Optical, physical, and chemical characterization of marine Black Carbon

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National Research Council Canada
Conseil national de recherches Canada

Outline

- BC mass concentration measurement challenges
- instrument calibration verification
- BC/aerosol properties of interest and measurement methods
- sample conditioning

ICCT UCR linkage

- NRC Canada is contributing to phase one of the ICCT UCR marine BC project.
- Transport Canada hopes to support the efforts of NRC Canada for this project in the future.
- The objective is to provide complementary data or support to the principle objectives of the ICCT UCR project

BC mass concentration measurement challenges

- all instruments measuring BC mass concentration do so indirectly, relying on knowledge of optical, physical, or chemical properties
- instruments are generally sensitive to interferences which depend on how they operate (underlying method and specific operating parameters)
- manufacturers implement different calibration principles
- a ‘bottled’ BC aerosol reference material does not exist
- impact of fuel type and engine load on BC characteristics and interferences not well known
- instrument contamination under harsh operating conditions possible (likely?)

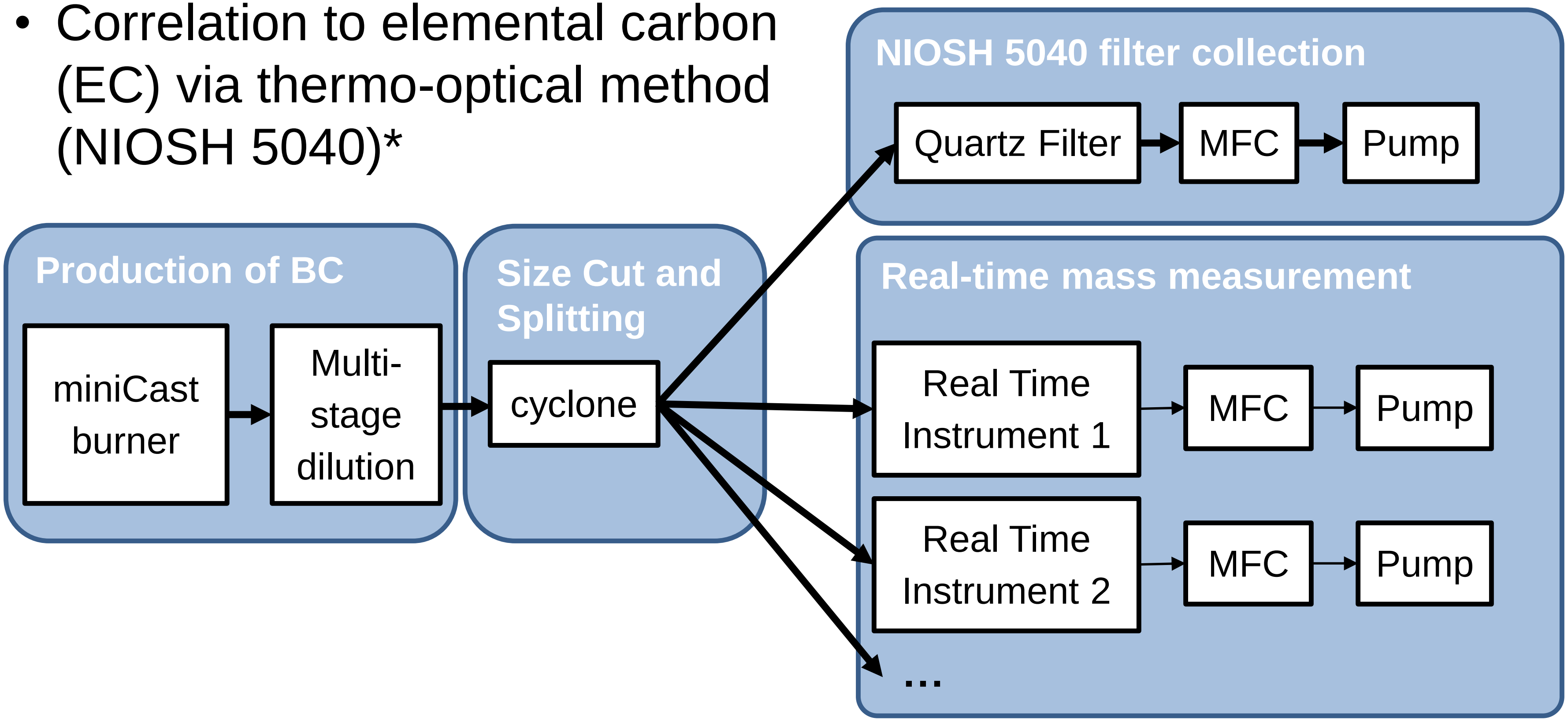
Mitigating the measurement challenges

- instrument calibration verification before and after campaign using flame generated BC with known characteristics
- verification of BC optical, physical, and chemical properties as a function of fuel type and engine load
- quantification of co-emitted species
- explore exhaust condition strategies

Instrument calibration verification

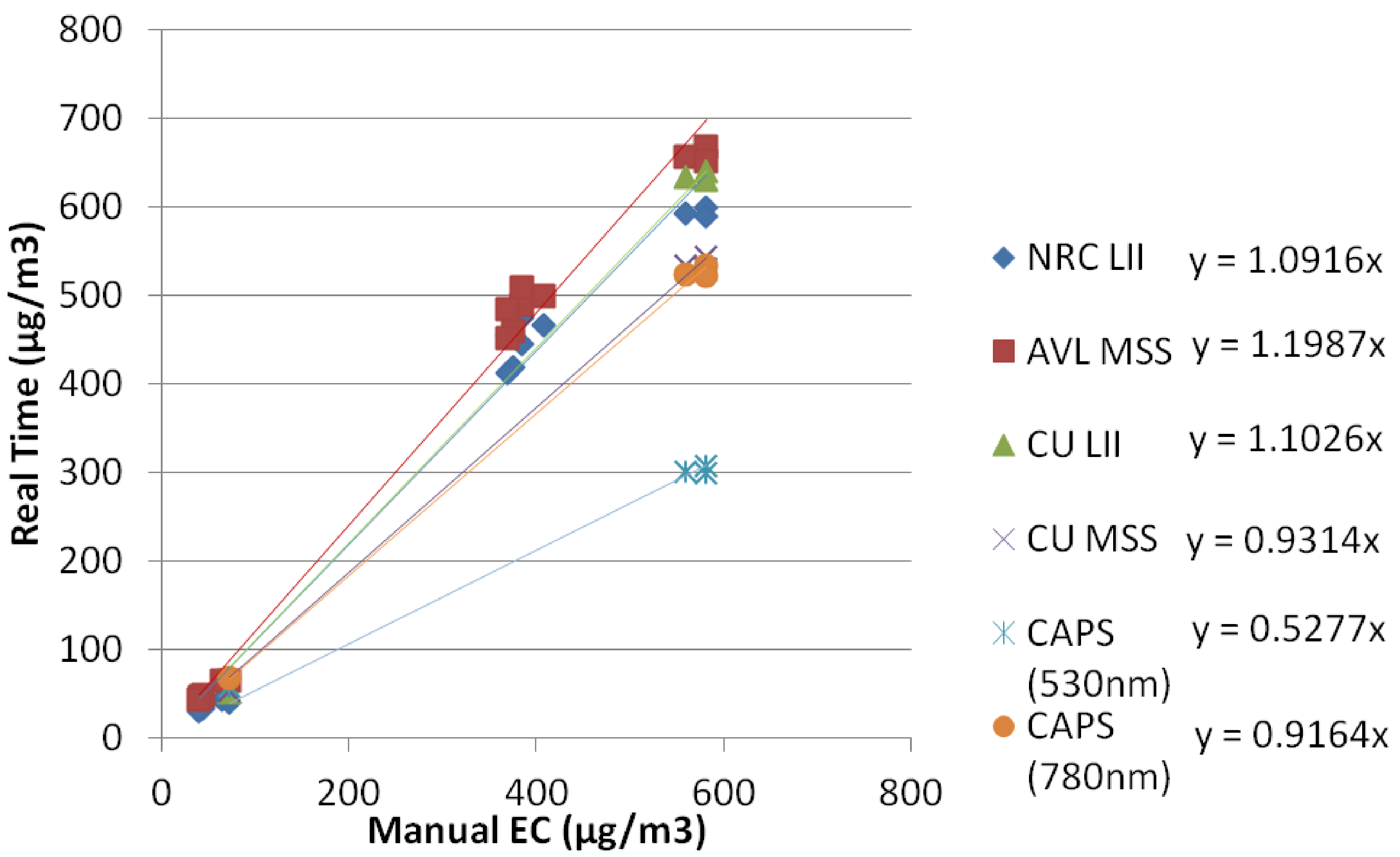
Calibration verification against Thermal Optical Method

- Correlation to elemental carbon (EC) via thermo-optical method (NIOSH 5040)*



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

Example of instrument comparison



Optical, physical, and chemical characterization

Characteristics of interest

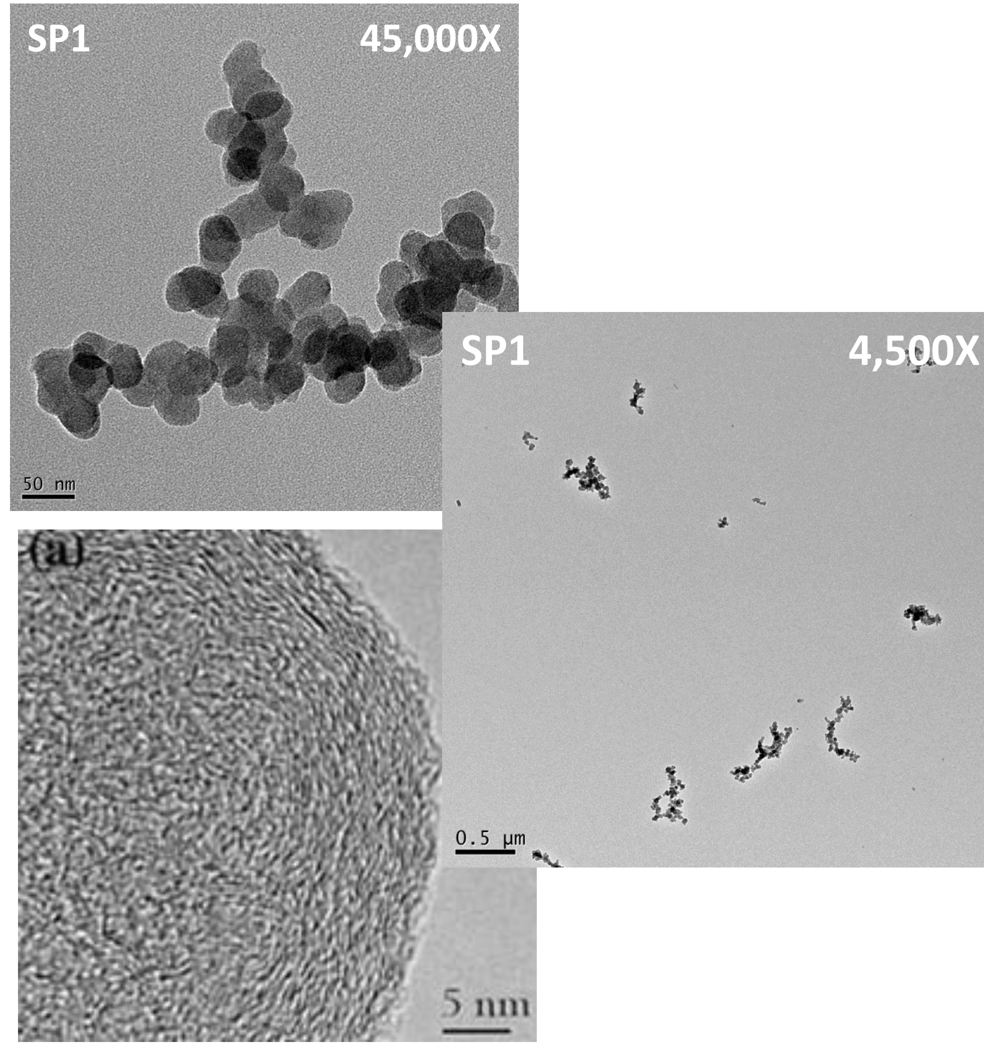
- spectral variability of light absorbing properties
  - often expressed as Angstrom absorption exponent (AAE)
  - MEPC 67/INF.31 suggests AAE ~ 1 as a criteria for BC
- TEM 'visual' of particles
  - size, shape, compactness, maturity, coatings
- RAMAN spectroscopy
  - internal bond structures, graphitization, bound organics
- volatile coating mass
- composition of organic particles
- composition of all particles and gas phase

Spectral optical properties

- cavity attenuation phase-shift PM single-scattering albedo (CAPS PM_{SSA})
  - extinction coefficient
  - total scattering coefficient
  - single-scattering albedo
  - 530, 660, 780 nm
- photoacoustic extinctiometer (PAX)
  - absorption coefficient
  - total scattering coefficient
  - 375, 534, 870 nm
- angstrom absorption exponent
  - can be determined from multi-wavelength data

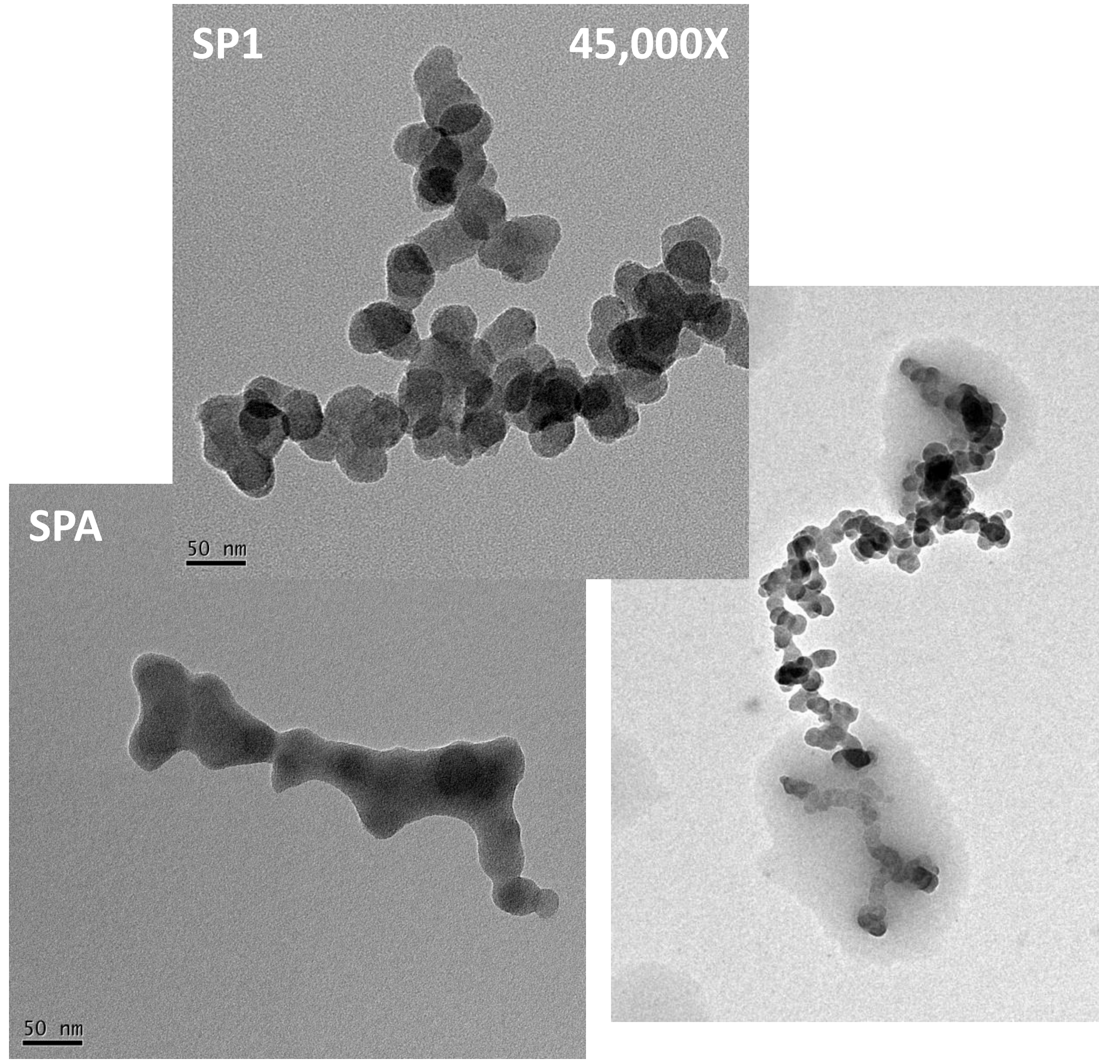
Quantitative TEM analysis

- primary particle size
- aggregate
  - size distribution
  - fractal structure
  - compactness
- internal structure
  - graphitic layer length and spacing



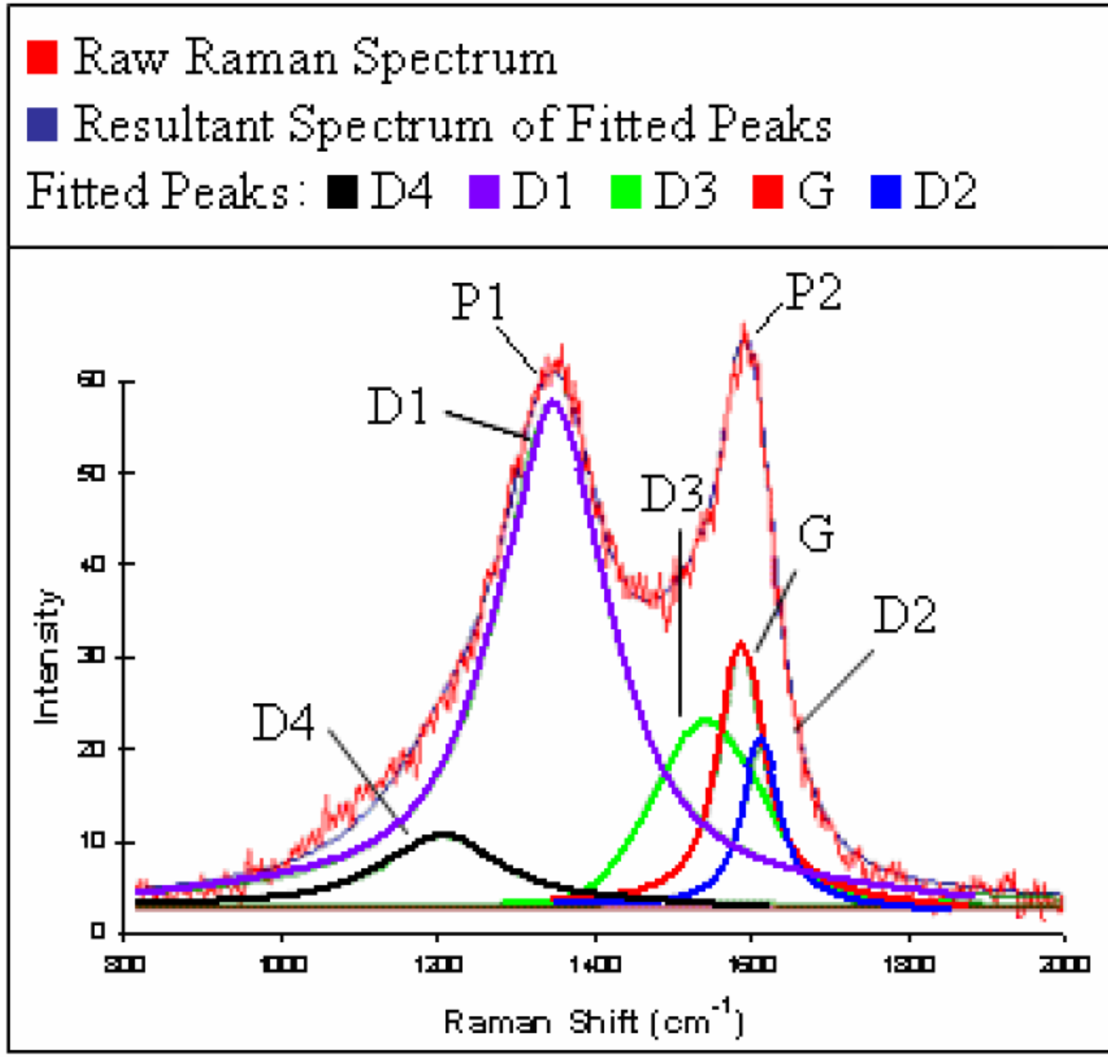
Qualitative TEM analysis

- particle maturity
- coatings
- other particles
  - solids
  - liquids
- particle collapse



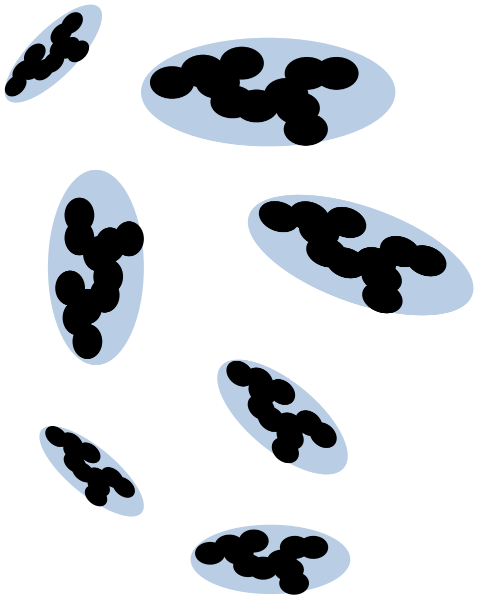
microRaman surface analysis of BC particles

- spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a material
- identifies internal structural features in carbon particles
  - bonding (sp^2 vs. sp^3)
  - degree of graphitization
    - G – graphitic
    - D1-D4 – defects/disorders
- possible finger-print for different sources



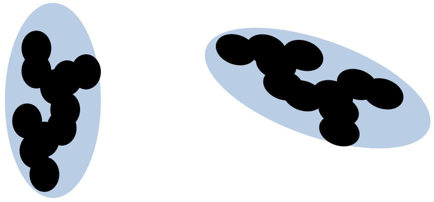
Quantification of BC coating mass using DMA, CPMA, denuder, and CPC

- start with an aerosol of coated particles



Quantification of BC coating mass using DMA, CPMA, denuder, and CPC

- start with an aerosol of coated particles
- size select particles using DMA



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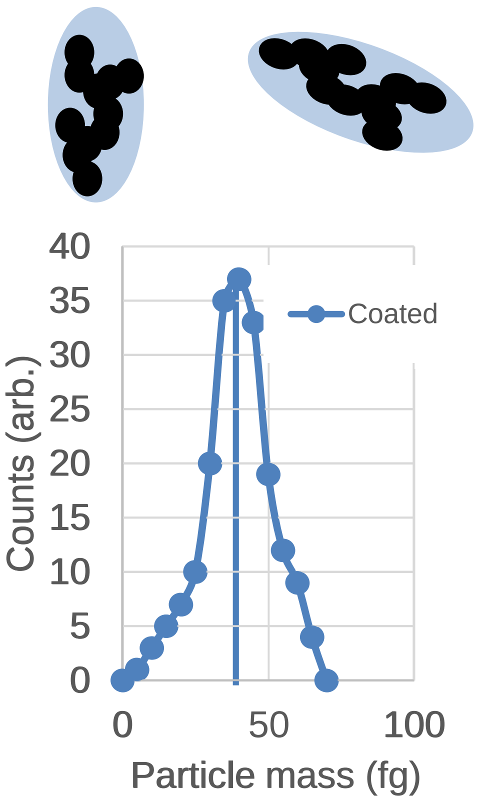
- measure peak particle mass for size selected mass with CPMA and CPC
  - represents mass of particles with coating



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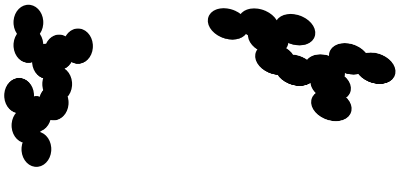

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Quantification of BC coating mass using DMA, CPMA, denuder, and CPC

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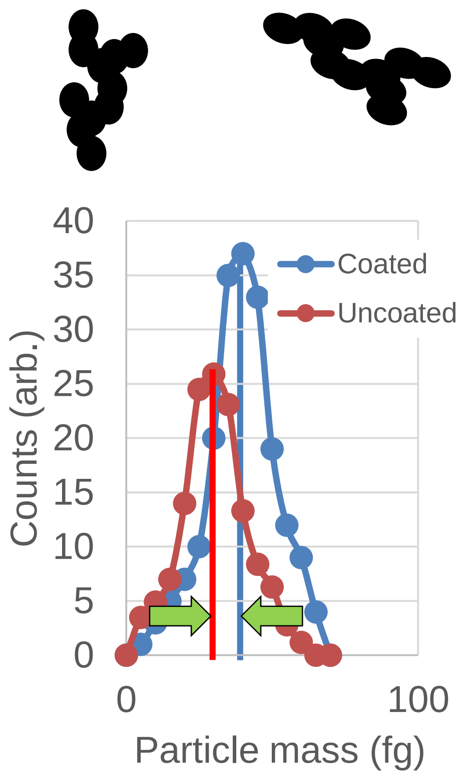
  - represents mass of particle with coating
- strip particles of coating
- measure peak particle mass for same size
- difference in mass is the coating mass
- can be done for a range of particle sizes



Sample conditioning

Sample conditioning

- brain storming ideas and looking for input from those with marine emission experience
  - dilution
  - heated dilution with evaporator tube
  - thermal denuder
  - thermal denuder with heated activated carbon
  - catalytic stripper
  - diffusion dryers/stripper which target particular gases that are problematic to instruments

Wrap up

- objective of this part of the campaign is to:
  - improve comparability of instruments
  - improve our understanding of marine engine generated BC particles and how they do or don't change with fuel and load
  - help to understand any differences observed amongst BC mass concentration instrument
  - explore mechanisms to condition exhaust before measurement to improve measurement accuracy
- we welcome ideas, criticisms, reality checks!

Thank you

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