The Centrifugal Particle Mass Analyser as a Fundamental Particle Mass Standard

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Cambridge Particle Meeting 2012

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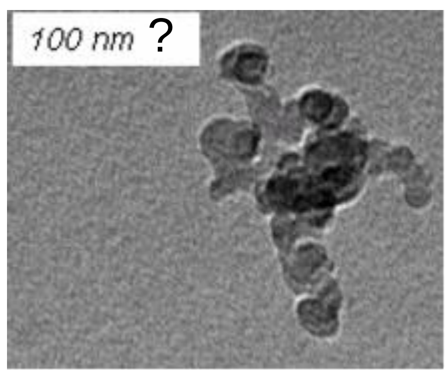
The need to measure sub-micron nanoparticle mass

- Many legislative metrics are expressed in terms of **mass** e.g. engine emissions in the U.S., ambient particle standards
- Combined with size measurement, one can determine:
  - Particle density
  - Particle fractal index and dynamic shape factor ⇒ particle morphology
- Particle “size” for a non spherical particle can be defined in many ways dependent upon measurement technique, ***but* particle mass is well defined – measurement is independent of morphology and composition**



Mass ≡ 0.52 fg

Size ~ 100 nm ???

Aerosol Particle Mass Analyser

- Developed by Ehara et al. (1996)
- Classifies particles by mass to charge ratio
- Opposing centrifugal and electric fields classify particles

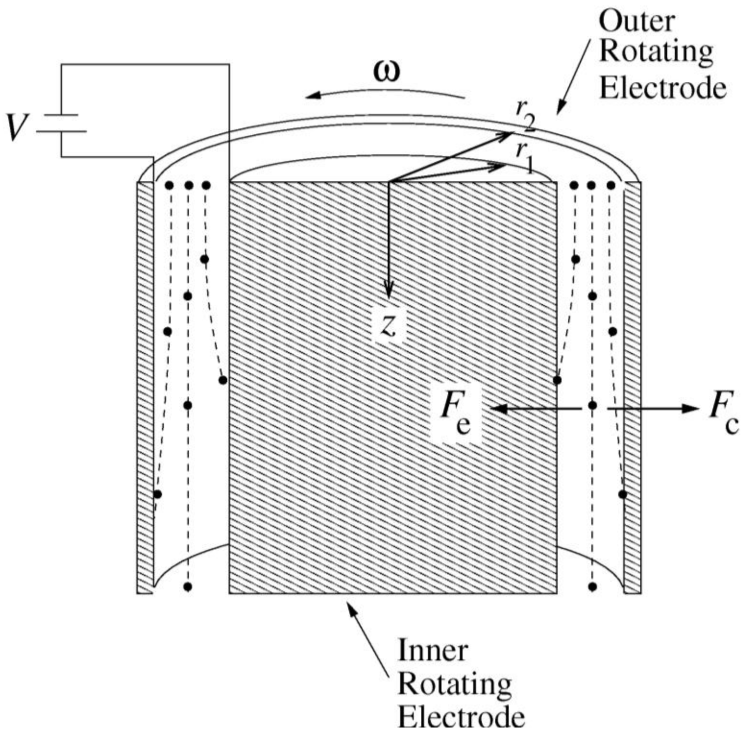


Diagram courtesy of J. Olfert

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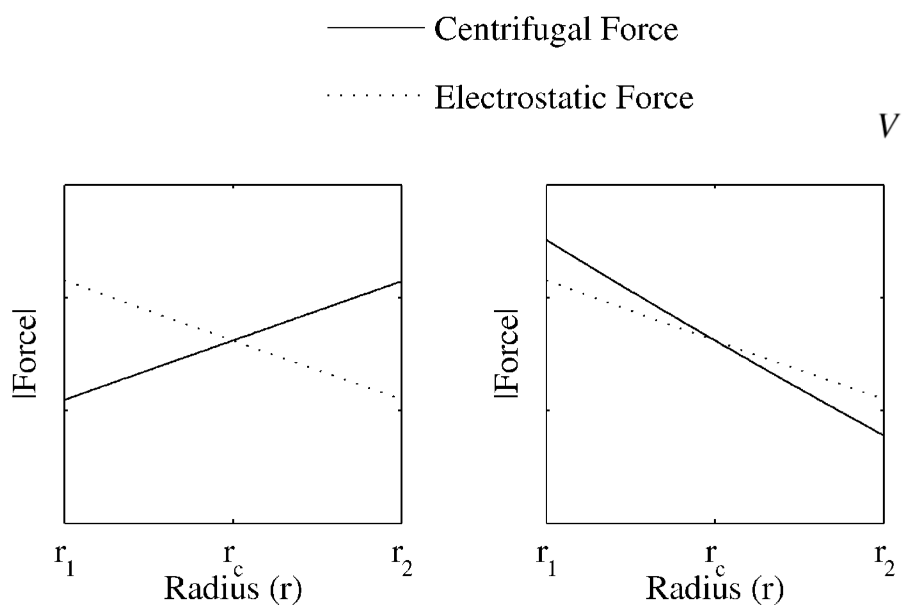
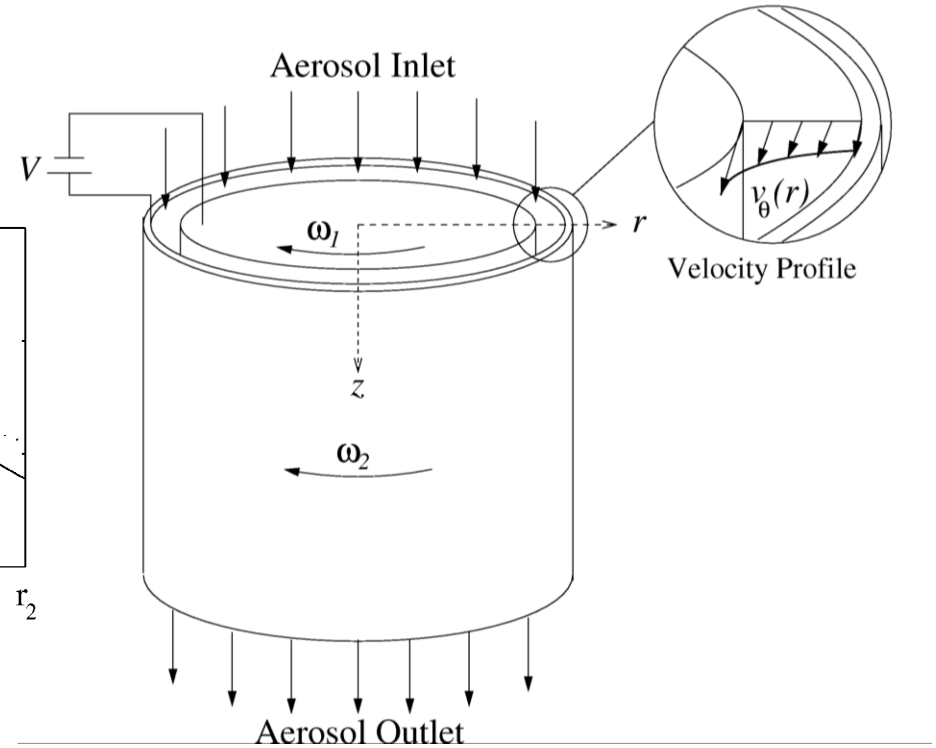
Centrifugal Particle Mass Analyser

- Concept by Mark Rushton and Kingsley Reavell (Cambustion) – also known as “Couette CPMA”
- Developed as a PhD project by Jason Olfert at Cambridge University (2003–2006)
- Cylinders rotate at *slightly* different speeds ⇒ Creates a velocity gradient (*Couette* flow) ⇒ Vary centrifugal force across radius ⇒ Forces balance across radius
- **Particles of correct mass pass through at all entry locations**



$\omega_i = \omega_o$ $\omega_i > \omega_o$



See: Olfert & Collings (2005). *J. Aero. Sci.*

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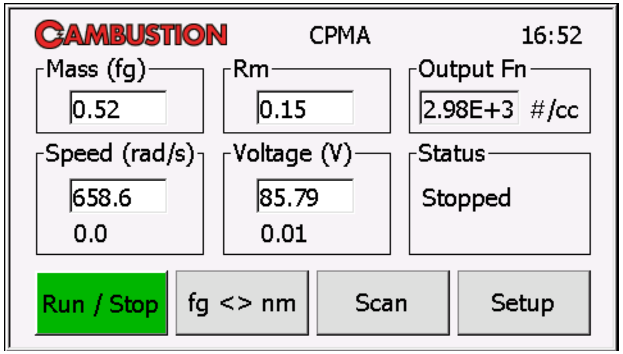
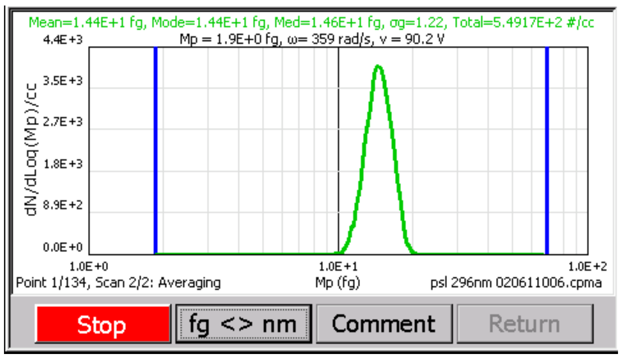
New Version (2012…)



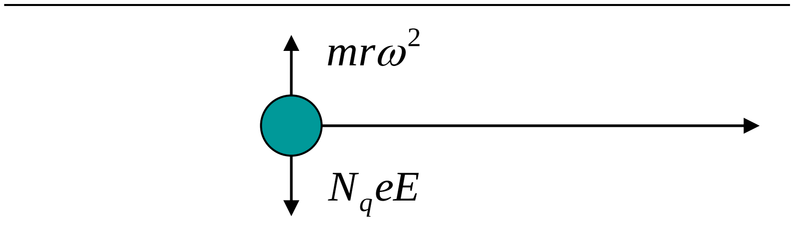


200 l × 120 ø mm classifier with 1 mm gap; 0.1–1000 V; 500–12,000 rpm

Set mass and resolution (FWHM) directly, rather than speed and voltage….

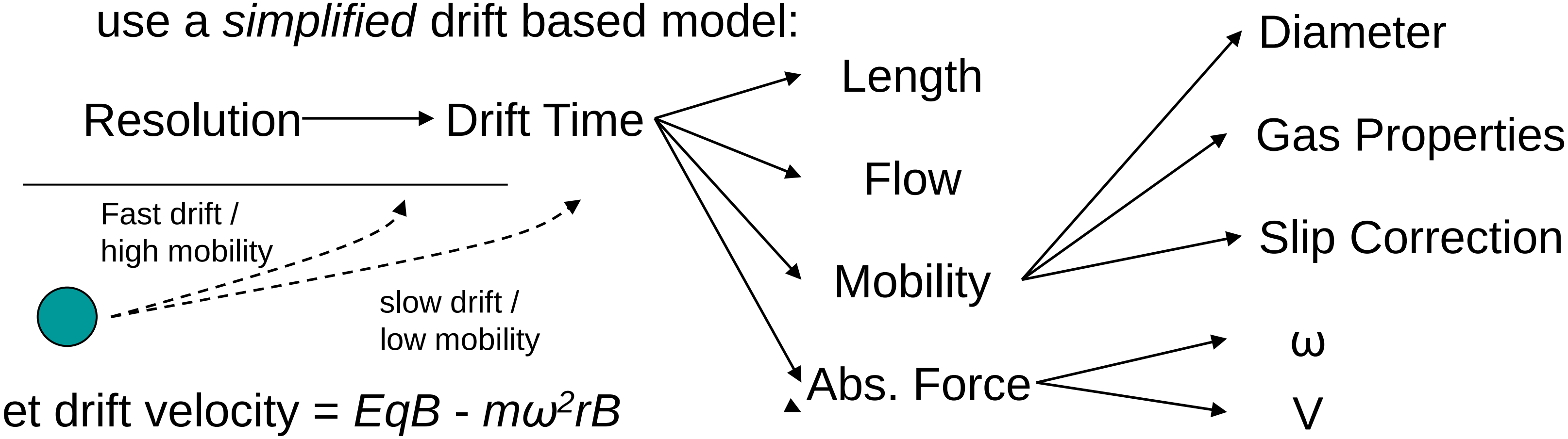
Mass setpoint and resolution

- CPMA selected centre mass is a simple function of the physical parameters of the CPMA, by balancing the forces:



$$\frac{m}{N_q} = \frac{eV}{r^2\omega^2 \ln\left\{ r_o / r_i \right\}}$$

- Unlike say a DMA, setpoint has no dependence on gas properties (e.g. temperature, pressure, viscosity, mean free path) or slip correction.
- Infinite choice of ω, V which balance for a given mass:charge — magnitude determines particle drift speed and hence resolution. We use a *simplified* drift based model:



Net drift velocity = $EqB - m\omega^2 rB$

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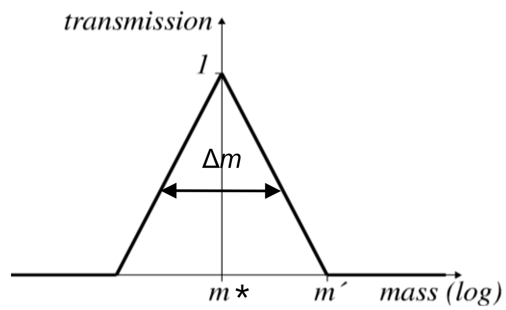
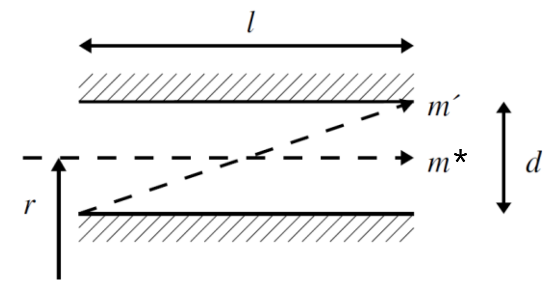
Resolution & Scanning

$$R_m \equiv \frac{m^*}{\Delta m_{\mathrm{FWHM}}}$$





A (good) approximation shows (Reavell *et al.* 2011): $\frac{m'}{m^*}\left(mr\omega^2\right) - \frac{q'}{q}\left(qE\right) = \frac{B}{B'}\frac{Q}{2\pi Blr}$

This is dependent upon mobility, *B*, hence $d_{\mathrm{p,mobility}}$

To calculate *ω* and *V* for a desired resolution, software needs mass:size model: $m_{\mathrm{p}} = \mathrm{A}\, d_{\mathrm{p}}^{\,i}$ (for unit density spherical particles, $A = (\pi / 6) \times 1000$ and $i = 3$). Mass setpoint accuracy still independent of all these factors, only needed for accurate resolution.

The *size* based resolution, $R_{\mathrm{s}} = \sim 3\ R_{\mathrm{m}}$ for spheres
For typical DMA resolution of $R_{\mathrm{s}} \sim 10$, the equivalent CPMA resolution, $R_{\mathrm{m}} \sim 3.03$

As the net drift velocity = $EqB - m\omega^2 rB$, *strictly speaking*, scanning the voltage whilst leaving the speed constant changes the resolution over the scan – the new CPMA allows simultaneous counter variation of *ω* and *V* to keep the resolution, *R*, constant.

DMA-CPMA System

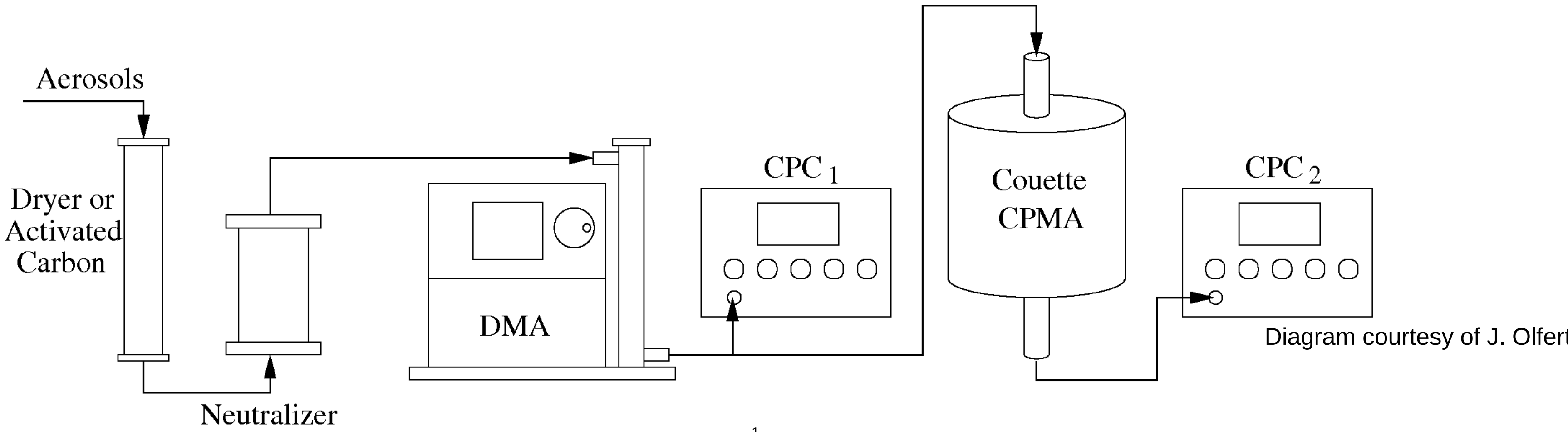
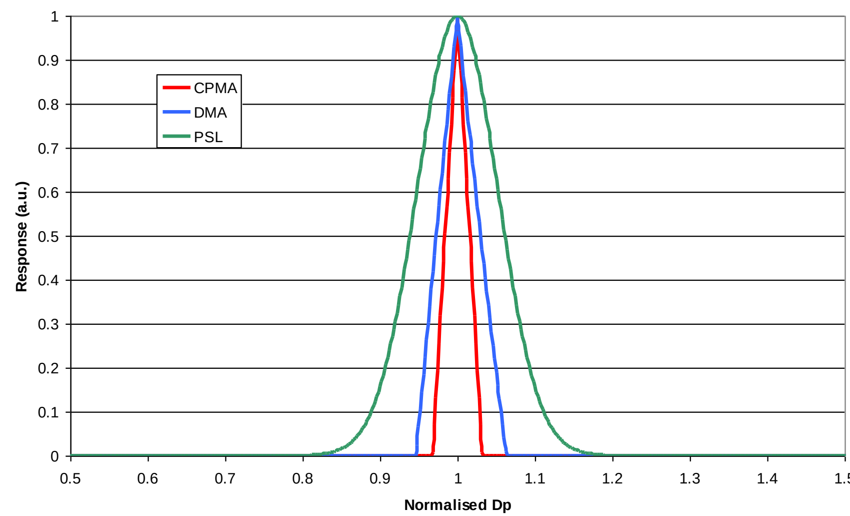


Diagram courtesy of J. Olfert

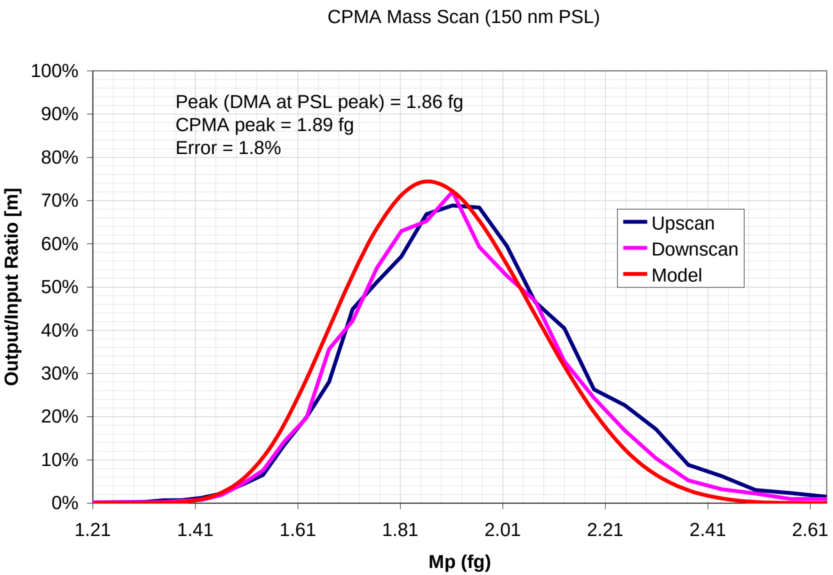
- PSL particles are nebulised, neutralised (charged) and passed through DMA
- CPMA step scanned – speed and voltage counter-varied to maintain same resolution.
- In the following examples, the CPMA's resolution is finer than the DMA's, therefore only a narrow "slice" is measured, so $N_{CPC2} < N_{CPC1}$.

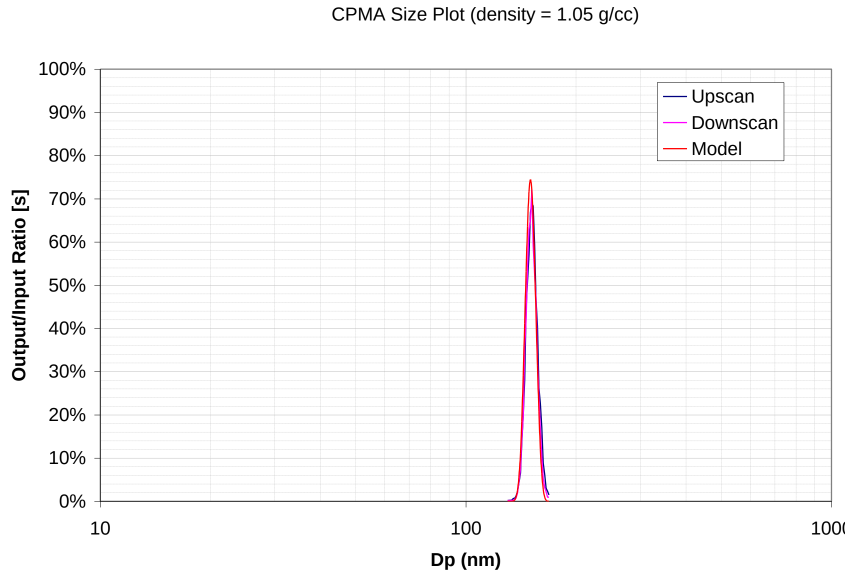


e.g. Thermo 102 nm PSL $d/\Delta d$ = 8.33, DMA $d/\Delta d$ = 20.0, CPMA $d/\Delta d$ = 31.0 ($m/\Delta m$ = 10.0)

PSL Results

150 nm PSL: CPMA R_m = 5.12 (R_d ~ 16.6), flow = 1.5 lpm; DMA sheath = 10 lpm, aerosol = 1 lpm





Similar width of distribution validates drift limited resolution model.
Though "traceable", PSL is not ideal for this experiment:

- Tolerance of 50 nm PSL is 7.3 nm = 15% in size; but ~45% in mass terms (~90% as a 95% C.I.) – as a mass "standard" almost meaningless
- Size alignment of PSL and DMA is critical
- Nebulised PSL actually bimodal: "Surfactant peak" can overlap PSL peak – density?

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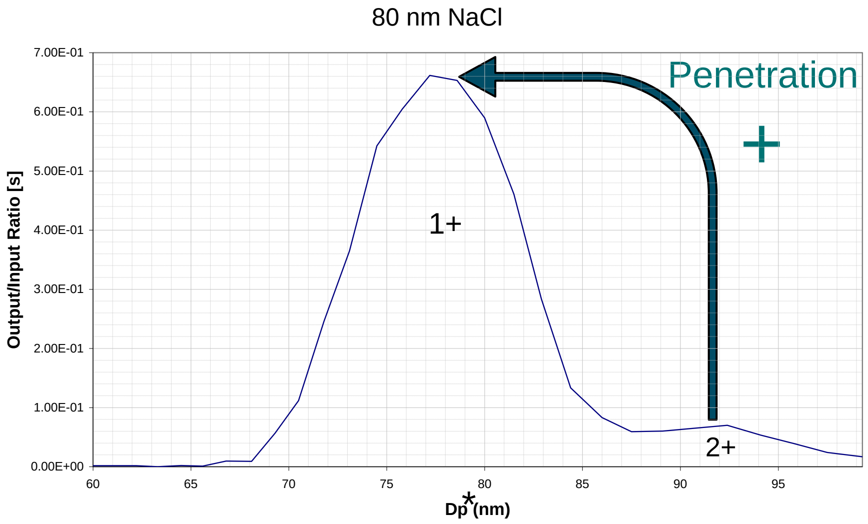
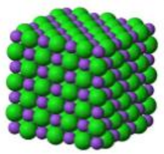
NaCl Experiments

- Cut nebulised NaCl aerosol with DMA, pass through CPMA
  - Calibrated DMA more accurate than PSL (esp. for D_p <100 nm)
  - No surfactant (no mixture of different densities)
  - Only 2 functions to convolute
  - Nebulised aerosol not monodisperse, doubly charged particles occur
  - Particles are not spherical (~cubic), must take account of shape factor (for *DMA* accuracy)





$$\chi_{f,\mathrm{NaCl}} = 1.08$$

$$\chi_f = \frac{d_{\mathrm{me}} C_c(d_{\mathrm{me}})}{d_{\mathrm{ve}} C_c(d_{\mathrm{ve}})}$$

$$m_{\mathrm{DMA}} = \frac{\pi}{6} \rho d_{ve}^{\ 3}$$

Much more on charge later…

NaCl Experiments: Uncertainties

- **DMA Mass**: ISO15900:2009 (Differential Electrical Mobility Analysis): $\frac{\Delta Z}{Z} \approx 2.2\%$

  $\frac{\Delta Z}{Z} \sim \frac{\Delta D}{D}; \frac{\Delta m_d}{m_d} \sim 3\frac{\Delta D}{D} = 6.6\%$; 95% C.I. $= 2\sigma =$ **13%** (neglecting errors in C_c and χ_f)

- **CPMA Mass**: 4 independent variables:

Quantity	Abs Tolerance (eqv. to 95% C.I.)	Δx/x 95% C.I.
Voltage (V)	-	1%
Angular Speed (ω)	-	1%
Inner Radius (r_i)	± 0.05 mm	-
Outer Radius (r_o)	± 0.05 mm	-

$$\frac{m_c}{q} = \frac{eV}{\left(\frac{r_o + r_i}{2}\right)^2 \omega^2 \log\left(\frac{r_o}{r_i}\right)}$$

$$\frac{\Delta m_c}{m_c} \approx \sqrt{\left(\frac{\Delta V}{V}\right)^2 + \left(2 \cdot \frac{\Delta \omega}{\omega}\right)^2 + \left(\frac{\Delta r_o}{r_o - r_i}\right)^2 + \left(\frac{\Delta r_i}{r_o - r_i}\right)^2} \text{ for } r_o \approx r_i$$

(tolerance on **gap**, r_o-r_i, dominates – changes electric field)

$$\frac{\Delta m_c}{m_c} \approx \sqrt{(0.01)^2 + (2 \times 0.01)^2 + \left(\frac{0.05}{1.00}\right)^2 + \left(\frac{0.05}{1.00}\right)^2} = \mathbf{7.5\%} \text{ (95\% C.I.)}$$

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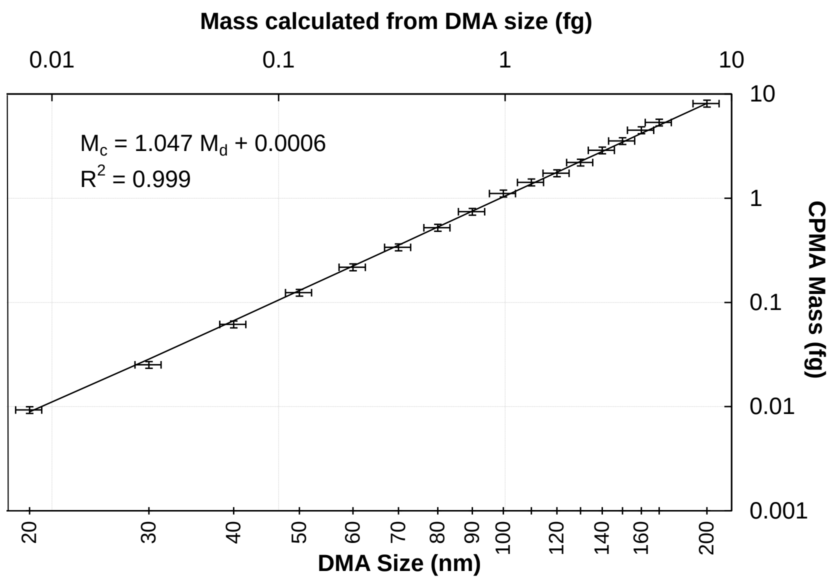
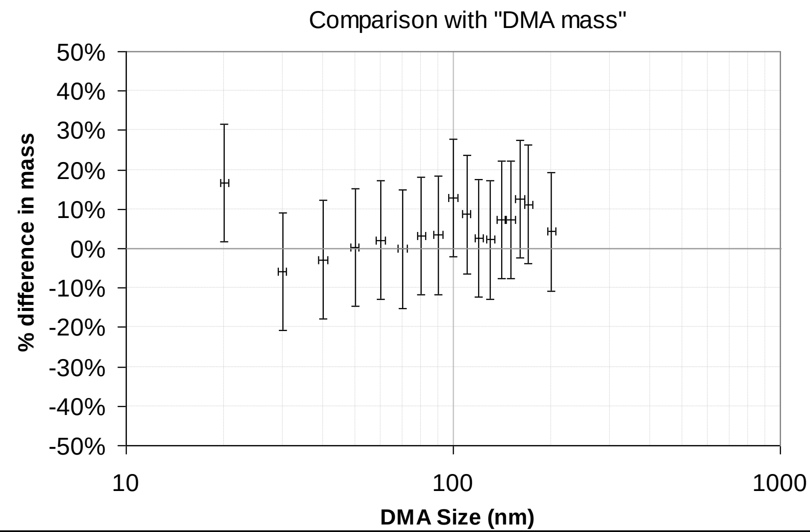
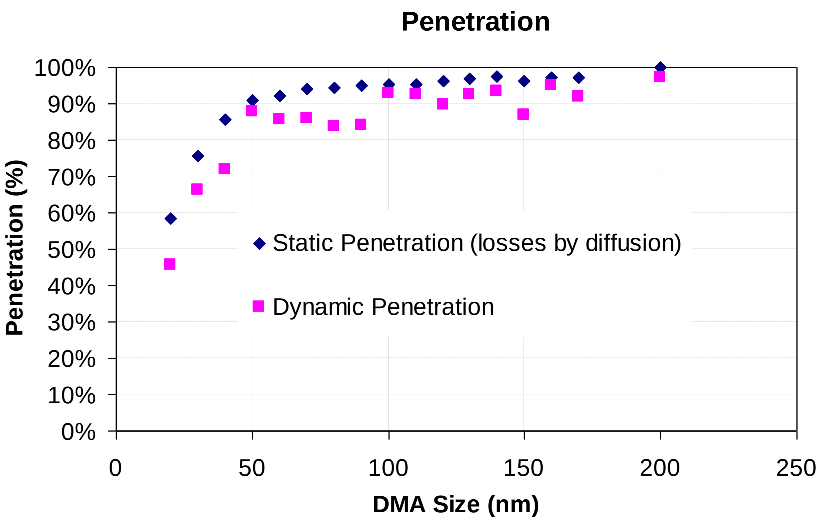
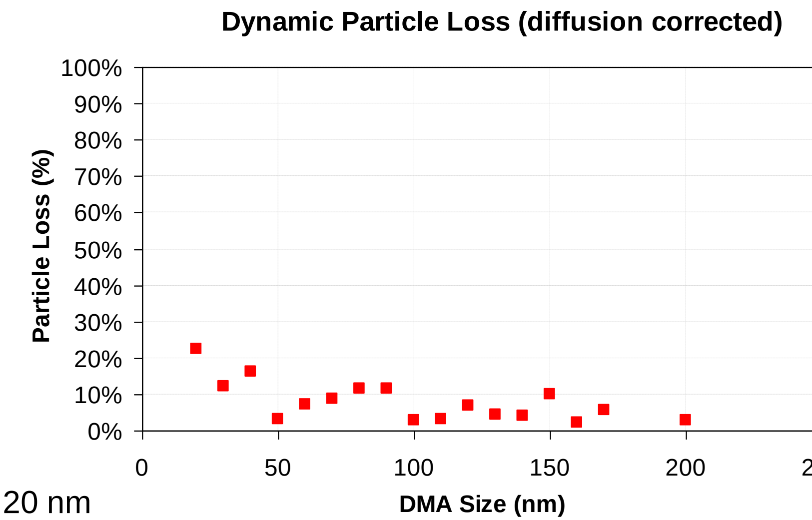
NaCl results: $R_m = 3$ ($R_s \sim 10$)



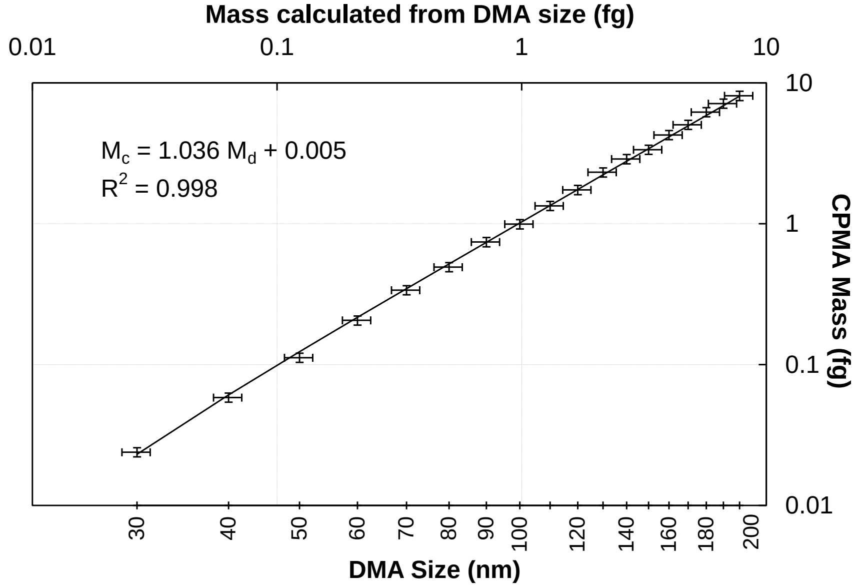


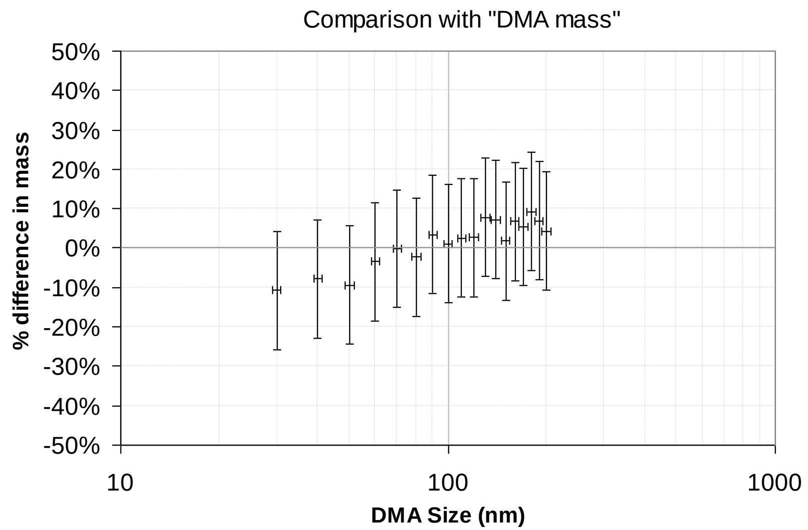


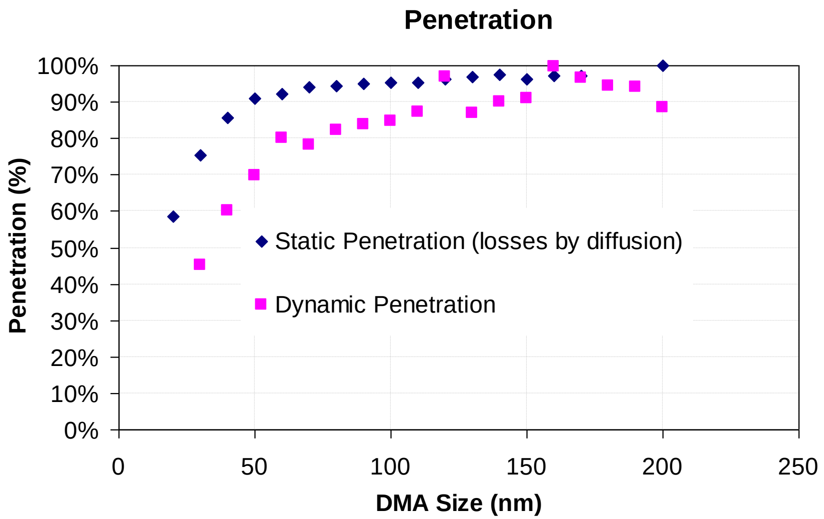
$d_{50,static}$ ~ 20 nm

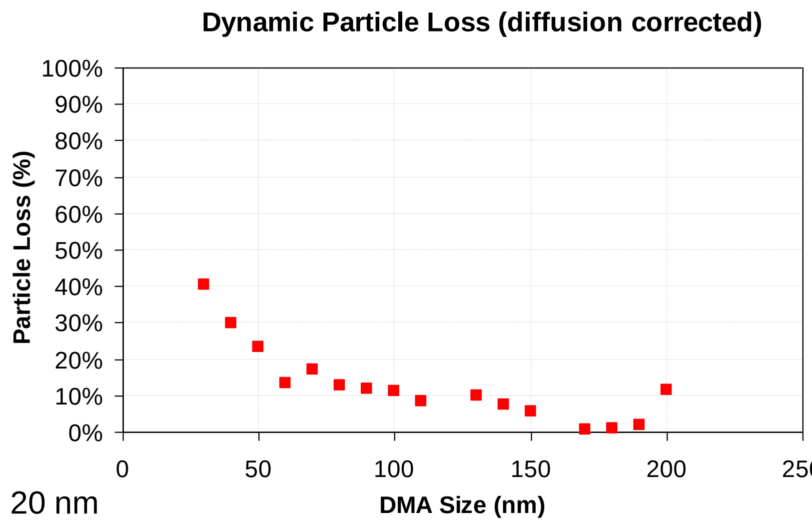


NaCl results: $R_m = 5$ ($R_s \sim 16$)









$d_{50,static} \sim 20$ nm

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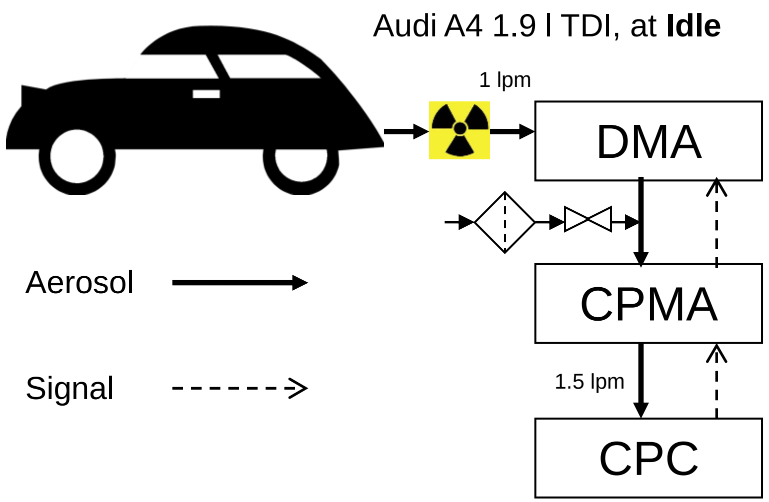
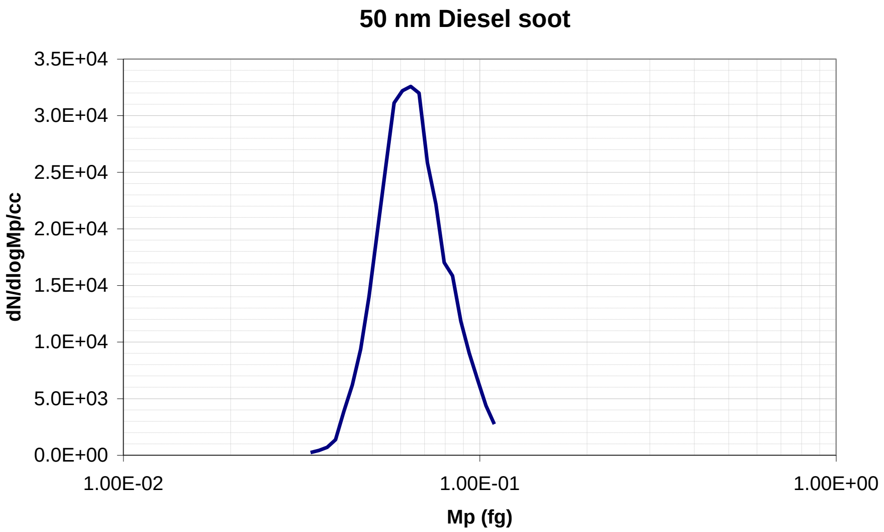
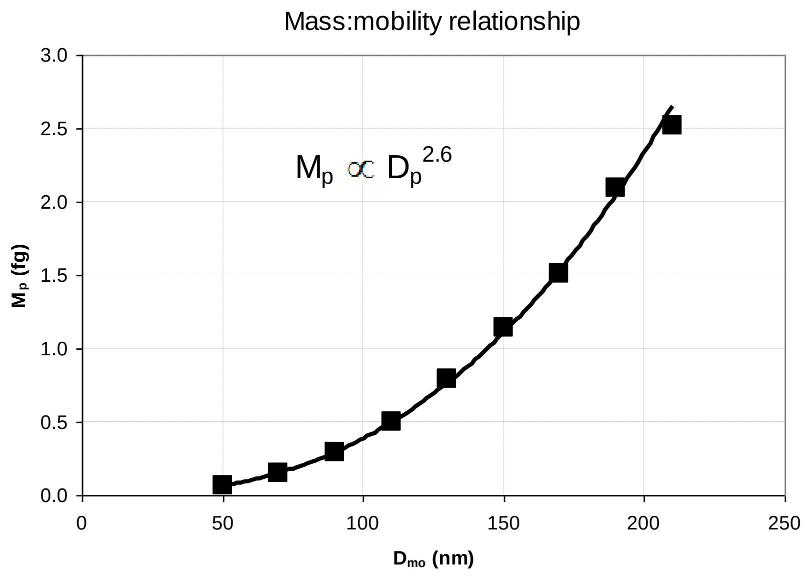
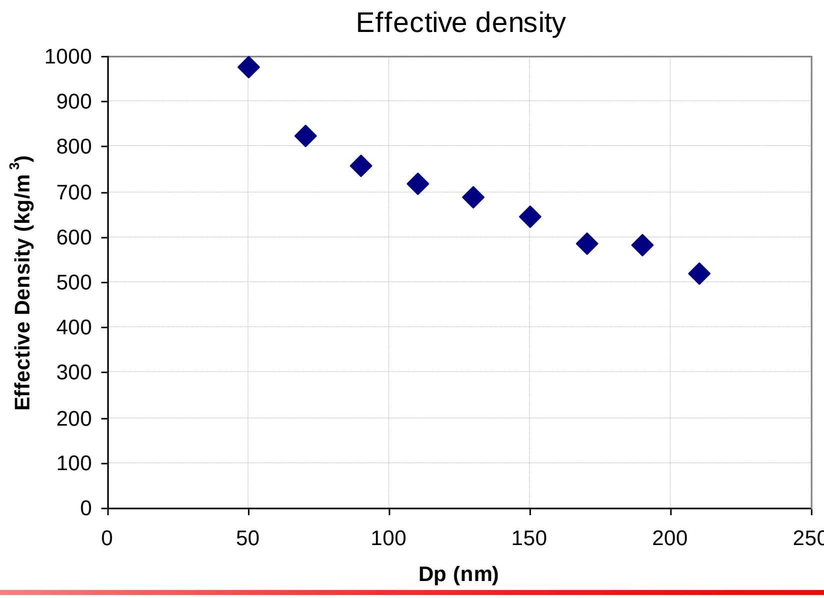
Density Measurement: Diesel Engine









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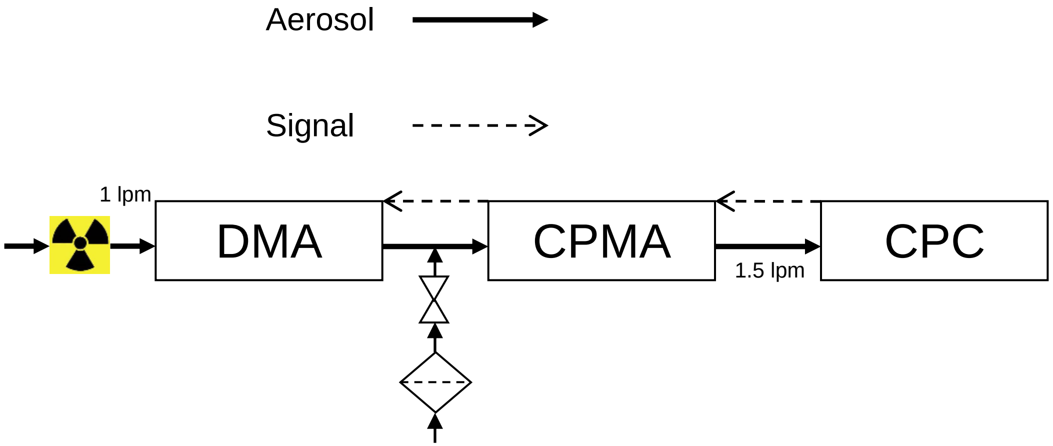
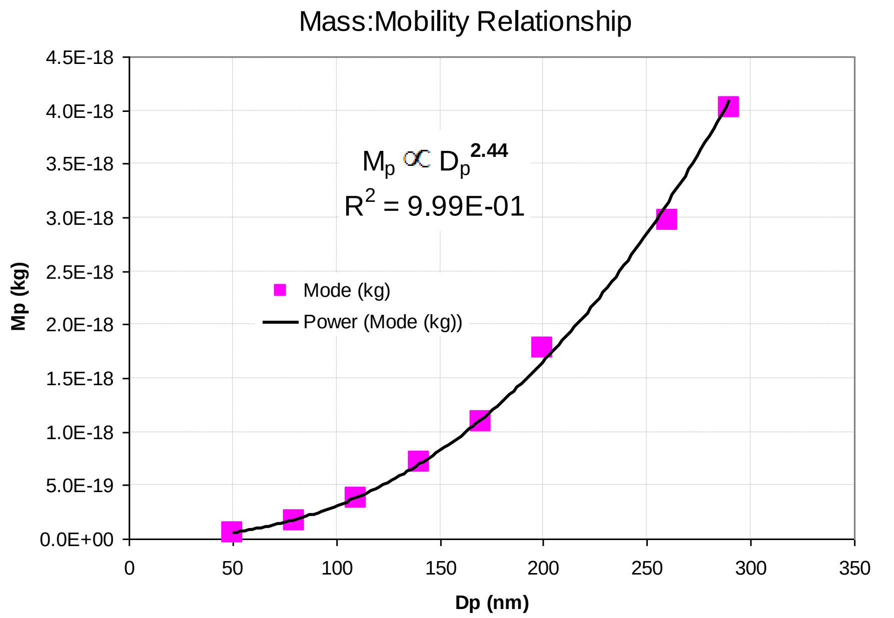
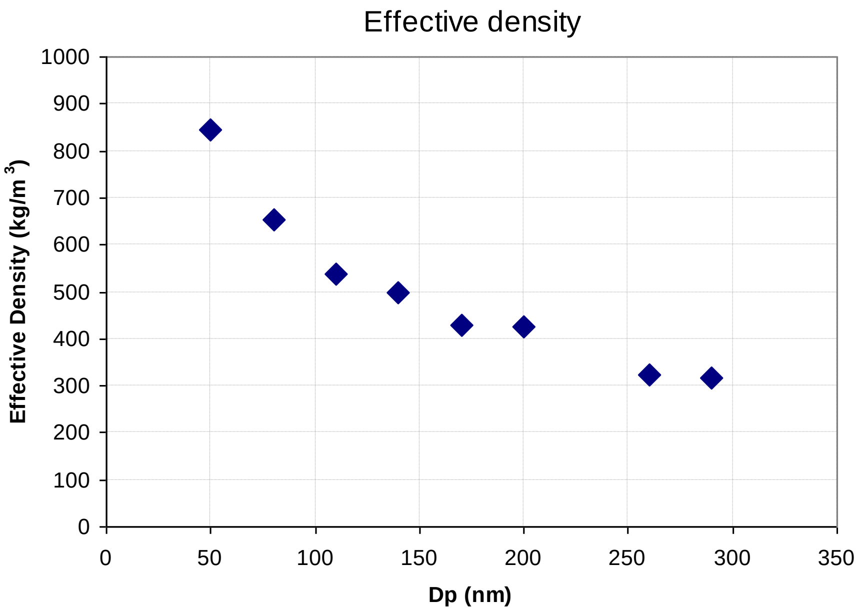
Density Measurement: Diesel Soot Generator







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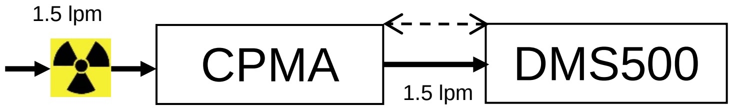
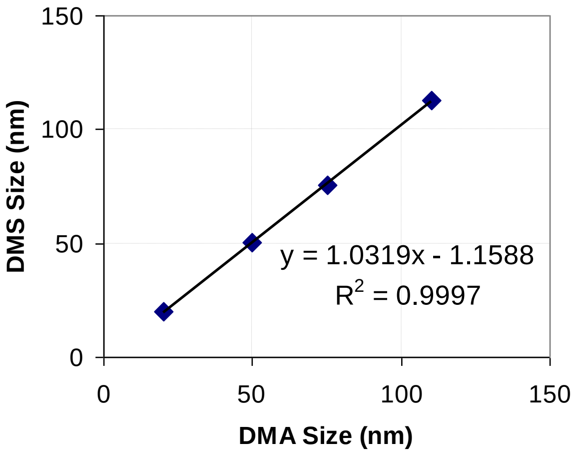
Tandem CPMA:DMS ...when speed is of the essence

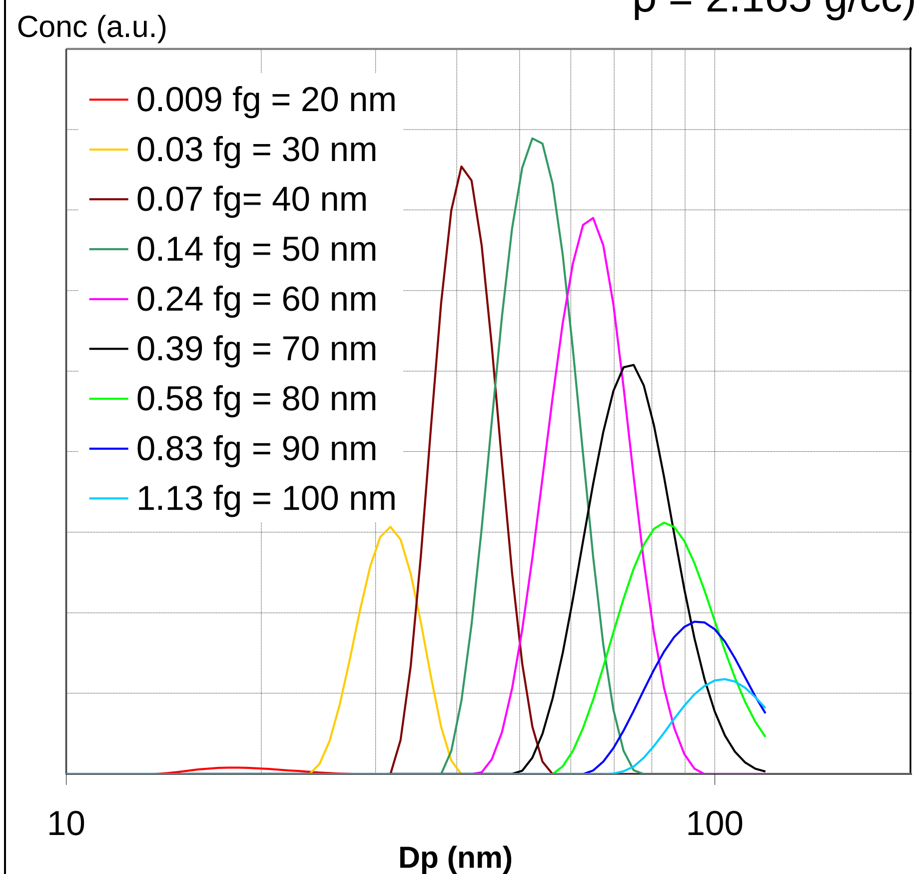
- M_p vs. D_{mo} obtained in < 5 minutes; just 1 CPMA scan
- Charge aerosol with neutraliser, scan CPMA, sample with modified DMS500:



- DMS Charger disabled
- Inversion matrix created assuming +1 pre-charged aerosol (10 nm – 150 nm, 64 classes per decade)
- 1.5 lpm sample flow
- Mass setpoint from CPMA logged to DMS
- Lognormal CMD from DMS logged to CPMA
- DMS Validated with monodisperse aerosol from DMA:



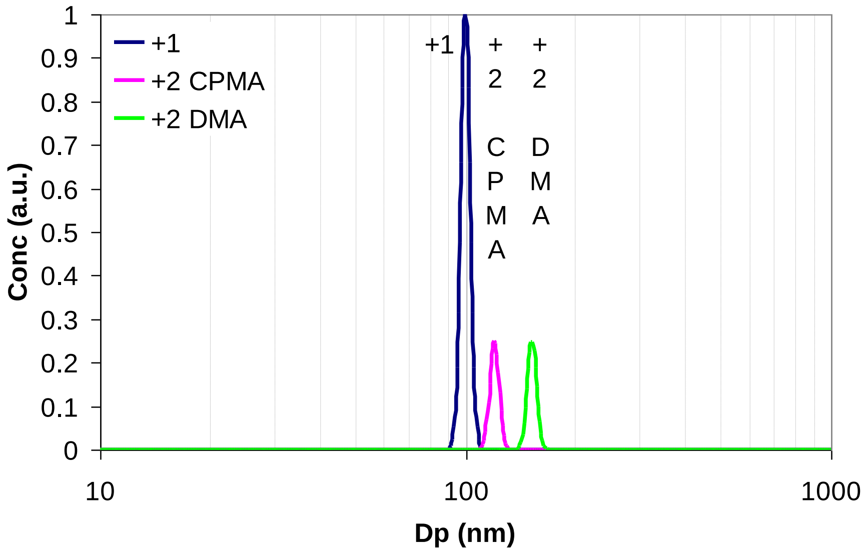
Example: NaCl (CPMA mass based on ρ = 2.165 g/cc):

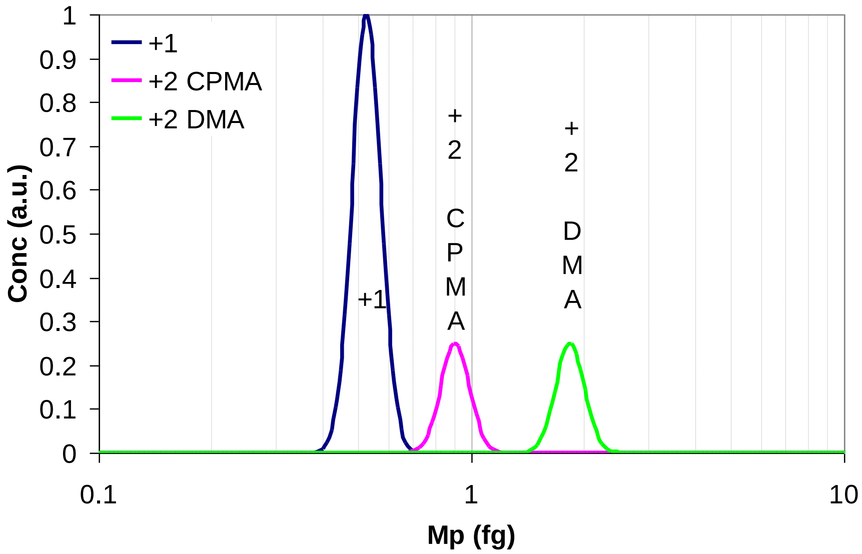


- Technique recently used on Gas Turbine engines…

Charge Effects – Downstream of DMA

- Strictly necessary to correct for multiple charges from Neutraliser - DMA system.
- e.g.: **100 nm** particle
  - **+2** particle from DMA (with same electrical mobility) at **152 nm** (mass **1.8 fg** at unit density)
  - These particles (still with 2+ charges) appear at **half** the mass of a 152 nm particle in the CPMA scan (2 charges): **0.9 fg**
  - observed +2 peak equivalent to **120 nm:**





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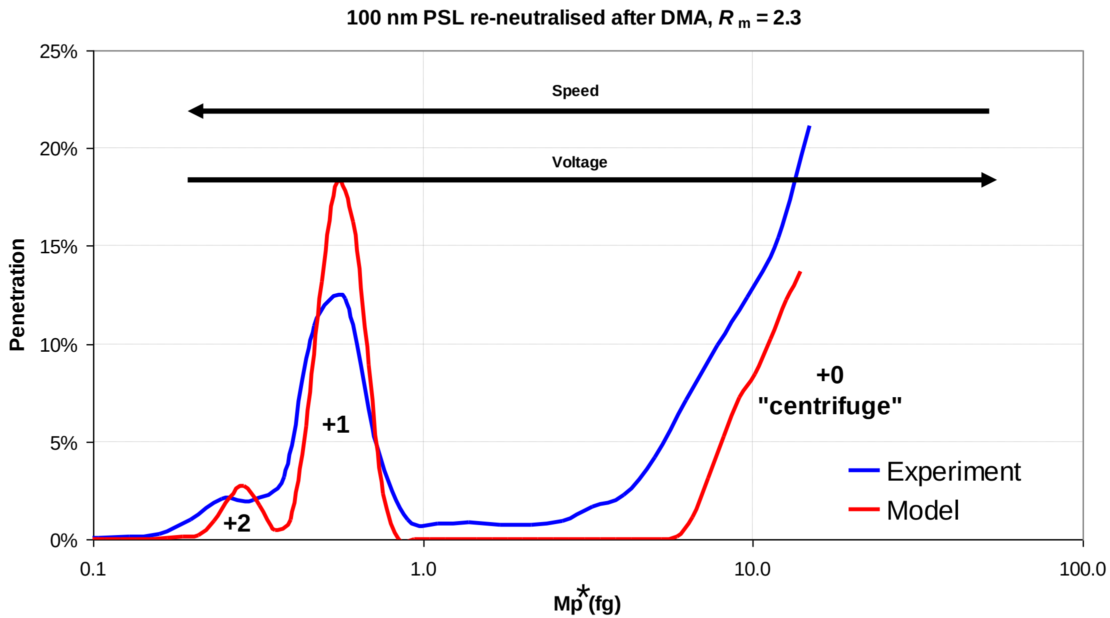
Charge Effects – Bipolar Equilibrium Charge

If used *directly* with a neutraliser (without a DMA) also need to account for *zero* charge state at sufficiently low speeds if used with CPC

DMA is there to remove PSL surfactant etc



- Charging models size based, hence a mass based model is weakly density dependent
- Inverse problem yet to be tackled
- If an electrometer is used when scanning — don't detect zero charge particles
    - Still need to correct concentration for their *absence*, and for the absence of –ve charged particles

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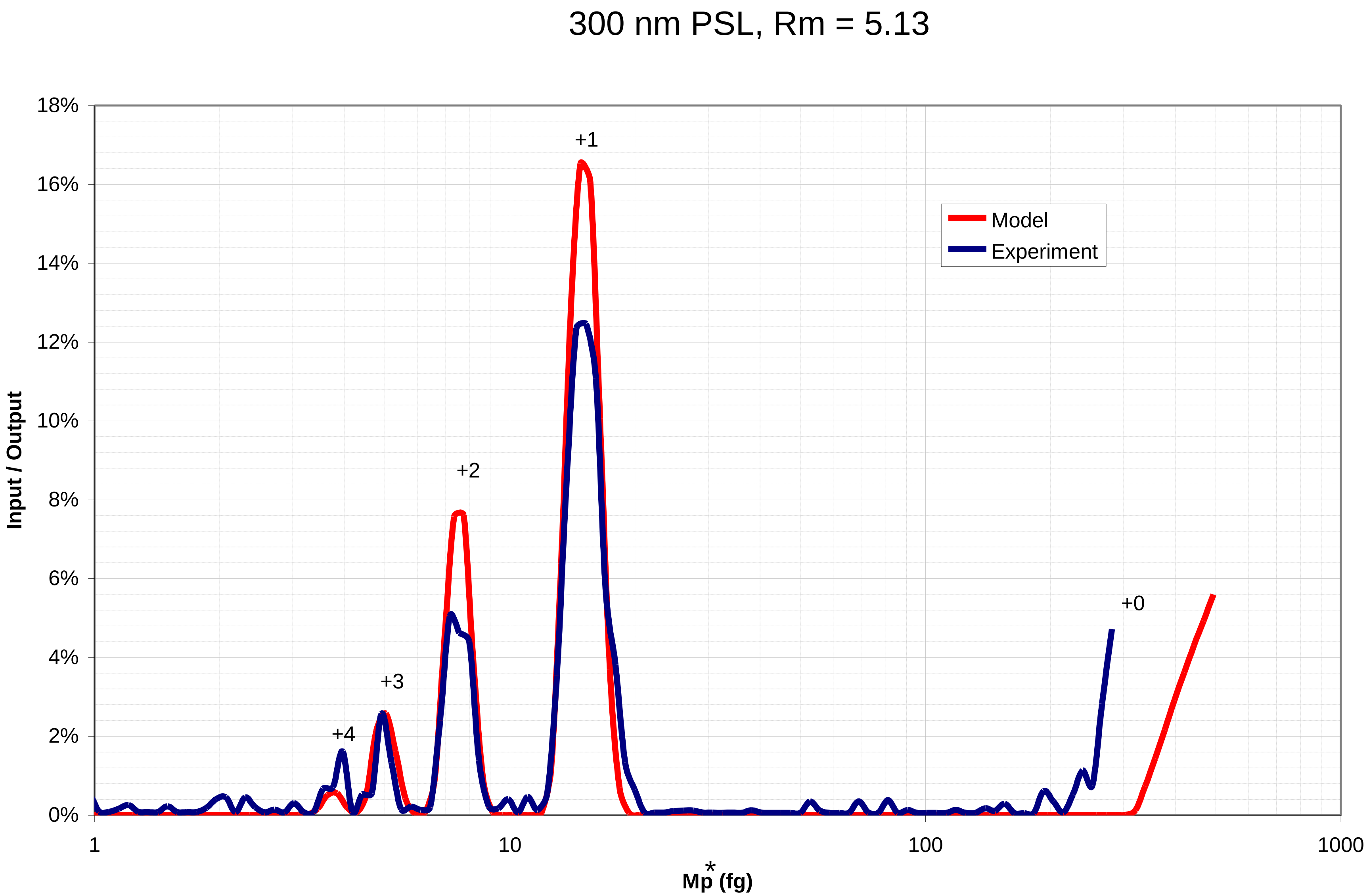
Higher resolution, bigger particles, more charges…

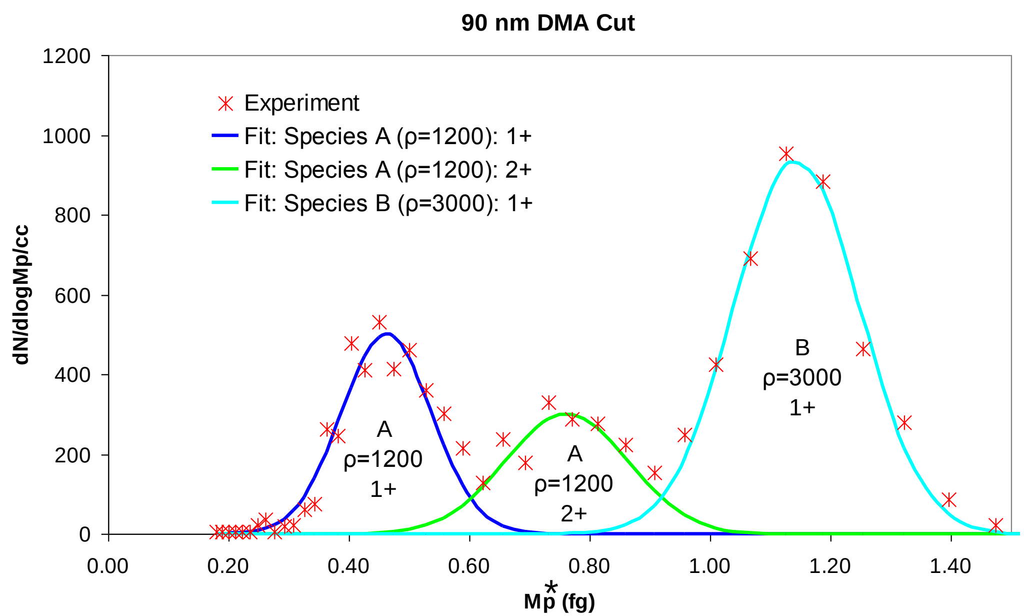


Liquefied Petroleum Gas Vehicle (preliminary data)

BMW 5 Series
LPG Conversion

Exhaust Ejector
Diluted to ~20:1
to reduce water
condensation

Low signal (clean
engine)



D_p →

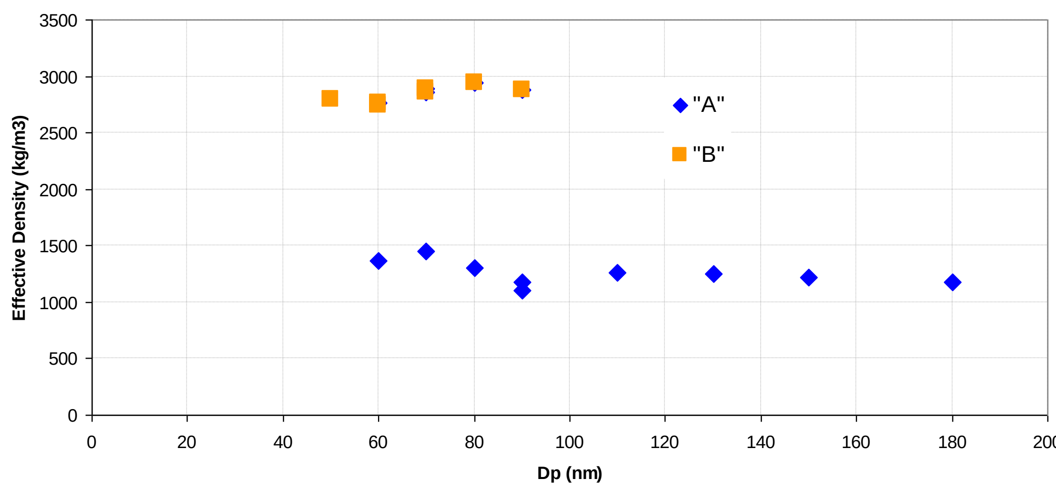
%A →

%B ←

A: soot or water?

B: ash? (lube oil)

TBC…



CPMA-Electrometer: A Suspended Mass Standard

- System appealing as “suspended mass standard” for instrument calibration
  - electrometer counts “**double** mass:charge” particles **twice** (etc), correcting for charge

Source → Charger → CPMA → Mass conc. instrument to be calibrated / Electrometer

M = mass *setpoint* (fg)

m_{total} = post CPMA mass *concentration* (fg/cc)

$$m_{\text{total}} = m_{+0} + Mn_{+1} + 2Mn_{+2} + 3Mn_{+3} + \ldots$$
$$= m_{+0} + M\left(n_{+1} + 2n_{+2} + 3n_{+3} + \ldots\right)$$
$$I_{\text{elec}} = Qe\left(n_{+1} + 2n_{+2} + 3n_{+3} + \ldots\right)$$
$$\therefore m_{\text{total}} = m_{+0} + \frac{MI}{Qe} = m_{+0} + M \times \text{"Indicated N/cc"}$$

Only necessary correction is for m_{+0} (-ve particles don’t pass)

… or ….

minimise m_{+0}:

- remove small particles
- use a unipolar corona charger. Also raises detection limit.

m_{total} = **mass *setpoint* × indicated electrometer *concentration*** + zero charge correction

Not true for DMA-Electrometer system – doubling ‘drag’ does not double concentration!

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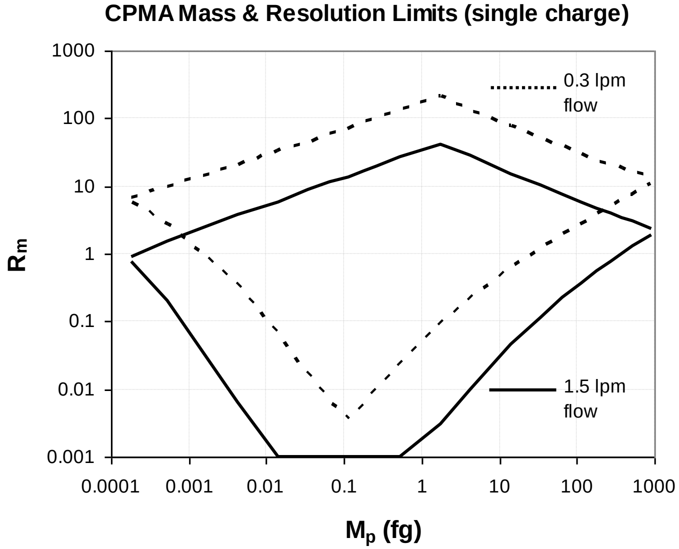
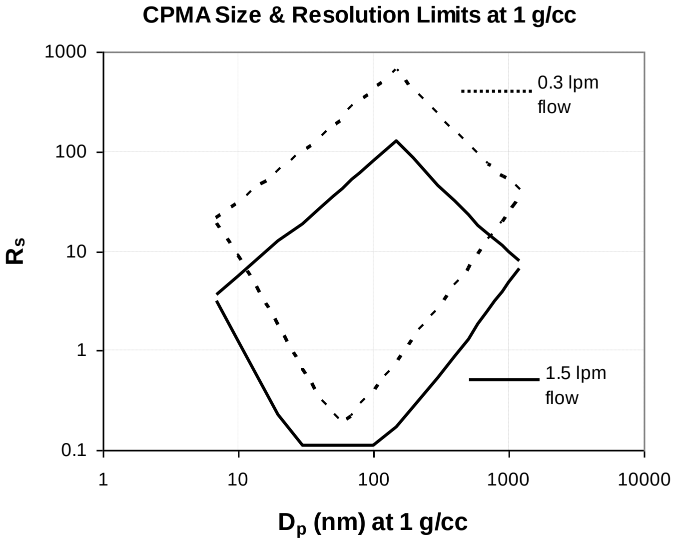
Applications & Specifications

- *Fundamental aerosol mass standard – calibrate AMS, black carbon detectors etc.*
- *Particle density / morphology (with DMA & CPC)*
- *Mass scan (with CPC or electrometer)*





- Classifier dimensions: 200 l × 120 ø mm, 1 mm gap
- Typical sample flow, 0.3 – 1.5 lpm
- Residence time ~ 3 s @ 1.5 lpm
- Operating parameters: 500 – 12,000 rpm, 0.1 – 1000 V
- I/O: Ethernet, RS232 / USB, 3 × analogue in, 3 × analogue out
- Integrated touchscreen controller, with step scan to USB drive

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Acknowledgements

- Dr Jason Olfert (University of Alberta)
- Professor Nick Collings (University of Cambridge)
- Andrew Todd (Cambustion)

Jon Symonds: jps@cambustion.com

www.cambustion.com/cpma

for more information including references

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