The Centrifugal Particle Mass Analyser as a Fundamental Particle Mass Standard

J.P.R. Symonds, K.St.J. Reavell, M.G. Rushton, C. Lowndes
Content

- Introduction – why mass?
- CPMA principle
- Setpoint and resolution
- Classifier evaluation – mass accuracy and penetration
- Tandem DMA-CPMA Experiments:
  - Diesel Vehicle Soot Density
  - DPG Soot Density
- Tandem CPMA-DMS experiments
- Charge effects
- LPG vehicle soot density
- CPMA-Electrometer System: A Suspended Mass Standard
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 \( \Rightarrow \) 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

\[
\text{Mass } \equiv 0.52 \text{ fg}
\]

\[
\text{Size } \sim 100 \text{ nm } ???
\]
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
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

\[ \omega_i = \omega_o \]
\[ \omega_i > \omega_o \]

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:

\[ m = \frac{eV}{N_q r^2 \omega^2 \ln \left( \frac{r_o}{r_i} \right)} \]

- 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 \( \omega, V \) which balance for a given mass:charge — magnitude determines particle drift speed and hence resolution. We use a simplified drift based model:

Resolution → Drift Time

- Fast drift / high mobility
- Slow drift / low mobility

Net drift velocity = \( EqB - m\omega^2rB \)
Resolution & Scanning

\[ R_m \equiv \frac{m^*}{\Delta m_{\text{FWHM}}} \]

A (good) approximation shows (Reavell et al. 2011):

\[ \frac{m'}{m^*} (m \omega^2) - \frac{q'}{q} (qE) = \frac{B}{B'} \frac{Q}{2\pi B l r} \]

This is dependent upon mobility, \( B \), hence \( d_{p,\text{mobility}} \)

To calculate \( \omega \) and \( V \) for a desired resolution, software needs mass:size model: \( m_p \)

\[ m_p = A d_p^i \] (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, \( R_s \approx 3 R_m \) for spheres

For typical DMA resolution of \( R_s \approx 10 \), the equivalent CPMA resolution, \( R_m \approx 3.03 \)

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

- 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 \( N_{\text{CPC2}} < N_{\text{CPC1}} \).

- e.g. Thermo 102 nm PSL \( \frac{d}{\Delta d} = 8.33 \), DMA \( \frac{d}{\Delta d} = 20.0 \), CPMA \( \frac{d}{\Delta d} = 31.0 \) (\( m/\Delta m = 10.0 \))
PSL Results

150 nm PSL: CPMA $R_m = 5.12$ ($R_d \sim 16.6$), 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?
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)

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

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

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

Much more on charge later...
NaCl Experiments: Uncertainties

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

\[
\frac{\Delta Z}{Z} \approx \frac{\Delta D}{D} ; \frac{\Delta m_d}{m_d} \approx 3 \frac{\Delta D}{D} = 6.6\%; \text{ 95\% C.I. = } 2\sigma = 13\% \text{ (neglecting errors in } C_c \text{ and } \chi_t)\
\]

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

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Abs Tolerance (equiv. to 95% C.I.)</th>
<th>( \Delta x/x ) 95% C.I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltage (V)</td>
<td>-</td>
<td>1%</td>
</tr>
<tr>
<td>Angular Speed (( \omega ))</td>
<td>-</td>
<td>1%</td>
</tr>
<tr>
<td>Inner Radius (( r_i ))</td>
<td>( \pm 0.05 \text{ mm} )</td>
<td>-</td>
</tr>
<tr>
<td>Outer Radius (( r_o ))</td>
<td>( \pm 0.05 \text{ mm} )</td>
<td>-</td>
</tr>
</tbody>
</table>

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

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

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

\[
\frac{\Delta m_c}{m_c} \approx \sqrt{(0.01)^2 + (2 \times 0.01)^2 + \left( \frac{0.05}{1.00} \right)^2 + \left( \frac{0.05}{1.00} \right)^2} = 7.5\% \text{ (95\% C.I.)}
\]
NaCl results: $R_m = 3$ ($R_s \sim 10$)

\[ M_c = 1.047 M_d + 0.0006 \]
\[ R^2 = 0.999 \]
**NaCl results:** $R_m = 5$ ($R_s \sim 16$)

\[
M_c = 1.036 M_d + 0.005 \\
R^2 = 0.998
\]

**Penetration**

- Static Penetration (losses by diffusion)
- Dynamic Penetration

**Dynamic Particle Loss (diffusion corrected)**

$\text{d}_{50,\text{static}} \sim 20 \text{ nm}$
Density Measurement: Diesel Engine

Audi A4 1.9 l TDI, at Idle

1 lpm

DMA

CPMA

1.5 lpm

CPC

Aerosol

Signal

50 nm Diesel soot

dN/dlogMp/cc

Effective density

Mass:mobility relationship

M_p ∝ D_p^{2.6}

Effective density (kg/m^3)

CPMA

CPC

Aerosol Signal

1 lpm

DMA

CPMA

1.5 lpm

CPC

50 nm Diesel soot

dN/dlogMp/cc

Effective density

Mass:mobility relationship

M_p ∝ D_p^{2.6}

Effective density (kg/m^3)
Density Measurement: Diesel Soot Generator

Density Measurement: Diesel Soot Generator

### Mass: Mobility Relationship

\[ M_p \propto D_p^{2.44} \]

\[ R^2 = 9.99 \times 10^{-1} \]

- **Mode (kg)**
- **Power (Mode (kg))**

### Effective Density

- **Dp (nm)**
- **Effective Density (kg/m\(^3\))**

---

**DPG**

Aerosol → DMA → CPMA → CPC

1 lpm

1.5 lpm

**Mass: Mobility Relationship**

\[ M_p \propto D_p^{2.44} \]

\[ R^2 = 9.99 \times 10^{-1} \]

- **Mode (kg)**
- **Power (Mode (kg))**
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:

- Technique recently used on Gas Turbine engines…

![Graph showing DMA and DMS size comparison](image)

\[
y = 1.0319x - 1.1588 \\
R^2 = 0.9997
\]

Example: NaCl (CPMA mass based on \( \rho = 2.165 \text{ g/cc} \)):

<table>
<thead>
<tr>
<th>Conc (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.009 fg = 20 nm</td>
</tr>
<tr>
<td>0.03 fg = 30 nm</td>
</tr>
<tr>
<td>0.07 fg = 40 nm</td>
</tr>
<tr>
<td>0.14 fg = 50 nm</td>
</tr>
<tr>
<td>0.24 fg = 60 nm</td>
</tr>
<tr>
<td>0.39 fg = 70 nm</td>
</tr>
<tr>
<td>0.58 fg = 80 nm</td>
</tr>
<tr>
<td>0.83 fg = 90 nm</td>
</tr>
<tr>
<td>1.13 fg = 100 nm</td>
</tr>
</tbody>
</table>

![Graph showing particle size distribution](image)
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**:
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

- 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
Higher resolution, bigger particles, more charges…

300 nm PSL, Rm = 5.13
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)

90 nm DMA Cut

- Experiment
- Fit: Species A (ρ=1200): 1+
- Fit: Species A (ρ=1200): 2+
- Fit: Species B (ρ=3000): 1+

\[ \text{D}_p \]
\[ \%A \]
\[ \%B \]

A: soot or water?
B: ash? (lube oil)
TBC...

Effective Density (kg/m³)

"A"
"B"
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

\[
m_{\text{total}} = m_{+0} + Mn_{+1} + 2Mn_{+2} + 3Mn_{+3} + \ldots
\]

\[
= m_{+0} + M \left(n_{+1} + 2n_{+2} + 3n_{+3} + \ldots\right)
\]

\[
I_{\text{elec}} = Qe \left(n_{+1} + 2n_{+2} + 3n_{+3} + \ldots\right)
\]

\[
\therefore m_{\text{total}} = m_{+0} + \frac{MI}{Qe} = m_{+0} + M \times "\text{IndicatedN/cc}" \]

\[
m_{\text{total}} = \text{mass setpoint} \times \text{indicated electrometer concentration} + \text{zero charge correction}
\]

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

• Dr Jason Olfert (University of Alberta)
• Professor Nick Collings (University of Cambridge)
• Andrew Todd (Cambustion)
Jon Symonds: ips@cambustion.com

www.cambustion.com/cpma
for more information including references