Calibration of Fast Response Differential Mobility Spectrometers

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Contents

The Need for Fast Response

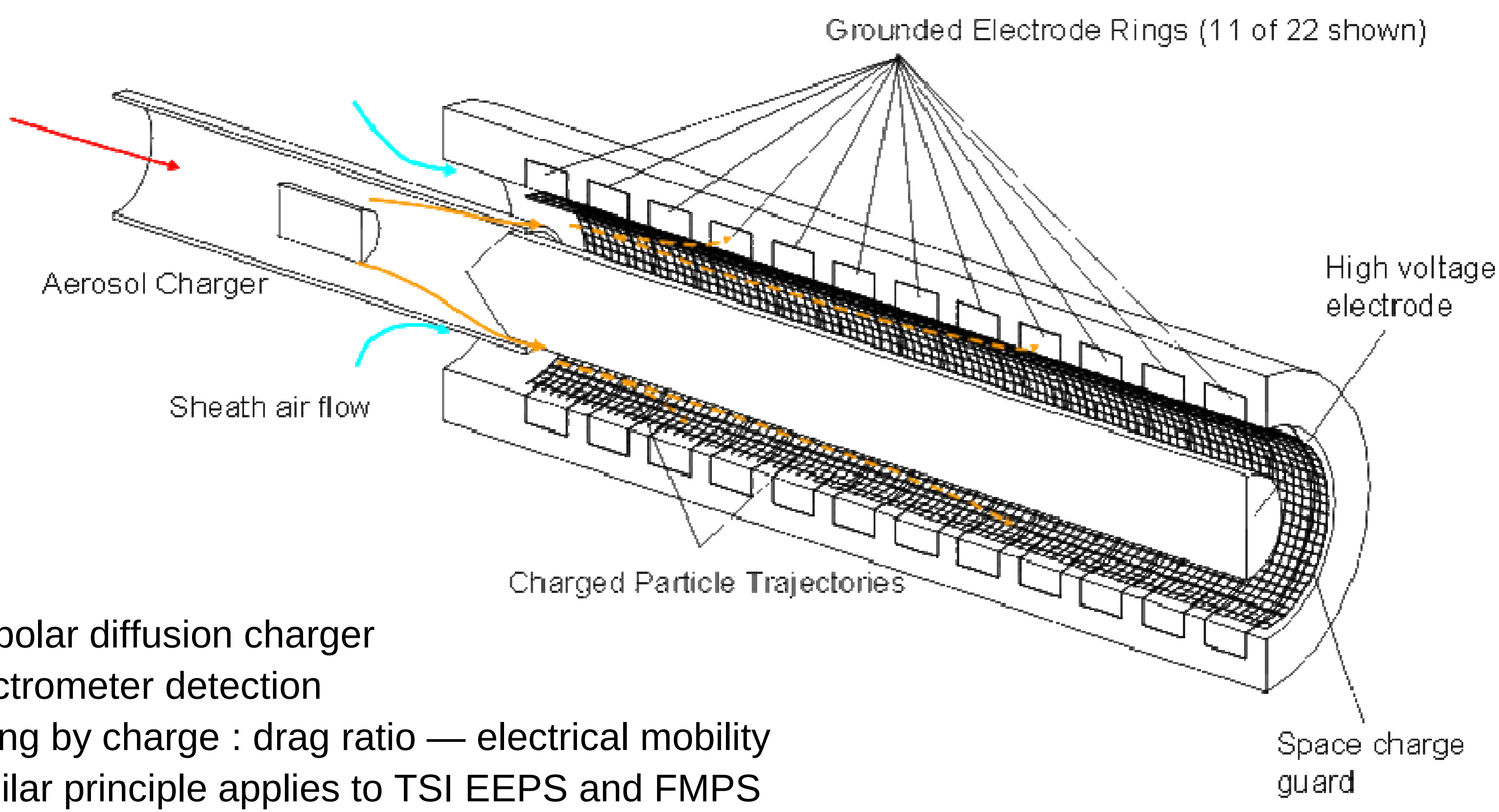
- Aerosols can change rapidly, SMPS scan can take 2 minutes.
- Fast response electrical mobility analysers:
  - Electrical Aerosol Spectrometer, Tartu University / Airel Ltd
  - Cambustion DMS500
  - TSI EEPS
  - TSI FMPS
  - Cambustion DMS50

- DMS Series and EEPS especially aimed at measuring engine exhaust aerosols
  - Adoption of such systems by automotive researchers ⇒ “order of magnitude accuracy” no longer good enough

- But… all such instruments currently compromise on sensitivity and spectral resolution over SMPS systems

This paper uses the DMS series an example. Both these instruments are available with integrated sampling and dilution systems, so this paper considers the ‘whole picture’ of calibration.

DMS Series Principle of Operation



- Unipolar diffusion charger
- Electrometer detection
- Sizing by charge : drag ratio — electrical mobility
- Similar principle applies to TSI EEPS and FMPS
- DMS500: 10 Hz data, 200 ms time response, 5 nm to 1 μm or 2.5 μm
- DMS50: 10 Hz data, 500 ms time response, 5 nm to 560 nm, 12 V operable

'Fast Response Classification of Fine Aerosols with a Differential Mobility Spectrometer'; Reavell, K. Proc. AGM Aerosol Soc. UK. 2002

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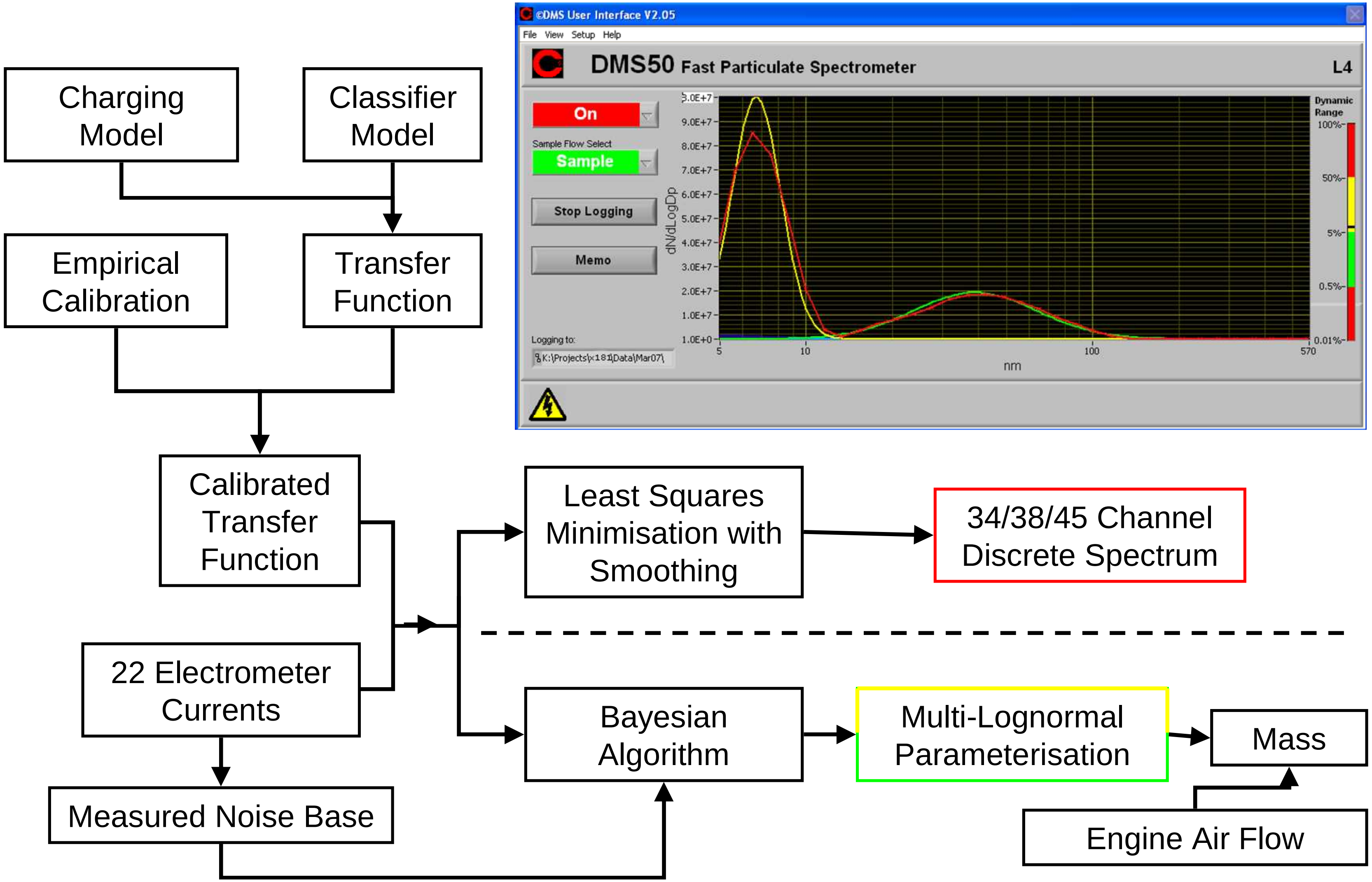
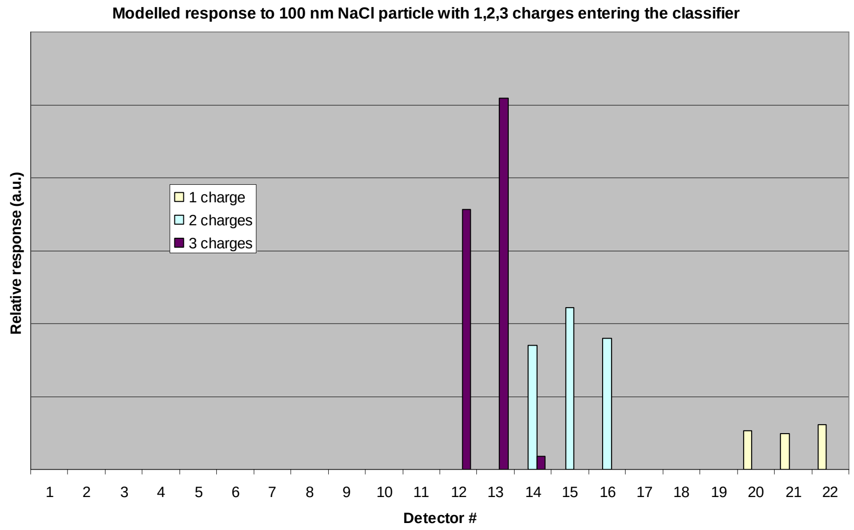
DMS Data Inversion

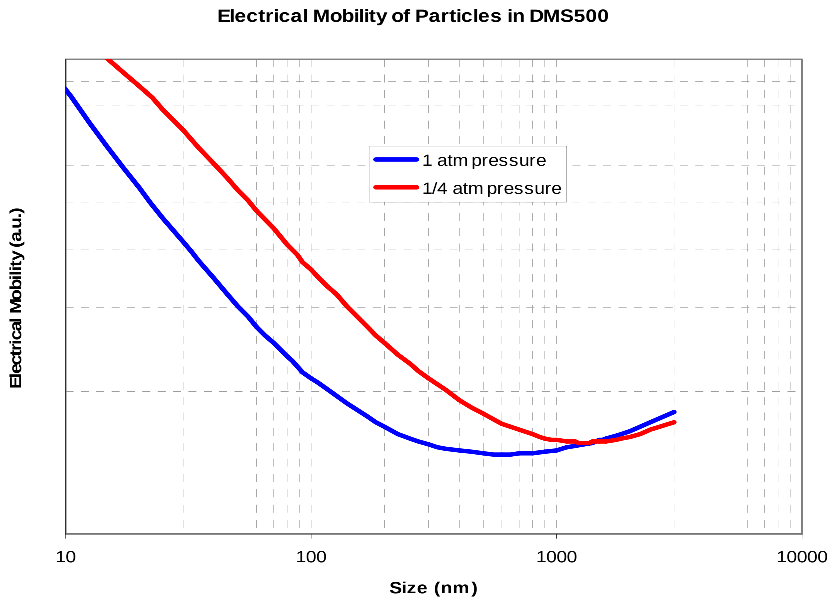


Particle Charging

- Unipolar Diffusion Charger
- Particles gain net, multiple, positive charge from corona discharge



- Bigger particles less mechanically mobile, but gain more charge
- Eventually, large particles become as electrically mobile as small particles: **Mobility Inversion**
- Inversion point moved to larger sizes by dropping pressure
- Cyclone important!



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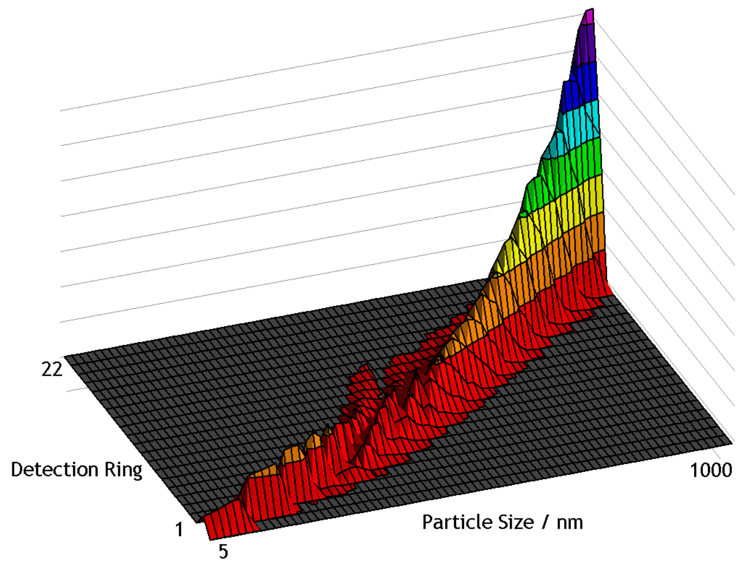
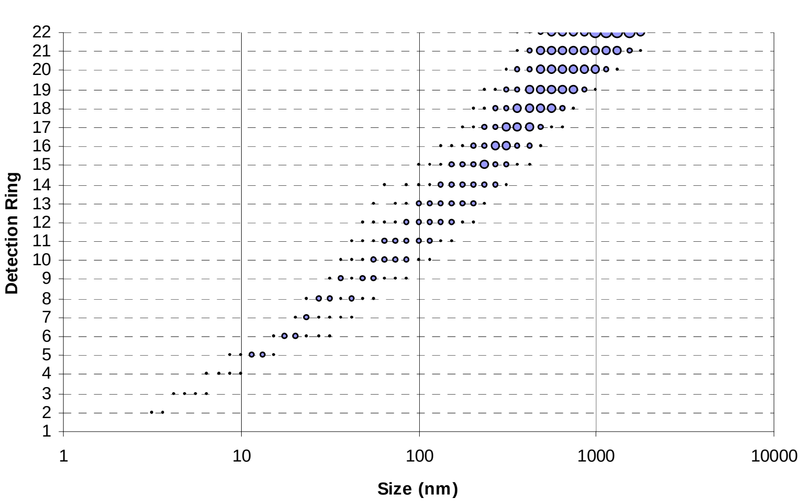
Instrument Transfer Function

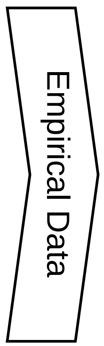
Initially generated from Monte Carlo simulation. For a random particle of a given size:

- Random charge state is selected from a calculated probability distribution for that sized particle
- Entry point to the classifier randomly selected, and particle's trajectory calculated to predict the landing detection ring and measured current.
- Repeated across all sizes for many particles →
- Empirically adjusted for every instrument during test using a linear transform ↓

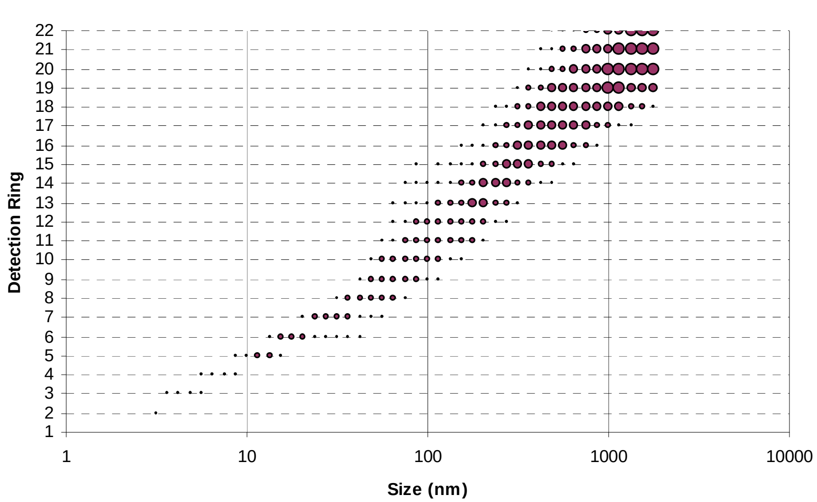


Modelled Transfer Function





Typical Adjusted Transfer Function



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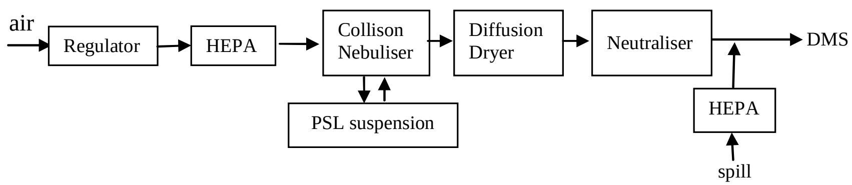
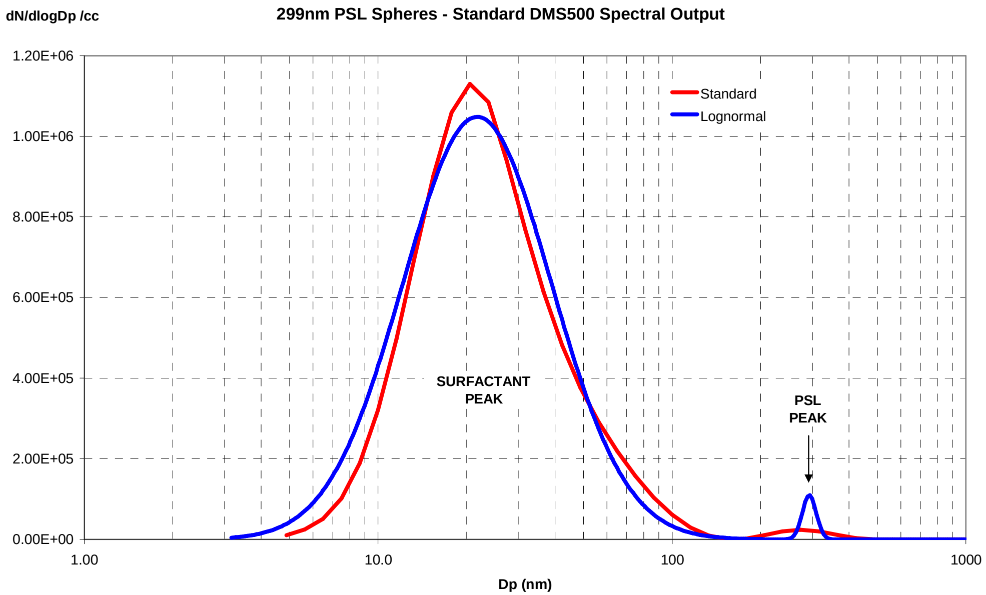
Size Calibration: PSL

- Duke Scientific (now Thermo Scientific) Polystyrene Latex Spheres
- NIST Traceable, traceability provided by microscopy
- Large surfactant / impurity mode makes unsuitable for smaller sizes:





- Lognormal parameterisation used for ease of analysis & improved apparent spectral resolution

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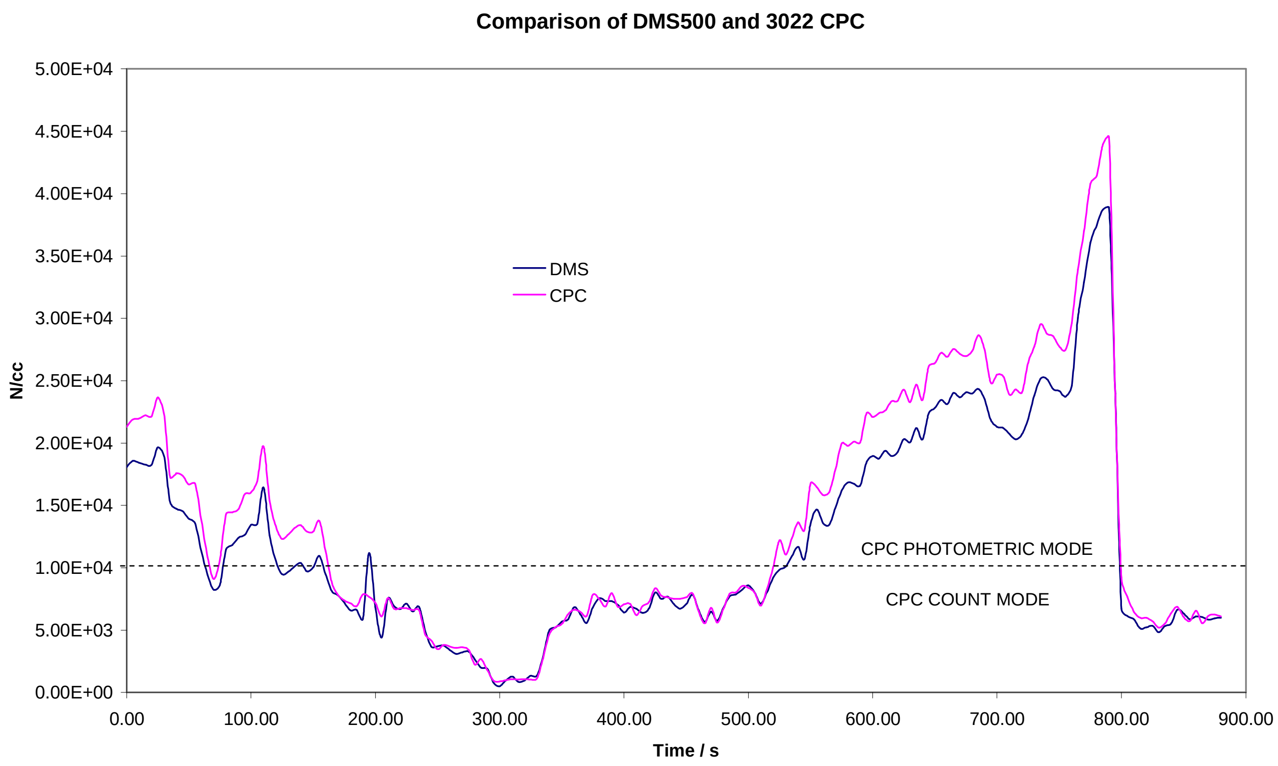
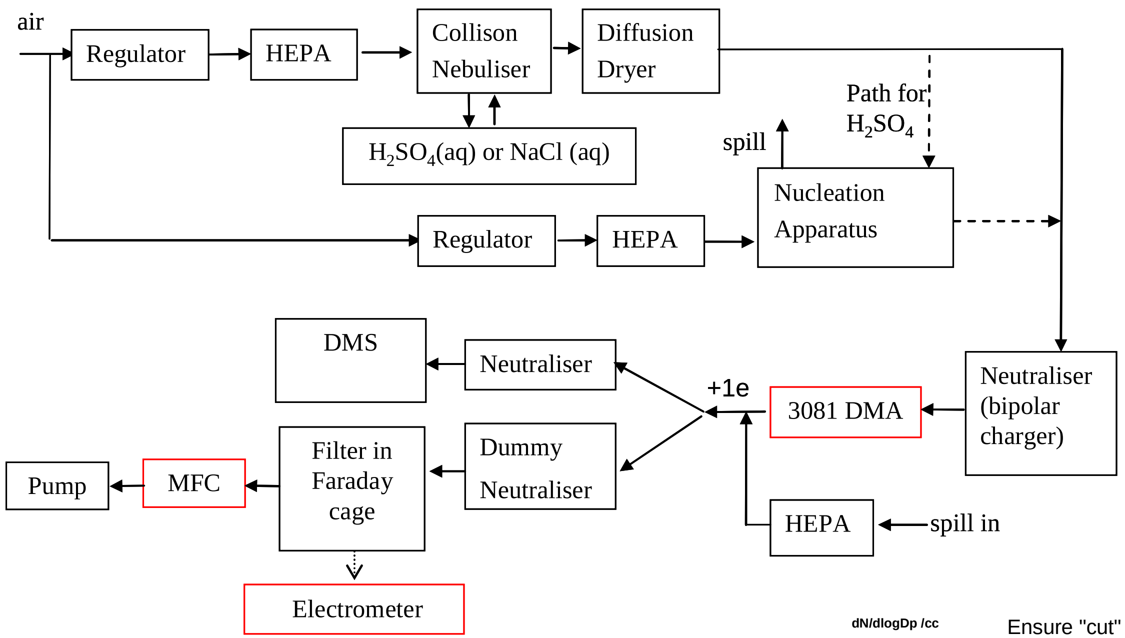
Gain Calibration

CPC not a primary standard in "photometric mode" at higher concentrations required by electrometer based fast response instruments.

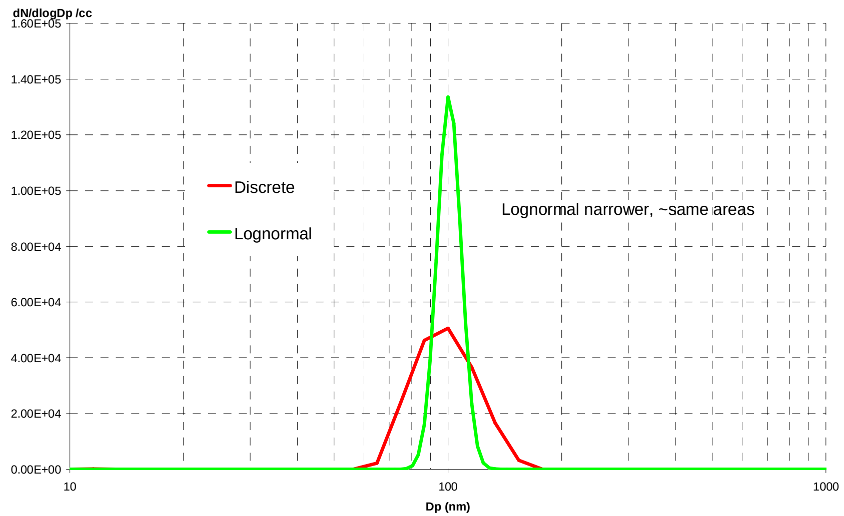
Hence go back to methodology based on that recommended for CPC calibration; the use of a standard electrometer: Liu and Pui (1974). Useful primary standard if can be ensured that each particle is singly charged….

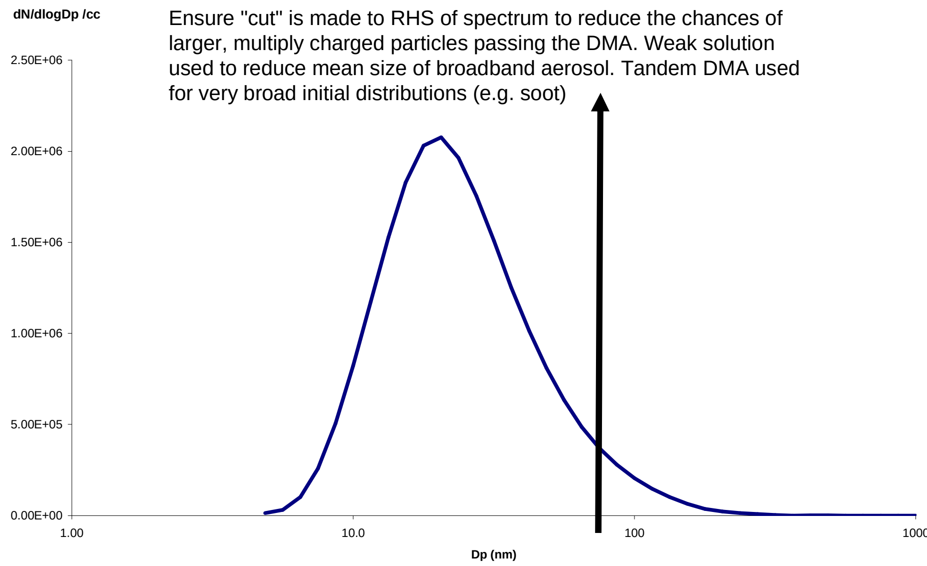


DMA / Electrometer-Based Calibration Setup



Cannot ensure single charge for largest particles, therefore rely on extrapolation of model for > 300 nm





Aerosol Sources

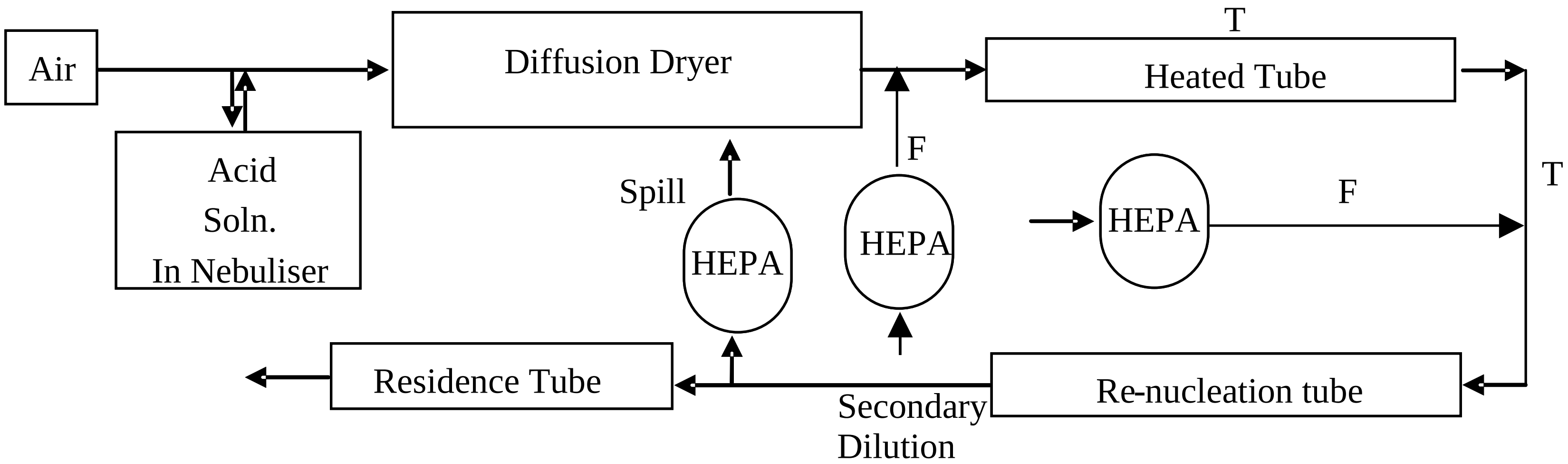
"Spherical Calibration" – GDI and Nucleation Mode

Size Range	Aerosol	Generation Method	Measure Gain?
5 – 50 nm	Sulphuric Acid	Nebuliser & Nucleation Rig (next slide)	Yes
50 – 300 nm	Sodium Chloride	Nebuliser	Yes
300 – 1000 (or 2500) nm	Polystyrene Latex Spheres (PSL)	Nebuliser	No

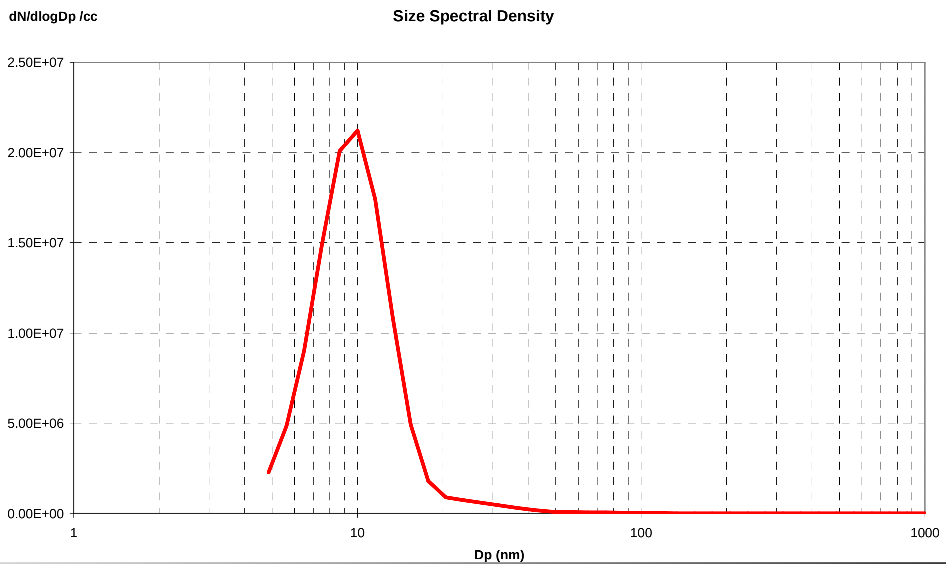
Soot Calibration – Diesel Accumulation Mode

- Soot from Propane Flame (mini-Cast), 50 – 300 nm (later…)

Nucleation Source (H_2SO_4)

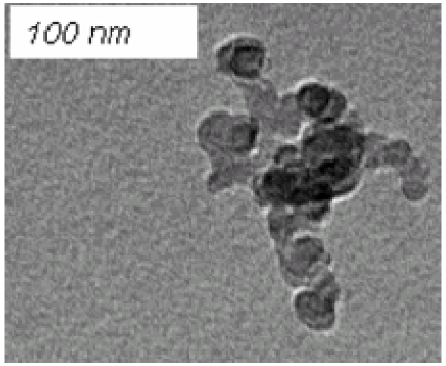


F – rotameter
T – thermocouple



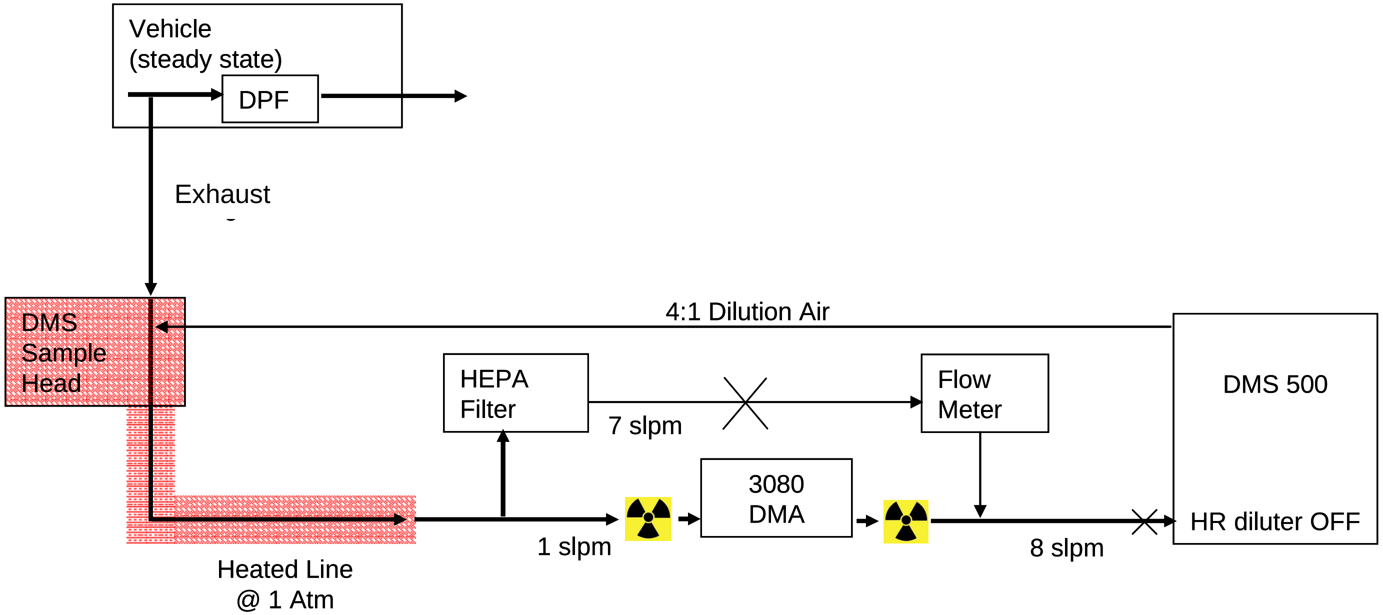
Effect of Morphology (1)

What size is this?

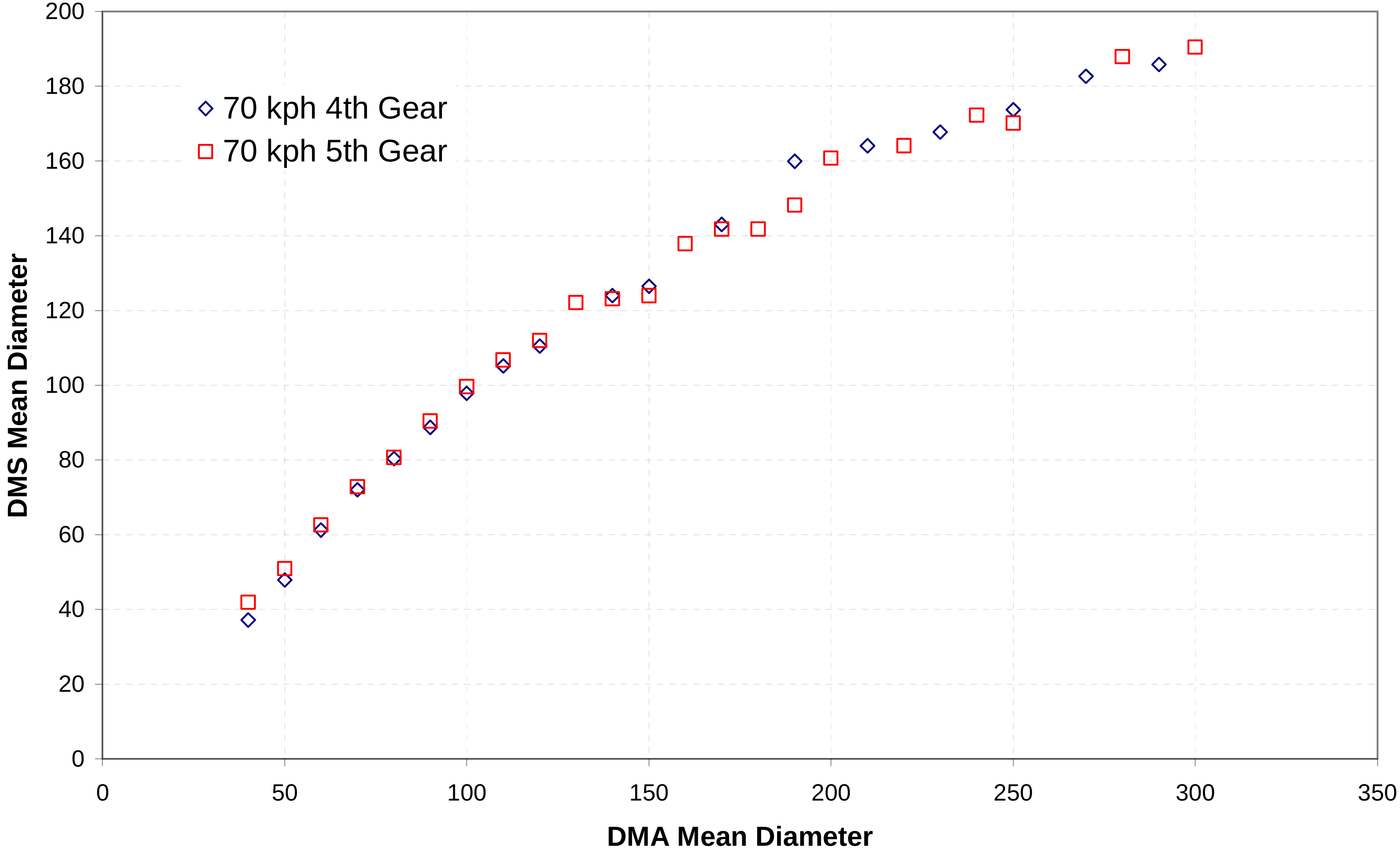


- DMS originally calibrated with spherical particles
- Compare DMA (mobility) sizing with DMS (electrical mobility) sizing for Diesel Agglomerates

Test apparatus



Effect of Morphology (2)



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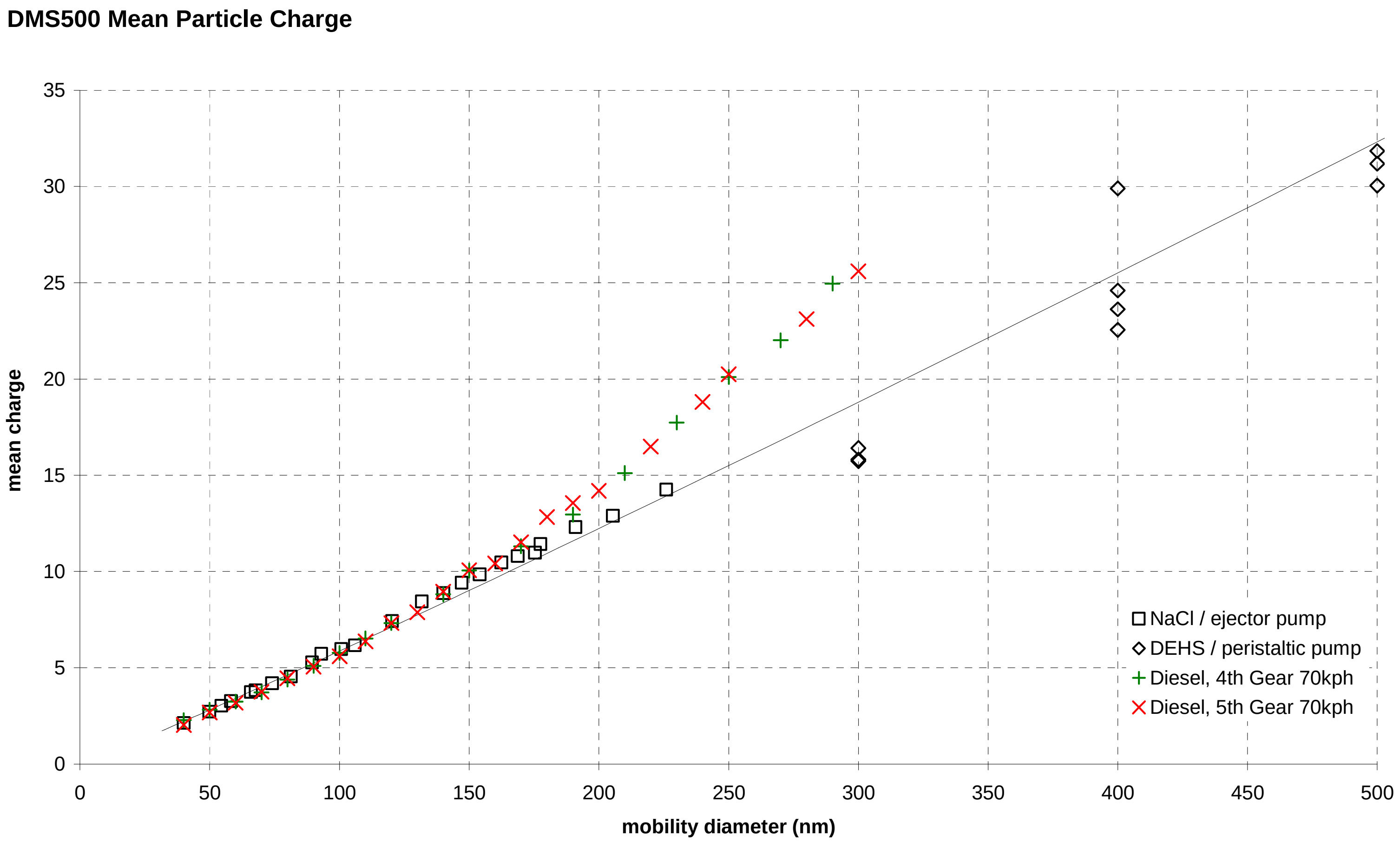
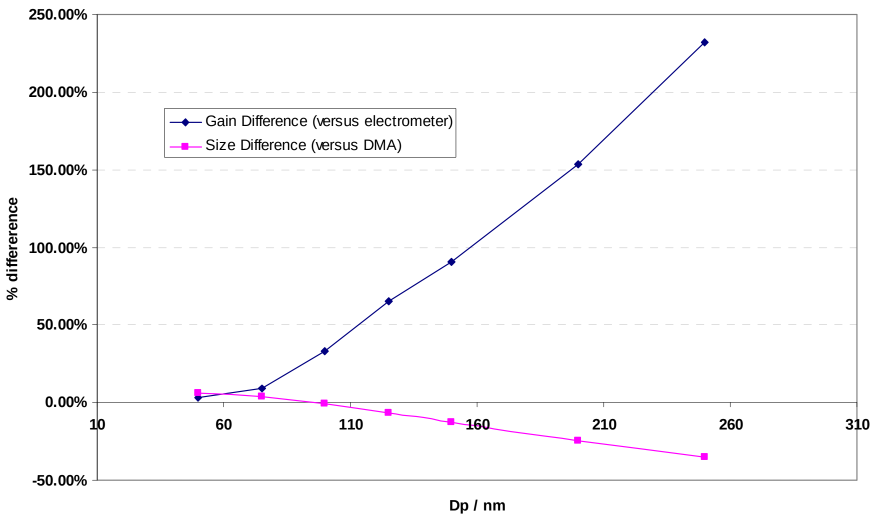
Effect of Morphology (3)



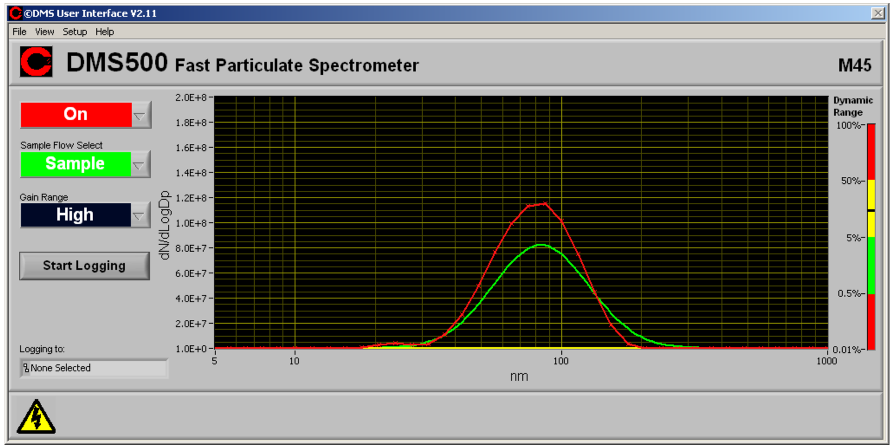
Effect of Morphology (4)

- Differences observed with DMA cut soot under a "spherical calibration":



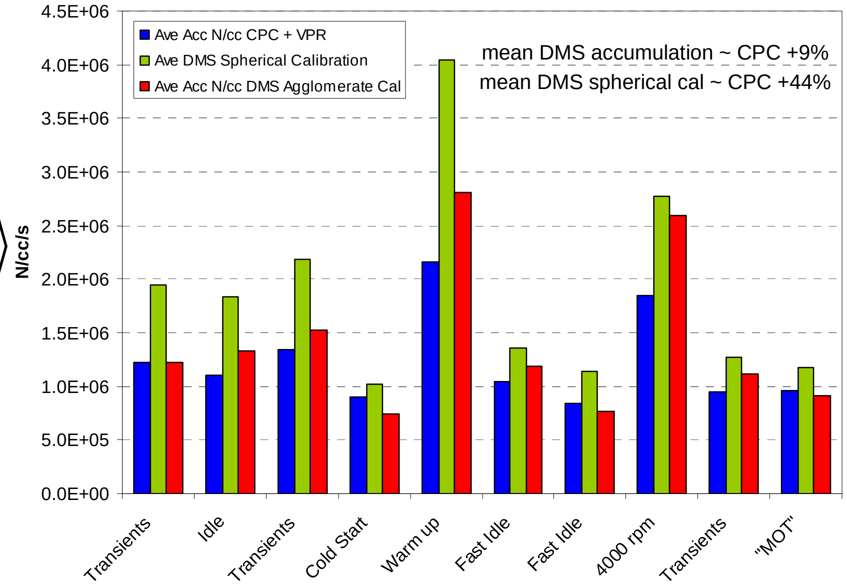
- Solution is to empirically calibrate with soot for use with Diesel emissions. Only calibrate accumulation mode of lognormal "fit" with soot; use this output for "solid particle number".

- Multiple charging / DMA size range / source particle size range makes this only workable up to ~ 300 nm (sufficient for most engine work)



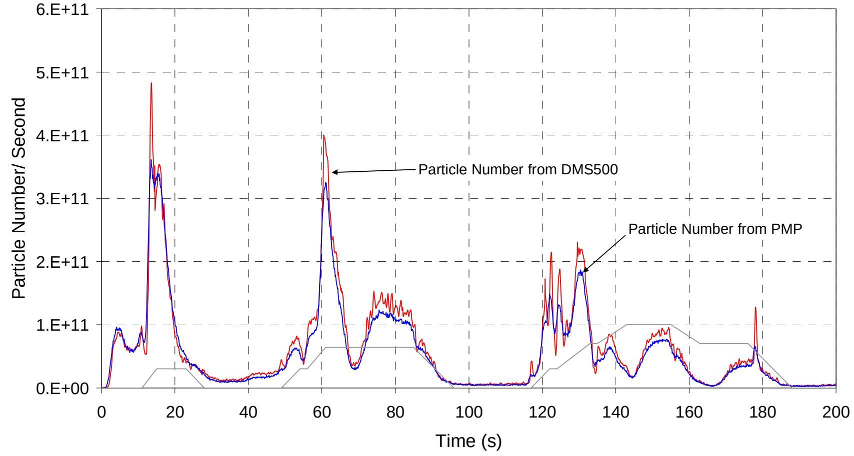
Results after “soot calibration”

Comparison of DMS with PMP system with Diesel soot; with and without “soot” calibration.



However, correlation for Gasoline Direct Injection (GDI) works best for original “spherical” calibration

$\Rightarrow$ **Need separate calibrations for GDI and Diesel soot in instruments with corona chargers.**



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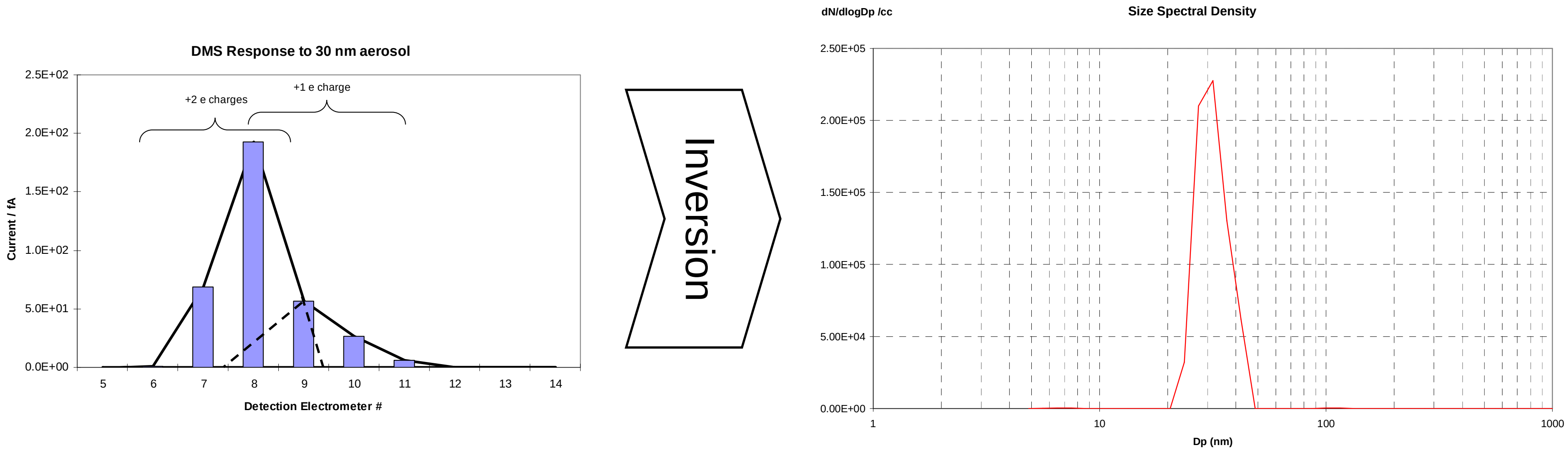
Calibration Artefacts: Multiple charging

- For a given size, each possible charge state produces a mobility response on the rings; data inversion deconvolutes this to give particle size spectrum
- Response to monodisperse (DMA "cut") salt aerosol below:



- Inversion problem hardest in 20 – 50 nm region, beyond that effect is blurred by mobilities becoming closer together with increasing mean charge.
- For work requiring high accuracy in this region with narrow aerosols (e.g. gas turbine studies), need careful "micro-calibration" at many sizes in this region to avoid multiple peaks transferring to spectrum

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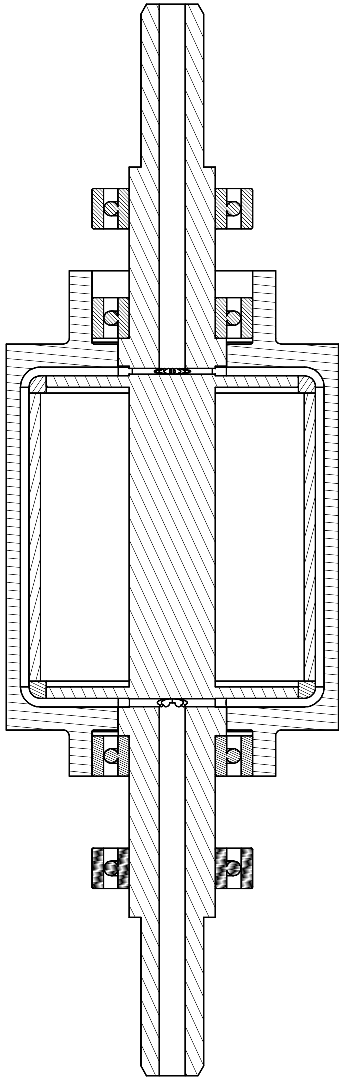
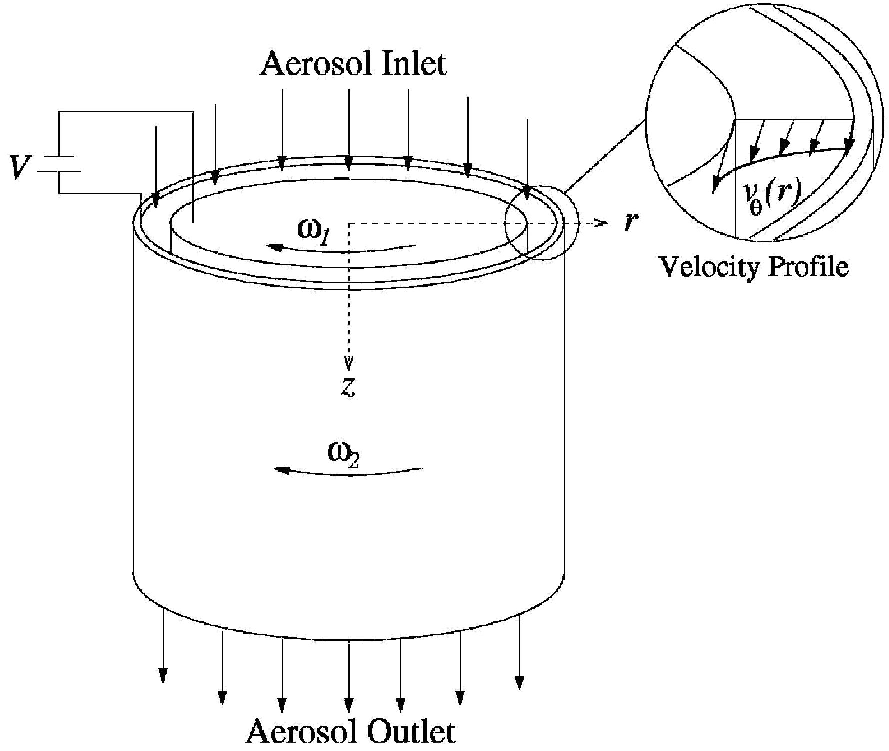
Relating Size to Mass: The CPMA



Classifies by Charge:Mass ratio, as DMA does for Charge:Drag ratio. Opposing electrical and centrifugal forces

Development of APM (K. Ehara *et al.*), but with inner and outer electrode rotating at different speeds, to create a stable field and higher throughput of particles (Reavell & Rushton)



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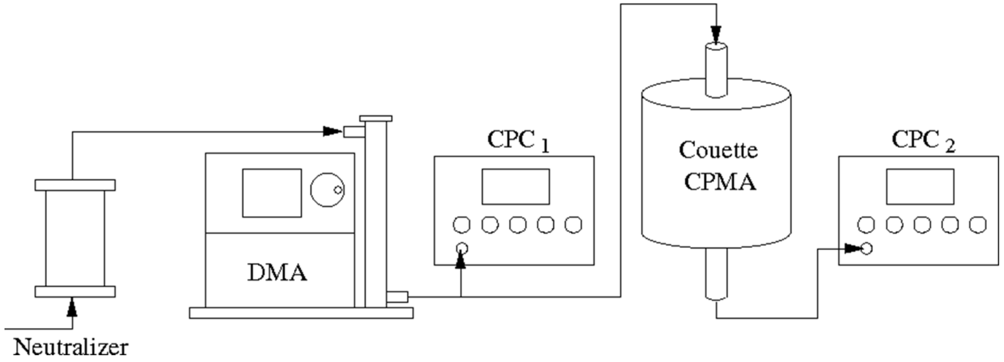
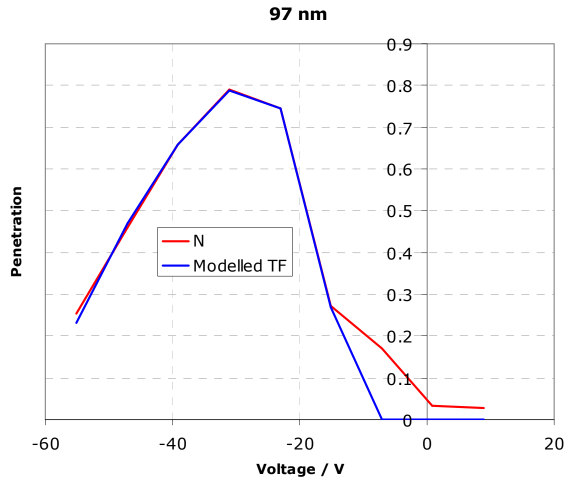
Measuring GDI Particle Mass (1)

1. Start with standard PSL particles of known size & density to calibrate system
2. Select size of particles with DMA ("size band-pass filter")
3. All particles leaving DMA are charged
4. Measure number of particles (Condensation Particle Counter)
5. Select mass of particles with CPMA ("mass band-pass filter")
6. Measure number of particles leaving CPMA (with 2nd CPC)
7. Ratio CPC readings to get penetration whilst varying CPMA voltage → transfer function
8. Peak voltage gives peak mass. System is now therefore calibrated with PSL
9. Repeat at the same size points with engine exhaust, peak in transfer function gives particle mass at that size.





$$m_c = \frac{neV_c}{\omega_c^2 r_c^2 \ln(r_2 / r_1)}$$

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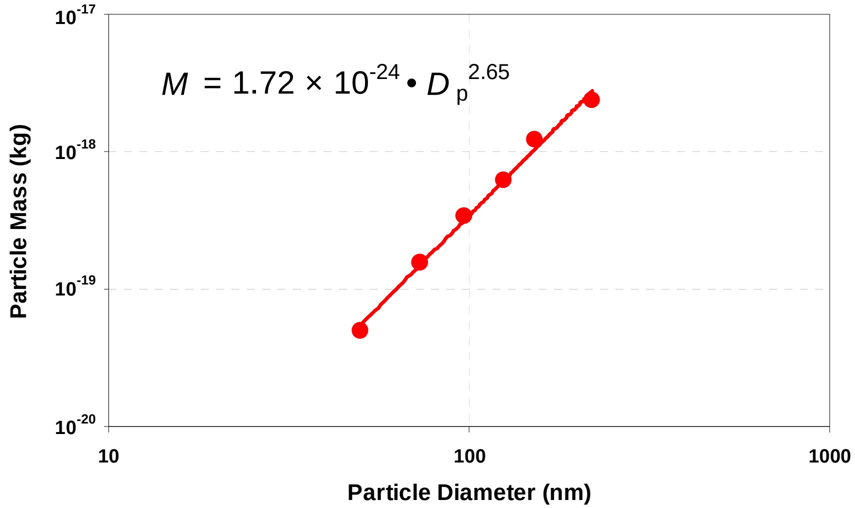
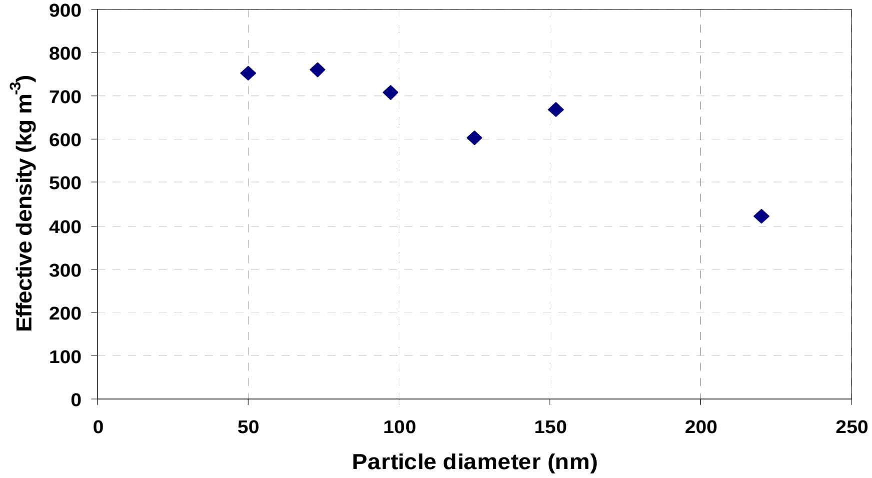
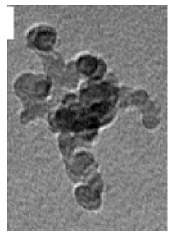
Measuring GDI Particle Mass (2)





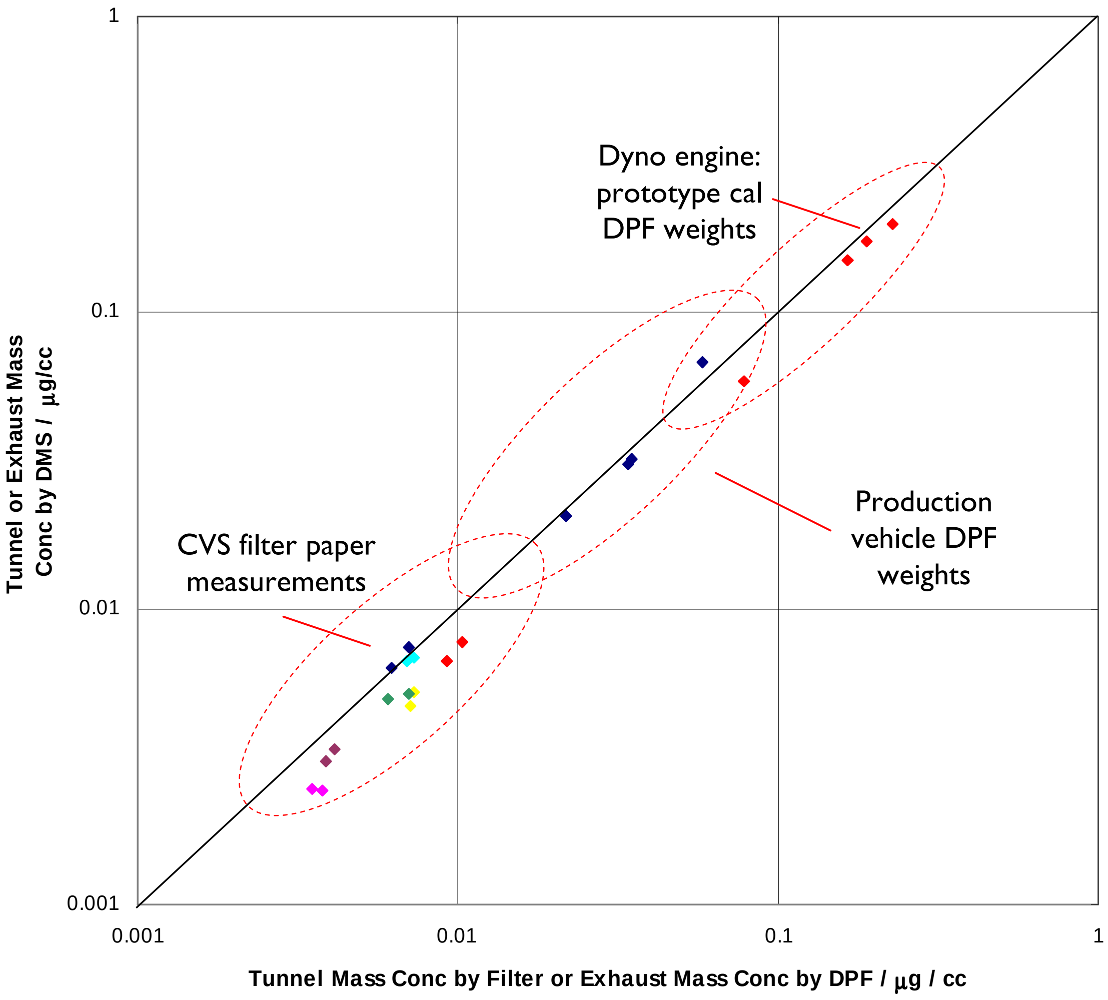
Density of particles emitted from a gasoline direct injection engine, J. Symonds, P. Price, P. Williams and R. Stone, ETH Conference on Nanoparticles, 2008

- Plot mass versus DMA cut size
- Gradient on log-log plot gives "fractal density factor" relating diameter to mass (would be 3 for spherical particles), D_f = 2.65 for these GDI particles



- Particles get less dense as they get bigger, due to "open structure"
- Equivalent measurements show D_f = 2.3 for Diesel
- Therefore GDI particles' structure less "open" than Diesel
- Probably due to "infill" by volatile material

Mass Calibration: Diesel Particles



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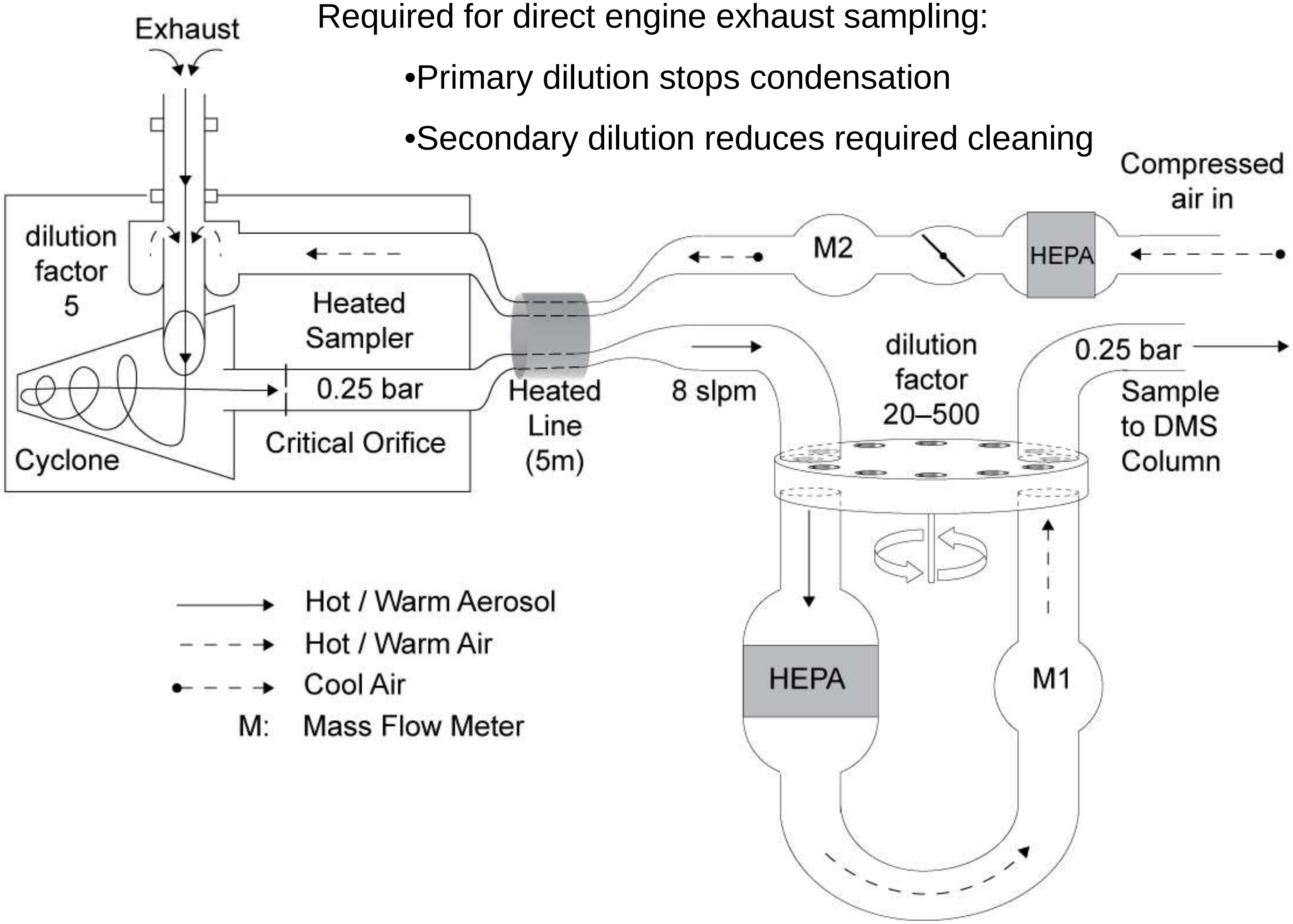
DMS500 Sampling & Dilution System

Required for direct engine exhaust sampling:

- Primary dilution stops condensation
- Secondary dilution reduces required cleaning



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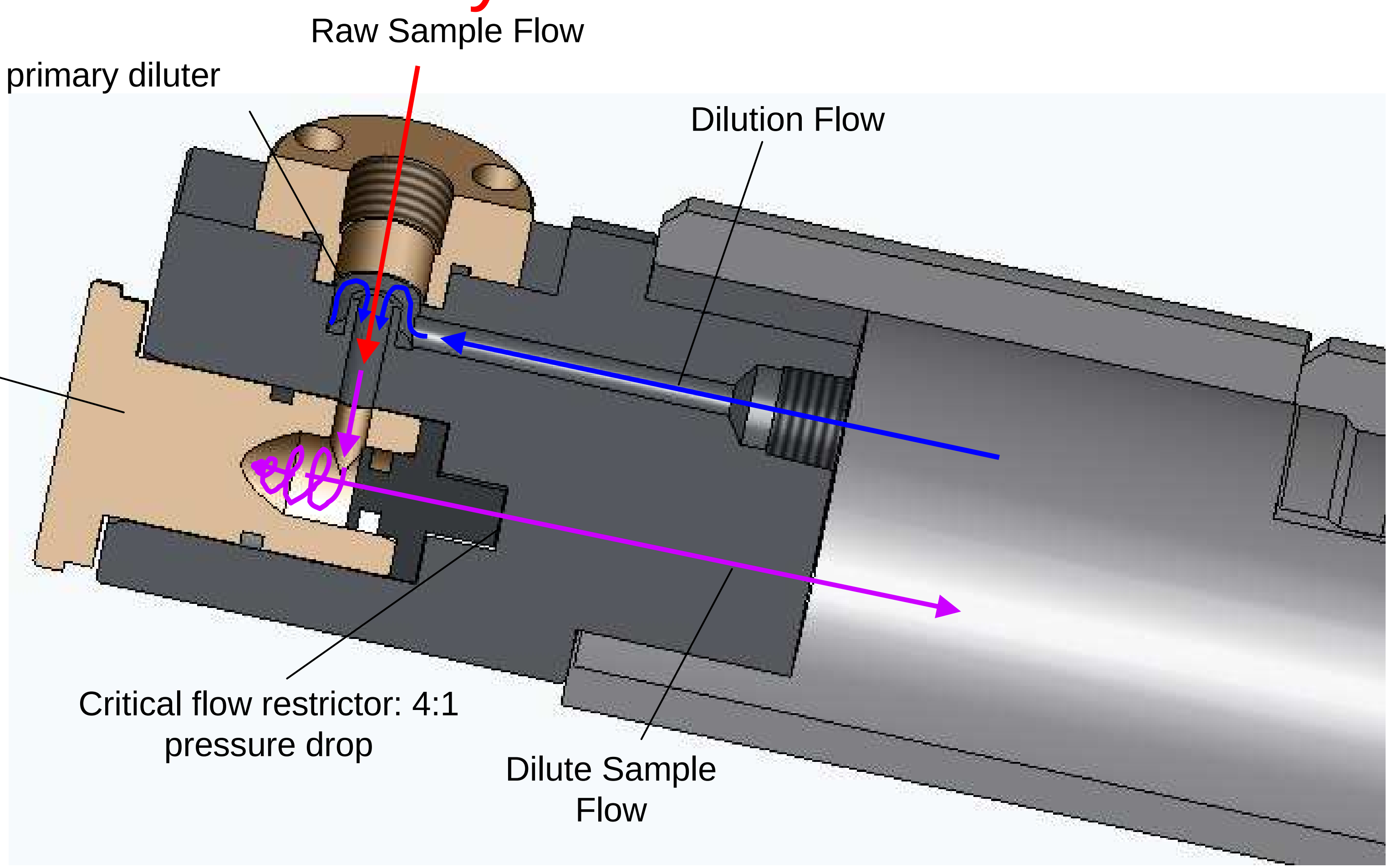
Primary Dilution



Raw Sample Flow (RSF) = Dilute Sample flow (DSF) – Dilution Flow (DF)

Dilution Factor (DF) = DSF/RSF = DSF/(DSF – DF)

$\therefore$ Need accurate co-calibration (in series) of both flow meters: @ DF = 5, 2% difference in flow $\Rightarrow$ 8% gain error

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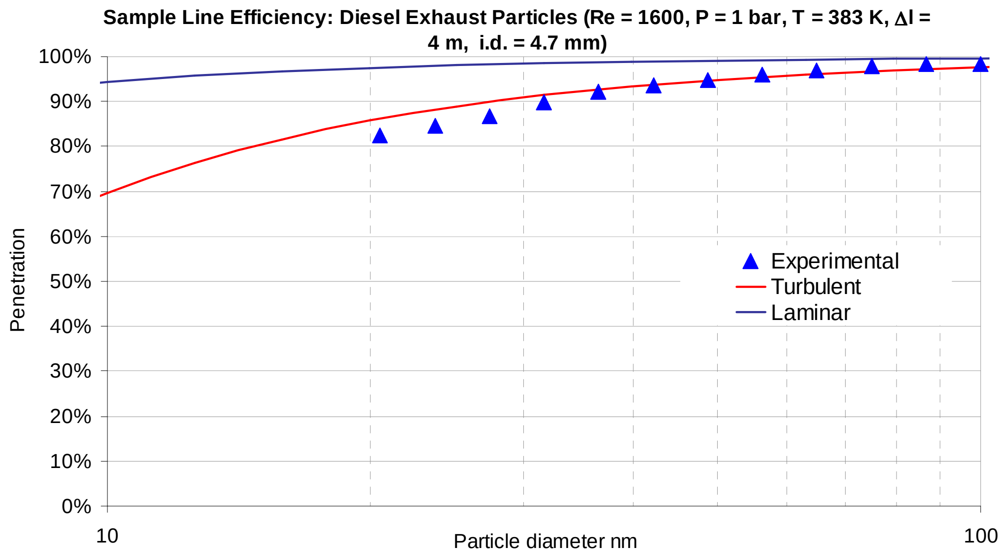
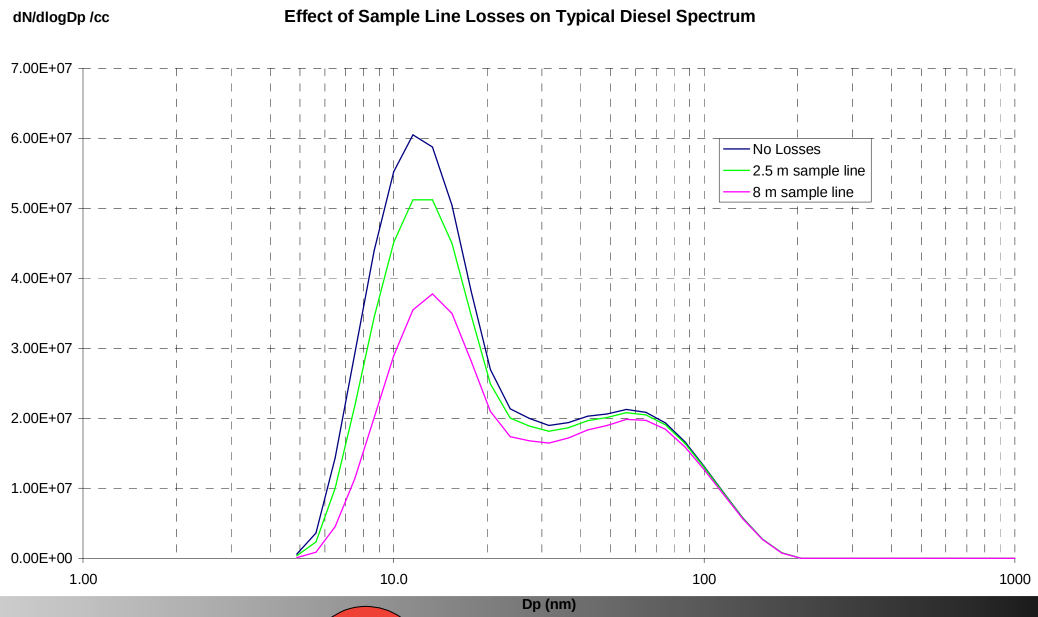
Sample Line Losses



Sample Line Losses Fit “Turbulent Model” given in Hinds even for laminar flow!



Symonds, Olfert & Reavell, 2007

Kumar, Fennell, Symonds & Britter, 2008

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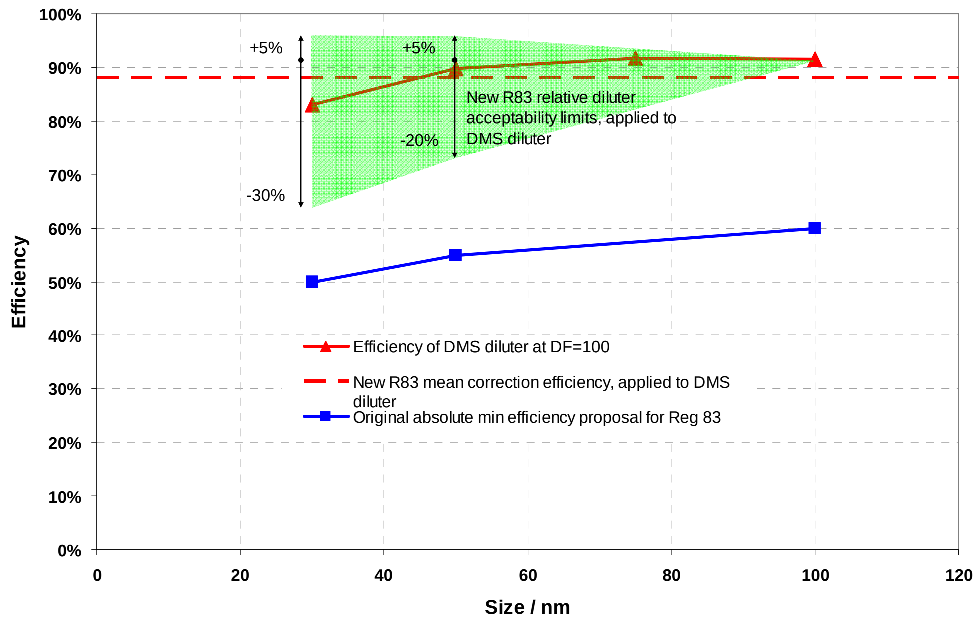
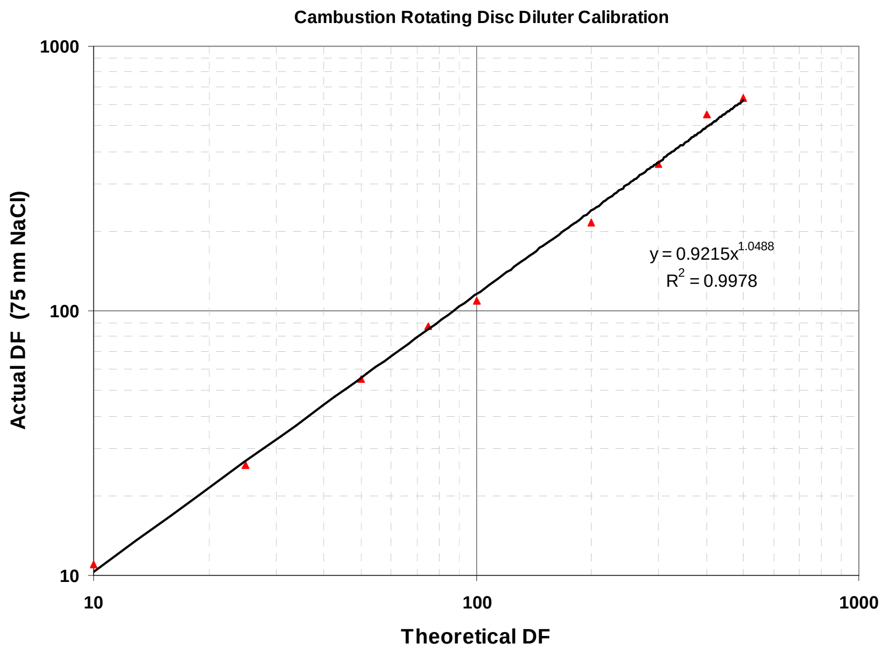
Rotating Disc Diluter Calibration

- Losses thought to be mainly particle diffusion to disc pocket walls:
  - Worse for small particles
  - Worse for higher dilution ratios (disc slower → more time to diffuse)
- Technically possible to apply size dependent correction, but would be impractical for every instrument.
- Broadband NaCl aerosol used to calibrate and check, size similar to engine soot…





Traceability

- Size (PSL)
  - Electron Microscopy
    - Length scale (possibly other nanospheres…)

- Size (DMA)
  - Physical characteristics of DMA, but ultimately final check from PSL sizing (as in ISO15900:2009)
    - Electron Microscopy
      - Length scale
- Number
  - Electrometer
    - Known current source (e.g. Keithley 5156)
      - Known voltage source
        - Josephson Junction Standard (relates frequency to voltage)
          - Caesium Standard
      - Known resistance
        - Quantum Hall Effect Standard
  - Mass flow meter
    - Piston Prover
      - Length scale
      - Clock
        - Caesium standard
      - Pressure / temperature standards

- Primary dilution traceable to mass flow meters
- Secondary dilution calibration only requires instrument to be linear in gain

Uncertainty Estimates

Size from DMA / PSL ~ Coefficient of variance of 5%, 95% CI = ±10% (assume ‘2k’)

Gain (no dilution) ~ CoV of 10%, 95% CI = ±20%

Gain (secondary dilution) ~ CoV of 10% (classifier) + CV of 10% (diluter) ~ CoV of 14% (assume independent), or 95% CI = ± 28%

Gain (primary & secondary dilution) ~ CoV of 10% (classifier) + CoV of 10% (2^{nd} diluter) + CoV of 8% (1st diluter, assuming 2% error in flows) ~ CoV 16%, or 95% CI = 32%

+ sample line losses…

In practice, generally much better agreement with “PMP” systems for particle number concentrations than this is achieved. Of course, these systems are also subject to their own uncertainties…

Mass Uncertainty = size CoV of 5% × 3 (each dimension is *not* independent) ~ 15%, + gain CoV of 10%, so CoV is at least 18% (95% CI ~ 36%) even with no dilution.

Summary of DMS Series Calibration

- Size Calibration:
  - Ultimately traceable to PSL spheres
    - Directly
    - via DMA using NaCl, H_2SO_4 or Soot aerosols
- Number Calibration
  - H_2SO_4 or NaCl or Soot particles charged and size selected with DMA
  - Concentration measured with electrometer and mass flow meter
- Morphological Effects
  - Need soot calibration for Diesel engines, up to 40% error in number concentration if not used
- Dilution and Sampling Systems
  - Effect on any measurement system can be significant & sobering…..

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Acknowledgements

'Team DMS R&D':

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Justin Hunt & Joe Evans (Cambustion)

CPMA Research: Jason Olfert (Universities of Cambridge & Alberta)

CPMA Data from GDI engine: Philip Price, Richard Stone (Oxford University), Paul Williams (Manchester University)

Sample Line Losses: Prashant Kumar (University of Surrey), Paul Fennell (Imperial College), Rex Britter (University of Cambridge), Jason Olfert

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