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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]
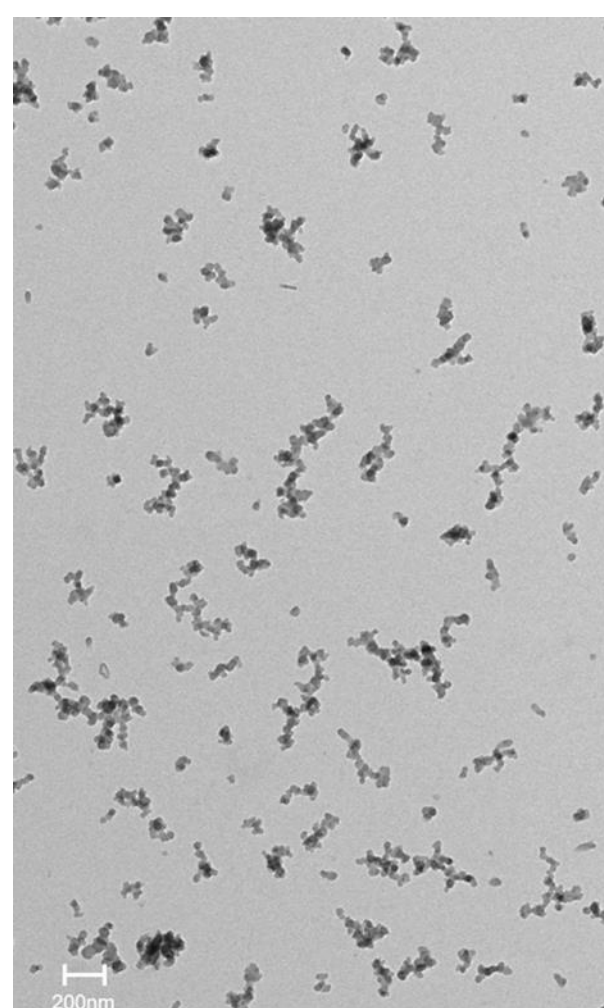
- strongly absorbs visible light
- is refractory with a vaporization temperature near 4000 K
- exists as an aggregate of small spheres
- is insoluble in water and common organic solvents
  1. Bond et al., "Bounding the role of black carbon in the climate system: A scientific assessment," Journal of Geophysical 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
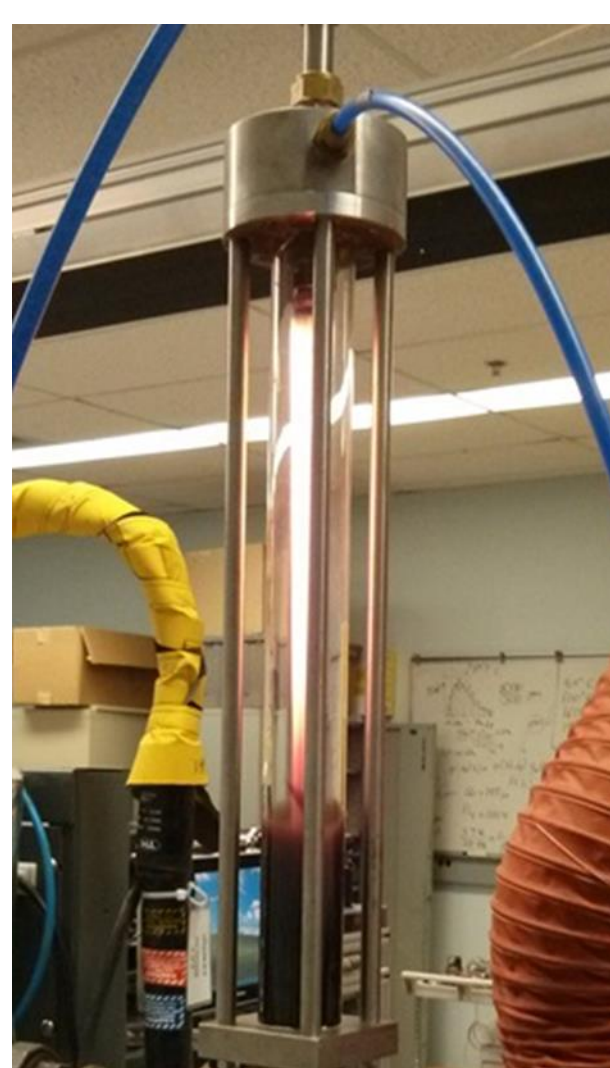
- Layout
  - 1.0 µm cyclones at 25 SLPM
  - SAE AIR6241 compliant splitters
  - equal length (2.0 m) heated conductive 3/8" tubing from splitters to all measurement devices
  - everything from inlet to first splitter to measurement devices heated to 60 C
  - two stage filter collection in SAE AIR6241 compliant housing
 - inverted flame burner with >95% elemental carbon (EC) PM content
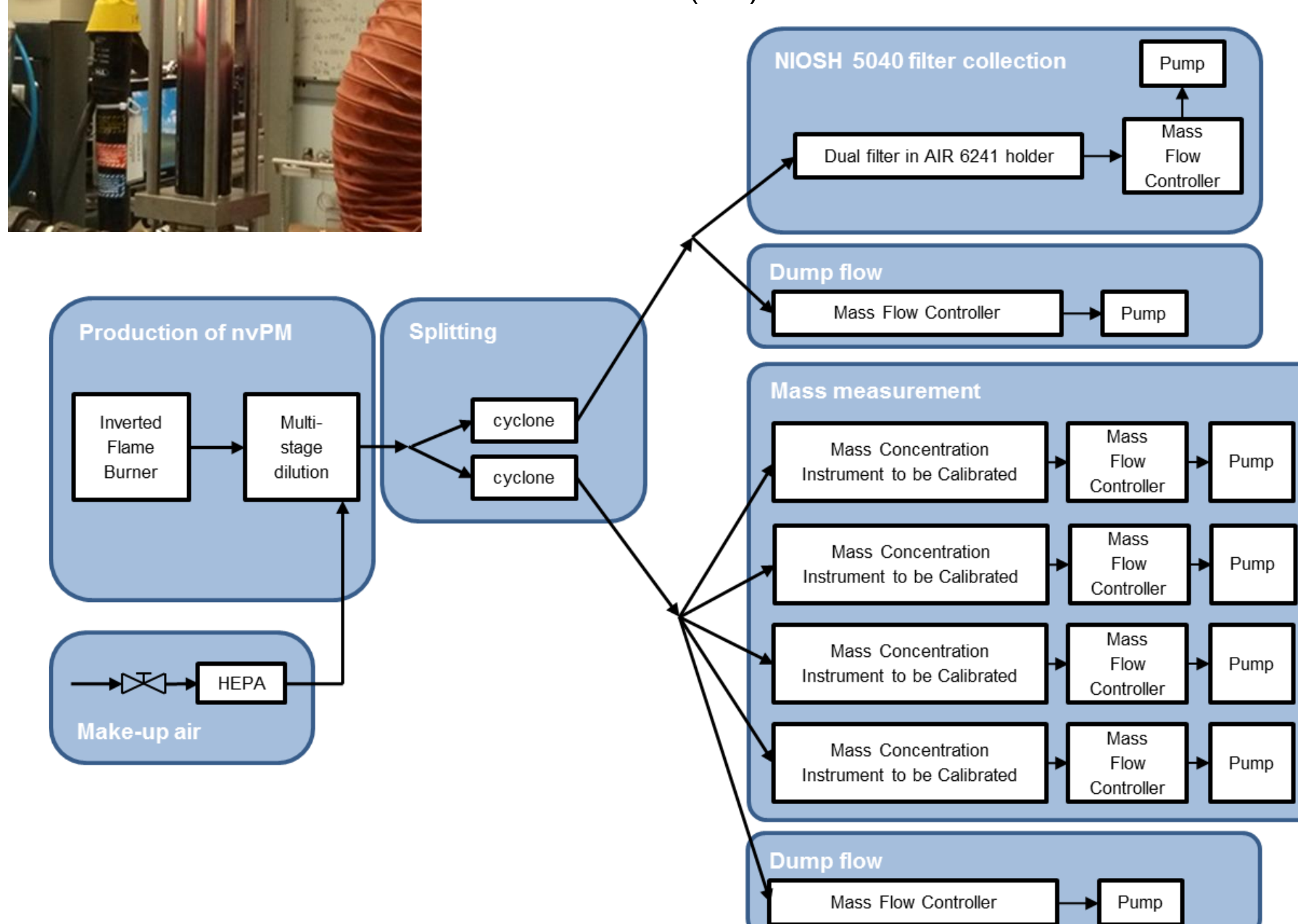
- The Artium LII 300 and AVL MSS measure mass concentration of black carbon suspended in the sample flow in real time.
- Output signals are proportional to mass concentration, but for accuracy the constant of proportionality must be found by calibration
  - SAE E-31 approved method is calibration by 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
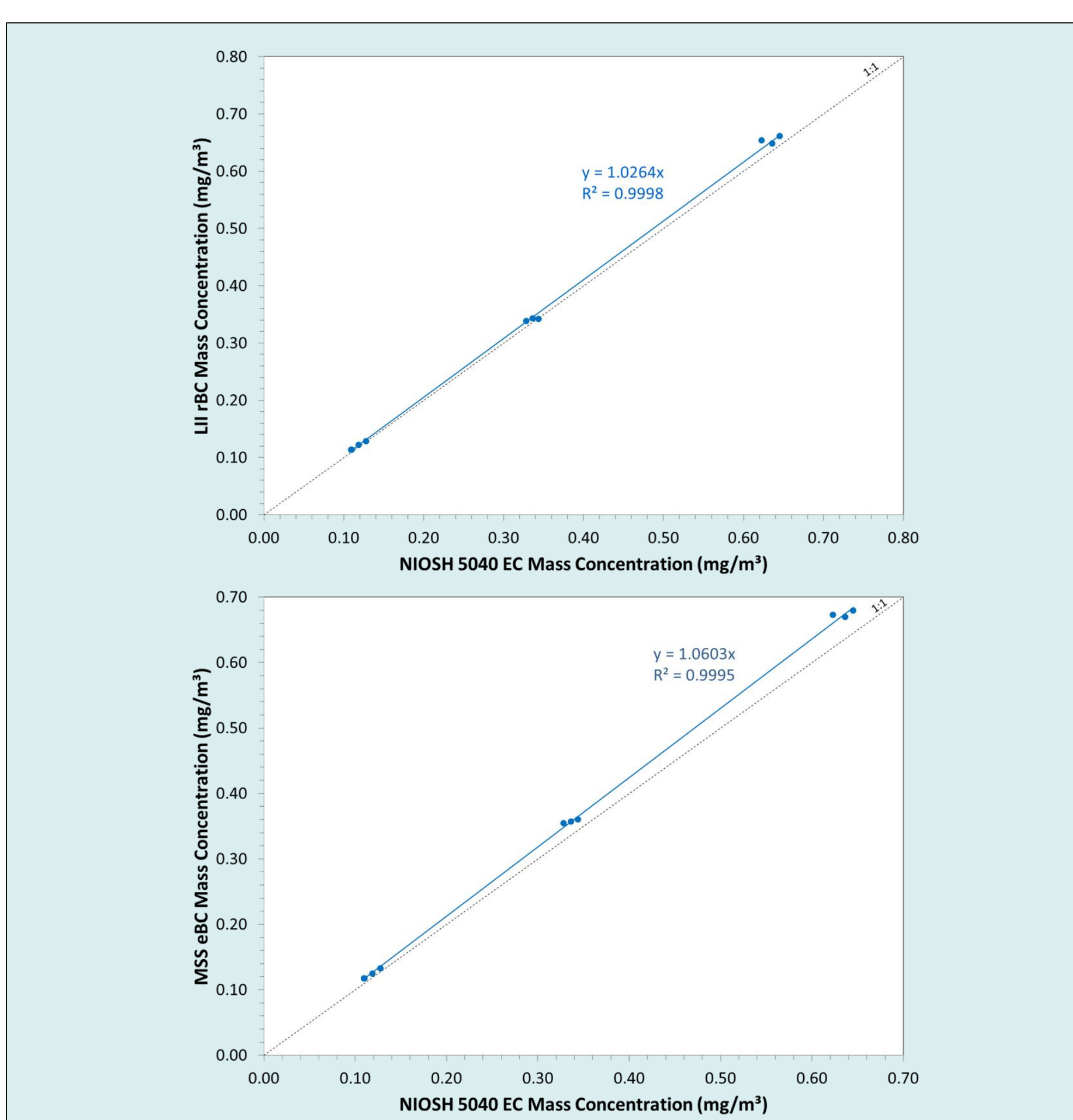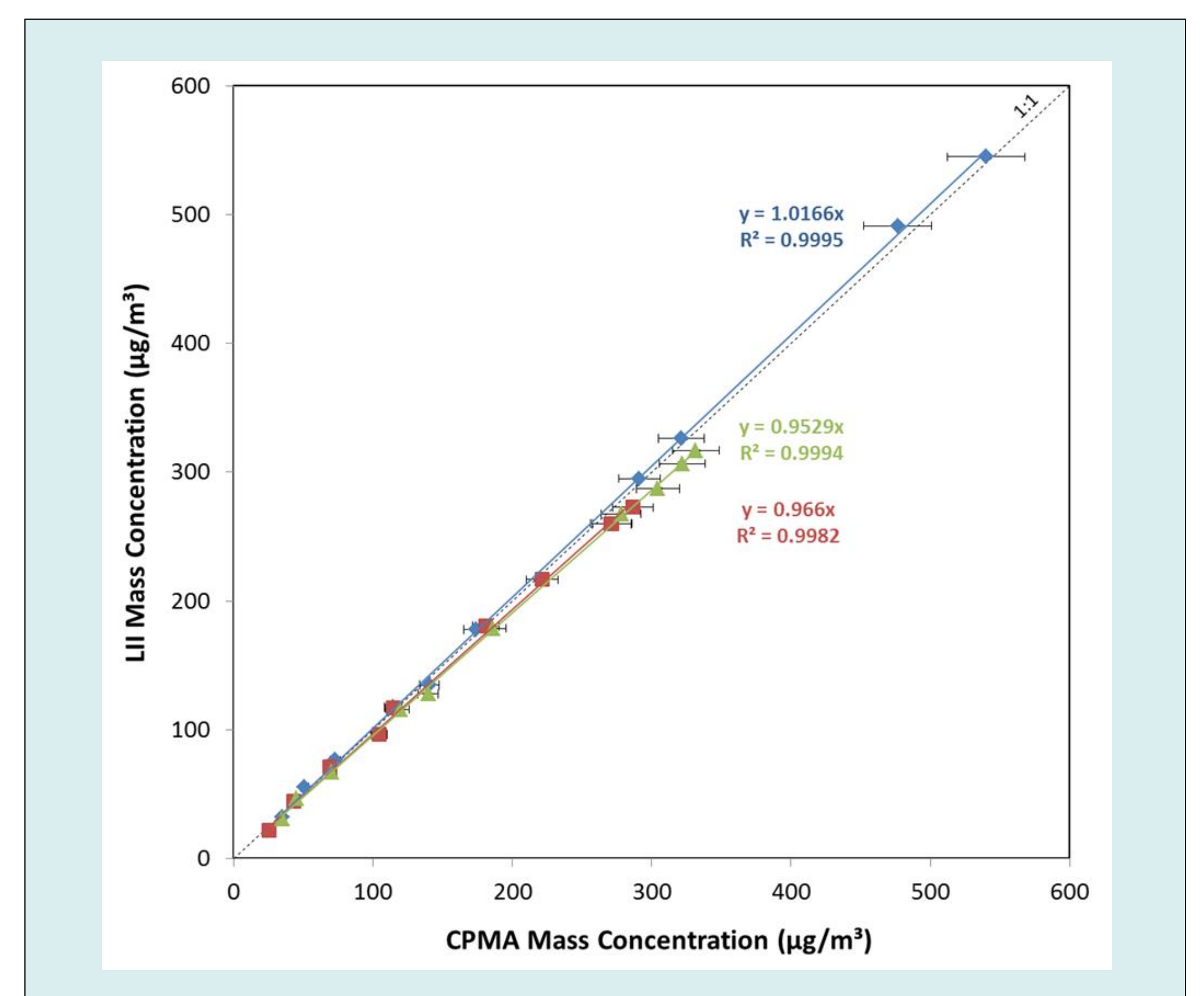
CPMA-ELECTROMETER METHOD[3]

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)
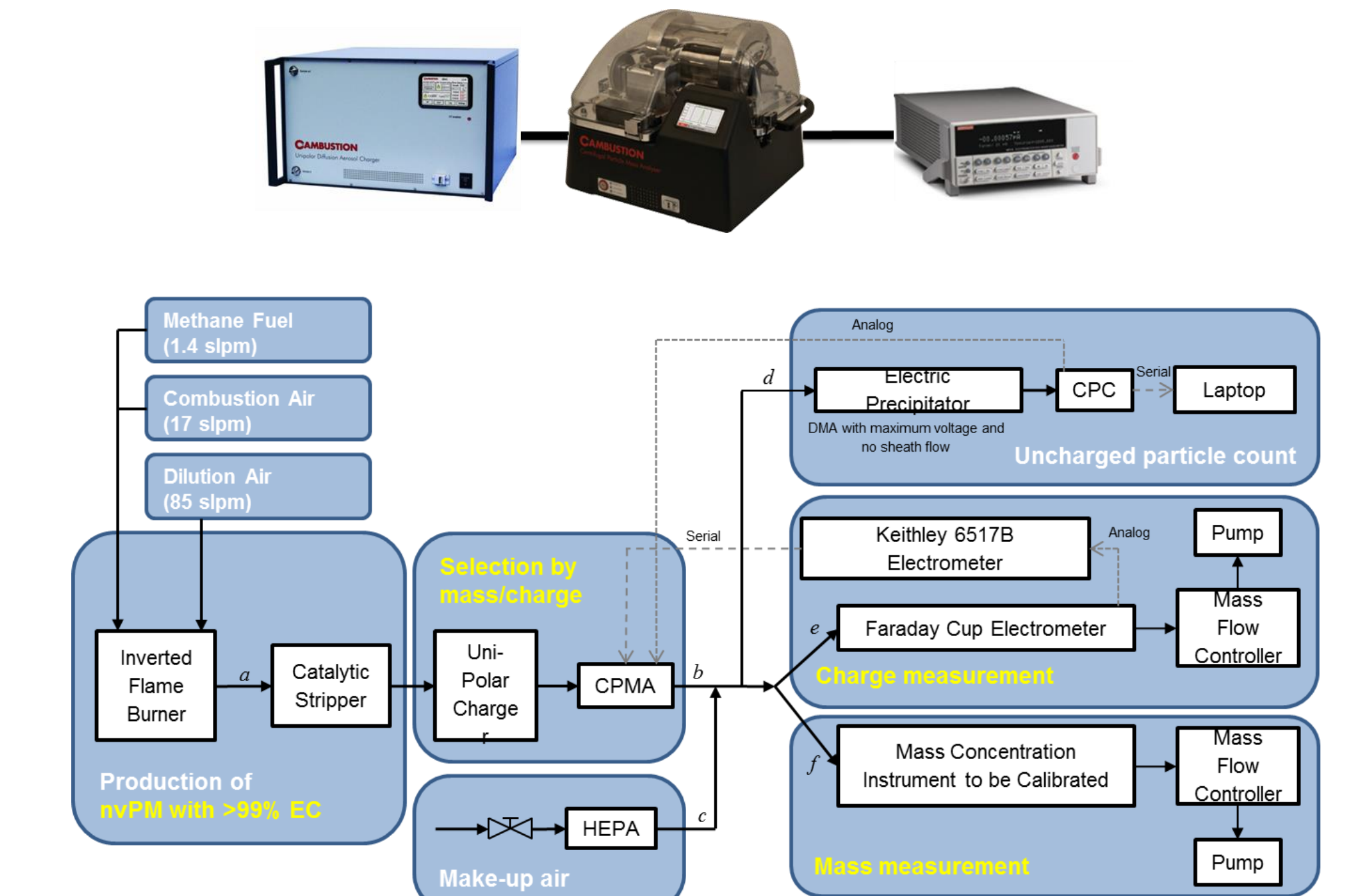
- Investigated potential sources of uncertainty
  - charge on particles appears to have minimal effect on measurements made by mass instruments
  - CPMA resolution setting appears to have minimal effect on measurements
  - improvements to electrometer to reduce noise and to UDAC to improve charging efficiency resulted in reducing overall uncertainty from 8.6% to 5.2% (k=2)

- Experiments so far have demonstrated a range of 1 – 500 µg/m3

$y = 1.0166x$
$R^2 = 0.9995$

$y = 0.9529x$
$R^2 = 0.9994$

$y = 0.966x$
$R^2 = 0.9982$

LII Mass Concentration (µg/m³) vs. CPMA Mass Concentration (µg/m³)

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

$y = 1.0264x$
$R^2 = 0.9998$

LII nBC Mass Concentration (mg/m³) vs. NIOSH 5040 EC Mass Concentration (mg/m³)

$y = 1.0603x$
$R^2 = 0.9995$

MSS eBC Mass Concentration (mg/m³) vs. NIOSH 5040 EC Mass Concentration (mg/m³)

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