A High Transmission Efficiency Centrifugal Particle Mass Analyser for Determination of Nanoparticle Mass and Morphology

Jonathan Symonds (Cambustion)
Arnaud Noirtin (Intertek)
Jason Olfert (University of Alberta)

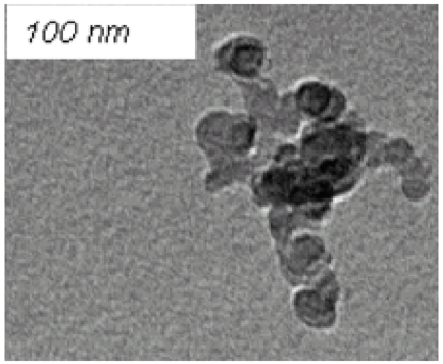
Nanosafe 2010, Grenoble

Contents

- The need to measure aerosol particle mass
- State of the art in aerosol nanoparticle mass measurement
- The Centrifugal Particle Mass Analyser (CPMA)
- Result from first prototype (2004)
  - Mass calibration of the CPMA
  - Differentiation of spherical and cubic particles
  - Fractal dimension measurement of
    - Diesel soot agglomerates
    - Gasoline soot particles
- Second prototype (2009)
- The forthcoming commercial version

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:
  - Size to mass calibration for size based instrumentation
  - Particle fractal dimension and dynamic shape factor ⇒ particle morphology
- Whilst particle size for a non spherical particle can be defined in many ways dependent upon measurement technique, **true particle mass is independent of morphology or composition**



Mass ≡ 0.52 fg

Size ~ 100 nm ???

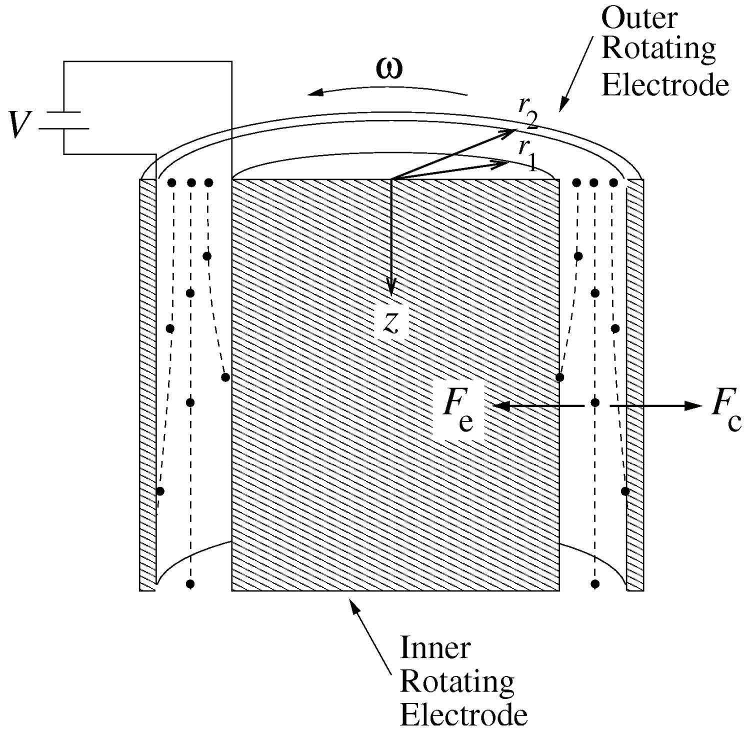
CAMBUSTION

State of the art of aerosol nanoparticle mass measurement

- Filter paper weighing
- Filter paper opacity (e.g. AVL 415)
- Microbalances (TEOM/QCM)
- Photo-acoustic / Micro Soot Sensor (PASS/MSS)
- By calculation from electrical mobility data e.g. SMPS (slow response), DMS (fast response) etc
- By calculation from aerodynamic diameter data e.g. DMM, APS, ELPI, MOUDI etc
- Aerosol Particle Mass analyser (APM)…..

Aerosol Particle Mass Analyser

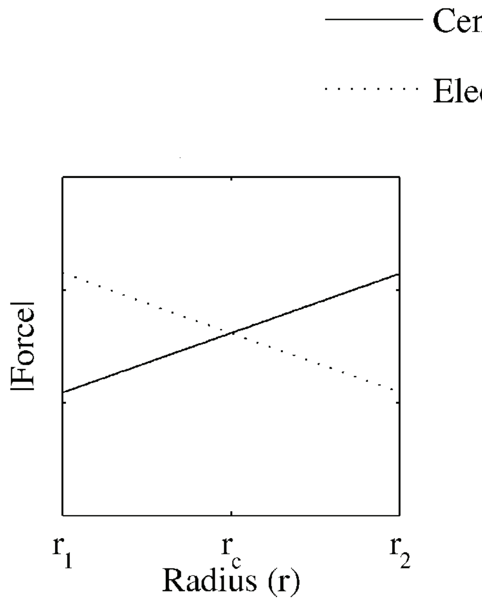
- Developed by Ehara et al. (1996)
- Classifies particles by mass to charge ratio
- Opposing centrifugal and electric fields classify particles



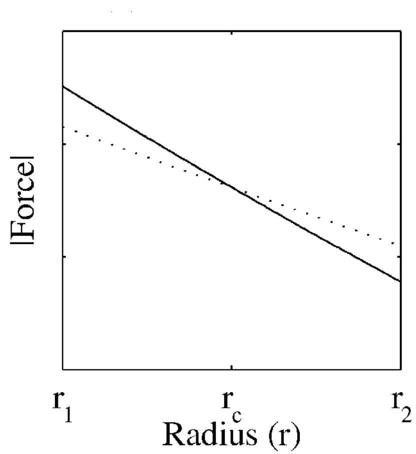
Line diagrams courtesy of J. Olfert

(Couette) Centrifugal Particle Mass Analyser (1)

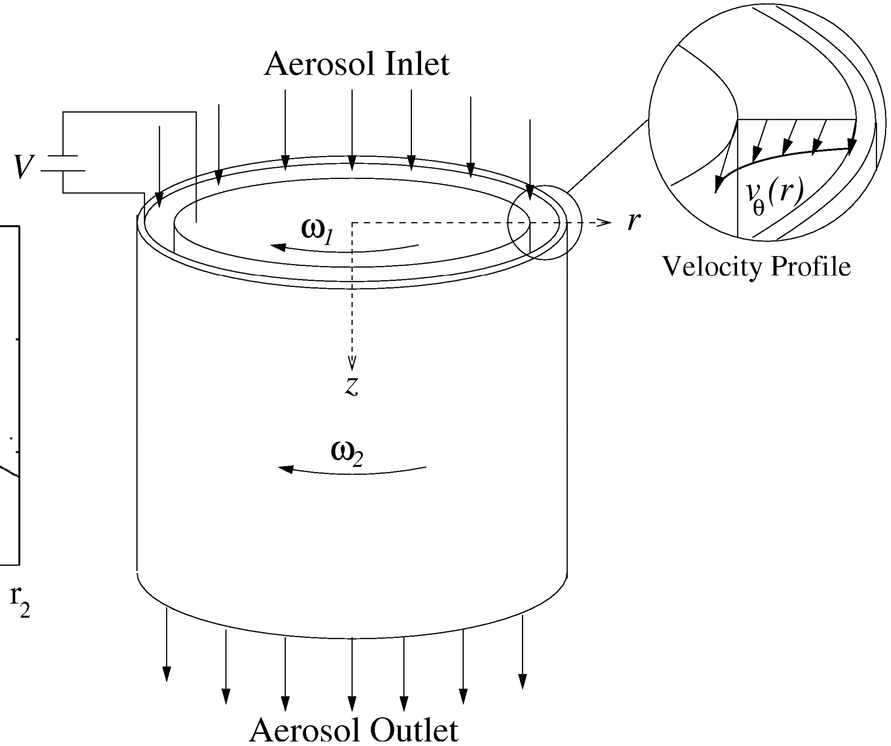
- Concept by K. Reavell and M. Rushton (Cambustion)
- Developed as a PhD project by Jason Olfert at Cambridge University (2003–2006)
- Cylinders rotate at *slightly* different speeds ⇒ Creates a velocity gradient (*Couette* flow) ⇒ Forces balance across radius
- **Particles of correct mass pass through at all entry locations**



$\omega_i = \omega_o$



$\omega_i > \omega_o$

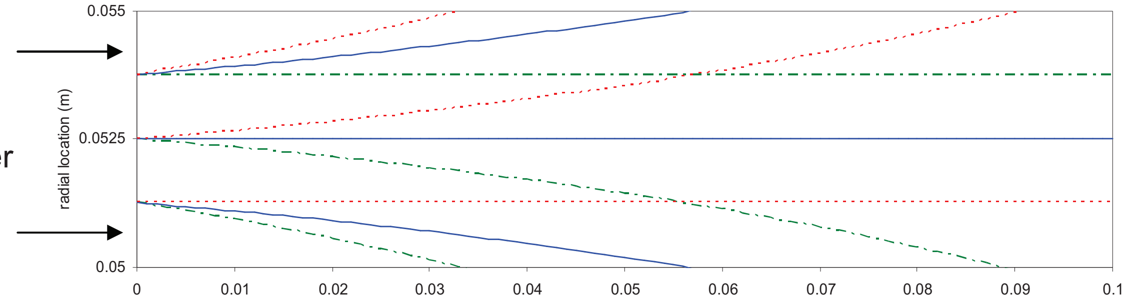


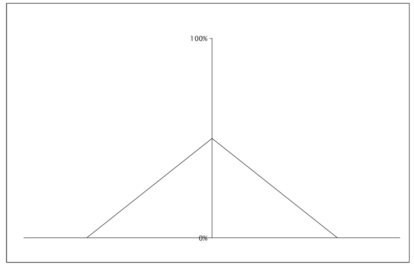
See: Olfert & Collings (2005). *J. Aero. Sci.*

CAMBUSTION

(Couette) Centrifugal Particle Mass Analyser (2)

$\omega_{inner} = \omega_{outer}$

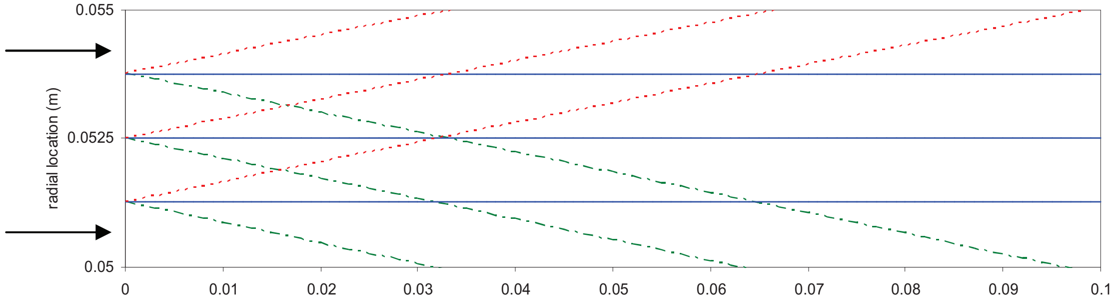


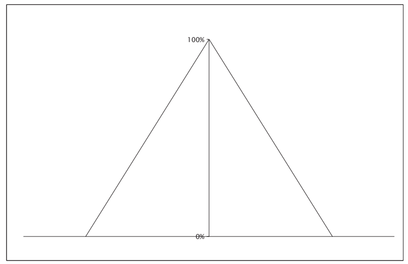


unstable transfer fn

Desired Mass Too Heavy Too Light

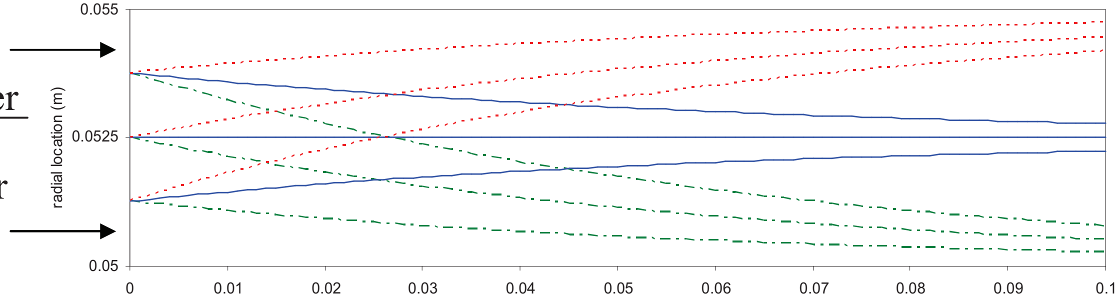
$\omega \propto 1/\text{radius}$

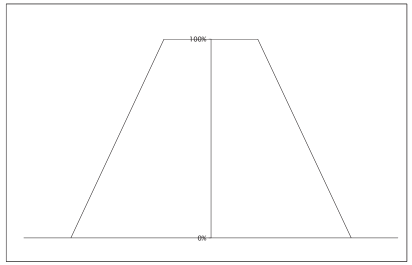




neutrally stable

$$\frac{\omega_{inner}}{r_{inner}} > \frac{\omega_{outer}}{r_{outer}}$$





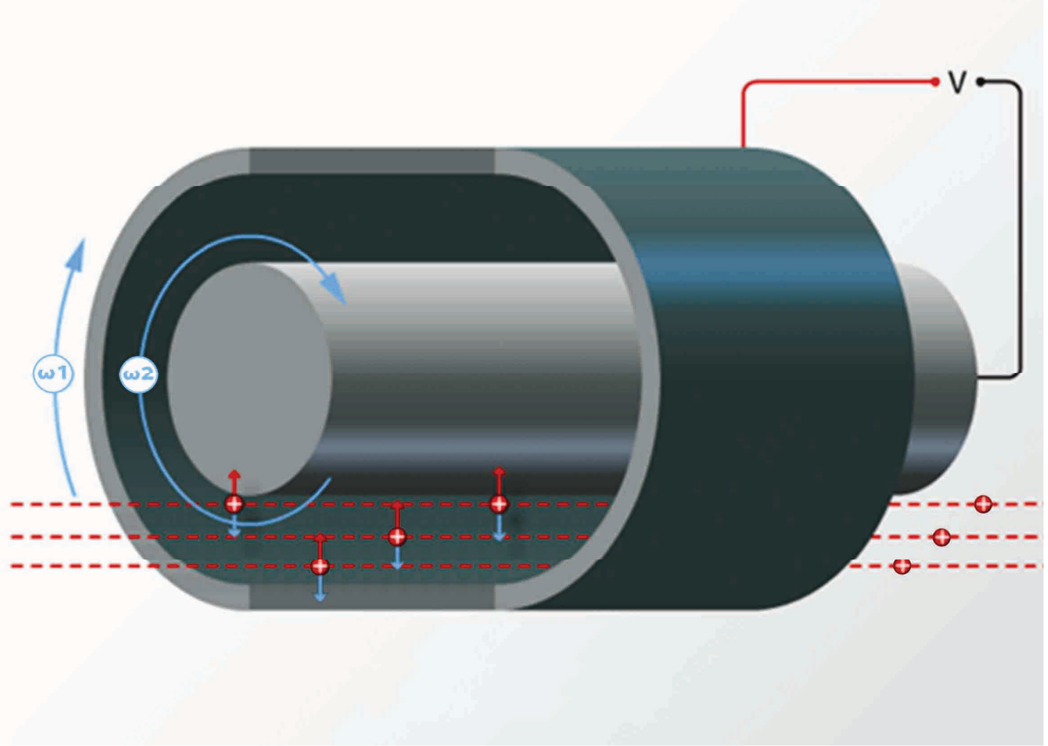
positive stability

CAMBUSTION

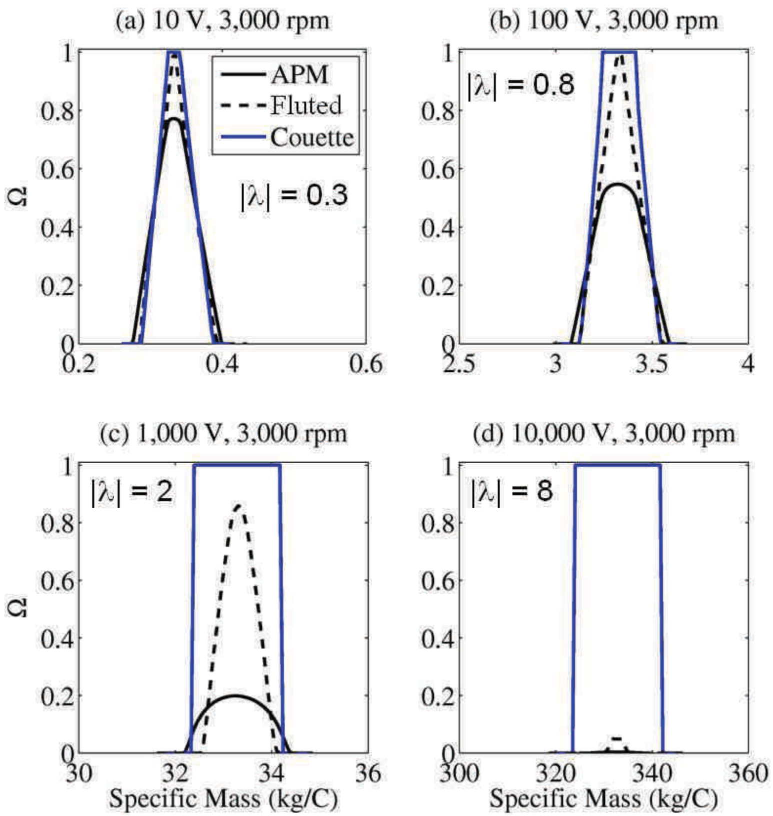
(Couette) Centrifugal Particle Mass Analyser (3)

- Particles of the correct mass:charge ratio pass through the classifier whatever their entry radius

  $\Rightarrow$ High transmission efficiency



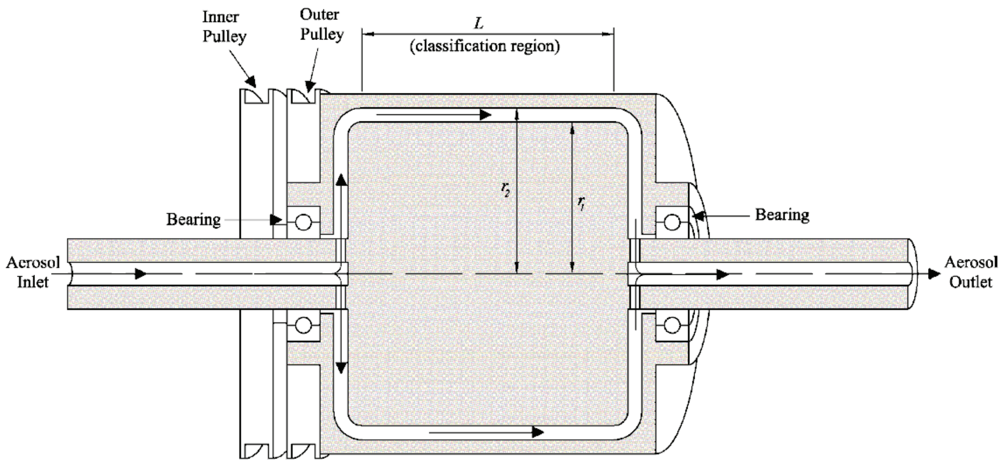
$\omega_{inner} > \omega_{outer}$

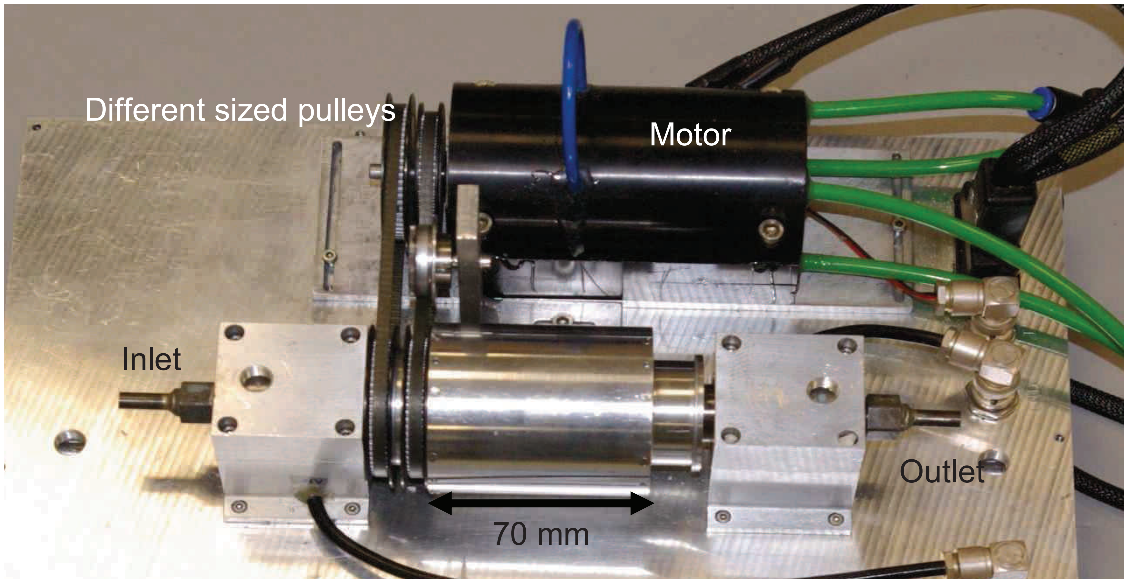


Theoretical transfer functions (+ve stability)

CAMBUSTION

CPMA: First Prototype (2004)

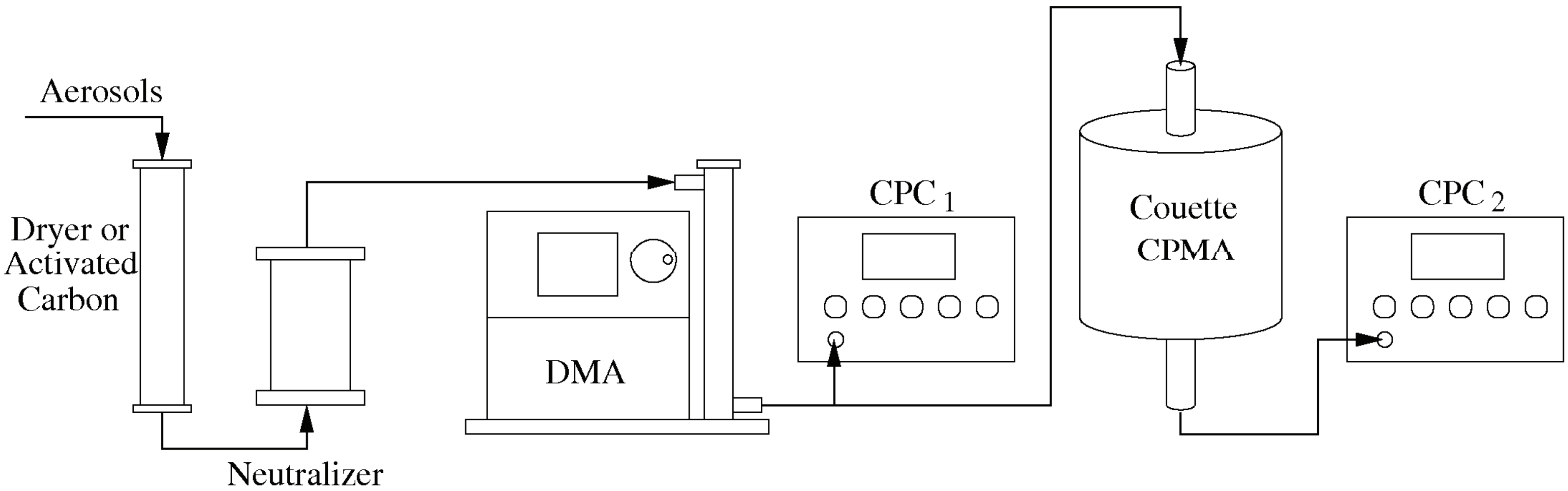




CAMBUSTION

First experiments: DMA-CPMA system

- A DMA and CPMA can be used to measure particle densities, fractal dimensions, and dynamic shape factors.
- Can determine size:mass relationship
- The experimental set-up used in this work is shown below:

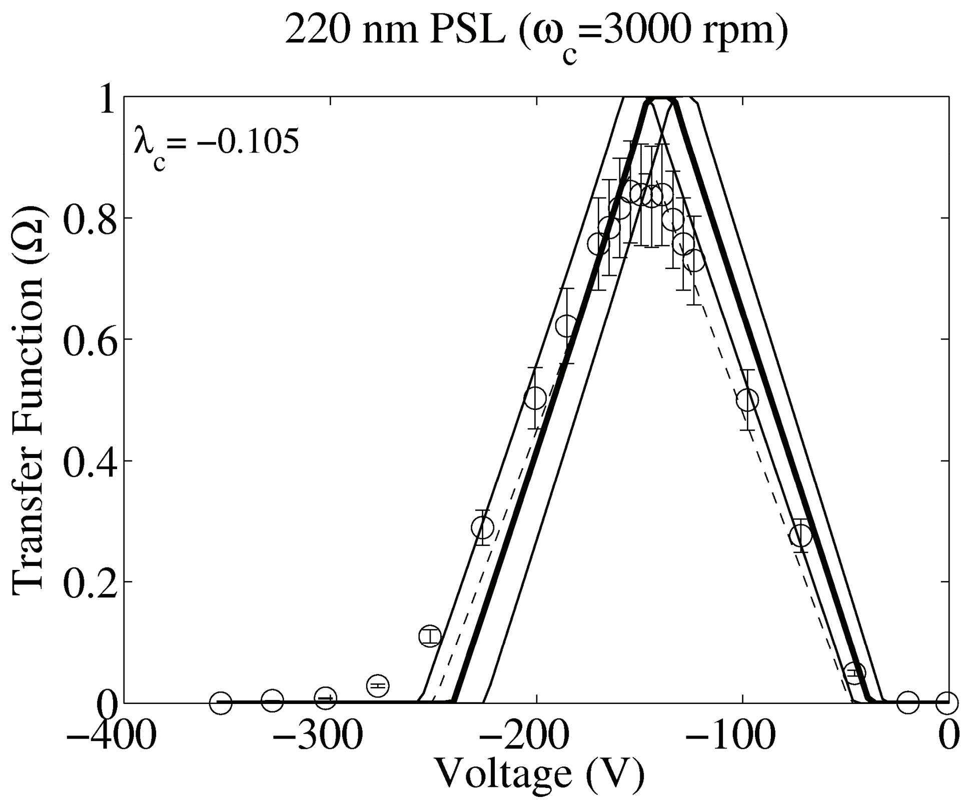


CAMBUSTION

First Prototype – Mass validation – PSL particles

$$m = \frac{qV_{\text{peak}}}{r_c^2 \omega_c^2 \ln(r_2 / r_1)}$$

All well defined quantities (except for q?); no dependence upon gas properties, slip correction etc.



E.g. 220 nm PSL:

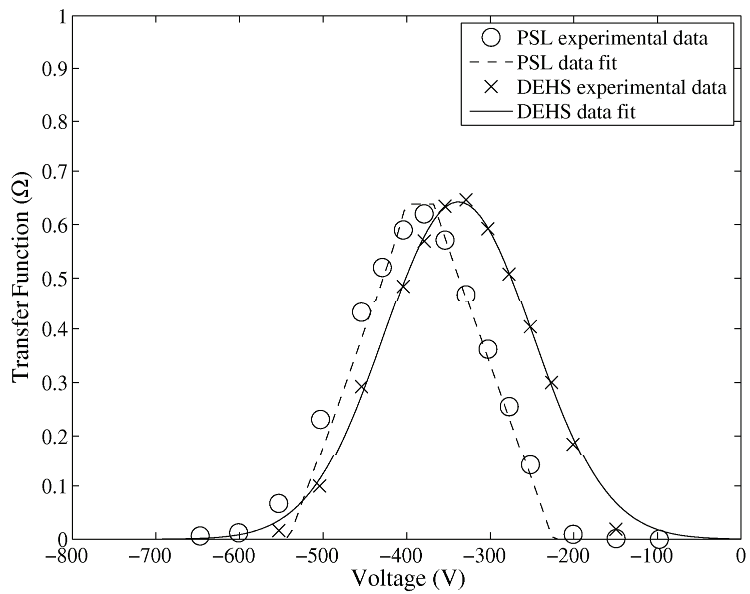
- m_{exp}= 6.25 femtograms
- m_{theo}= 5.85 fg (6.7% error)
- Error mostly likely due to “end effects” – more later…
- Some particles losses; mostly likely due to impaction before and after classifying region.

Olfert & Collings (JAS, 2005)

Density Measurement

$$\rho_{test} = \rho_{PSL} \frac{V_{CPMA,test}}{V_{CPMA,PSL}}$$

- DEHS aerosol (nebulised in alcohol, dried). Compare peak mass voltage with that from PSL at the same DMA selected size, given PSL density = 1.05 g/cm^3:



- Measured density = 0.926 g/cm^3 c.f. 0.914 g/cm^3 known, an error of 1.3%

Dynamic Shape Factor Measurement

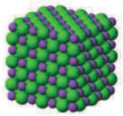
•Dynamic shape factor (Kasper, 1982; ratio of resistive force compared to a spherical particle of same volume):

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

where d_{me} is the mobility equivalent diameter, d_{ve} is the volume equivalent diameter and $C_c()$ are the relevant slip correction factors. It can be shown that:

$$d_{\mathrm{ve}} = d_{\mathrm{me}} \sqrt[3]{\frac{\rho_{\mathrm{PSL}} V_{\mathrm{test}}}{\rho_{\mathrm{test}} V_{\mathrm{PSL}}}}$$

•Select (cubic) NaCl particles with DMA at 299 nm, compare with spherical PSL:

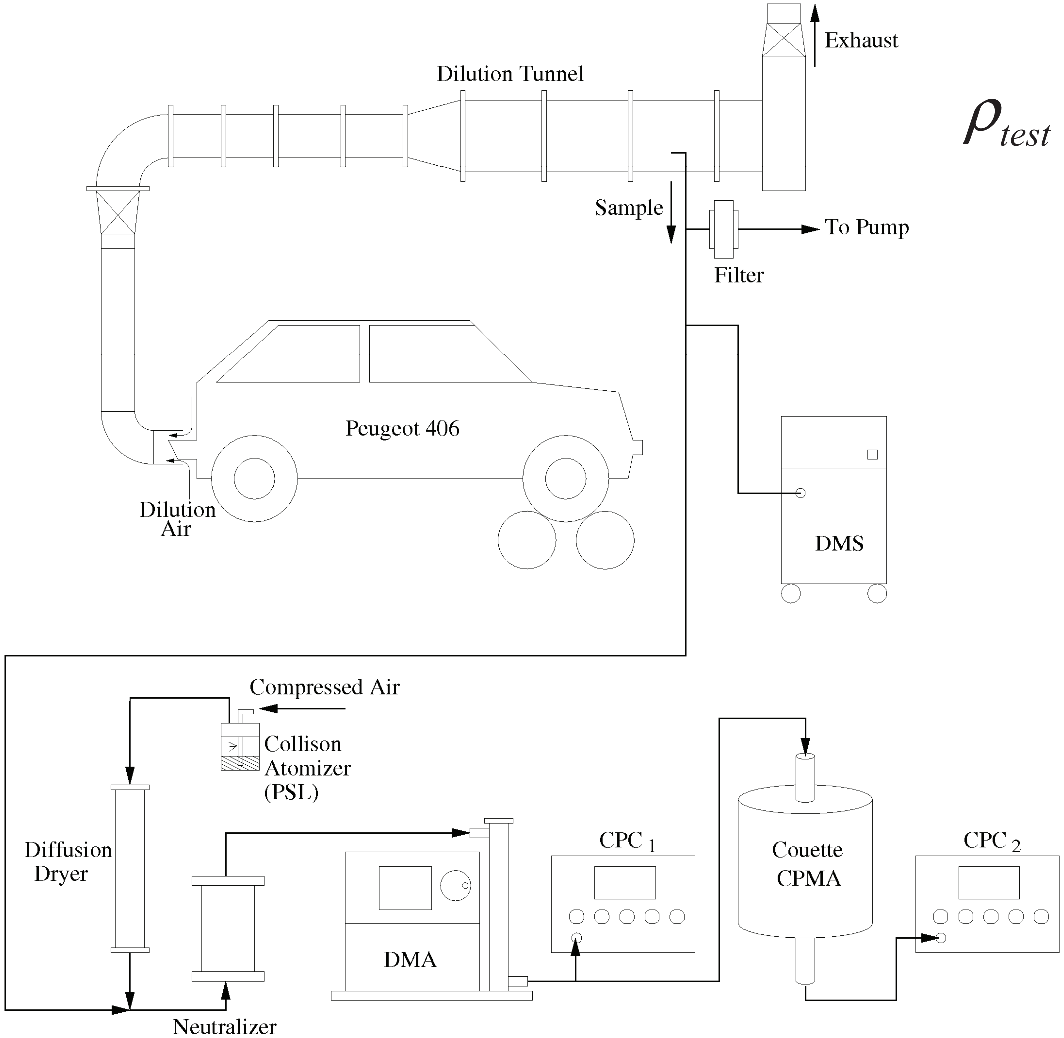


$$\chi_{f,\mathrm{NaCl}} = 1.08$$

which agrees with other studies.

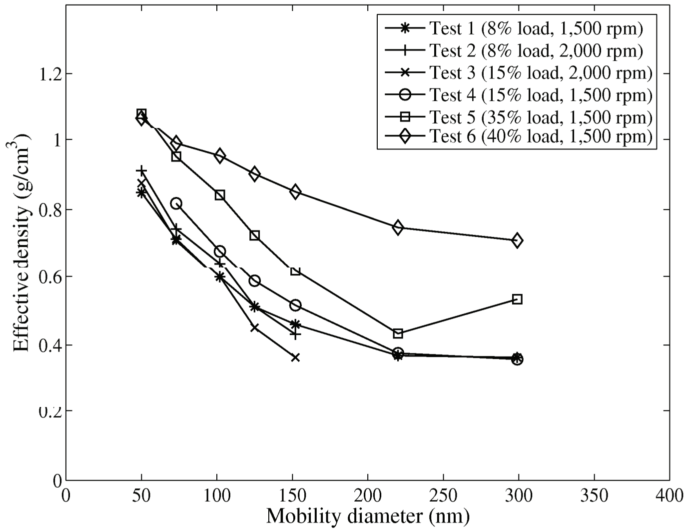
CAMBUSTION

Fractal Dimension Determination – Diesel (1)



$$\rho_{test} = \rho_{PSL} \frac{V_{CPMA,test}}{V_{CPMA,PSL}}$$

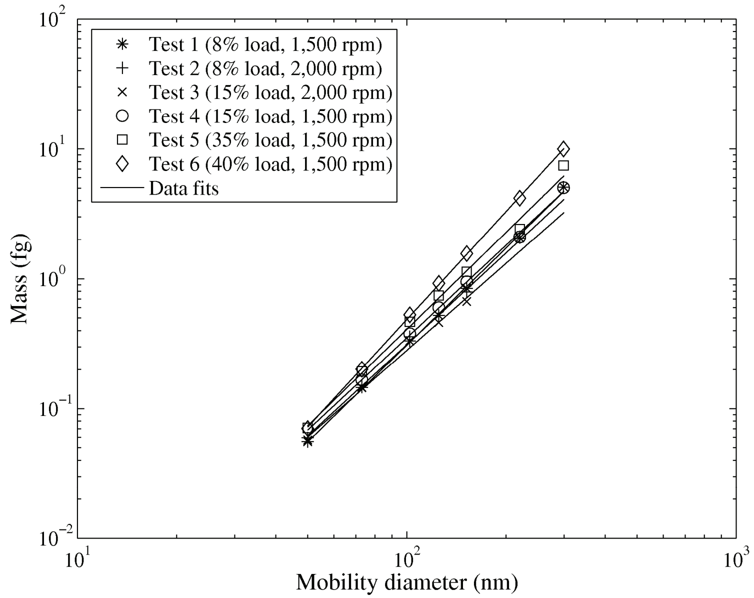
$$M \propto d^{Df}$$



Olfert, Symonds & Collings (JAS 2005)

CAMBUSTION

Fractal Dimension Determination – Diesel (2)



$M \propto d^{D_f}$

$\Rightarrow D_f$ = gradient of (log) graph

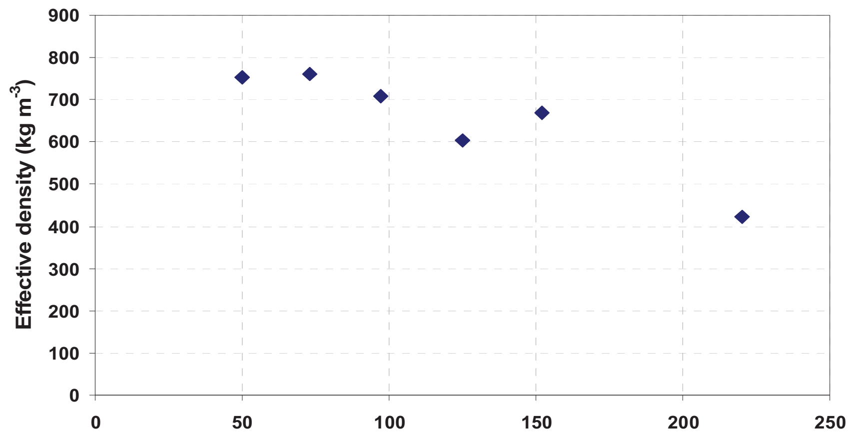
Increased load $\Rightarrow$
Increased catalyst temperature $\Rightarrow$
Increased sulphate desorption $\Rightarrow$
Sulphate "infill" on agglomerates $\Rightarrow$
Higher D_f ($\rightarrow$ 3)

Test	Engine load (%)	Engine speed (rpm)	Dilution ratio	Average DOC temperature (°C)	Fractal dimension
1	8	1500	6.2:1	197	2.48 ± 0.10
2	8	2000	4.0:1	204	2.34 ± 0.20
3	15	2000	3.9:1	250	2.22 ± 0.30
4	15	1500	5.8:1	240	2.36 ± 0.16
5	35	1500	2.8:1	310	2.47 ± 0.24
6	40	1500	2.7:1	336	2.76 ± 0.06

Olfert, Symonds & Collings (JAS 2005)

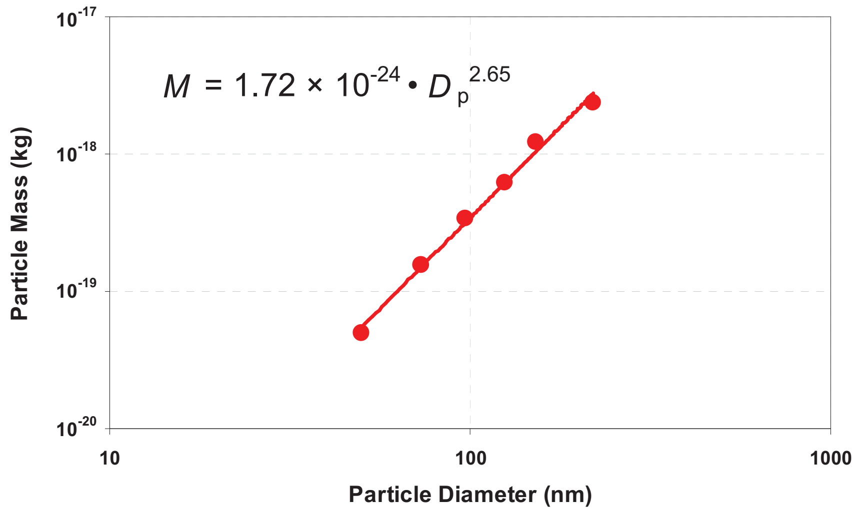
Fractal Dimension Determination – Gasoline

- Gasoline Direct Injection Engine (GDI)
- Low speed, light load
- Homogenous fuel:air



- *D_f = 2.65 for these conditions*
- Less fractal than Diesel
- Adsorbed material
- OC:EC higher for GDI

$\Rightarrow$ *Use different density for e.g. mass calculation with DMS series fast mobility analysers*



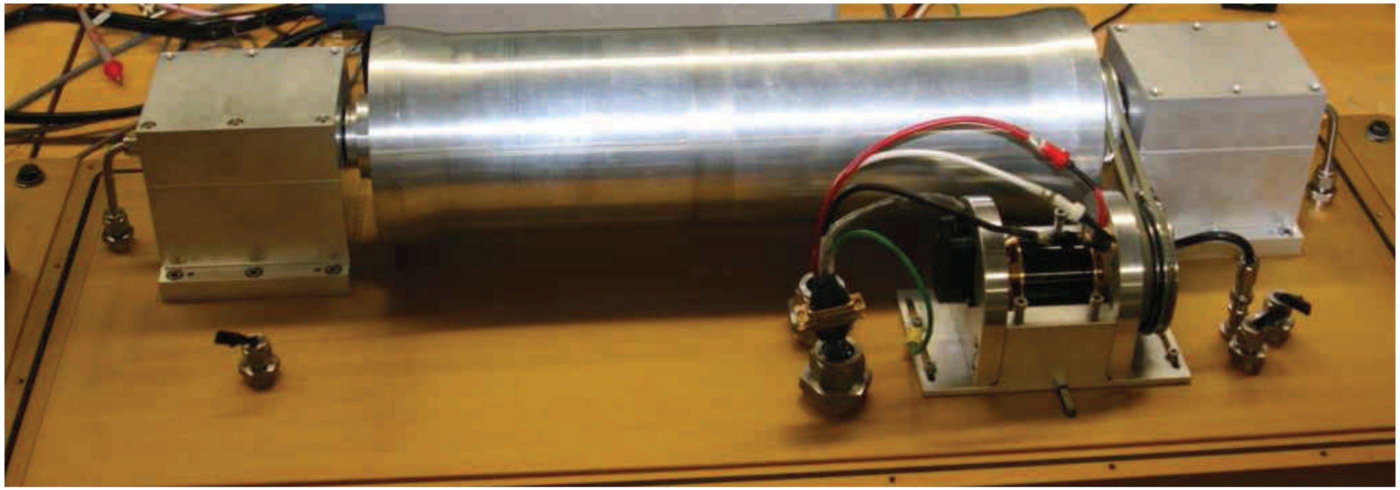
Symonds, Price, Williams and Stone (EAC, 2008)

CAMBUSTION

Second Prototype – Design

- First prototype showed concept well however it can be improved
  - "End effects" in fields at flow entry are large
  - Lower resolution than possible; length ≡ resolution

⇒ Second prototype longer (400 mm c.f. 70 mm)
  - Longer length means higher resolution *without* higher losses; particles of the correct mass kept from the walls
  - Improved design at entry and exit to the classification region & sealing
  - Better accuracy



CAMBUSTION

Second Prototype – Results

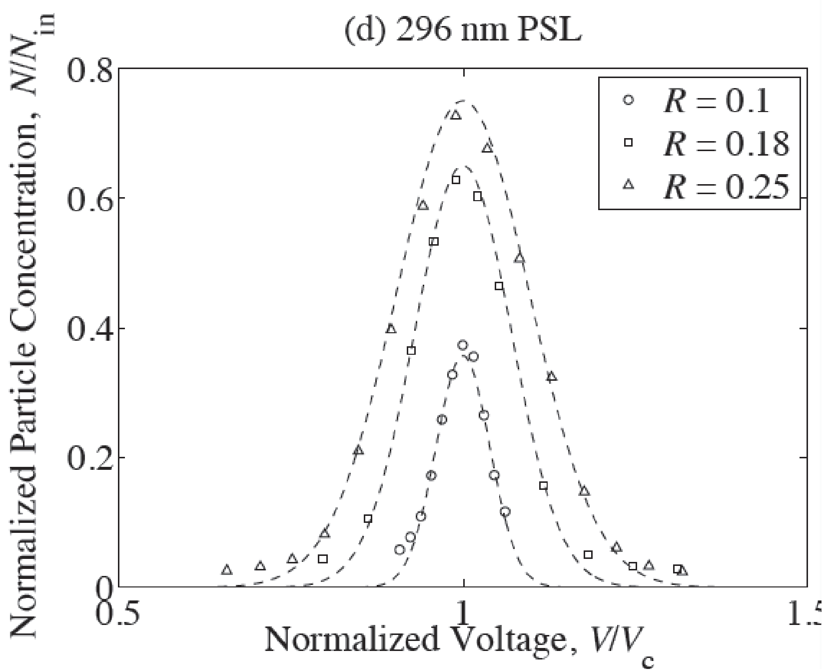


Table 1: Experimental Results

PSL size (nm)	PSL mass (fg)	PSL uncertainty (fg)	CPMA mass (fg)	Resolution (FWHM)	% difference
70±3	0.19	±0.03 (±13%)	0.17	0.1	-8%
102±3	0.58	±0.05 (±9%)	0.52	0.1	-10%
151±4	1.89	±0.16 (±8%)	1.85	0.1	-2%
296±6	14.3	±0.8 (±6%)	14.2	0.1	-1%

Olfert *et al*. IAC (2010)

⇒Higher resolution, better accuracy than first prototype

CAMBUSTION

Commercial Version (coming soon…)

- Half the length of second prototype to reduce weight (200 mm), still very high resolution
- 0.5 ag – 500 fg (~ 10 nm – 1000 nm for unit density)
- Up to 1.5 slpm sample flow ("High flow" CPC)
- Ability to step scan to generate mass spectrum when used with a CPC (analogue of DMPS for mass)
- Applications
  - As an alternative to a DMA for selecting monodisperse aerosol without morphological bias
  - As an absolute mass standard for calibration of instruments [protoype 1 used for this purpose in recent U.S. intercomparison study (Cross *et al.* AS&T 2010)]
  - To determine particle morphology and fractal dimension when used with a DMA
  - To produce particle mass spectra
- Final design details to be decided….

Acknowledgements

- Jason Olfert (Univ. of Alberta, previously Univ. of Cambridge)
- Nick Collings (Univ. of Cambridge)
- Philip Price (Ford UK), Paul Williams (Univ. Manchester) & Richard Stone (Univ. Oxford)
- T. Johnson, B. Wu, N. Olmedo, C.S. Stout (Univ. of Alberta)
- Kingsley Reavell, Mark Rushton, Charlie Lowndes & Andrew Ellison (Cambustion)

For more information on the CPMA contact:
Jon Symonds: jps@cambustion.com
or
Arnaud Noirtin: arnaud.noirtin@intertek.com (in France)
or visit
www.cambustion.com/cpma
(including reference list)