Behaviour of Non- and Multiply-Charged Aerosols in the Centrifugal Particle Mass Analyzer

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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 \( \Rightarrow \) particle morphology
- Particle “size” for a non spherical particle can be defined in many ways dependent upon measurement technique, \textit{but particle mass is well defined – measurement is independent of morphology and composition}

\[ \text{Mass } \equiv 0.52 \, \text{fg} \]
\[ \text{Size } \sim 100 \, \text{nm} \]
Centrifugal Particle Mass Analyzer

- Improvement to Aerosol Particle Mass Analyzer (APM) concept (Ehara, 1996)
- Concept by Mark Rushton and Kingsley Reavell (Cambustion) – also known as “Couette CPMA” (2003)
- Developed as a PhD project by Jason Olfert at Cambridge University (2003–2006) – First Prototype
- Cylinders rotate at *slightly* different speeds (inner>outer) ⇒ Creates a velocity gradient (*Couette* flow) ⇒ Vary centrifugal force across radius to match electric force ⇒ Forces balance across radius
- **Particles of correct mass:charge pass through at all entry locations; theoretically 100% transmission.**

Diagram courtesy of J. Olfert

New Version (2012…)

200 l × 120 ø mm classifier with 1 mm gap; 0.05–1000 V; 500–12,000 rpm

Longer classifier ⇒ finer resolution without greater losses (except for diffusion)

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

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

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

- 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:

Net drift velocity = \( E q B - m \omega^2 r B \)
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 $N_{CPC2} < N_{CPC1}$.

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

CPMA flow = 1.5 lpm ($R_m = m / \Delta m_{FWHM}$); DMA sheath = 10 lpm, aerosol = 1 lpm

CPMA Mass Scan, 150 nm PSL, $R_m = 5.13$

- Peak (DMA at PSL peak) = 1.86 fg
- CPMA peak = 1.89 fg
- Error = 1.8%

CPMA Mass Scan, 300 nm PSL, $R_m = 10$

- Peak (DMA at PSL peak) = 14.94 fg
- CPMA peak = 14.80 fg
- Error = 0.2%

150 nm PSL, $R_m = 5.13$, CPMA Size Plot (density = 1.05 g/cc)

300 nm PSL, $R_m = 10$, CPMA Size Plot (density = 1.05 g/cc)
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:

- In theory, relative position of the +1 and +2 peaks gives just enough degrees of freedom to estimate density pre-factor and index for mass:size relationship from just one scan – but not recommended for good accuracy.
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 ($\rho=1200$): 1+
Fit: Species A ($\rho=1200$): 2+
Fit: Species B ($\rho=3000$): 1+

90 nm DMA Cut on "Unit Density" Size Scale

Experiment
Fit
Raw mobility spectrum

Concentration - DMA Cut / CMA Scan (dN/dlogDp/cc)

Concentration - Overall Mobility Spectrum (dN/dlogDp/cc)

Effective Density (kg/m³)

Dp
%A
%B
A: soot or water?
B: ash? (lube oil)
TBC…
Charge Effects – Bipolar Equilibrium Charge (1)

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

PSL → DMA → CPMA → CPC

DMA is there to remove PSL surfactant etc

![Diagram showing charge effects and penetration graph](image)

100 nm PSL re-neutralised after DMA, \( R_m = 2.3 \)

**Penetration**

- Speed
- Voltage

"centrifuge"

"+0"

"+1"

"+2"

**Experiment**
Charge Effects – Bipolar Equilibrium Charge (2)

- 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
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

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

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

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

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

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

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.
Conclusions

• CPMA useful calibration standard for other instruments for mass
• Scanning downstream of a DMA (density measurement) requires charge correction
• To extend CPMA-CPC system to analogue of SMPS system in the future will require a charge correction algorithm – including the zero / negative charge states
• CPMA-Electrometer system useful as a suspended mass concentration standard – *double-charged double-mass particles counted twice*. Zero charged particles must be corrected for *or* minimised (e.g. by using a corona charger)
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www.cambustion.com/cpma
for more information including references 2005 – 2011

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