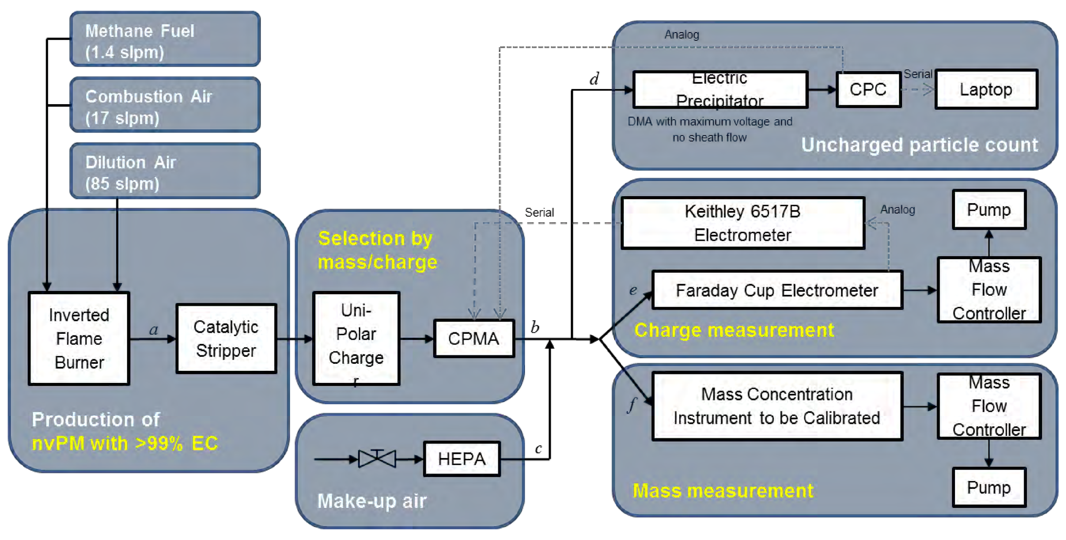
- The Artium LII 300 and AVL MSS measure mass concentration of black carbon suspended in the sample flow in real time.
- Output signals are proportional to mass concentration, but for accuracy the constant of proportionality must be found by calibration
  - SAE E-31 approved method is calibration by the NIOSH 5040 standard, a filter-based method that measures the quantities of organic carbon (OC) and elemental carbon (EC) by reduction to methane and analysis in a flame ionization detector (FID)
  - filter paper measurements are slow and expensive to collect and analyze, need careful handling, and are often subject to sampling artifacts that reduce accuracy



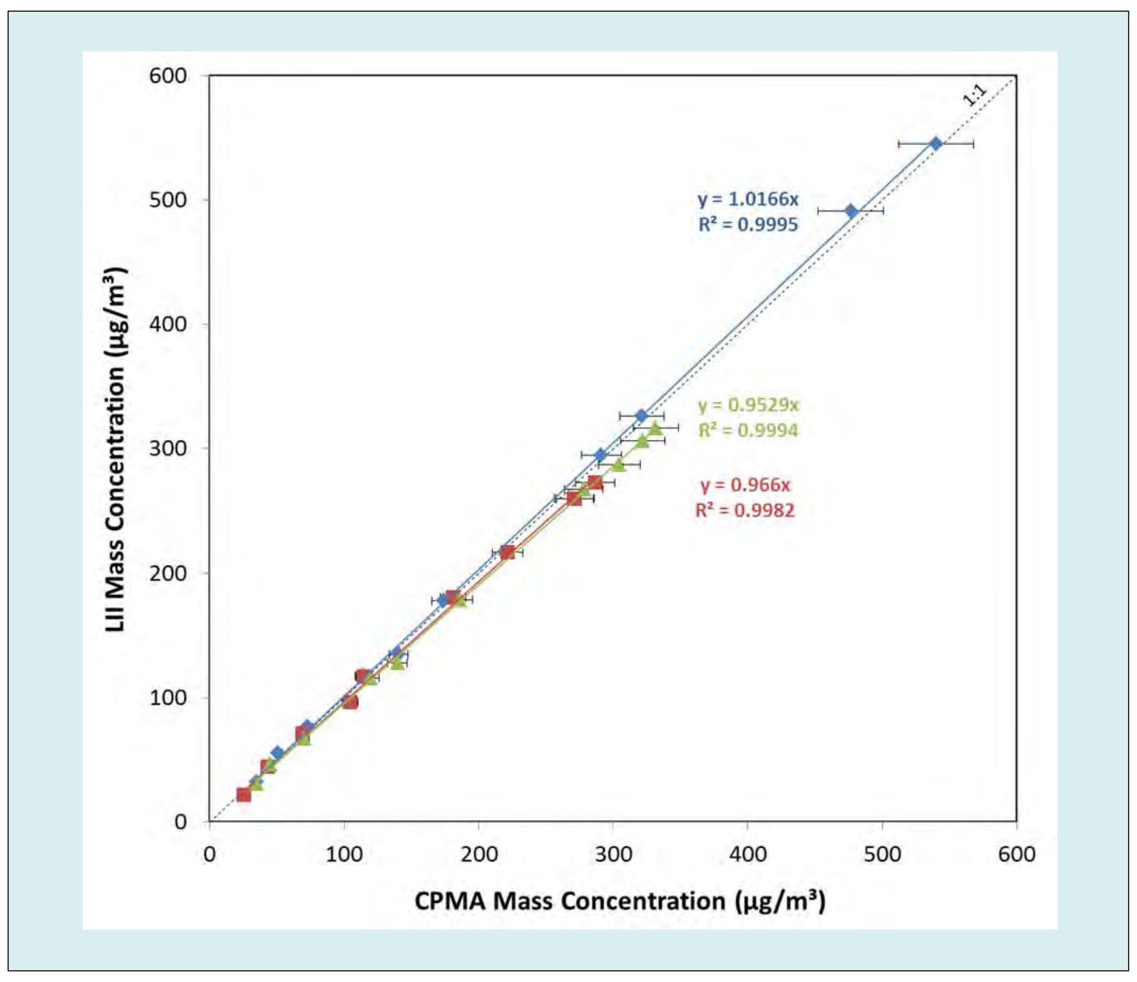
CPMA-ELECTROMETER METHOD[3]

3. Symonds et al., "The CPMA-Electrometer System—A Suspended Particle Mass Concentration Standard," Aerosol Science and Technology, 47:i-iv (2013)

- Traceable – function of rotational speed, voltage, flow rate, current, and electron charge (physics-based approach)
- Uncertainty of ~5%
- 10 point calibration in less than one hour
- Excellent method for low mass concentrations (< 100 μg/m3)



- Investigated potential sources of uncertainty
  - charge on particles appears to have minimal effect on measurements made by mass instruments
  - CPMA resolution setting appears to have minimal effect on measurements
  - improvements to electrometer to reduce noise and to UDAC to improve charging efficiency resulted in reducing overall uncertainty from 8.6% to 5.2% (k=2)
- Experiments so far have demonstrated a range of 1 – 500 μg/m^3



SUMMARY

- Airborne particulate matter has significant, detrimental effects on health, visibility, and climate
  - $PM_{2.5}$ mass concentration measurements, while important, are a poor overall indicator of these effects
- PM metrology is required
  - to improve reliability and repeatability of measurements, and to reduce uncertainty
    - critically important to climate change modelling
    - necessary to improve association between health effects and PM properties
  - for sound policy decisions and regulations
- Quality of measurements and intercomparability need to be improved
  - size and size distribution
  - composition
  - surface area and surface reactivity
  - optical properties (absorption and scattering)
  - mass of smaller size fractions (PM1.0)
- Black Carbon is one of the best PM targets due to co-benefits in reducing climate forcing and improving human health
- SAE AIR6241, employing NIOSH 5040 is an effective method for assessing BC mass concentration
- CPMA-electrometer system is a viable option for calibration of aerosol mass concentration instruments
  - highly linearly correlated
  - lower uncertainty, averaging 5.2% (k=2), and much quicker than NIOSH 5040 method

OUR PARTNERS

UNIVERSITY OF ALBERTA