Supplementary Information:

Coalescence Sampling and Analysis of Aerosols using Aerosol Optical Tweezers

Allen E. Haddrell,¹ Rachael E.H. Miles,¹ Bryan R. Bzdek,¹

Jonathan P. Reid,^{1,*} Rebecca J. Hopkins^{2,*} and Jim S. Walker³

¹ School of Chemistry, University of Bristol, Bristol, BS8 1TS, UK
² DSTL, Porton Down, Salisbury, SP4 0JQ, UK
³ BIRAL, Unit 8, Harbour Road Trading Estate, Portishead, Bristol, BS20 7BL, UK

SI.1 The Application of the Volume Fraction Mixing Rule to Estimate the Number of Accreting Droplets Required to Change the Droplet Refractive Index

The droplet refractive index following the coalescence sampling can be estimated from the expression:

$$n_{drop} = x_{smp} n_{smp} + x_{aer} n_{aer}$$
(S1)

in the limit of small changes in refractive index. Here, *n* denotes refractive index (n-RI), *x* denotes the volume fraction and the subscripts *smp* and *aer* refer to the aqueous NaCl solution of the sampling droplet and the coalescing aerosol, respectively. The change in particle refractive index, δn_{drop} , due to the presence of the accreted aerosol component is given by

$$\delta n_{drop} = \left[(1 - x_{aer}) n_{smp} + x_{aer} n_{aer} \right] - n_{smp} \tag{S2}$$

where the volume fraction of the aqueous NaCl in the new particle has been written in terms of the volume fraction of the accreted aerosol. Rearrangement allows the volume fraction of the accreted aerosol in the final droplet to be calculated.

$$x_{aer} = \frac{\delta n}{n_{aer} - n_{smp}} \tag{S3}$$

The original volume of the aqueous NaCl probe droplet is known, with the volume fraction this constitutes in the droplet following the accreted aerosol equivalent to $1 - x_{aer}$. We again neglect the hygroscopicity of the accreted aerosol, so *aer* can be taken as being equivalent to the properties of the accreted aerosol alone in the absence of water.

SI.2 Derivation of the Equations for Estimations of Expected Accretion Flux for Sampling Droplet

To estimate an expected accretion flux for the sampling droplet, we first assume that the flowing aerosol size distribution can be described by a typical log-normal distribution in particle diameter, D_p , specifying the mean particle diameter, \overline{D}_p , the geometric standard deviation of the size distribution, σ_g , and the total aerosol number concentration, N_{γ}^{41}

$$n_N^0(\log D_p) = \frac{dN}{d\log D_p} = \frac{N}{(2\pi)^{1/2}\log\sigma_g} \exp\left(-\frac{(\log D_p - \log \overline{D}_p)^2}{2\log^2\sigma_g}\right)$$
(S4)

with a mass concentration of M (µg m⁻³). Typical size distributions used in this work are shown in Figure 2(a). The flow rate of gas carrying the ambient aerosol into the trapping cell is denoted by F and is typically 200 cm³ min⁻¹. Then, the mass flux of aerosol into the optical tweezers cell per second (Δm , g s⁻¹) in which the sampling droplet is captured can be written as:

$$\Delta m = \frac{F \times M \times 10^{-6}}{60} \tag{S5}$$

A schematic of the cell, with internal volume $\sim 3 \text{ cm}^3$, is shown in the insert to Figure 2(b), with the cell flushed completely on a timescale of ~ 1 s. Computational fluid dynamics simulations have indicated that the aerosol flow is not uniformly dispersed over the cross-section of the cell, with aerosol flowing preferentially along a straightline trajectory from the inlet to outlet, on the axis of the trapped droplet. However, we assume here that the aerosol flow is dispersed over the full cross-sectional area of the cylindrical cell, flowing from the inlet, across the cell diameter and through the outlet, an assumption that will give a lower limit for the accretion flux. At the centre of the cell, in the vicinity of the sampling droplet, the cell cross-section can be approximated as the product of the height and diameter. The cross-sectional area of the droplet is dependent on the droplet radius. Thus, the fractional area of the aerosol flow intercepted by the sampling droplet, *f*, can be estimated from the ratio of the cross-sectional areas of the sampling droplet and the total aerosol flow (the height *h* multiplied by the width (diameter) *w* of the trapping cell).

$$f = \frac{\pi r_{smp}^2}{h \times w} \tag{S6}$$

Then, the accreted mass of aerosol sampled by the trapped droplet per second, Δm_{smp} , can be estimated from:

$$\Delta m_{smp} = f \times \Delta m \tag{S7}$$

A further correction may be necessary to account for the possibility that optical forces near the trap site may enhanced the capture cross-section of the sampling droplet. A correction factor for enhancements in collection efficiency, *C*, can be included in Equation (S7):

$$\Delta m_{smp} = C \times f \times \Delta m \tag{S8}$$

We will show later that this approach provides an excellent estimate of the sampling efficiency, with a correction factor of order unity. Thus, given the complexities involved in understanding this problem, we consider that this framework can provide an adequate representation of the coalescence capture strategy using optical tweezers.

Finally, the change in solute mass within the sampling particle, Δf_{solute} , over a time interval Δt can be determined. The mass of solute in the sample droplet, initially only NaCl, can be determined from the initial sampling droplet volume, the droplet density, ρ , and the mass fraction of solute (*MFS*) in the droplet that ensures equilibrium between the gas phase (at the RH of the measurement) and condensed phase.

$$\Delta f_{solute} = \frac{3\Delta m_{smp} \times \Delta t}{4\pi r_{smp}^3 \rho \times MFS}$$
(S9)

For the sample NaCl droplet, the dependence of *MFS* on relative humidity can be calculated from standard thermodynamic models such as E-AIM (http://www.aim.env.uea.ac.uk/aim/aim.php).

SI.3 Determination of Diameter Growth Factor from Refractive Index and Droplet Diameter

First, the measured value of n-RI at a particular instant can be used to infer the mass fraction of sodium chloride (*MFS*) in the droplet using the molar refraction mixing rule (described in detail in SI, Figure S3). This allows the mass growth factor to be estimated, $GF_m(RH)$, from the relationship:

$$GF_m(RH) = \frac{m_{solute} + m_{water}}{m_{solute}} = \frac{1}{MFS}$$
(S10)

where m_{solute} is the mass of sodium chloride in the droplet and m_{water} is the mass of water. In addition, the absolute mass of solute can be determined accurately by assuming the well-established relationship between hygroscopic growth (in this case, mass growth factor) and the mass of water, using the E-AIM model (http://www.aim.env.uea.ac.uk/aim/aim.php). From the known density of a dry sodium chloride particle, this dry particle mass can be reported as a dry size, r_{dry} . Thus, the reported droplet radius can be expressed as $GF_d(RH)$ at every time point:

$$GF_d(RH) = \frac{r_{wet}}{r_{dry}}$$
(S11)

Figure S1: Summary of uncertainty in measurements of size, n-RI and Raman intensity ratio recorded over a period of 200 s for droplets of differing size and composition. Each point represents a measurement made on a different sampling droplet: black open circles, measurements with aqueous sodium chloride droplets, 8 droplets total; blue filled circles, measurements with aqueous sucrose-sodium chloride droplets, 6 droplets total. The standard deviation determined for the RH measurement is also shown.



Figure S2: (a) Number of coalescing particles required to lead to the specified size change for a 3 μ m radius sampling droplet. (b) Number of coalescing particles required to lead to the specified size change for a 8 μ m radius sampling droplet. (c) Number of coalescing particles required to lead to the specified RI change for a 3 μ m radius sampling droplet. (d) Number of coalescing particles required to lead to the specified RI change for a 8 μ m radius sampling droplet.







Figure S4: A typical measurement of the size and RI of a sample sodium chloride droplet as the RH of the gas phase varies (between 96 and 72 %), and the stability in retrieved droplet size and variation in growth factor.





Figure S5: Expanded view of the coalescence sampling event shown in Figure 5.

Figure S6: Experimental configuration for sampling measurements with accumulation mode aerosol generated with an atomiser.

