Calibration of Black Carbon Instruments with the CPMA-Electrometer Reference Mass Standard (CERMS)

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Outline

Background
• techniques for measuring black carbon (BC)
• standards for aerosol instrument calibration
• the CPMA-electrometer reference mass standard (CERMS)

Results
• calibration of a number of instruments
• calibration of an instrument with a number of sources

Mass closure
• demonstration of mass closure when compared to elemental carbon (EC) from thermal optical analysis (TOA)

Summary
Techniques for measuring black carbon (BC)

A non-exhaustive list of methods/instruments for measuring BC

Aerosol absorption methods
- CAPS PMssa

Photoacoustic methods
- PAX, MSS, PASS

Filter-based methods
- MAAP, PSAP, Aethalometer

Evolved carbon methods
- TOA

Laser-induced incandescence
- LII 300, SP2

The reported values depend both on the characteristics of the source particles used in the calibration and the reference method applied, neither of which are unique or traceable.

- equivalent black carbon (eBC)
- elemental carbon (EC)
- refractory black carbon (rBC)
Calibration of Condensation Particle Counters

\[ N = \frac{I}{Q e} - N_{\text{multiply-charged}} \]

- charge
- classify
- compare to reference

Measures the current, \( I \), which is proportional to number of charges detected.
CPMA-electrometer reference mass standard (CERMS)

\[ m_{total} = m_0 + M_1 I / Q_e \]

- charge
- classify
- compare to reference

Centrifugal Particle Mass Analyzer (CPMA)

CPMA mass/charge setpoint depends on three traceable parameters:
• rotational speed (traceable)
• voltage (traceable)
• radial dimensions of the classifier
  • (optional traceable gauging certificate available from Cambustion)

Unlike a DMA, the setpoint does not depend upon the gas properties (such as viscosity and mean free path) or ambient conditions (temperature and pressure)

Classification not affected by particle morphology or composition

\[
M_1 = \frac{M}{N_q} = \frac{eV}{\left(\frac{r_o + r_i}{2}\right)^2 \omega^2 \ln\left(\frac{r_o}{r_i}\right)}
\]

Image from Jon Symonds, Cambustion
Benefits of CERMS

All aspects of the CERMS technique are traceable to the SI Measurement of a well-defined quantity: total post-CPMA suspended PM mass

CERMS has low uncertainty\(^1\)
- Repeatability was 1.1\% (k = 1)
- Intermediate precision was 2.1\% (k = 1)
- Resulting uncertainty (coverage factor, k = 2) was 3.0\%

Rapid (<2 hours experiment time) with potential for same day determination of calibration factor

Additional benefits for determining aviation engine emissions BC mass
- Demonstrated to low concentrations (1 µg/m\(^3\))
- on-site calibration
- gas turbine engine as the source of BC emissions

CERMS apparatus for calibration with lab soot generator

- **Input Air**: 7.5 lpm
- **Propane**: 0.0625 lpm
- **Mini-Inverted Soot Generator (MISG)**
  - **350 °C Catalytic stripper**
  - **80°C heated line**: 5.5 lpm

**Aerosol Generation**

**Unipolar Diffusion Aerosol Charger (UDAQ)**

**Centrifugal particle mass analyzer (CPMA)**

**TSI E3088B electrometer**

**Dilution Air**: 1.5-7 lpm

**BC Mass Instrument**

**BC Mass Instrument Under Calibration**

**Filters for determining EC/TC and fC**

**Quartz filter**

**Quartz filter**

**Bypass lines**

**Teflon filter**

**Quartz filter**

**Pump**: 5 lpm
Calibration of LII 300 determined from CERMS with lab soot from MISG

When referenced to denuded soot (nvPM):

\[ rBC = (0.78 \pm 0.05) \cdot \text{nvPM}_{\text{CERMS}} + (0.2 \pm 0.1) \]

- \( rBC \) is refractory black carbon (LII 300)
- residuals are in the range of \( \pm 0.1 \, \mu g/m^3 \)
- fit intercept nearly zero (below the LOD of the instrument)
- note that for this source, the effect of the catalytic stripper (VPR) is negligible
Calibration of PAX determined from CERMS with lab soot from MISG

When referenced to nvPM,

\[ eBC = (0.999 \pm 0.001) \cdot \text{nvPM}_{\text{CERMS}} - (1.05 \pm 0.02) \]

- eBC is equivalent black carbon (i.e., calculated from absorption measurements with light-absorption-per-gram assumed as 7.5 m² g⁻¹ at 550 nm)
- > 2 µg eBC m⁻³, the calibration verifies the traditional optical PAX calibration
- < 2 µg eBC m⁻³, RH-related baseline problems become evident: CERMS provides the LOD of the instrument
Calibration of LII 300 and MSS determined from CERMS with soot from large inverted burner
CERMS Apparatus for calibration of a mass instrument on a gas turbine engine

**Diagram Description**

- **Heated Dilution Air** enters the system.
- **350 °C Catalytic Stripper**.
- **Unipolar Diffusion Aerosol Charger (UDAQ)**
- **Centrifugal Particle Mass Analyzer (CPMA)**
- **TSI E3068B Electrometer**
- **BC Mass Instrument**
- **Filters for determining EC/TC and f_c**
- **Aerosol Generation**
- **Aerosol Classification**
- **SI-Traceable Mass Quantification**
- **BC Mass Instrument Under Calibration**
Calibration of MSS+ with CERMS using a gas turbine engine as the source – nvPM

Calibration Factor

- Calibrated using the CERMS approach in under 2 hours, on-site at an OEM test cell
- For this MSS+, using the Gnome gas turbine engine as the source, the slope relating the LII response to nvPM is 0.96 ± 0.04 with a small offset due to baseline effects

Graph showing linear fit with intercept and slope values,
Linear fit ± 10%
Intercept = 3.6 ± 1.2
Slope = 0.96 ± 0.04
 Calibration of LII 300 with CERMS using a gas turbine engine as the source – \( \text{nPM} \)

**Calibration Factor**

- Calibrated using the CERMS approach in under 2 hours, on-site at an OEM test cell
- For this LII 300, using the Gnome gas turbine engine as the source, the slope relating the LII response to \( \text{nPM} \) is \( 0.63 \pm 0.02 \)
Calibration of LII 300 with TOA using Gnome as the source – EC

Calibration Factor
• Determined using the SAE ARP6320\(^1\) method using EC collected on filters and thermal-optical analysis
• For the same LII 300, using the Gnome gas turbine engine as the source, the slope relating the LII response to EC is \(0.68 \pm 0.02\)

\[\text{Slope} = 0.679 \pm 0.016 \quad \text{Correlation} = 0.9982\]

\(^1\)SAE ARP6320 - Procedure for the Continuous Sampling and Measurement of Non-Volatile Particulate Matter Emissions from Aircraft Turbine Engines, 2018
Demonstration of Closure Between CERMS and PM Mass from TOA

Compare total PM mass from TOA to that from CERMS

- thermal-optical analysis (TOA) measures total carbon mass (TC), and operationally defines OC and EC fractions
- VOC contamination of the TOA filter was subtracted
- division of TC into OC and EC is often poorly defined for combustion samples
- as TC does not include all elements present in nvPM samples, it can be converted to total PM mass concentration
- %C is the mass fraction of carbon in the PM measured by elemental analysis (EA), $f_C$

Summary

CERMS (CPMA-Electrometer Reference Mass Standard) has been demonstrated for rapid, low uncertainty calibration of a range of BC instruments using a number of BC sources

This study has successfully demonstrated operation of a CERMS calibration of mass instruments using a gas turbine engine as the source

- Rapid (<2 hours experiment time) with same-day determination of calibration factor
- May be performed on-site
- Sensitive to very low concentrations, relevant to nvPM mass concentrations from modern gas turbine engines
- Instrument responses are linear with respect to CERMS regardless of instrument detection methodology or source
The **CPMA** classifies particles by mass/charge ratio

An aerosol **electrometer** measures total particulate charge, so a **CPMA-electrometer** measures total particulate mass.
What about uncharged particles?

They are generally close to zero, even so, they can be directly measured using an electrostatic precipitator to remove charged particles.

Measures the current, $I$, which is proportional to number of charges detected.

Particle source

- Unipolar charger
- Centrifugal Particle Mass Analyzer
- Aerosol electrometer
- Electrostatic Precipitator
- Mass instrument to calibrate
- Pump