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Extended Abstract

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Title: The CPMA-Electrometer System as a Traceable Mass Concentration Standard

Abstract:

The abstracts for papers and posters must contain unpublished information on your research subject: background, investigation methods, results and conclusions. Graphs and references are very welcome. Acronyms should be avoided. Abstracts with < 300 words can not be considered. General information on products which are already commercially available can not be accepted as presentations for the conference but are very welcome at the exhibition of particle filter systems and nanoparticle measurement instruments.

The use of gravimetric techniques to calibrate real-time aerosol mass instrumentation (such as Aerosol Mass Spectrometers, or those instruments which utilise Laser Induced Incandescence (LII) or Photoacoustic measurement techniques) has a number of drawbacks. Filter paper measurements are prone to artefacts from any volatile material which could become absorbed on the paper, and it takes considerable time to collect enough mass on a filter paper to make a measurement. Validation of the instrumentation under real-time transient conditions is impossible using a gravimetric method. Other techniques (such as classifying using a DMA) do not actually directly measure mass at all, and require assumptions to be made about material density and morphology.

The Centrifugal Particle Mass Analyzer (CPMA, Olfert and Collings (2005)) classifies nanoparticles by their mass-to-charge ratio, by subjecting them to opposing electric and centrifugal fields. As such, if set to select particles of mass M_{+1} with one charge, particles of mass $2M_{+1}$ with two charges will also be selected, and so on. An aerosol electrometer with a known flow passing through it fundamentally measures charge concentration. Thus if an aerosol electrometer is placed downstream of a CPMA, given each charge represents here a quantum of mass M_{+1}, by measuring the charge concentration and multiplying it by M_{+1}, one has a measure of the total mass concentration downstream of the CPMA:

$$m_{\text{total}} = m_0 + \frac{M_{+1}I}{Qe}$$

where m_0 is the mass concentration of any uncharged particles which pass through the CPMA (see below), I is the current measured by the electrometer and Q is the flow through the electrometer.

By splitting the flow prior to the electrometer, this can provide a source of aerosol of known mass concentration for calibration of real-time mass instrumentation, for example instruments which use Laser Induced Incandescence (LII) or photoacoustic techniques, or aerosol mass spectrometers. Figure 1 shows the suggested scheme.
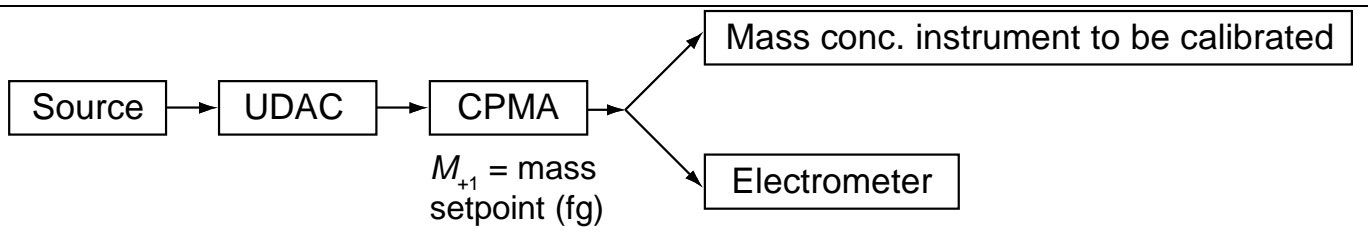
m_{total} = mass *setpoint* × indicated electrometer *concentration* + zero charge correction

Figure 1: The Proposed Scheme

The aerosol electrometer cannot account for uncharged particles, and some sufficiently light uncharged particles will pass through the CPMA at sufficiently slow speeds. It is possible to at least put an upper limit on this effect by the use of an electrostatic precipitator and a CPC to measure the population of uncharged particles, and by calculating a "cut-off" diameter for particles passing through the CPMA at a given speed.

To minimize the population of uncharged particles, we suggest the following three steps:

- use a unipolar charger
- run the CPMA at the highest possible speeds (highest resolution)
- set M_{+1} to select particles from the leading edge of the underlying distribution

Using these suggestions, it is possible to reduce this source of error to just a few parts per million (see full paper for an example). In addition, the high average charge imparted by the unipolar charger improves the sensitivity of the electrometer. It is possible in practice with this method to generate mass concentrations from less than 1 µg m^{-3} to several mg m^{-3}.

M_{+1} is a well-defined property, and itself depends *only* on well-defined, traceable quantities: the speed of rotation and potential difference across the CPMA electrodes, the radii of the electrodes, and the elementary charge constant:

$$M_{+1}r\omega^2 \qquad \qquad M_{+1} = \frac{eV}{r^2\omega^2 \ln\left\{ r_o / r_i \right\}}$$
$$eV / r \ln(r_0 / r_i)$$

This contrasts, for example, with the "size" classification of a DMA, which depends on many gas properties (temperature, pressure, viscosity) as well as the slip correction factor, and indeed particle morphology.

A comparison of this method was made with gravimetric filter paper measurements (Figure 2). A nebulized oil aerosol of low volatility was charged with a Unipolar Diffusion Aerosol Charger (UDAC, Cambustion), and classified by a CPMA. The post-CPMA flow was split between an aerosol electrometer and a TX40 filter paper, with a controlled flow passing through it. The filter paper was weighed before and after periods of loading, and M_{+1} was varied to give a range of mass concentrations between 0.2–4.4 mg m^{-3}. In this experiment we found the two techniques agreed to within 6%, with good linearity. Unlike gravimetric techniques, this method is ideal for direct real-time instrument calibration, and is not subject to artifacts due to volatile aerosols.
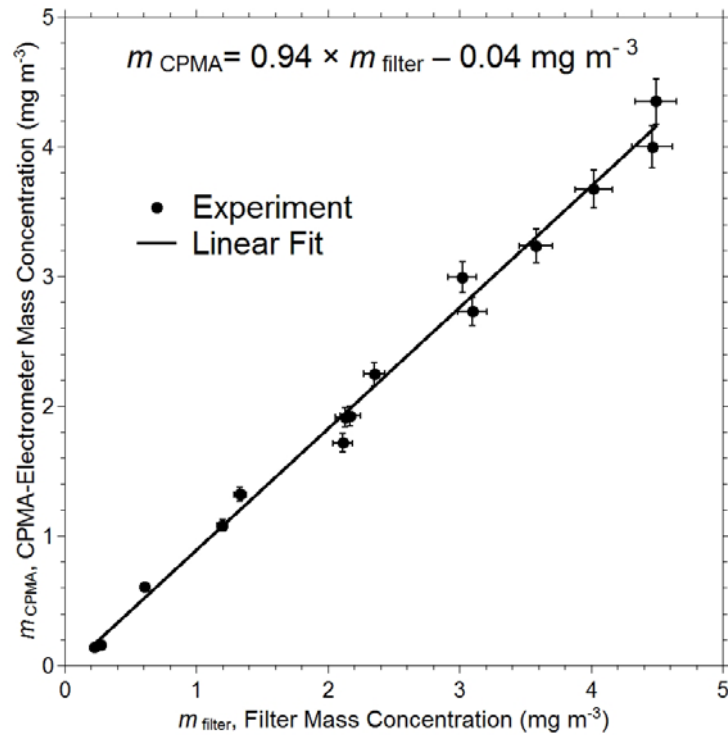
$$m_{CPMA} = 0.94 \times m_{filter} - 0.04 \text{ mg m}^{-3}$$

Figure 2: Comparison with Gravimetric Method

References:

Olfert, J. & Collings, N., *Journal of Aerosol Science*, **36** 1338–1352 (2005)
Symonds, J.P.R., Reavell, K.St.J., Olfert J.S. *The CPMA-Electrometer System—A Suspended Particle Mass Concentration Standard*, Aerosol Science and Technology (Aerosol Research Letter), vol. 47(8), pp. i–iv (2013)

Short CV:

Dr Simon Payne is a R&D Engineer at Cambustion. He holds a PhD from the University of Cambridge, based on research into the fundamental processes of the deposition of soot onto Diesel Particulate Filters.

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The CPMA-Electrometer System as a Traceable Mass Concentration Standard

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Introduction

The use of gravimetric techniques to calibrate real-time aerosol mass instrumentation (such as Aerosol Mass Spectrometers, or those instruments which utilise Laser Induced Incandescence (LII) or Photoacoustic measurement techniques) has a number of drawbacks. Filter paper measurements are prone to artefacts from any volatile material which could become absorbed on the paper, and it takes considerable time to collect enough mass on a filter paper to make a measurement. Validation of the instrumentation under real-time transient conditions is impossible using a gravimetric method. Other techniques (such as classifying using a DMA) do not actually directly measure mass at all, and require assumptions to be made about material density and morphology.

The Centrifugal Particle Mass Analyser (CPMA) (Olfert & Collings, 2005) is a development of the Aerosol Particle Mass (APM) Analyser (Ehara et al., 1996), which classifies particles by their mass to charge ratio by using opposing electric and centrifugal fields. Particles enter a classification region between two rotating concentric cylinders, between which a potential difference is applied. In the specific case of the Cambustion CPMA, these cylinders spin at very slightly different speeds, which creates a stable system of forces, which improves the classification performance in terms of penetration and resolution (see Olfert and Collings, 2005; Symonds et al., 2012).

Fig 1. Cambustion CPMA

In the past, DMAs have been used to calibrate mass-based instruments — but this requires assumptions to be made about particle density and morphology. Indeed, a DMA actually measures electrical mobility; the "size" inferred by a DMA is dependent upon many factors such particle morphology, the temperature, pressure and viscosity of the gas, as well as the empirical Cunningham slip correction. By contrast, the CPMA mass setpoint, assuming particles are singly charged (hereafter referred to as M_{+1}) depends only on the rotational speed, voltage, classifier cylinder radii and elementary charge — all well defined, easily traceable quantities:

$$M_{+1} = \frac{eV}{r^2 \omega^2 \ln\left\{r_o/r_i\right\}}$$

Both instruments usually suffer from the possibility of multiply-charged particles — however, the technique described here uniquely for the CPMA (or APM) actually uses this to its advantage.
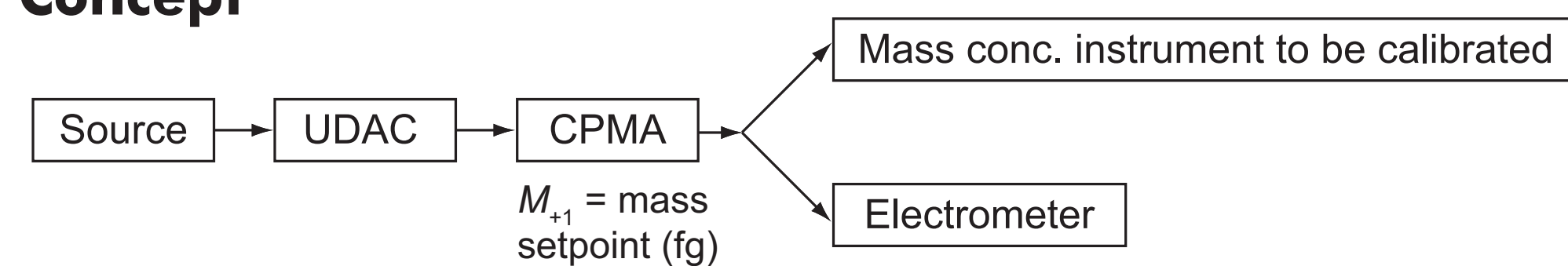
Concept

Fig 2. The Concept

A broad source of aerosol particles is charged using a Unipolar Diffusion Aerosol Charger (UDAC, Cambustion, Fig. 3). This uses a corona to place a high net positive electrical charge on the aerosol particles, and is based on the charger used in the Cambustion DMS500 fast response aerosol size spectrometer; the principle is described by Biskos et al. (2005). It has re-circulating, filtered sheath flows to keep the charger clean.
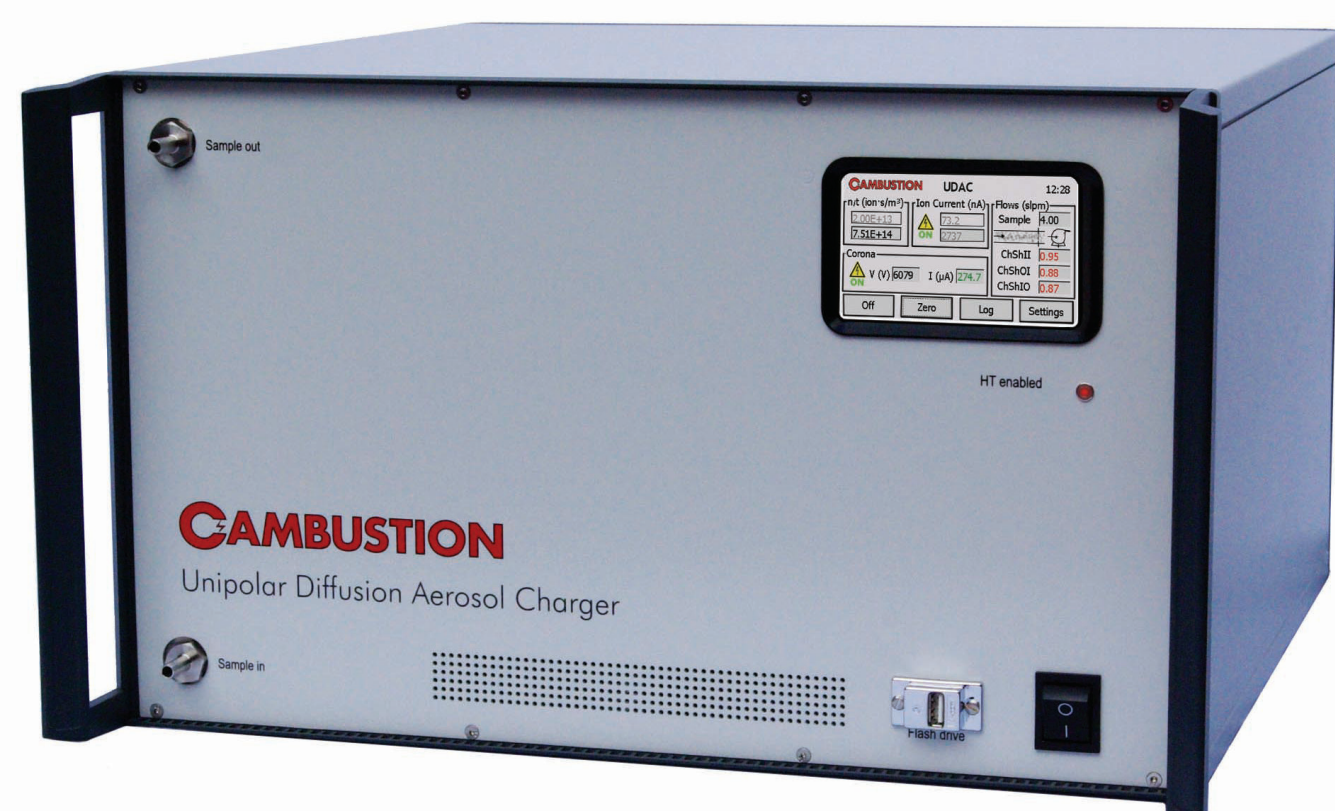

Fig 3. Unipolar Diffusion Aerosol Charger (Cambustion)

The stream of charged particles is classified by mass to charge ratio by the CPMA which is set to select those particles with a single charge at a mass M_{+1}. It will also select those particles with two charges which are of mass $2\,M_{+1}$, those with three charges of mass $3\,M_{+1}$, etc. From this we note that the charge state of a particle leaving the system also indicates the mass of the particle, in terms of the number of "units" of M_{+1}. Fig. 4 shows a theoretical size spectrum of the output of this system, showing the individual charge states.
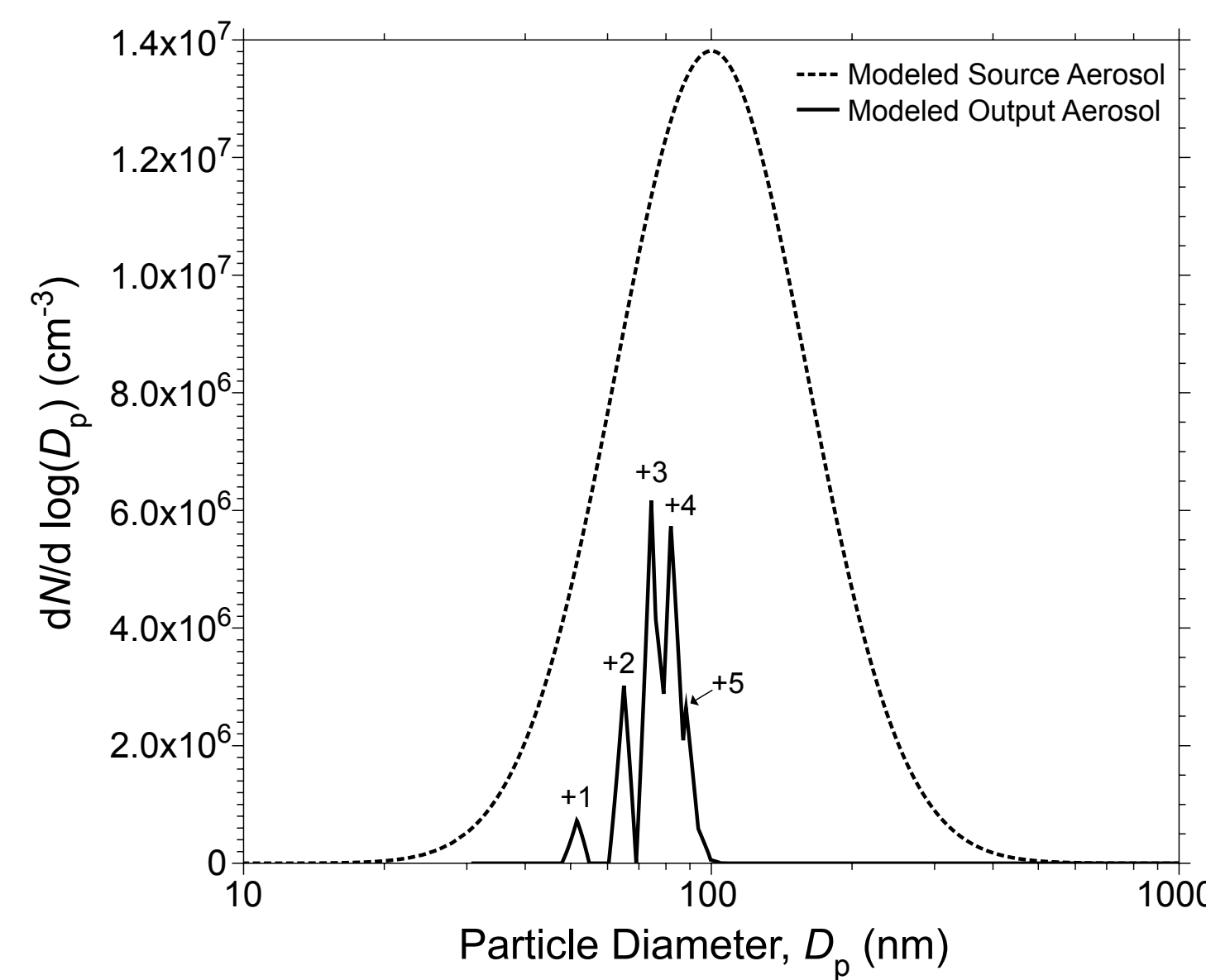

Fig 4. Theoretical output of UDAC-CPMA system for a 100 nm source aerosol of GSD 1.6, and charger $n_i t$ of 5.4×10^{13} ions m^{-3} s

We then split the post-CPMA aerosol between an aerosol electrometer and a challenge instrument which we wish to calibrate (for example: an AMS, LII or PASS). The total mass concentration (m_{total}) downstream of the CPMA is given by:

$$m_{total} = m_0 + M_{+1}n_{+1} + 2M_{+1}n_{+2} + 3M_{+1}n_{+3} + \ldots$$
$$= m_0 + M_{+1}\left(n_{+1} + 2n_{+2} + 3n_{+3} + \ldots\right)$$

where n_i is the number concentration of particles of charge state i, and m_0 is the mass concentration of any uncharged particles which can pass through the CPMA at sufficiently slow speeds (see below). The current measured by the electrometer is

$$I = Qe\left(n_{+1} + 2n_{+2} + 3n_{+3} + \ldots\right)$$

for flow Q and elementary charge e. Noting that the term in parentheses is common to both equations, it can be eliminated to give

$$m_{total} = m_0 + \frac{M_{+1}I}{Qe}.$$

Thus it follows that the total mass concentration measured by the challenge instrument is simply the singly-charged mass setpoint of the CPMA, multiplied by the charge concentration indicated by the electrometer (I/Qe), plus a correction for any uncharged particles. As we shall see, this correction can easily be made negligible.

Uncharged Particles

At sufficiently slow speeds, sufficiently light uncharged particles may pass through the CPMA, and will not be detected by the electrometer. Even though these lightest particles will inherently give only a small contribution to the total mass (as m_0), it is prudent to minimise this effect or account for it. This is why a unipolar charger is suggested — this will place a large net positive charge on particles, thus decreasing the likelihood of uncharged particles. In addition, the high level of charge will also increase the electrometer signal, thus overcoming one of the normal disadvantages of those devices — that of sensitivity. For the aerosol shown in Fig. 4, and a typical electrometer, the minimum mass concentration available for calibration is just 0.6 µg m^{-3} (Symonds et al., 2013).

Running the CPMA at higher speed (higher resolution) will increase the centrifugal force to reduce the effect of uncharged particles. Finally, by setting M_{+1} to be on the leading edge of the underlying source distribution, the available population of the smaller, uncharged particles can be greatly attenuated.
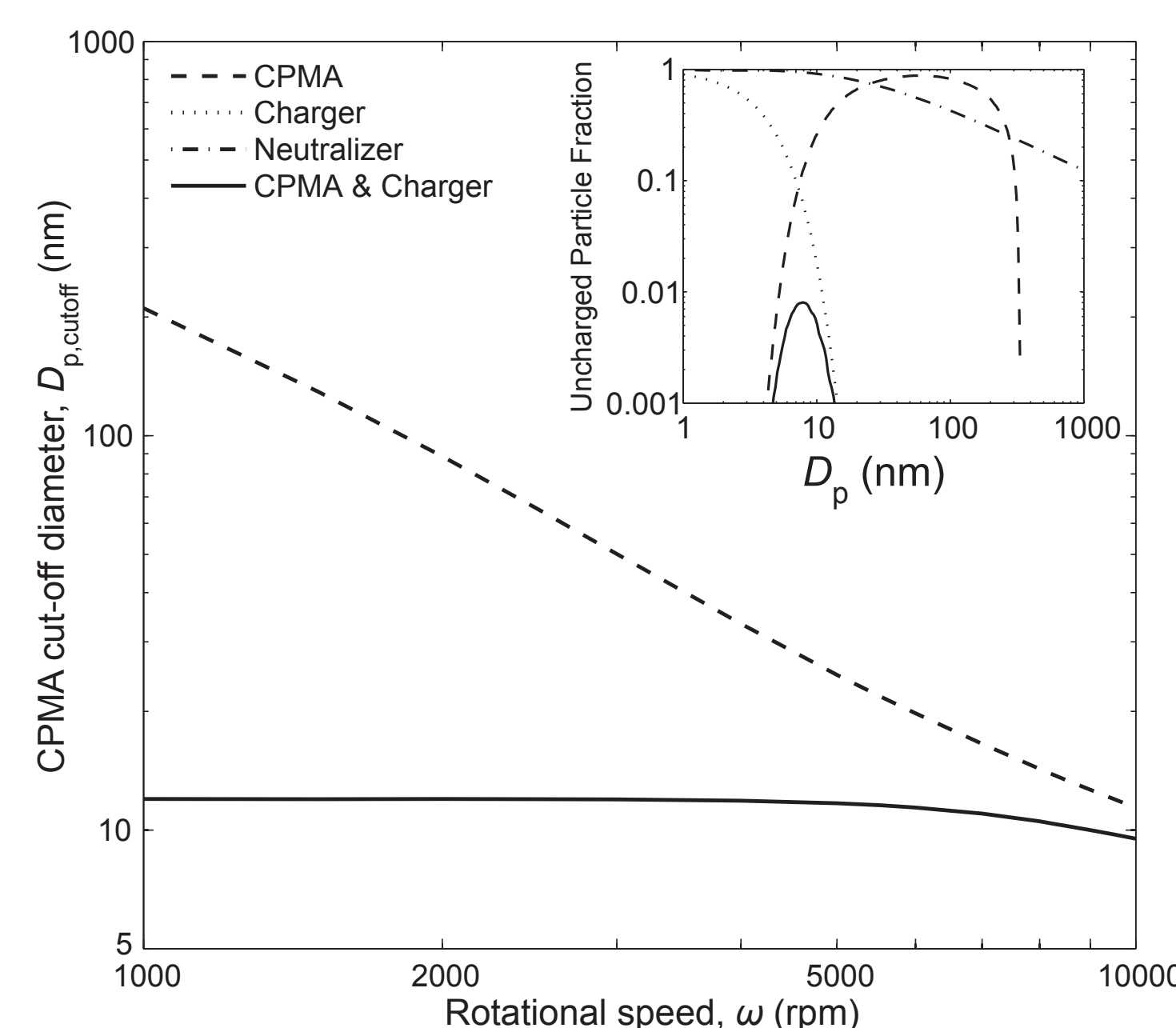

Fig 5. Theoretical Penetration of Uncharged Particles

The inset of Fig. 5 shows the fraction of uncharged unit-density particles against size passing through either a unipolar charger and a bipolar neutraliser, through a CPMA running at a rotational speed of 1000 rpm, and also downstream of a unipolar charger and CPMA in series (solid line). In this latter case, very few uncharged particles >10 nm will be present. The very high fraction of uncharged particles from the bipolar neutraliser shows that this is unsuitable for use with this method.

The main part of Fig. 5 shows the effective cut-off diameter, $D_{p,cutoff}$ (defined as the 95th percentile uncharged particle size which can pass) as a function of CPMA speed, at a flow rate of 1.5 lpm. As an example, Jing mini-CAST soot particles were charged with

a UDAC at an ion concentration - time product $n_i t = 5.4 \times 10^{13}$ ions m^{-3} s, and selected with the CPMA at $M_{+1} = 0.52$ fg (≈ 100 nm). Using a Cambustion Electrostatic Precipitator and a TSI 3775 CPC, the number concentration of uncharged particles downstream of the CPMA (n_0) was measured to be just 5.14 cm^{-3}. One can assess the the maximum contribution of m_0 from $D_{p,cutoff}$ and n_0 as

$$m_{0,max} = n_0 \frac{\pi}{6} \rho_{eff} D_{p,cutoff}^3$$

for effective density ρ_{eff} (Symonds et al., 2013). At 4 lpm sample flow and rotational speed $\omega = 7224$ rpm, $D_{p,cutoff}$ was calculated to be 26 nm, giving $m_{0,max} \approx 0.047$ fg cm^{-3}. Compared with the measured value of ($M_{+1}I/Qe$) of 7.6×10^4 fg cm^{-3}, this represents a maximum systematic error due to uncharged particles of just 0.62 ppm in this case.

Error Analysis

By using the law of propagation of uncertainties, the standard uncertainty in M_{+1} can be approximated by

$$\frac{\Delta M_{+1}}{M_{+1}} \approx \sqrt{\left(\frac{\Delta V}{V}\right)^2 + \left(2 \cdot \frac{\Delta \omega}{\omega}\right)^2 + \left(\frac{\Delta r_o}{r_o - r_i}\right)^2 + \left(\frac{\Delta r_i}{r_o - r_i}\right)^2}.$$

The probability distribution of the radii can be considered uniform, and according to NIST guidelines, for a gauging accuracy of ± 10µm their standard uncertainties can be estimated as $10\sqrt{3}$ µm. Assuming standard uncertainties in V and ω of 0.5%, $M_{+1}/\Delta M_{+1} \approx 1.4\%$. Propagating this further with standard uncertainties in I and Q from the aerosol electrometer measurement of 1% each, gives an overall combined standard uncertainty in m_{total} of $\approx 2\%$. Due to the finite width of the CPMA transfer function, if the source aerosol is not evenly distributed in mass with respect to M_{+1} an additional 0.8–1.5% standard uncertainty is introduced — see Symonds et al., (2013).

Experimental Validation

The UDAC-CPMA-Electrometer system was compared with the gravimetric technique at steady state. A challenge aerosol of Kurt J. Lesker diffusion pump oil type 704 was used, chosen for its very low vapour pressure. A TX40 filter paper through which a controlled flow of 2 slpm was drawn was used in place of the challenge instrument. A radioactive neutraliser was placed directly upstream of the filter paper to avoid any static effects due to the high level of charge on the aerosol. Filter papers were weighed using a Mettler-Toledo UMX2 balance, before and after loading, and the concentration calculated from the mass difference and flow. The electrometer was a HEPA filter in a Faraday cage, connected to a Keithley 6514 electrometer. The charge concentration is read directly into the CPMA from the electrometer over a serial connection, and the CPMA multiplies this by the chosen M_{+1} to give a direct read-out on its screen of m_{total}, also logged to a data file. M_{+1} was varied between 0.52–4.2 fg ($\approx$97–194 nm). The CPMA resolution, $R_m = M_{+1}/\Delta M_{+1,FWHM}$, = 5.
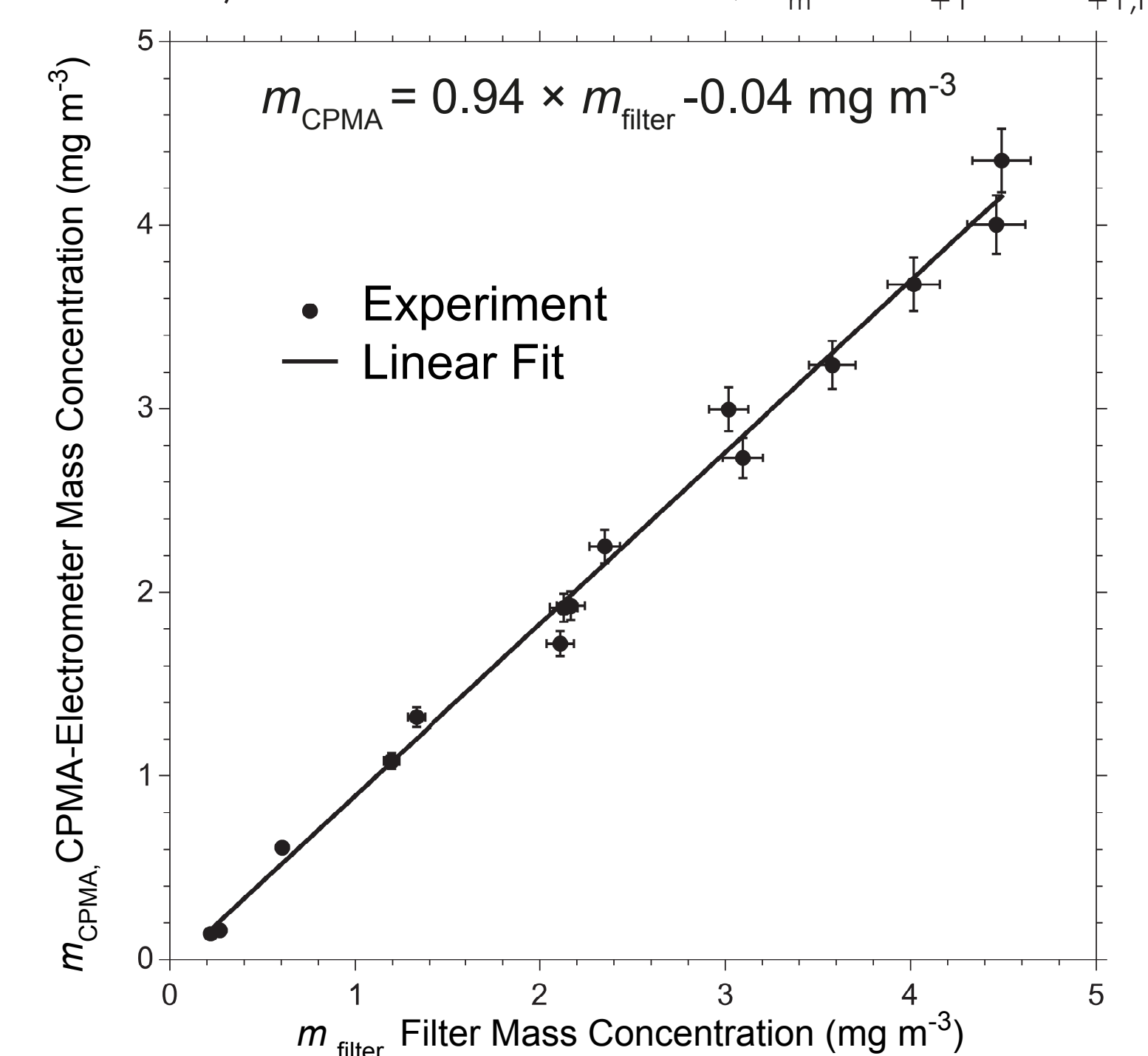

Fig 6. Comparison with the gravimetric method

The results in Fig. 6 show just a 6% disagreement with the gravimetric method. There is of course uncertainty in the gravimetric method, even when using a non-volatile aerosol.

Conclusions

The UDAC-CPMA-Electrometer system is a fundamentally traceable source of particles of known mass concentration for real-time instrument calibration. Further work is underway applying this method to the calibration of LIIs and PASSs, with promising results.

References

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