

Droplet activation of wet particles: the Wet CCN approach

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Droplet activation of wet particles: development of the Wet CCN approach

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Abstract

Relationships between critical supersaturation required for activation and particle dry diameter have been the primary means for experimentally characterizing cloud condensation nuclei (CCN) activity; however, use of the dry diameter inherently limits the application to cases where the dry diameter can be used to accurately estimate solute volume. This study challenges the requirement and proposes a new experimental approach, Wet CCN, for studying CCN activity without the need for a drying step. The new approach directly measures Köhler curves under sub-saturated conditions. The experimental setup consists of a humidity-controlled differential mobility analyzer and a CCN counter; wet diameter equilibrated at known relative humidity is used to characterize CCN activity instead of the dry diameter. The experimental approach was validated against ammonium sulfate, glucose and non-spherical ammonium oxalate monohydrate. Further, the approach was applied to a mixture of non-spherical iodine oxide particles. The Wet CCN approach successfully determined the hygroscopicity of non-spherical particles by collapsing them into spherical, deliquesced droplets. We further show that the Wet CCN approach offers unique insights to the physical and chemical impacts of the aqueous phase on CCN activity; a potential application is to investigate the impact of evaporation/co-condensation of water-soluble semi-volatile species on CCN activity.

1 Introduction

In addition to their key roles in the prediction of climate changes (IPCC, 2007), clouds are also important drivers of atmospheric chemistry, impacting aerosol formation, modification, and removal (Graedel and Weschler, 1981; Blando and Turpin, 2000; Ervens et al., 2011). One aspect of clouds that is presently not well understood is the beginning of their lifetime: cloud droplet activation. The aerosol particles that serve as nuclei for cloud droplets are called cloud condensation nuclei (CCN). The number concentration

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hydrate formation, also leading to overestimates of dry solute mass; and evaporative loss of some aerosol components (e.g., Prenni et al., 2001; Hori et al., 2003; Mikhailov et al., 2004). An additional complication is that dry non-spherical particles may collapse when exposed to high humidity (e.g., Martin et al., 2013), so that the volume change upon wetting cannot be used to deduce the amount of water added to the particle.

To address these challenges, this study developed a new experimental approach, “Wet CCN”, to characterize hygroscopicity without the need for accurate characterization of the particle dry diameter. Proof-of-concept experiments were carried out with lab standards as well as for iodine oxide particles (IOP). Previous studies observed that IOP contributed to new particle formation in coastal areas; however, there has been debate over its chemical identity as inferred from hygroscopicity measurements (Jimenez et al., 2003; McFiggans et al., 2004; Murray et al., 2012; Saiz-Lopez et al., 2012). IOP was reported to have characteristics that are particularly suited for testing the utility of the Wet CCN approach: nucleated particles are non-spherical; there is the potential for the formation of hydrates ($I_2O_5 \cdot H_2O$); and IOP appears to retain water when dried. Based on the findings from these laboratory studies, the limitations and potential applications of the new approach were assessed.

2 Theoretical development

The Wet CCN approach builds upon the conventional CCN analysis, hereafter called the “Dry CCN” approach, which uses the dry diameter as a key constraint. The following theoretically describes the approach: first, based on the traditional form of Köhler theory (Pruppacher and Klett, 1997), and then a commonly used single parameter hygroscopicity representation, κ -Köhler theory (Petters and Kreidenweis, 2007).

2.1 Wet CCN approach based on Köhler theory

Köhler theory predicts saturation ratio S over an aqueous droplet (Pruppacher and Klett, 1997)

$$S = a_w \exp\left(\frac{4\sigma_{s/a}\bar{V}_w}{RTD}\right) \quad (1)$$

5 where a_w is the activity of water in solution, $\sigma_{s/a}$ is the surface tension of the solution/air interface, \bar{V}_w is the partial molar volume of water, R is the universal gas constant, T is temperature, and D is the diameter of the droplet. S is equivalent to the relative humidity, RH, expressed as a fraction. There are a number of equivalent ways to represent the activity of water. Using activity coefficient (γ_w) and mole fraction of water (x_w):

$$10 \quad S = \gamma_w x_w \exp\left(\frac{4\sigma_{s/a}\bar{V}_w}{RTD}\right) \quad (2)$$

$$S = \gamma_w \left(1 + \frac{n_s \bar{V}_w}{\frac{\pi}{6} D^3 - n_s \bar{V}_s}\right)^{-1} \exp\left(\frac{4\sigma_{s/a}\bar{V}_w}{RTD}\right) \quad (3)$$

15 where n_s is the moles of solute, and \bar{V}_s is the partial molar volume of solute. By making assumptions about γ_w and $\sigma_{s/a}$, S can be mapped as a function of D (Eq. 3) through the entire range of S (Fig. 1: assuming ideal solution of glucose starting with 100 nm dry diameter, and $\sigma_{s/a} = \sigma_{w,pure}$). Figure 1 illustrates the key concept of the Wet CCN method; one can measure the hygroscopicity of wet aerosol by constraining the trajectory of S vs. D , which can be performed without measuring the x -intercept, as is done in the Dry CCN method.

20 As is evident from Eq. (3), a number of parameters affect the trajectory of S vs. D . For instance, γ_w may impact hygroscopic growth under sub-saturated conditions. In addition, at the point of activation, n_s is related to the critical saturation ratio (S_c : the

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maximum of S in Eq. 3) and $\sigma_{s/a}$ by the following approximation, which assumes that the solution is dilute such that the volume occupied by the solute can be neglected relative to the droplet volume, and the solution is ideal ($\gamma_w = 1$) (Seinfeld and Pandis, 2006):

$$n_s = C \frac{\sigma_{s/a}^3(T)}{\ln^2 S_c} \quad (4)$$

where $C = \frac{128\pi\gamma_w^{-2}}{81R^3T^3}$ and $\sigma_{s/a}(T)$ is the temperature-dependent surface tension of the solution/air interface (Christensen and Petters, 2012).

Due to difficulties in determining each unknown parameter explicitly, a lumped parameterization remains a practical approach to representing the hygroscopicity of the aerosol. Thus, the Wet CCN approach is described below in the framework of the single-parameter fit, κ -Köhler theory.

2.2 Wet CCN approach based on κ -Köhler theory

Petters and Kreidenweis (2007) defined the hygroscopicity parameter, κ , as follows:

$$\frac{1}{a_w} = 1 + \kappa \frac{V_s}{V_w} \quad (5)$$

where V_s is the volume of solute and V_w is the volume of water.

From Eqs. (5) and (1),

$$S = \frac{D^3 - D_{\text{dry}}^3}{D^3 - D_{\text{dry}}^3(1 - \kappa)} \exp\left(\frac{A}{D}\right) \quad (6)$$

where D_{dry} is the dry diameter ($D_{\text{dry}}^3 = 6V_s/\pi$).

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Assuming κ is constant throughout the entire range of S (the sensitivity to the assumption is discussed in the following section), S can be mapped as a function of D for different D_{dry} and κ (Fig. 2, $\kappa = 0.001\text{--}1.2$, $s_c = 0.25\%$ where $s_c = S_c - 1$). The contours of κ illustrate that κ can be determined by measuring particle wet diameters (D) equilibrated at a certain humidity (S) before activation at the critical saturation ratio (S_c), unlike the Dry CCN method that measures D_{dry} (D -intercept of the κ -Köhler curves) of particles for a certain S_c .

2.3 Sensitivity analysis: impact of $\kappa_{\text{gf}} \neq \kappa_{\text{CCN}}$

The assumption that κ is constant throughout the entire range of S may not be valid in some cases; for instance, κ of secondary organic aerosol (SOA) at sub-saturated conditions (κ_{gf} calculated from a growth factor determined by a hygroscopicity-tandem differential mobility analyzer, H-TDMA) are often observed to be lower than that determined at super-saturated conditions (κ_{CCN} determined by a CCN counter) (Prenni et al., 2007; Petters et al., 2009b; Wex et al., 2009; Massoli et al., 2010). The possible causes include non-ideality and solubility of complex organic mixtures (Petters et al., 2009b).

To evaluate the impact of κ_{gf} and κ_{CCN} on the κ -contour (Eq. 6, Fig. 2) individually, the following combines conventional formulations for κ_{gf} and κ_{CCN} (Petters and Kreidenweis, 2007):

$$D = D_{\text{dry}} \left(1 + \kappa_{\text{gf}} \frac{a_w}{1 - a_w} \right)^{1/3} \quad (\text{sub-saturated}) \quad (7)$$

$$D_{\text{dry}} = \left(\frac{4A^3}{27\kappa_{\text{CCN}} \ln^2 S_c} \right)^{1/3} \quad (\text{super-saturated}) \quad (8)$$

where $A = \frac{4\sigma_{\text{s/a}} M_w}{RT\rho_w}$. Eq. (8) shows that κ_{CCN} and S_c effectively select for the sphere equivalent particle dry diameter. Similarly, Eq. (7) shows that the wet particle diameter

is determined by κ_{gf} and water activity (a_w) (RH can be converted into a_w by Eq. 1). Note that Eq. (8) is valid for $\kappa_{\text{CCN}} > 0.2$, but may be used for $\kappa_{\text{CCN}} > \sim 0.01$ if small numerical errors are acceptable (Petters and Kreidenweis, 2013).

5 Considering sub-saturated hygroscopic growth and cloud droplet activation as continuous steps, as shown in Fig. 1, Eqs. (7) and (8) can be combined to eliminate D_{dry} .

$$D = \left(\frac{4A^3}{27\kappa_{\text{CCN}} \ln^2 S_c} \right)^{1/3} \left(1 + \kappa_{\text{gf}} \frac{a_w}{1 - a_w} \right)^{1/3} \quad (9)$$

Equation (9) suggests that if $\kappa_{\text{gf}} = \kappa_{\text{CCN}} = \kappa$, one set of D , S_c , and a_w measurement is enough to determine κ . However, when $\kappa_{\text{gf}} \neq \kappa_{\text{CCN}}$, Eq. (9) is indeterminate, and simply reading κ values from the κ -contour (Fig. 2) may result in error. The sensitivity of κ determined by the κ -contour (Fig. 2) to the assumptions on κ_{CCN} and κ_{gf} is evaluated in Fig. 3. κ_{CCN} determines the D -axis intercept (D_{dry}) and κ_{gf} determines the extent of the hygroscopic growth (shape of the curves); Fig. 3 shows that the Wet CCN measurement is more sensitive to κ_{CCN} than κ_{gf} , especially in the low to mid RH ($< 70\%$) range, as seen in the gap between contours (mostly determined by D_{dry} and κ_{CCN}). Note that when $\kappa_{\text{gf}} < \kappa_{\text{CCN}}$, the κ value inferred from the contours (calculated by Eq. 6) are (erroneously) higher than κ_{CCN} (Fig. 3b), in which case a more appropriate way is to curve-fit data using Eq. (9) to acquire κ_{gf} and κ_{CCN} separately.

3 Experimental methods

3.1 Dry CCN and Wet CCN

The Wet CCN experimental setup is similar to that used for the Dry CCN approach and described elsewhere (Petters et al., 2007), except that the aerosol sample is equilibrated to a known relative humidity prior to size-selection (Fig. 4). The sample humidity

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was controlled in a similar way as in Suda and Petters (2013): the sample air was passed through Nafion tubes (PermaPure, MH-110, O.D. 0.27 cm, length 30.5 cm) with temperature-controlled water (Cole-Parmer, 6-liter Programmable Digital Controller Refrigerated/Heated Circulating Bath, EW-12118-30) circulating in the annular region.

5 Both the aerosol sample flow and the sheath flow were humidified. The relative humidities in both flows were measured by humidity sensors (Rotronic, Hygroclip). The humid aerosol flow was introduced into a chamber holding four ^{210}Po strips to equilibrate the aerosol charge distribution. A differential mobility analyzer (TSI 3071A) operating at 9 L min^{-1} sheath flow and 1.4 L min^{-1} monodisperse flow was used to select a quasi-
10 monodisperse sample of humidified particles; the voltage was increased stepwise to select particles with mobility diameters ranging from 40 nm to 300 nm. The recirculating sheath flow of the DMA was slightly dried by flowing dry air through a Nafion tube (PermaPure, MH-110) before humidification in order to avoid condensation in the line. The monodisperse aerosol flow was split and sent to a condensation particle counter (CPC, TSI 3010) to record total particle number concentration and to a Droplet Measurement Technologies Cloud Condensation Nuclei Counter (DMT CCNC) (Roberts and Nenes, 2005), held at a fixed supersaturation, to record activated droplet number concentrations. Calibration of supersaturation was carried out by observing activation of ammonium sulfate (Fisher Scientific, > 99 %, A702) and using $\kappa = 0.6$ based
20 on E-AIM calculation (Wexler and Clegg, 2002; Petters and Kreidenweis, 2007; Kreidenweis et al., 2009). Experiments were conducted using particles composed of glucose (Sigma-Aldrich, D-(+)-glucose, > 99.5, G8270), ammonium oxalate monohydrate (Sigma-Aldrich, > 99.5 %, 09898), ammonium nitrate (Fisher Scientific, > 98 %, A676), and iodine oxide particles (IOP) as described below. Ammonium sulfate, glucose, ammonium oxalate, and ammonium nitrate aerosols were generated from aqueous solutions using a TSI 3076 constant output atomizer.

25 Wet particle diameter D was measured as the activation diameter, D_{50} , at which 50 % of particles activated into droplets. Example data for ammonium sulfate activation are shown in Fig. 5 where the activation curves (activated fraction vs. diameter) of dry

and wet ammonium sulfate are compared. For a given critical supersaturation (s_c) set by the CCNC, the shift in activation curve in Fig. 5 is only due to the presence of water since the moles of solute needed for activation (n_s) are independent of the liquid water content of the initial aerosol. Note that when the sample is dry, D_{50} equals D_{dry} .

3.2 Generation of iodine oxide particles (IOP)

Experiments were carried out in a 65 L stainless steel tank operating as a batch reactor (Fig. 6). The reactor was flushed with O_3 generated by an ozone generator (Teledyne Instruments, Model 703) to reach estimated initial O_3 concentrations of 1–2 ppm. CH_2I_2 (99 %, Sigma Aldrich, 158429) was injected into the reactor by doping 1 μ L of 10 vol% solution of CH_2I_2 in methanol on glass wool in a manifold and gently flushing 3 L of warm air through the manifold (calculated concentration of CH_2I_2 0.47 ppm). Due to the small size of the reactor, experiments were carried at concentration ranges several orders of magnitude higher than previous chamber studies (Jimenez et al. (2003), CH_2I_2 : 0.015–50 ppb, O_3 : 100–500 ppb, 28 m³ Caltech indoor chamber). Higher concentrations may impact aerosol composition by influencing reaction kinetics and partitioning of higher volatility products to the condensed phase. Therefore caution must be taken in extrapolating the results to atmospheric conditions. The scope of the IOP experiments in this study is to evaluate the applicability of the Wet CCN approach to a previously studied system producing non-spherical particles with unknown composition. Jimenez et al. (2003) observed qualitatively different hygroscopicities of IOP formed in dry vs. humid conditions, with the humid reaction producing non-hygroscopic IOP and the dry reaction producing highly hygroscopic IOP, possibly due to differences in gas-phase chemistry.

3.3 CCN state space

The contours of κ calculated from κ -Köhler theory are a simple graphical way to acquire κ for wet particles. In the general case, the intercept of the curve is determined by κ_{CCN}

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and the shape by κ_{gf} . When a trajectory of data points deviates from an isoline, κ_{gf} and κ_{CCN} may be acquired separately by curve fitting as discussed above (Sect. 2.3). Additionally, physical processes impacting the state of CCN can be probed in detail when certain assumptions can be made, as indicated in Fig. 7.

κ -Köhler curves for a setpoint of $s_c = 0.25\%$ in the CCN instrument are shown in Fig. 7. The shaded region in Fig. 7 represents particle equilibration at very low RH (that is, the typical drying step to determine the volume of solute present). The endpoints of the κ isolines in this region indicate the dry critical diameter required for activation at $s_c = 0.25\%$ of a particle of composition κ , that is, the typical findings from the Dry CCN method, which uniquely relates D_{dry} , s_c , and κ . For example, a 90 nm dry particle with composition represented by $\kappa = 0.3$ would just activate under the selected s_c of 0.25%. In the Wet CCN method applied to this same example particle composition, particles are equilibrated at various relative humidities and size-selected while wet; the (wet) D_{50} values determined for $s_c = 0.25\%$ are expected to trace out the $\kappa = 0.3$ isoline.

For all particles for which the Dry CCN method may be expected to yield accurate estimates of κ , the Wet CCN method outlined above – that is, identifying a representative κ by experimentally tracing out a constant- κ isoline – is expected to yield similar results for κ . However, the Wet CCN method can provide additional information about the physical state of the particle being probed, in addition to providing an accurate assessment of κ for particles for which the Dry CCN method fails. The locations of measurements in the S vs. D_{50} space, hereafter called Wet CCN state space, can potentially be used to infer that dry test particles are non-spherical, have collapsed when exposed to water vapor, or undergo efflorescence. As shown in Fig. 7, collapse of a non-spherical particle into a more spherical shape would result in a gap between D_{dry} that the Dry CCN method would “erroneously” provide and a κ isoline with the “correct” representative κ value obtained from the observations at high equilibration RH. Efflorescence would be manifested as an unchanging D_{50} in the CCN instrument, regardless of the choice of initial equilibration RH; again, the “correct” representative κ value is expected at high equilibration RH. This behavior is properly labeled efflorescence since atomized

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particles are passed through the Nafion tube at $RH \sim 100\%$ and remain in a metastable state until RH drops below the efflorescence RH , which is the feature of this method enabling the use of spherical, deliquesced particles.

Phase partitioning, i.e., evaporation or co-condensation, of semivolatile compounds (Topping and McFiggans, 2012; Topping et al., 2013) may also occur during hygroscopic growth and cloud droplet activation. For instance, a number of studies reported evaporation (as a result of chemical decomposition) of ammonium nitrate (Mikhailov et al., 2004; Svenningsson et al., 2006; Gysel et al., 2007; Wu et al., 2013) and organic acids (Prenni et al., 2003) during H-TDMA measurements. Semivolatile compounds may evaporate inside the CCNC (Asa-Awuku et al., 2009; Romakkaniemi et al., 2013).

The impact of phase partitioning on the Wet CCN method should depend on two major factors: (1) where the shift in partitioning occurs, particularly whether upstream or downstream of the DMA, and (2) whether evaporation is reversible, i.e., whether evaporated semi-volatiles come back into the particle phase upon re-humidification within the CCNC. If evaporation of semi-volatiles occurs upstream of the DMA (e.g., during humidification in a Nafion tube) irreversibly, then D_{50} will deviate from a κ isoline. Again, the changes in κ_{gf} impact the shape of the S vs. D trajectory and κ_{CCN} impacts the D -intercept (D_{dry}) (Fig. 3). At higher RH ($> \sim 70\%$), the parameters other than particle composition (e.g., non-ideality, solubility) strongly influence κ_{gf} , and thus the impacts of phase partitioning are less likely to be experimentally isolated. On the other hand, measurements at low to mid RH ($< \sim 70\%$) are strongly dependent on κ_{CCN} and thus sensitive to small changes in the solute composition.

However, if the evaporation occurs after DMA selection (e.g., within the CCNC), the observed κ would be biased low by overestimating V_s , which is a common issue resulting in biases in the Dry CCN method. If the presence of water suppresses evaporation (e.g., by Raoult's effect), data in the CCN state space is expected to deviate from a κ isoline; however, currently the relative importance of evaporation upstream or downstream of the DMA is unknown. Combining the Wet CCN method and an evaporation

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model that predicts particle changes in the CCNC (Romakkaniemi et al., 2013) may shed light on the issue.

In summary, the applications of the Wet CCN state space (Fig. 7) are as follows:

1. In the simplest case where particles can be assumed to be spherical, non-volatile, and $\kappa_{\text{CCN}} = \kappa_{\text{gf}}$, κ can be inferred from the contour onto which experimental data fall. Although the Dry CCN method is sufficient to acquire κ_{CCN} , the Wet CCN method is an effective way to evaluate the validity of the assumptions needed to apply the Dry CCN method.
2. When particles are assumed to be spherical and non-volatile but $\kappa_{\text{CCN}} \neq \kappa_{\text{gf}}$, the simple interpretation from the κ -contour is misleading (lower κ_{gf} results in higher κ inferred from the contour, Fig. 3b). In this case, κ_{CCN} and κ_{gf} can be determined separately by curve-fitting data to Eq. (9) (S can be converted into a_w by Eq. 1).
3. When dry particles are assumed to be non-volatile and non-spherical, and wet particles are spherical, the Wet CCN method provides an accurate estimate of κ without being affected by particle shape. Furthermore, the gap between a Dry CCN measurement and a Wet CCN measurement (e.g., difference in derived κ) can be used to infer the dynamic shape factor (the ratio of the mobility diameter of a non-spherical particle to its volume-equivalent diameter).
4. When κ can be reasonably estimated from particle composition, then the phase partitioning process can be evaluated since κ and V_s (impacted by evaporation) are coupled parameters (Eq. 5). The challenge is to evaluate the partitioning at different locations (e.g., before/after the DMA), which may require additional assumptions or modeling (e.g., Romakkaniemi et al., 2013).

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4 Results and discussions

4.1 Validation results

Results of Wet CCN analysis for ammonium sulfate and glucose particles, as well as a model prediction for ammonium sulfate, are shown in Fig. 8. The theoretical line represents D_{dry} (x -intercepts) calculated by assuming $\kappa_{\text{CCN}} = 0.6$ (Petters and Kreidenweis, 2007) and subsequent hygroscopic growth taking into account non-ideality of ammonium sulfate solutions using E-AIM (Wexler and Clegg, 2002). The observations for ammonium sulfate agreed well with the E-AIM prediction. These data are not redundant with the calibration, since the saturation ratio in the CCNC was calibrated using dry ammonium sulfate particles, as is standard practice, which adjusts the D -intercept (D_{dry}); the observation is consistent with the expected deviation from the $\kappa = 0.6$ isoline due to non-ideality predicted by E-AIM. Efflorescence of ammonium sulfate was observed at $\text{RH} \sim 35\%$, also in agreement with prior work (Seinfeld and Pandis, 2006). The measurements for glucose particles ($\kappa \sim 0.2$) were in agreement with a previous characterization study using the H-TDMA technique (Suda and Petters, 2013), and were also consistent with the estimated range of $\kappa = 0.14\text{--}0.2$ reported in Petters et al. (2009). Recent additional high accuracy CCN measurements found $\kappa_{\text{CCN}} = 0.154$, as one would predict for an ideal solution (unpublished data).

The Wet CCN approach was applied to ammonium oxalate monohydrate particles as an example system of non-spherical crystals (Hori et al., 2003), for which the Dry CCN method will overestimate solute volume and underestimate κ . Previous studies reported a large range of $\kappa = 0.24\text{--}0.48$ for ammonium oxalate monohydrate (Hori et al., 2003; Petters et al., 2009a). The Wet CCN observations (Fig. 8) suggested a transition from a non-spherical crystal with void spaces, into an aqueous solution droplet. The estimates of apparent κ for the dry crystals were in agreement with the range in previous studies; on the other hand, κ of fully dissolved ammonium oxalate was equivalent to that of ammonium sulfate ($\kappa = 0.6$).

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For comparison, κ can be estimated assuming surface tension and solubility do not play a role, and the solution behaves ideally (Raoult's law holds) (Kreidenweis et al., 2009; Petters et al., 2009a):

$$\kappa_{\text{Raoult}} = \nu \frac{\rho_s M_w}{\rho_w M_s} = \nu \frac{f_w}{f_s} \quad (10)$$

5 where ν is the number of ions the solute dissociates into, ρ_s is the density of solute, ρ_w is the density of water, M_w is the molecular weight of water, M_s is the molecular weight of the solute, f_w is the molar volume of water, and f_s is the molar volume of the solute. Using Eq. (10) and molar volume of ammonium oxalate ($94.7 \text{ cm}^3 \text{ mol}^{-1}$) (Haynes, 2013), κ_{Raoult} of ammonium oxalate is estimated to be 0.57 (ν is assumed to be 3).

10 Efflorescence of ammonium oxalate monohydrate was observed at $a_w \sim 0.5$, which is in agreement with a previous study employing the electrodynamic balance (EDB) technique (Peng and Chan, 2001). The effective κ of ammonium oxalate particles reported here for the Wet CCN technique narrowed down the previously large range in estimates. This measurement demonstrated that the Wet CCN method can determine the solute volume and κ of non-spherical water-soluble crystals, regardless of their hydration states.

4.2 Iodine oxide particles

20 Results of representative experiments carried out in dry (reactor RH < 10%) and humid conditions (reactor RH \sim 65%) are shown in the Wet CCN state space in Fig. 9. For the dry generated particles, the D_{50} of dry particles (\sim 80 nm at RH \sim 10%) clearly deviated from the trend at higher equilibration RH, suggesting non-sphericity and collapse when wetted; the κ of fully dissolved IOP was observed to be in the range of 0.5–0.6, close to that of ammonium sulfate ($\kappa \sim$ 0.6). Assuming I_2O_5 (molar volume $69.5 \text{ cm}^3 \text{ mol}^{-1}$) hydrating to become two HIO_3 , as the first order approximation, κ_{Raoult}

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in an ideal solution is calculated to be 0.51 (further dissociation of HIO_3 would enhance κ_{Raoult}).

The comparison of the Dry CCN and the Wet CCN measurements provides quantitative insights on particle shape and density. The ratio of the κ measured by the Dry CCN ($\kappa = 0.17$) to the Wet CCN κ (0.5–0.6) suggests that the non-spherical dry particle volume was observed to be 2.9–3.5 times larger than the equivalent volume of spherical particles (note that κ and V_s are coupled parameters, Eq. 5). Assuming material density of 5 g cm^{-3} (c.f., I_2O_5 density: 4.98 g cm^{-3} , CRC handbook) (Haynes, 2013), the effective density of non-spherical particle would be $1.4\text{--}1.7 \text{ g cm}^{-3}$. Jimenez et al. (2003) estimated the effective density of non-spherical IOP to be $0.86\text{--}1.22 \text{ g cm}^{-3}$ by comparing the (vacuum) aerodynamic diameter and the mobility diameter. The difference in the effective densities indicates that IOP produced in this study was more compact than that in their study; a possible reason for the discrepancy of particle shape is the different gas and particle concentration levels (Jimenez et al., $\text{CH}_2\text{I}_2 < 50$ ppb; this study $\text{CH}_2\text{I}_2 \sim 500$ ppb), but a definitive explanation requires further experimental evaluation.

On the other hand, particle generation reactions carried out under humid conditions resulted in nearly non-hygroscopic particles (large D_{50} without S dependence). The unchanging D_{50} with respect to S suggests that particles were effloresced. Thus, observed D_{50} was extrapolated down to $S = 0$ and κ was calculated to be ~ 0.06 .

A similar observation regarding a strong dependence of hygroscopicity on relative humidity during the particle generation reactions was made by Jimenez et al. (2003) semi-quantitatively using a H-TDMA. In their humid experiments (reactor RH $\sim 65\%$), the hygroscopic growth factor (final diameter/initial diameter) remained nearly 1, that is, little to no water uptake was observed; on the contrary, in the dry experiment (reactor RH $< 2\%$), IOP started collapsing when exposed to RH beyond 23%, and then the particle regained its initial size at RH $\sim 85\%$ by hygroscopic growth of the collapsed particles, indicative of high κ (Fig. 7 in Jimenez et al., 2003). The low hygroscopicity particles (generated in humid experiments) were inferred to be I_2O_4 based on its lack of water solubility (prolonged treatment in excess of water decomposes I_2O_4 into I_2

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and HIO_3) (Daehlie and Kjekshus, 1964), instead of highly soluble I_2O_5 (263 g of I_2O_5 per 100 g of H_2O (Kumar et al., 2010)); note that this solubility is sufficient for CCN activation, i.e. deliquescence RH is less than the critical saturation ratio and cloud droplet activation is determined by κ_{CCN} (Petters and Kreidenweis, 2008).

5 However, a later study investigated the elemental composition of IOP generated photochemically by I_2 and O_3 and suggested that the main constituent is likely to be I_2O_5 (Saunders and Plane, 2005). Hence, the apparent contradiction has been a matter of debate (Murray et al., 2012; Saiz-Lopez et al., 2012). To address the contradiction, Murray et al. (2012) investigated the hygroscopicity of iodic acid (HIO_3), a hydrated
10 form of I_2O_5 , using EDB. They observed surprisingly low hygroscopicity ($\kappa = 0.024$) for this highly soluble inorganic compound. The reason for the weak hygroscopic growth was unclear, but one hypothesis was formation of polymeric structures that lead to strongly non-ideal behavior (Murray et al., 2012).

The reason for the discrepancy of particle hygroscopicity depending on “reaction
15 humidity” (not to be confused with “measurement humidity” in the Wet CCN method), remains unclear. κ of the ideal solution of I_2O_5 would be as high as typical inorganic salts (as discussed above), which appears to be consistent with the dry reaction experiments in this study and the experiments reported by Jimenez et al. (2003); in contrast, κ of humid reaction experiments was observed to be much lower ($\kappa = 0.06$), which was
20 consistent with humid reaction experiments in Jimenez et al. (2003), as well as with EDB analysis of HIO_3 by Murray et al. (2012) ($\kappa = 0.024$). Although further studies are needed to resolve the dichotomy, considering the significance of IOP in the marine and coastal environment (Saiz-Lopez et al., 2012), the humid reaction experiments yielding low κ IOP are expected to be more atmospherically relevant.

25 4.3 Ammonium nitrate

Evaporation of volatile compounds after DMA sizing (inside a CCNC) would result in overestimation in D_{50} determined by the Dry CCN method (Asa-Awuku et al., 2009; Romakkaniemi et al., 2013). Recently, Romakkaniemi et al. (2013) modeled

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evaporation and co-condensation inside the DMT CCNC (the same instrument as used in this study) using a computational fluid dynamics model. In a test case for ammonium nitrate particles, simulation results showed that evaporation of ammonium nitrate led to a reduction in effective dry diameter by 10 to 15 nm for particles having initial diameters between 40 and 120 nm (Romakkaniemi et al., 2013).

As the first step to evaluate the impact of evaporation on the Wet CCN method, ammonium nitrate was tested experimentally (Fig. 10). The theoretical prediction was made by using $\kappa = 0.73$ (Kreidenweis et al., 2009) for the D -intercept (D_{dry}) and calculating hygroscopic growth ($S > 0$) using E-AIM (Wexler and Clegg, 2002) with and without the assumption of volume additivity (black and gray solid lines). The observed $D50$ trend was significantly larger than the E-AIM prediction, with a difference of approximately 15 nm at $s_c = 0.4\%$. The extent of the gap is consistent with Romakkaniemi et al. (2013). In contrast, Svenningsson et al. (2006) did not observe significant evaporation of NH_4NO_3 ; Petters and Kreidenweis (2007) analyzed the data in terms of κ and acquired $\kappa = 0.67$. The discrepancy may be due to the different operating temperatures of CCNCs. Svenningsson et al. used a thermal gradient diffusion Cloud Condensation Nucleus spectrometer (CCN spectrometer, University of Wyoming, CCNC-100B) that generates supersaturation by cooling the bottom plate thermoelectrically (Snider and Brenguier, 2000); on the other hand, the DMT CCNC generates supersaturation by creating a positive temperature gradient (Roberts and Nenes, 2005). Asa-Awuku et al. (2009) compared the DMT CCNC and a static diffusion CCN counter that operates below room temperature and concluded that secondary organic aerosol generated by β -caryophyllene ozonolysis evaporated significantly in the DMT CCNC due to the higher operating temperature.

The observation suggests that the presence of water in the Wet CCN method did not suppress evaporation (as a result of chemical decomposition) of NH_4NO_3 significantly. Although higher relative humidity lowers the NH_4NO_3 dissociation constant (Stelson and Seinfeld, 1982), the higher temperature and the wall wetted by pure water in a CCNC might have enhanced the removal of particle phase NH_4NO_3 (Romakkaniemi

et al., 2013). Further studies are needed for determining the upper limit of volatility for compounds for which the Wet CCN method can accurately determine κ .

5 Limitation and potential application of Wet CCN approach

It remains challenging to experimentally constrain individual physicochemical parameters such as surface tension, molar volume, solubility, and activity coefficient since they all affect the trajectory of S vs. D (Fig. 1) in different ways. Therefore, parameterization of hygroscopicity using a parameter such as κ , which folds in effects from these other variables into a single observable property, remains a practical approach. Application of the Wet CCN method to single-component particles is relatively straightforward if solutes are effectively non-volatile and wet particles are dissolved and spherical (e.g., ammonium oxalate monohydrate). Crystal shape (which affects DMA sizing) and the presence of hydrated water in the particle volume are no longer an issue if fully deliquesced droplets can be used for characterization, as in the Wet CCN method. However, particles with a non-spherical rigid backbone may remain non-spherical even after wetting, re-introducing uncertainty in the sizing of the wet particle.

If evaporation/co-condensation of volatile compounds occurs after DMA sizing, it will lead to overestimation/underestimation in D_{50} determination, both in the Dry CCN and the Wet CCN measurements; however, the feature of the Wet CCN comes into play if the presence of water in the particle phase impacts evaporation/co-condensation. If water significantly suppresses evaporative loss of semi-volatile species (by Raoult's effect), then the Wet CCN approach allows for an experimental look at this problem. If evaporation/co-condensation occurs and results in significant changes in hygroscopicity before DMA sizing, data points in the Wet CCN state space are expected to deviate from κ isolines as described in Fig. 7. However, concentration dependent non-ideality (γ_w) (e.g., AS in Fig. 8) or phase separation in complex mixtures may also result in deviation from κ isolines due to the change in κ_{gf} especially at higher RH ($> \sim 70\%$)

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(Fig. 3); therefore, again, the Wet CCN measurement at higher RH ($>\sim 70\%$) needs to be treated with caution (Fig. 3).

Thus the major limitation of the Wet CCN technique appears to be the uncertainty in identifying the cause of observed deviations from κ isolines. The potential sources of such deviations include (1) shape changes, (2) concentration dependent non-idealities (impacting κ_{gf} , not κ_{CCN} : Fig. 3), (3) solubility limits of complex mixtures, and (4) evaporation/co-condensation. At minimum, deviation from κ isolines can be used as a flag for further investigation of physical/chemical processes involving the aqueous phase that may not be apparent, or may be overlooked, in measurements made via the conventional Dry CCN method.

6 Conclusions

This study developed the conceptual basis of the Wet CCN technique, based on simple modifications of existing conventional approaches, which we term Dry CCN methods. The Wet CCN method is the direct measurement of κ -Köhler curves in humid (sub-saturated) conditions, as opposed to the Dry CCN method that constrains only the dry portion of κ -Köhler curves. In the Wet CCN method, particles are not dried before sizing, enabling a series of applications to systems where dry particle characterization is difficult due to complex particle shapes or solute compositions (e.g., hydrate formation). The Wet CCN approach was evaluated using ammonium sulfate, glucose, and non-spherical ammonium oxalate monohydrate particles, and was shown to produce estimates of κ consistent with, or improved from, those previously reported in the literature. Further, the Wet CCN approach was applied to iodine oxide particles, which are non-spherical and have unknown chemical composition. Different measured hygroscopicities of IOP when they are formed in dry vs. humid reactions conditions were consistent with observations in a previous study (Jimenez et al., 2003). Ammonium nitrate was observed to evaporate significantly even with the Wet CCN method. Care must be taken in identifying the cause of deviations of measurements from κ isolines in

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the CCN state space, as particle shape effect, concentration dependent solution non-idealities, solubility limitations, and evaporation/co-condensation of volatile species can all result in such deviations and may be difficult to separate observationally.

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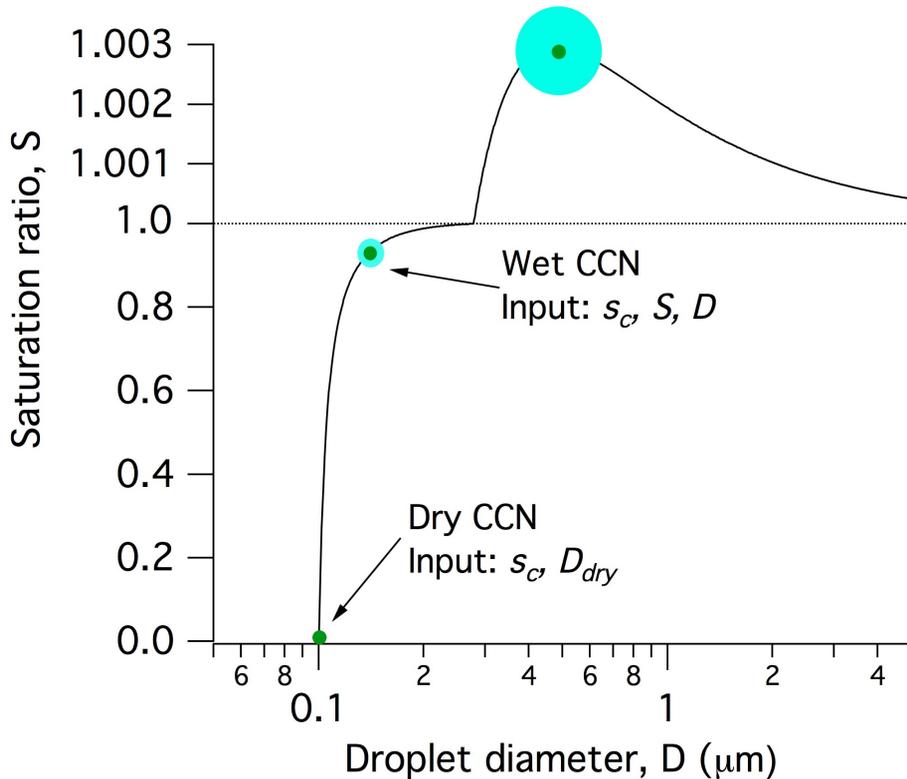


Fig. 1. Illustration of Wet CCN approach. Instead of dry diameter (D_{dry}), droplet diameter (D) at a certain saturation ratio (S) can be used to characterize the trajectory of Köhler curve (depends on hygroscopicity). The line represents Eq. (3) assuming an idealized solution of glucose ($\gamma_w = 1$, $\bar{v}_w = 18.0 \text{ cm}^3 \text{ mol}^{-1}$, $\bar{v}_s = 117 \text{ cm}^3 \text{ mol}^{-1}$, $n_s = 4.50 \times 10^{-18} \text{ mol}$) and that the droplet surface tension is equal to that of water. The scale of the y axis is changed at $S = 1$. The inserts are shown as core-shell morphology to visualize that the amount of solute (green circle) is constant; wet glucose is expected to be a homogeneous solution.

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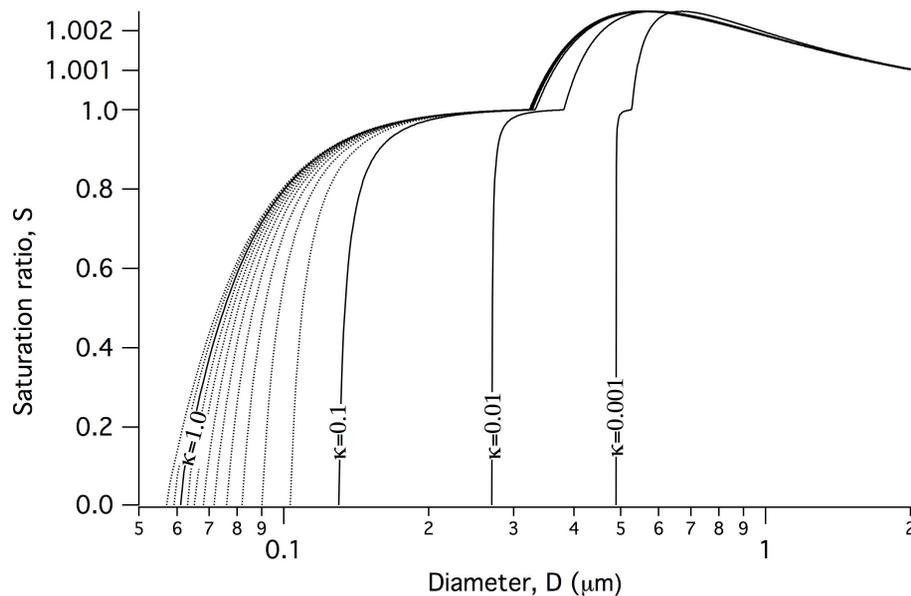


Fig. 2. Calculated saturation ratios of water (S) as functions of (wet) diameter (D) for $0.001 < \kappa < 1.2$ compounds (s_c : 0.25 %).

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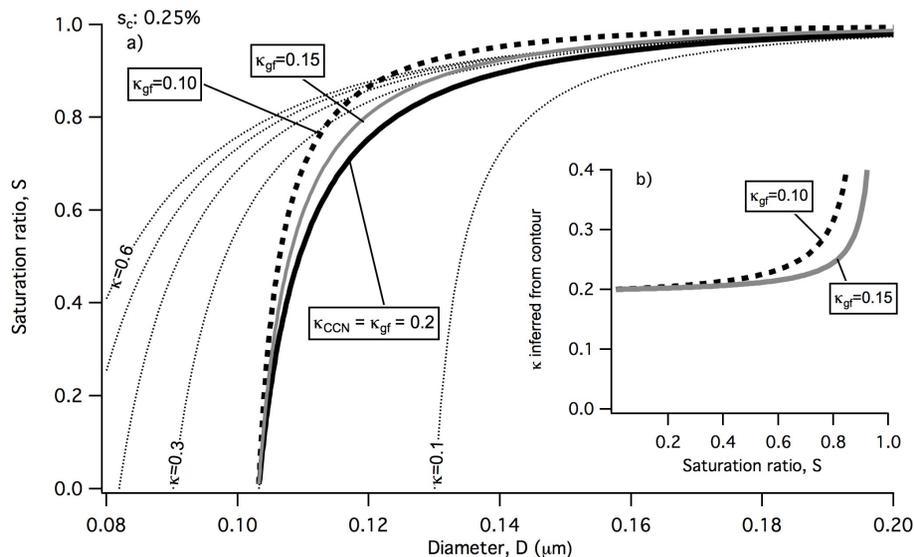


Fig. 3. Evaluation of the impact of κ_{gf} on the Wet CCN analysis (s_c : 0.25%). The uncertainties in κ_{gf} , as represented by the labeled curves, significantly impact the κ value inferred from the contour (calculated by Eq. 6) especially at higher RH (above $\sim 70\%$). When data points deviate from κ isolines, further analysis such as curve fitting is necessary.

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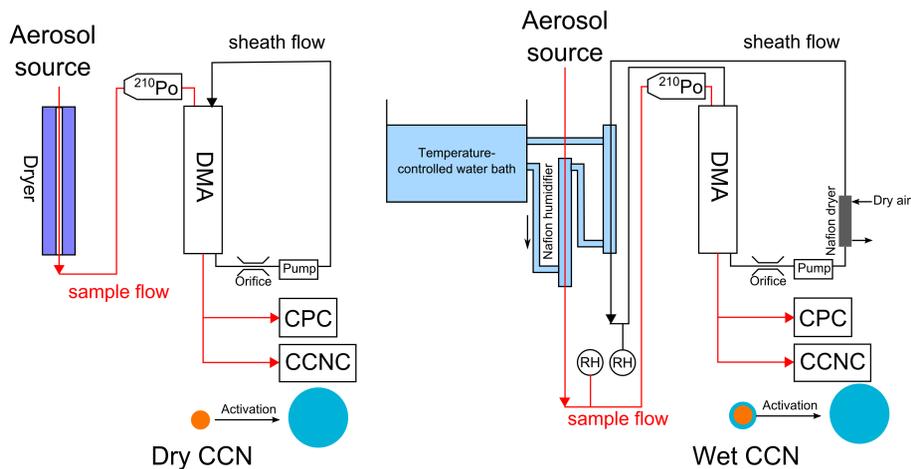


Fig. 4. Experimental setup for Dry CCN and Wet CCN analyses.

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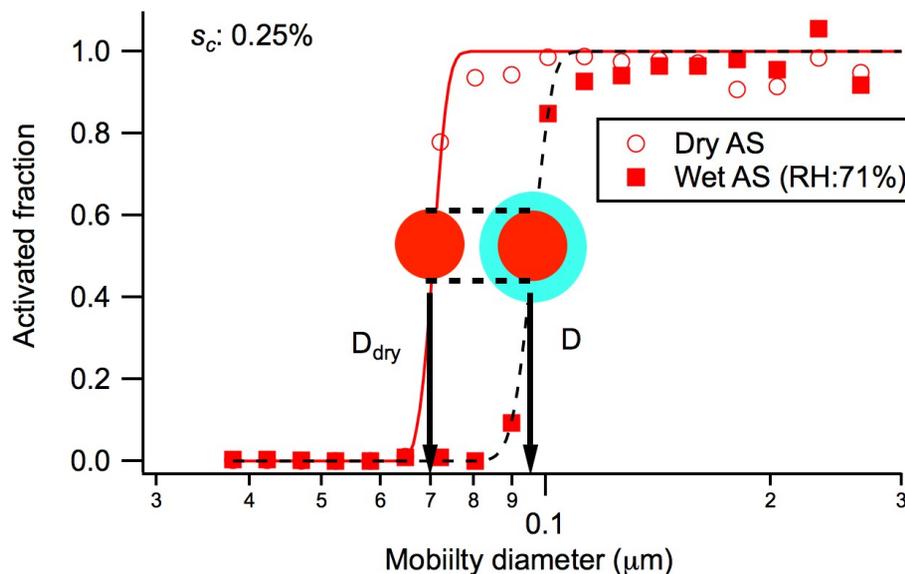


Fig. 5. Example activation curve of dry and wet ammonium sulfate (AS) particles. At a given critical supersaturation (s_c), the moles of AS needed for activation at this supersaturation are fixed, irrespective of initial particle state. Therefore, the activation curve of wet AS is shifted toward larger particles size (D), compared to dry AS (D_{dry}). The shift corresponds to the water content of the humidified particle.

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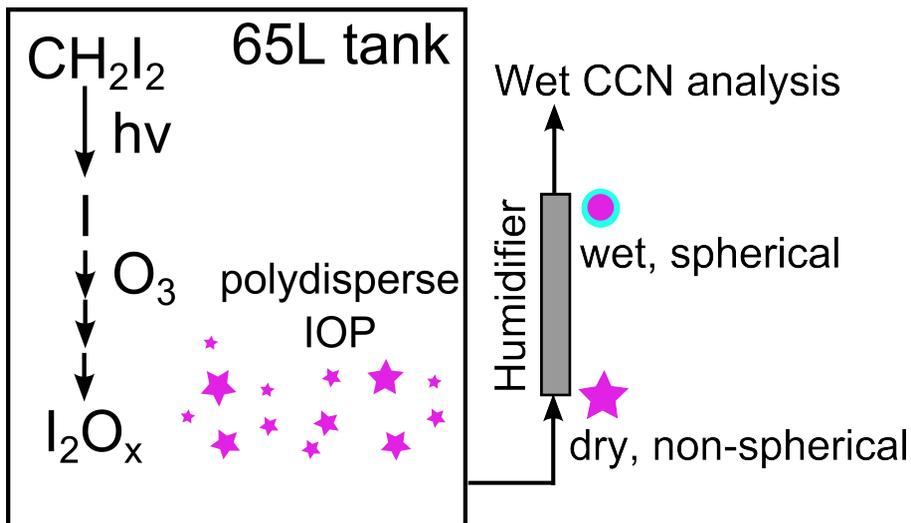


Fig. 6. Schematic of Wet CCN measurement of non-spherical iodine oxide particles (IOP). The non-spherical particles are passed through the humidifier (a part of the Wet CCN experimental setup) such that they collapse into wet spherical particles.

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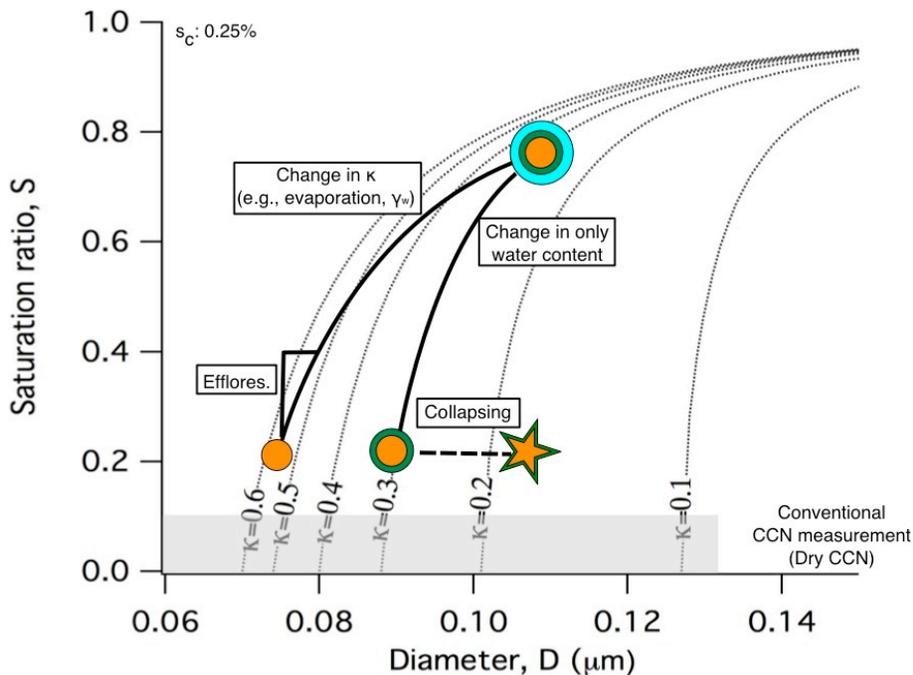


Fig. 7. Illustration of CCN state space. Orange: hygroscopic fraction of aerosol, green: less hygroscopic fraction, blue: water.

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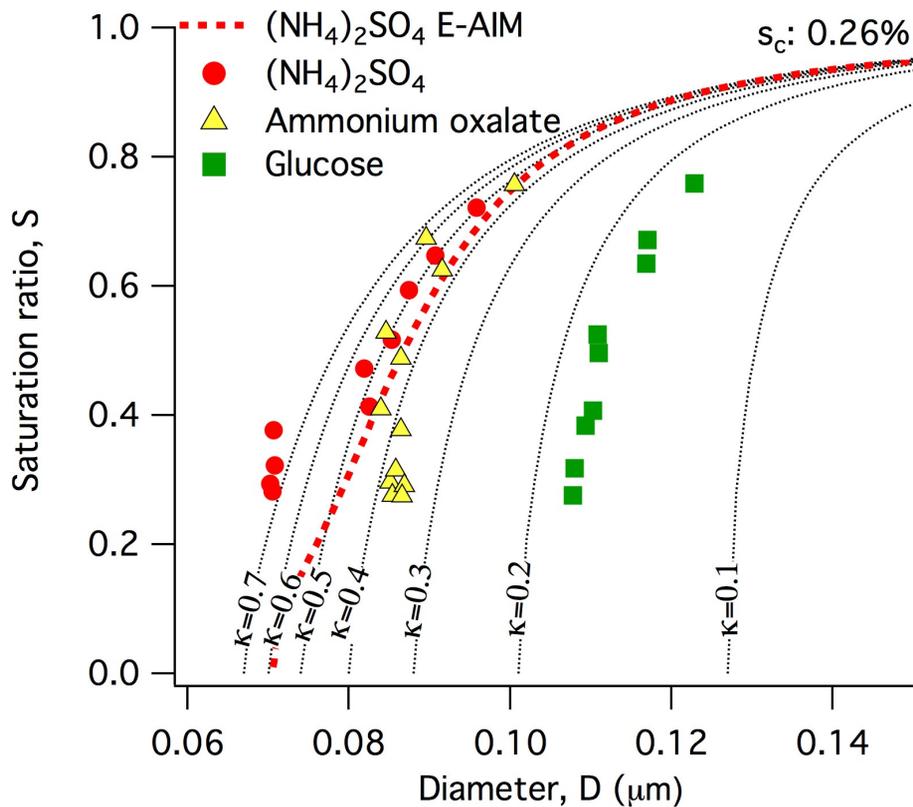


Fig. 8. Data obtained using the Wet CCN method for ammonium sulfate, glucose, and ammonium oxalate particles. Theoretical prediction for $(\text{NH}_4)_2\text{SO}_4$ is made by assuming $\kappa = 0.6$ at the Dry CCN condition (x intercept, $S = 0$) and calculating the subsequent hygroscopic growth ($a_w > 0$) by E-AIM (assuming volume additivity).

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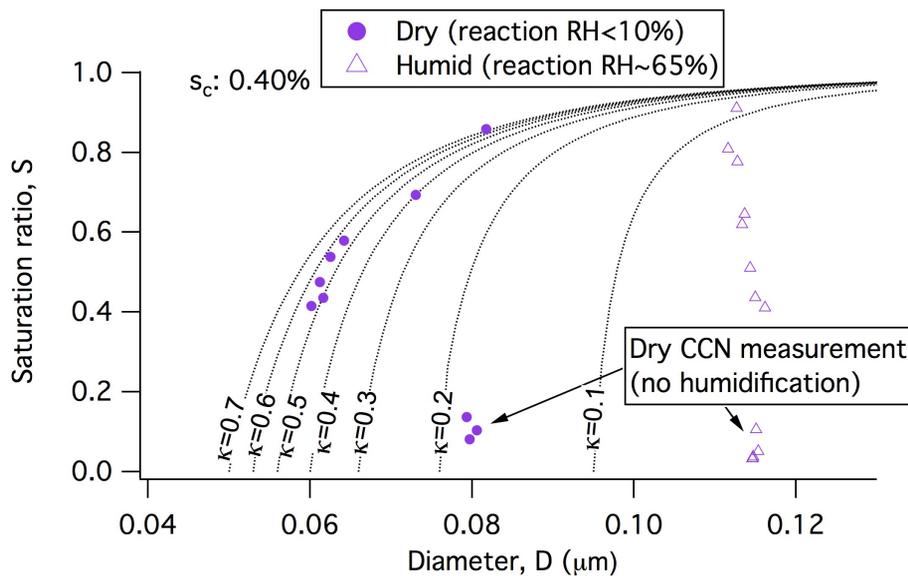


Fig. 9. Wet CCN measurements for iodine oxide particles produced by CH_2I_2 photolysis and oxidation by O_3 . Aerosol generation experiments were carried out at two humidity conditions as shown.

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