

Effect of the Uncertainty in Density of Polystyrene Latex (PSL) Spheres on the Calibration of Aerosol Instruments

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1 Introduction

Calibrated polystyrene latex (PSL) nano- and microspheres are commonly used by both manufacturers and users of aerosol sizing instruments to check accuracy and precision. This has worked well traditionally for instruments that use electrical mobility or light scattering as a measurement principle, but there is now an increasing trend towards the use of alternative sizing metrics (e.g., mass, aerodynamic diameter) in the aerosol community.

When calibrated PSL spheres are used as a reference for instruments measuring mass and aerodynamic diameter, the density of the material must also be known along with the particle size to calculate the metric of interest. However, most PSL manufacturers only certify the particle diameter, and the quoted density is that of the bulk material, which is often not confirmed by measurement.

The increase in uncertainty must therefore be taken into account when checking the sizing accuracy of popular classifiers such as the Aerodynamic Aerosol Classifier (AAC) and the Centrifugal Particle Mass Analyzer (CPMA).

Here we derive typical uncertainties in the conversion from mobility diameter (d_m) to aerodynamic diameter (d_a) and mass (m), and compare the sizing accuracy of the AAC by using calibrated PSL particles and DMA-classified Diethylhexyl-Sebacate (DEHS) droplets.

2 Uncertainty analysis

Mass

Mass is expressed as a function of d_m and the (effective) particle density ρ_p :

$$m = \rho_p d_m^3$$

The fractional uncertainty can be readily derived according to the variance formula for propagation of uncertainties:

$$\left(\frac{\sigma_m}{m}\right)^2 = \left(\frac{\sigma_{\rho}}{\rho_p}\right)^2 + \left(3\frac{\sigma_{d_m}}{d_m}\right)^2$$

Aerodynamic diameter

The aerodynamic diameter is defined as:

$$\tau = \frac{\rho_0 d_a^2 C_c(d_a)}{18\eta} = \frac{\rho_p d_m^2 C_c(d_m)}{18\eta}, \quad C_c(d) = 1 + \frac{2\lambda}{d} \left[A + B \exp\left(-C\frac{d}{2\lambda}\right) \right]$$

where ρ_0 is the unit density (1 g/cm^3), λ is the mean free path, $A = 1.165$, $B = 0.483$, $C = 0.997$.

The dependence of both aerodynamic and mobility diameter on the Cunningham slip factor make the uncertainty in d_a more difficult to evaluate. Ignoring the uncertainty in C_c itself (mainly due to temperature and pressure affecting λ), two limiting cases give:

$$d_m \rightarrow \infty : C_c(d) \rightarrow 1, \quad d_a = d_m \sqrt{\frac{\rho_p}{\rho_0}}$$

$$d_m \rightarrow 0 : C_c(d) = \frac{2\lambda}{d}(A+B), \quad d_a = d_m \frac{\rho_p}{\rho_0}$$

Overall, the relative uncertainty in d_a can therefore be constrained as:

$$\left(\frac{1}{2}\frac{\sigma_{\rho}}{\rho_p}\right)^2 + \left(\frac{\sigma_{d_m}}{d_m}\right)^2 \leq \left(\frac{\sigma_{d_a}}{d_a}\right)^2 \leq \left(\frac{\sigma_{\rho}}{\rho_p}\right)^2 + \left(\frac{\sigma_{d_m}}{d_m}\right)^2$$

In addition, to minimize uncertainty in the aerodynamic diameter, it is preferable to use materials with a density below 1 g/cm^3 , as the non-linearity of the Cunningham slip correction in this case results in a smaller relative uncertainty for d_a compared to the original one in d_m .

3 Density of size-calibrated PSL spheres

Literature studies have showed that the density of PSL nanospheres typically varies by 1-2% around its bulk density value of 1.05 g/cm^3 (Ehara et al, 2006; Tadjiki et al, 2017).

The former study, in particular, determined the density of different batches of PSL particles by observing the buoyancy in sodium chloride solutions of calibrated density. Following a similar method, we tested various PSL bottles from different manufacturers, both in date and past the quoted expiration date.

The PSL suspensions were first centrifuged, then resuspended and "washed" in ultrapure water and centrifuged again to obtain a PSL paste. This paste was then added into sodium chloride solutions of calibrated density. The suspensions were mixed well, and then allowed to settle in a temperature-controlled environment at 20°C . The density was determined by observing whether the PSL particles sank or floated in any given solution (Fig. 1).

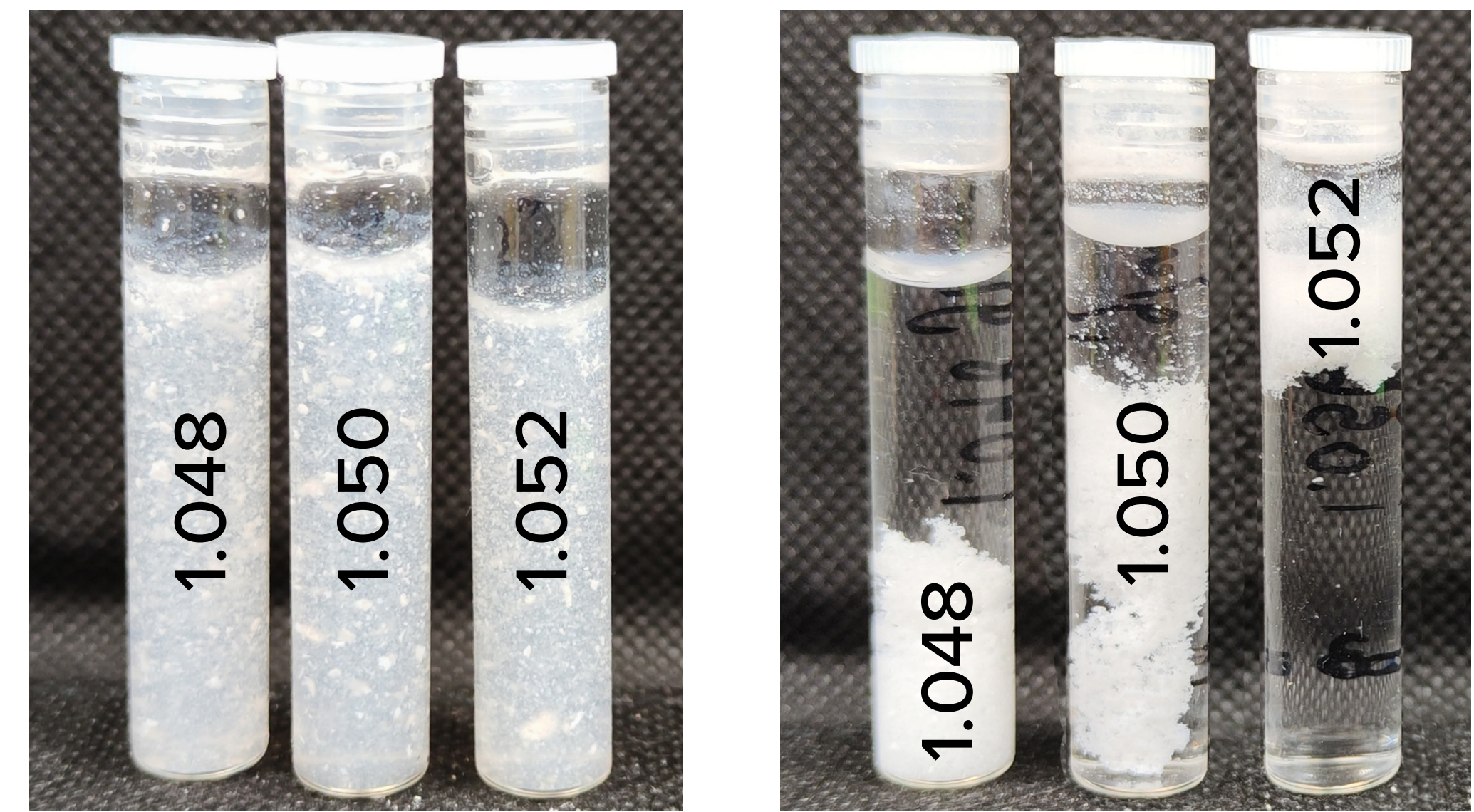


Figure 1: PSL particles with a density of 1.051 g/cm^3

The PSL particles measured here show a smaller deviation from the bulk value than is reported in the literature. A small difference can be observed between expired batches and in-date ones. The higher density value for the PSL particles manufactured by JSR is consistent with the results reported by Ehara et al (2006), who determined the density to be $\sim 1.055 \text{ g/cm}^3$ for particles by the same manufacturer.

The average density of in-date PSL was determined to be in this case: $1.049 \pm 0.001 \text{ g/cm}^3$ (Fig.2).

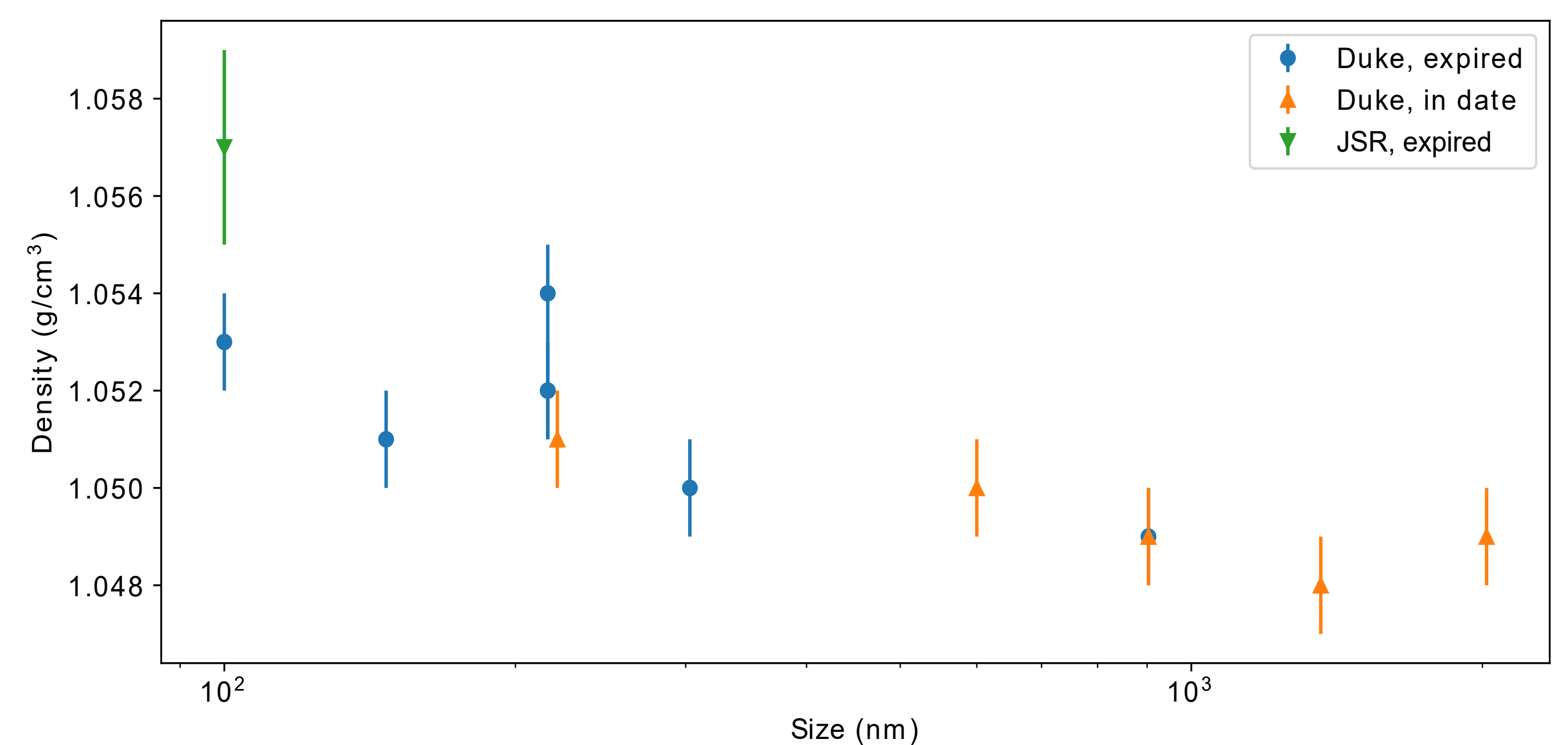


Figure 2: Measured density of PSL particles

4 PSL vs DEHS as test aerosol for the AAC

Using a high resolution on a DMA can provide a suitable calibration aerosol for the AAC, as the latter can easily distinguish the multiply-charged peaks (Fig. 3).

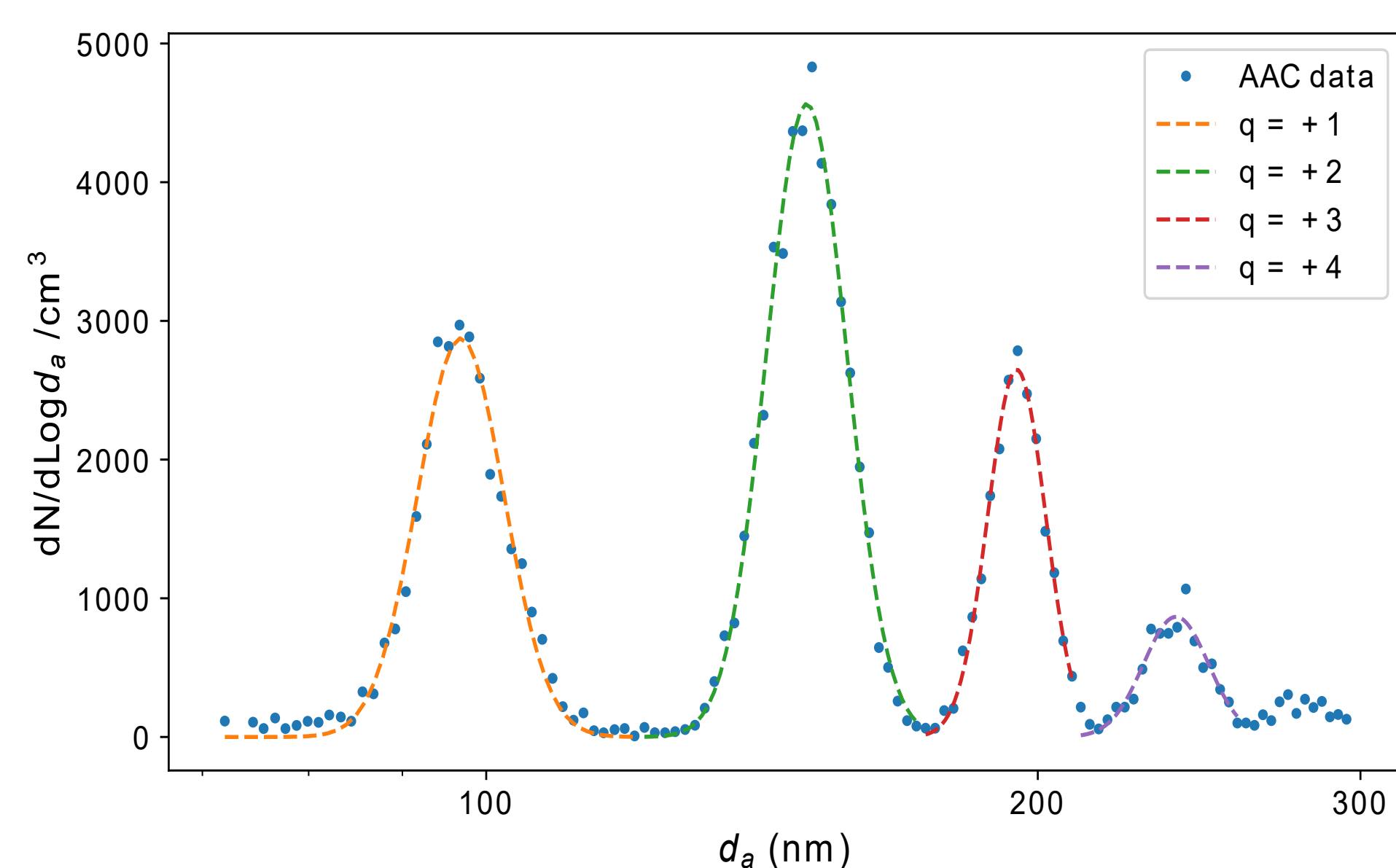


Figure 3: AAC scan of the challenge DEHS aerosol generated by the DMA.

The uncertainty expected from different test aerosols can be determined from the analysis above, based on the relative uncertainty in the input quantities.

Typical uncertainties in the examples here are:

	PSL	DMA-classified DEHS
ρ_p relative uncertainty	0.3% - 1%	0.1%
d_m relative uncertainty	1% - 3%	2% - 3%
d_a relative uncertainty	1% - 3%	2% - 3%

When using a calibrated DMA there is therefore little difference in the expected uncertainty in aerodynamic diameter of PSL or DEHS.

Advantages of the latter include:

- A more stable aerosol; when using Collison nebulizer the concentration of PSL particles drops visibly between repeated scans, and the peak is barely visible after ~ 15 min. On the other hand, the output of non-volatile droplets can remain stable over a couple of hours.
- Greater flexibility in the choice of aerosol size at a lower cost.
- More easily distinguished peaks, due to the absence of dried surfactant particles.

It is worth noting as well that PSL particles can degrade over time, and that storage conditions can impact their life-time, affecting measurements of both mobility and aerodynamic size.

Figure 4 shows the accuracy of the AAC as tested using both calibrated PSL particles and DMA-classified DEHS droplets.

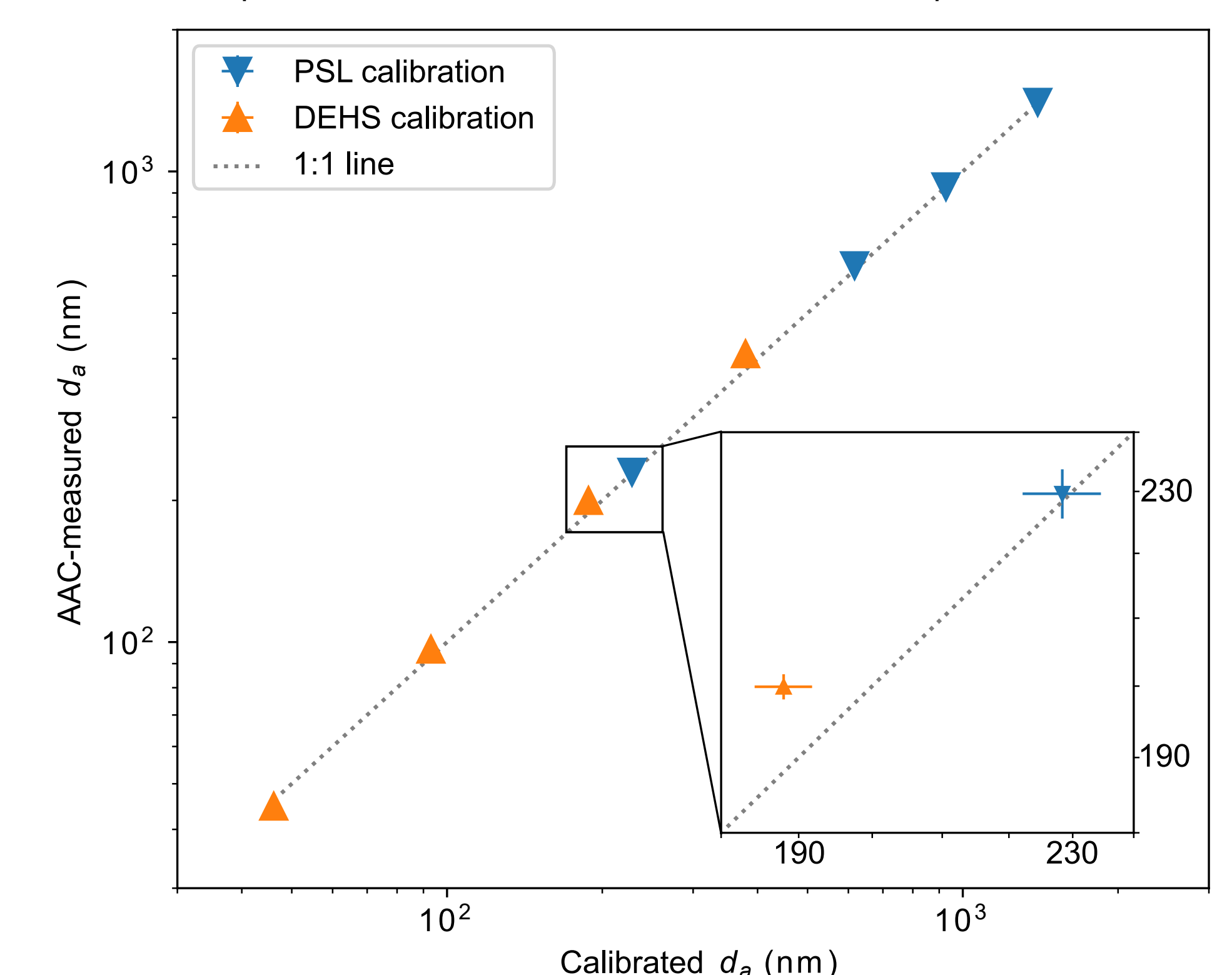


Figure 4: AAC accuracy measured using calibrated PSL spheres and DEHS droplets.

5 Conclusions

The mass and aerodynamic diameter of particles generally have a larger uncertainty than their mobility diameter. For mass-based instruments, the uncertainty on d_m is magnified and the "calibrated" mass uncertainty which is achievable from a size-based standard is very large. Aerodynamic diameter, on the other hand, is more sensitive to the particle density - especially at smaller sizes due to the effect of the non-linear Cunningham slip correction. Size-calibrated PSL particles can still give useful information regarding the accuracy of instruments such as the AAC or CPMA, but the expected uncertainty needs to be revisited compared to mobility-based instruments. However, DMA-classified spherical particles of known density can also be a practical alternative to PSL, as the generated aerosol is more stable and can have lower uncertainty in density and hence mass or aerodynamic diameter.

