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Metrology for Aerosol Emissions from Hydrocarbon Sources

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Overview

Context

Issues for Measurement of Aerosol Particles

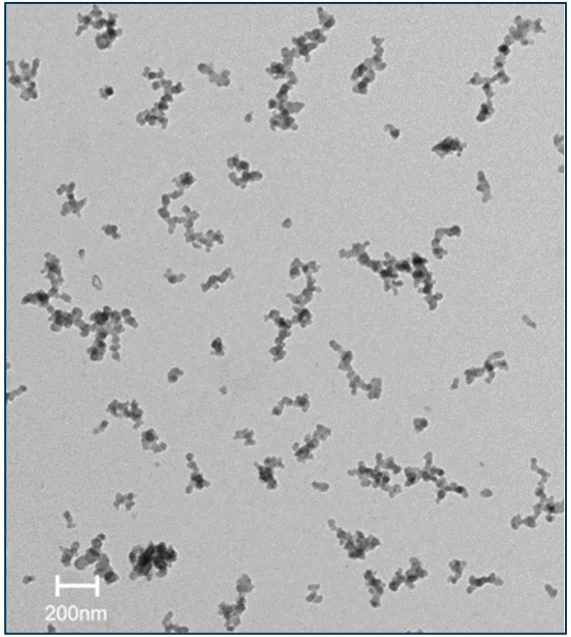
Focus on Mass and Absorption

Current method for mass – TOA (thermal optical analysis)

CERMS (CPMA-electrometer reference mass standard)

Size-dependent MAC (mass absorption cross-section)

Outlook



ABOVE TEM image of combustion-generated particles

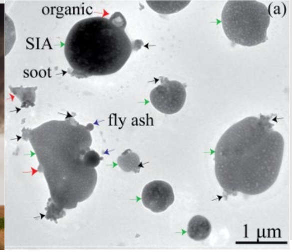
Aerosol Emissions from Hydrocarbon Combustion

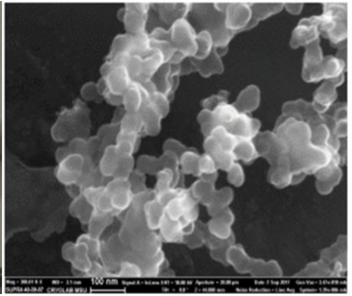
Anthropogenic and biogenic sources

- Fossil fuel combustion, biofuel combustion
  - Road and off-road vehicles, ships, rail, aircraft, industry, heating, cooking, wildfires, etc.

Primary emissions are black carbon, organic, and ash particles

- Can also lead to secondary aerosols through condensation of sulphates, nitrates, etc. and atmospheric photochemistry to produce secondary organic aerosols (SOA)





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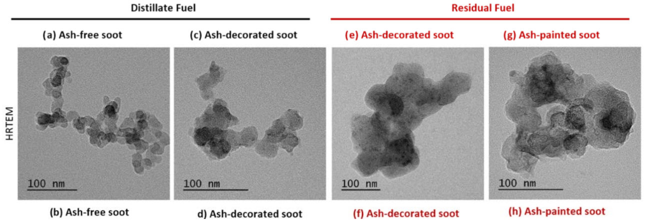


Biomass burning: Image sources here and here
Flare: image source here
Ships: image sources here and here

Aerosol Impacts

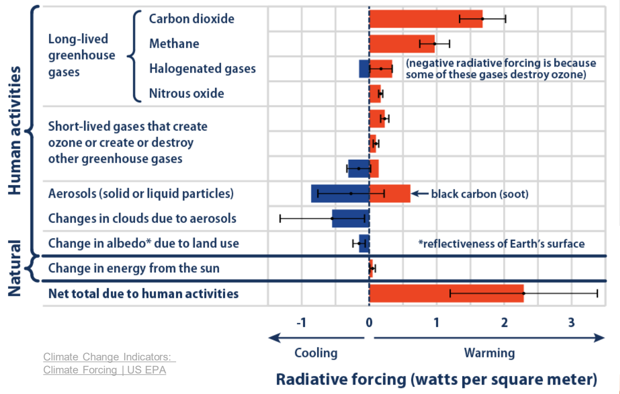
Climate Change

- positive forcing due to absorption (black carbon)
- negative forcing due to scattering (all atmospheric aerosols)

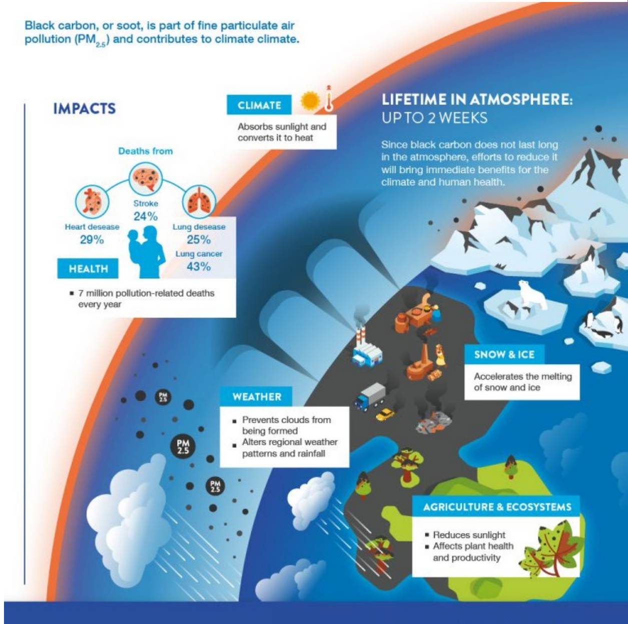
Health

Air Quality


Air quality: differences in visibility due to aerosols



Climate Change Indicators: Climate Forcing | US EPA



www.ccacoalition.org/en/slcps/black-carbon

Aerosol Impacts

Climate Change

- positive forcing due to absorption (black carbon)
- negative forcing due to scattering (all atmospheric aerosols)

Health

Air Quality

What needs to be measured?

- **mass concentration**
- number concentration
- size and size distribution
- composition
- surface area and surface reactivity
- internal structure (crystallinity)
- optical properties (**absorption** and scattering)

Many Methods to Measure Aerosol Nanoparticles

Filter based/offline methods

- gravimetric
- thermal optical analysis
- surface enhanced Raman

Single particle methods

- condensation particle counter
- scanning mobility particle sizer
- differential mobility analyzer
- centrifugal particle mass analyzer (CPMA)

Filter/optical methods

- smoke number
- aethalometer
- multi-angle absorption photometer

Aerosol/optical/real time methods

- laser-induced incandescence (LII)
- cavity attenuation phase shift PM single-scattering albedo (CAPS PMssa)
- photoacoustic extinctiometer (PAX)

Microscopy

- TEM, SEM, AFM

Measurement Issues for Aerosol Particles (I)

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. $PM_{2.5}$)

number concentration can be made traceable

- ISO/FDIS 27891 - Aerosol particle number concentration -- Calibration of condensation particle counters

Measurement Issues for Aerosol Particles (II)

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 – diffusion, thermophoretic, impaction, inertial,…
    - agglomeration
    - evaporation/condensation

Measurement Issues for Aerosol Particles (III)

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

Measurement Issues for Aerosol Particles (IV)

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.

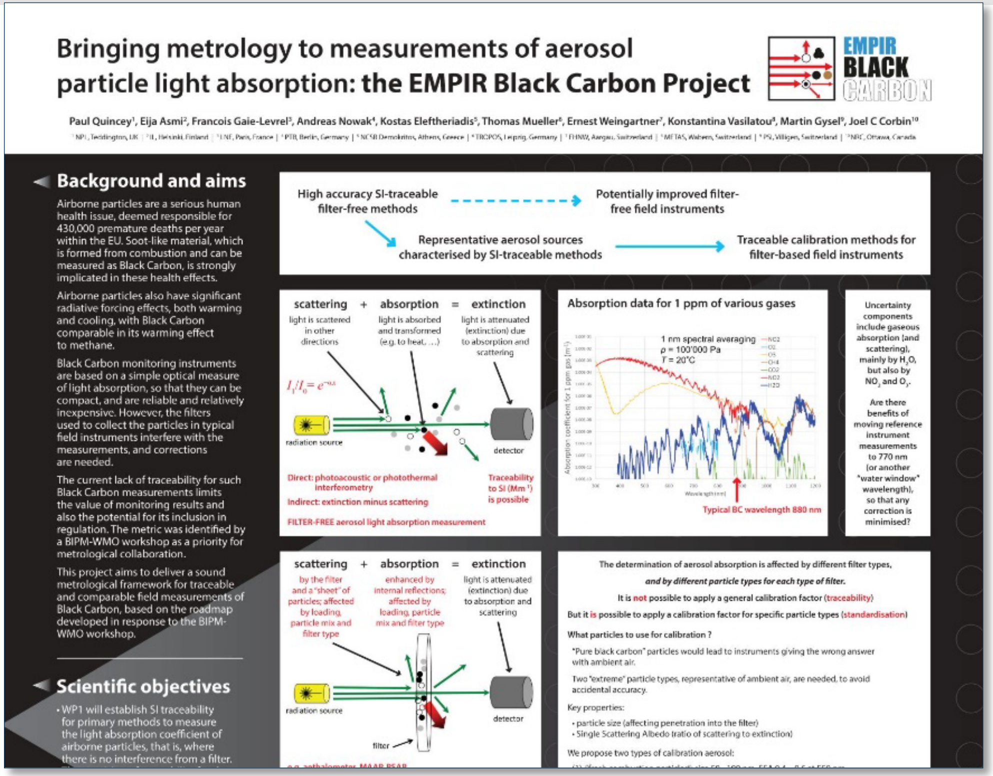
EMPIR Black Carbon (BC Traceability by NMIs)

Outcomes:

Lack of SI traceable calibration sources for absorption (WP1) impacted the project's course and WP2 and WP3 could not be fulfilled

Work was done on these packages, but could not be firmly placed on a metrological basis

A need for SI traceable calibration sources for absorption remains

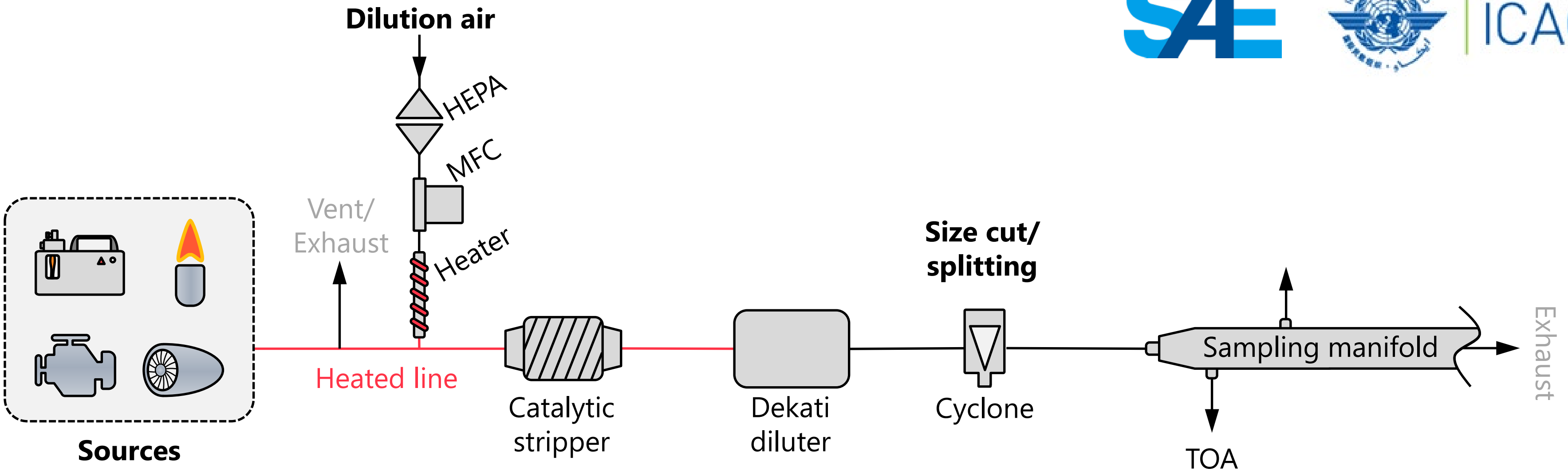


Current method for calibration of instruments for black carbon mass concentration

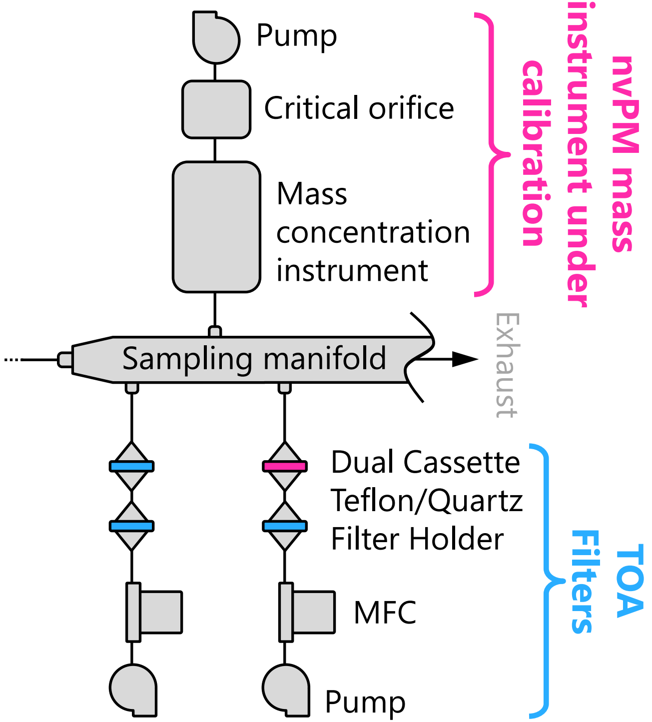
For aircraft engine emissions, particles that remain condensed at 350°C are defined as nonvolatile particulate matter (nvPM)

- Similar to solid PM as defined by Particulate Measurement Programme (PMP) in EU
- Conventional method for calibration is to relate mass concentration as determined by black carbon mass concentration instruments to elemental carbon (EC) as determined by thermal optical analysis (TOA)
  - nvPM mass ≈ black carbon (BC) mass
- Calibration method assumes that nvPM mass concentration ≈ EC mass concentration
  - Does not account for mass of bound O and H in BC carbon matrix
  - Does not account for mass of organics that remain on surface of BC particles

Calibration of BC Mass Concentration Instruments – Sampling Apparatus



Calibration of BC Mass Concentration Instruments – TOA Filter Collection Apparatus



nvPM mass instrument (nvPMmi) calibration

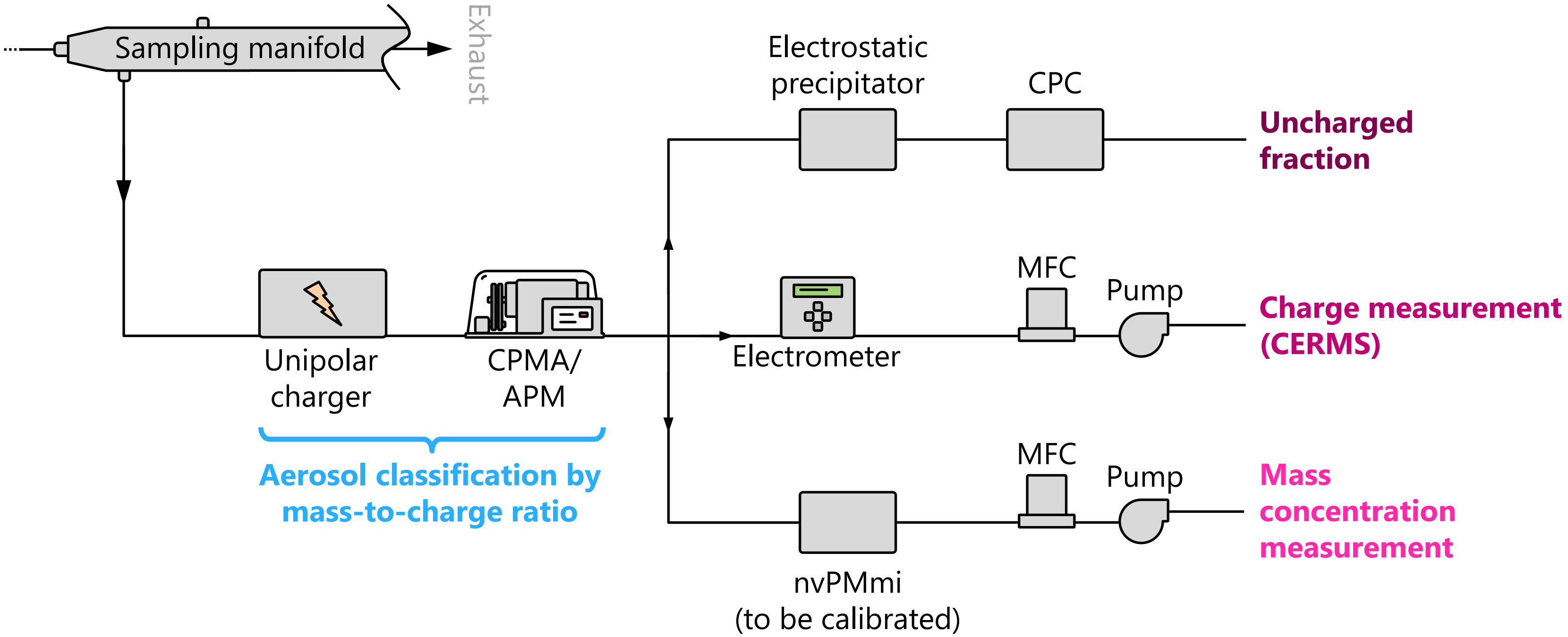
- Nonvolatile particulate matter (nvPM) mass concentration calibrated using elemental carbon (EC) as determined by thermal optical analysis (TOA) as the reference
- Accepted as a certification requirement for aircraft engine emissions by ICAO and adopted by governments worldwide

This is the conventional approach

- Measurement of mass concentration 50 – 500 µg/m^3
- Relative expanded uncertainties (95% confidence level) of 15-20 %
- Particle diameter range: 10 nm – 1 µm mobility diameter
- Standardized as SAE ARP6320A (2021)

But no CMCs

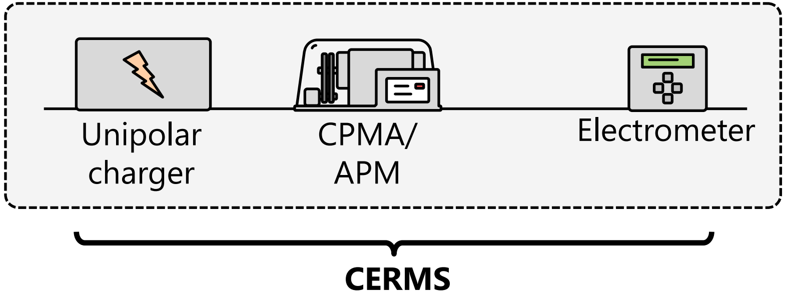
Development of Aerosol Mass Calibration at NRC: CPMA-Electrometer Reference Mass Standard



Development of Aerosol Mass Calibration at NRC

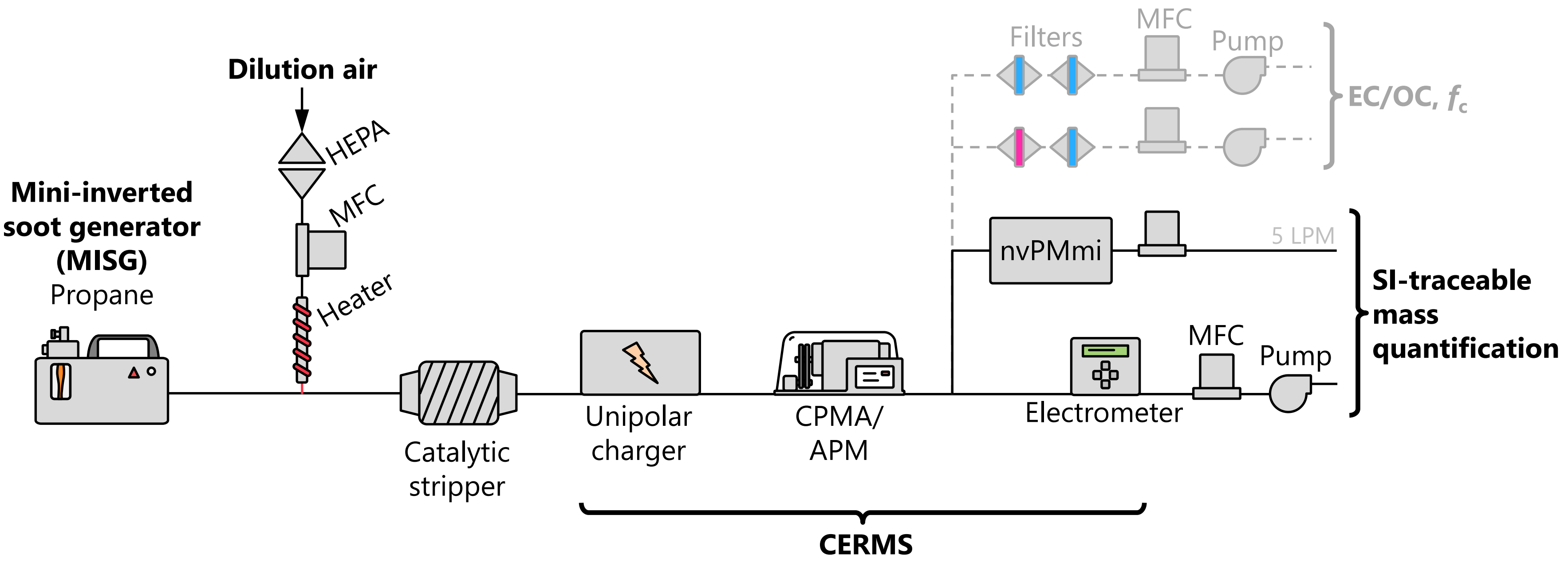
CPMA-Electrometer Reference Mass Standard (CERMS)

- Demonstrated for black carbon (BC) mass concentration instruments:
  - Artium Technologies LII 300, DMT PAX, AVL MSS
- An ILC is planned for March 2023 with NRC, University of Alberta, and Missouri University of Science and Technology
- Plan to test forthcoming NMIJ mass calibrated sphere reference material



1. J. Titosky et al. (2019). Aerosol Science and Technology. doi:10.1080/02786826.2019.1592103
2. J. C. Corbin et al. (2018) 10th International Aerosol Conference, Poster 13CB.5.
3. M. Dickau et al. (2015) Aerosol Science and Technology, doi:10.1080/02786826.2015.1010033

Development of Aerosol Mass Calibration at NRC: Mass Closure with Conventional TOA Method



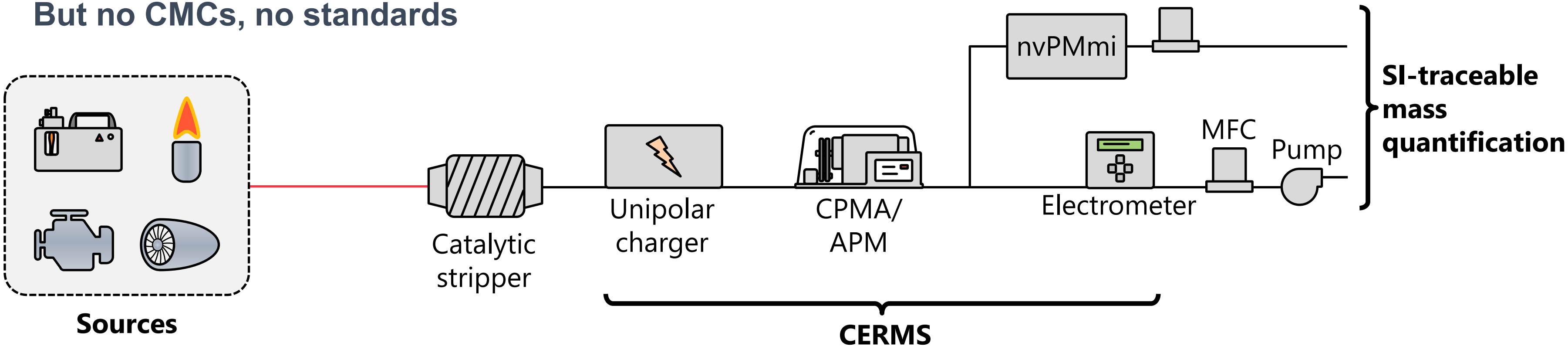
1. J. Corbin et al. (2020) Aerosol Science and Technology. doi:10.1080/02786826.2020.1788710

Development of Aerosol Mass Calibration at NRC: Status

State of the art

- Traceable measurement of mass concentration in the range 0.1 – 500 µg/m^3
- Relative expanded uncertainties (95% confidence level) of 3-5 %
- Particle diameter range: 10 nm – 1 µm mobility diameter,

But no CMCs, no standards



Example calibration with CERMS using an aircraft engine as the source

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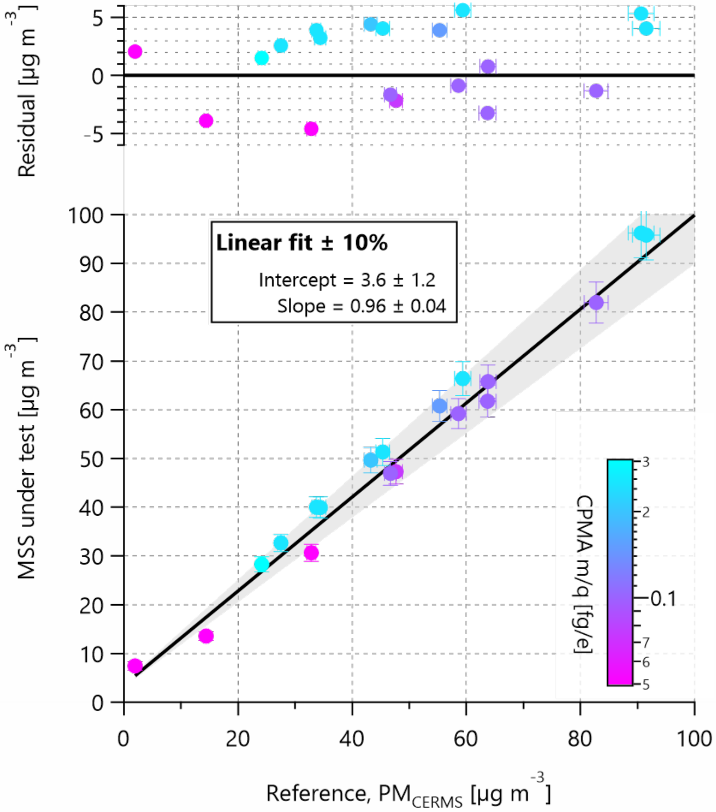
Calibration Factor

- Calibrated using the CERMS approach in under 2 hours, on-site at an OEM test cell
- For this instrument, using an aircraft gas turbine engine as the source, the slope relating the MSS response to nvPM is 0.96 ± 0.04, with an intercept of 3.6 ± 1.2 μg/m^3



Calibration Method Uncertainty

CERMS has uncertainty = 3%

- Repeatability was 1.1% (k = 1)
  - several measurements with same instrument, same lab, same operator, short period of time
- Intermediate precision was 2.1% (k = 1)
  - several measurements with different instrument, different lab, same operator, long period of time
- Resulting uncertainty (coverage factor, k = 2) was 3.0%

TOA has uncertainty = 20%

- Same laboratory variability is 13% (k = 2)
- Laboratory-to-laboratory variability is 16% (k = 2) from interlaboratory comparison of 20 filters
- Combined uncertainty (coverage factor, k = 2) is 20%

CERMS has significantly lower uncertainty than TOA

Aerosol Absorption:
MAC (mass absorption cross-section)

MAC

$$\frac{\text{Absorption coefficient}}{\text{Mass concentration}} = \frac{\beta_{abs}}{M}$$

EC

(poorly defined)

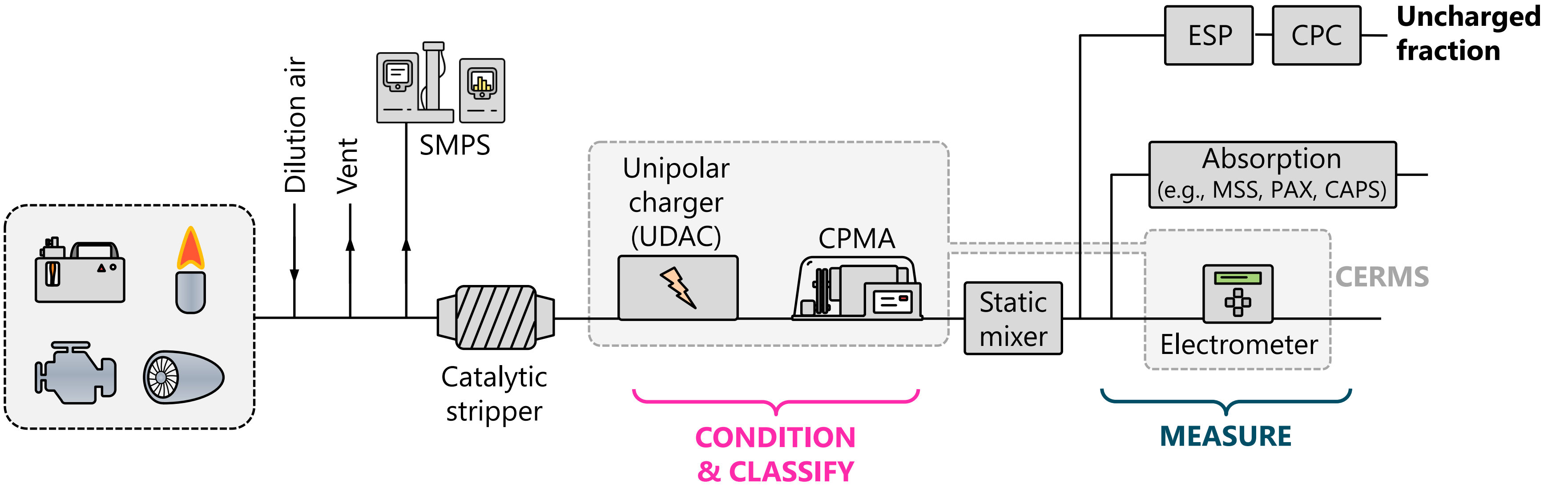
$$\frac{\beta_{abs}}{M_{EC}}$$

Soot

(most common)

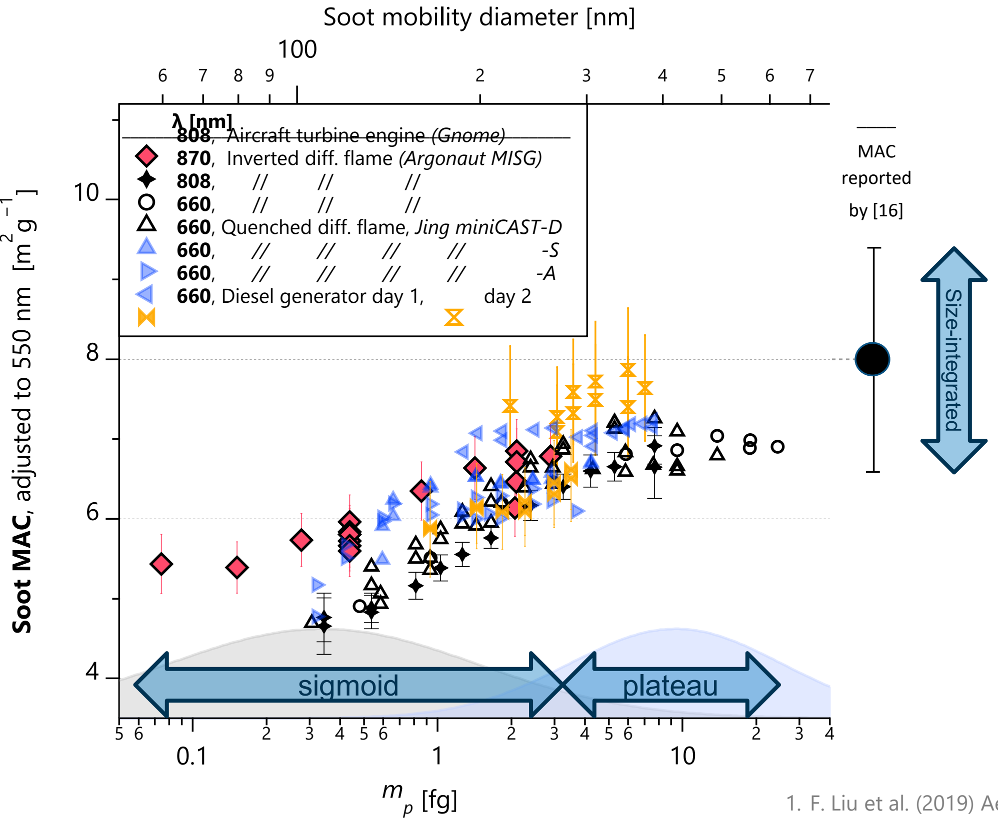
$$\frac{\beta_{abs}}{M_{nvPM}}$$

Determination of mass absorption cross-section (MAC) – size dependence



1. J. C. Corbin et al. (2022) Carbon. https://doi.org/10.1016/j.carbon.2022.02.037

Measured MAC for four aerosol sources



- consensus value of MAC[1]
  - **8.0 ± 1.4 m²/g** at 550 nm (k=2)
- size-resolved MACs observed for multiple diffusion flames and real-world sources
- trends vary between sources
- effect has largest impact for smallest soot particles (i.e., aviation, new automotive)
- not predicted by any literature hypothesis
- smaller MAC at smaller sizes is attributed to decreased soot maturity (degree of graphitization)

1. F. Liu et al. (2019) Aerosol Science and Technology. doi:10.1080/02786826.2019.1676878

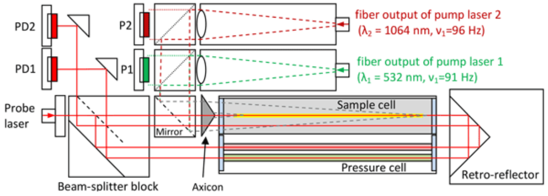
Outlook

National Institute of Advanced Industrial Science and Technology
National Metrology Institute of Japan

There is a need for traceability for mass and absorption measurements of aerosol emissions

- CERMS is a promising start for mass traceability
  - needs ILCs, confirmation with reference materials (see research[1] by Keiji Takahata, NMIJ/AIST), and standards
  - selectivity may be an issue (if specific components of aerosol emissions are being targeted)
- for absorption, photothermal interferometry (PTI) is promising as a traceable method that does not rely on extinction and scattering
  - see recent research[2] by Luka Drinovec, Haze Instruments towards a method for reference aerosol absorption measurements
- for organics, sulphates, and ash, the metrology needs are much greater
  - issues with partitioning due to temperature and dilution, and with oxidation[3]

NMIJ CRM 5722-a:
Monodisperse 300 nm PSL
Certified mass: 17 fg



1. Keiji Takahata et al. (2020) Aerosol Science and Technology. doi: 10.1080/02786826.2020.1787324
2. Luka Drinovec et al. (2022) Atmospheric Measurement Techniques. doi: 10.5194/amt-15-3805-2022
3. Allen Robinson et al. (2007) Science. doi: 10.1126/science.1133061

THANK YOU

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