Cloud Nucleating Activity of Non-Spherical Particles: Application of Wet CCN Measurement to Iodine Oxides

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Introduction

Aerosols impact cloud reflectivity and cloud residence time by acting as cloud condensation nuclei (CCN). Traditional lab methods for measuring properties dictating CCN activity (Figure 1) are unable to accurately measure particles with irregular (non-spherical) geometry such as iodine oxides. Here we apply a novel wet CCN measurement method (Figure 3) that collapses fractal iodine oxide particles to provide an accurate measurement of water uptake and CCN activity of irregular particles.

Fractal iodine oxide particles form through oxidation of molecular iodine and other iodic compounds released in coastal regions by algae. Subsequent condensation forms small nuclei that agglomerate into larger irregular, particles. Figure 2 shows prior attempts to measure hygroscopicity, or water uptake, of iodine oxides using traditional methods. Traditional methods to measure κ, the hygroscopicity parameter, use dried particles modeled as a sphere to calculate the amount of solute present (Petters and Kreidenweis 2007). Findings in Figure 2 were inconclusive because the fractal particles collapsed when exposed to elevated relative humidity.

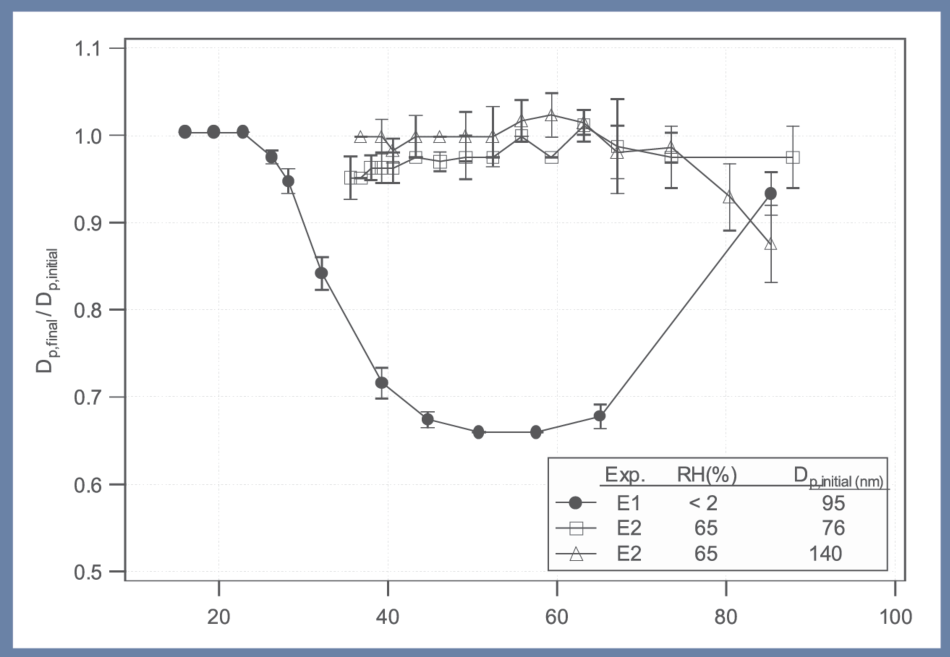

Figure 2 (above): Previous measurements of IOP hygroscopic growth
Jimenez et al. measured the hygroscopic growth of iodine oxide particles (IOPs) generated from CH_2I_2 and ozone in the presence of UV using a hygroscopic tandem differential mobility analyzer (HTDMA) in 2003. Figure 7 from the Jimenez et al. 2003 paper is reproduced above. The ratio of particle diameter after water uptake to particle diameter before water uptake (Dp,final and Dp,initial, respectively) is graphed against varying relative humidity (RH). Ratios below 1 indicate the particle became smaller when exposed to elevated RH. A ratio of 1 indicates no water uptake. E1, when the particle was generated in RH below 5%, shows ratios below 1, giving inconclusive information about the hygroscopicity of iodine oxides using the traditional method. E2 and E3 show no hygroscopic growth for particles generated in a reactor with RH of 65%.
The Jimenez et al. results motivated application of the wet CCN method to IOPs generated at different levels of RH.

Acknowledgements

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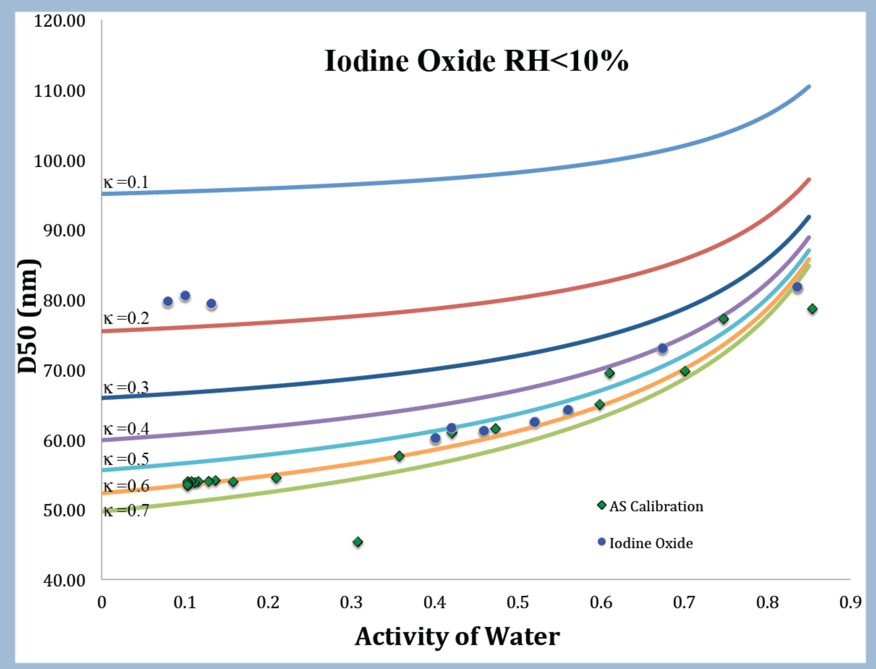
Figure 4 (right): Iodine oxides RH<10%

Changes in observed hygroscopicity (κ) are illustrated by plotting D_{50} (the diameter at which 50% of CCN activate to cloud droplets) at varying water activities (aw). Measurements are compared to isokappa lines. The isokappa lines calculate the D_{50} for a given κ, saturation ratio, and aw as seen in eq. 1.
Ammonium sulfate (AS), used for calibration, is accurately measured using the traditional method as it follows the same isokappa line of 0.6 with varying aw.
The fractal iodine oxide particles have an observed κ below 0.2 for traditional (dry) measurements. At higher aw, observed κ is nearer to 0.6.



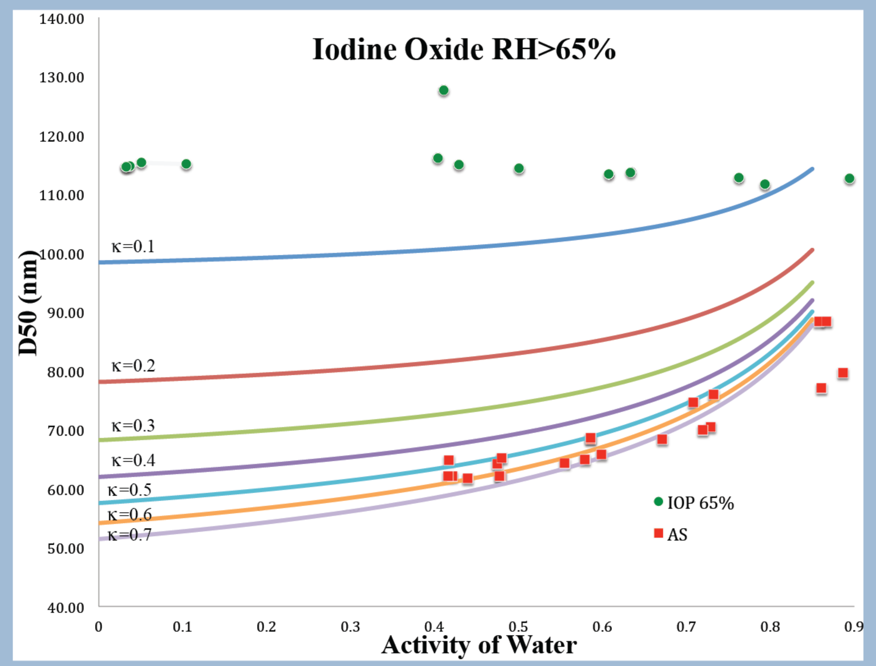


Figure 5 (left): Iodine oxides RH>65%

Changes in observed κ for particles generated at RH>65% are plotted in the same space as shown in Figure 4. Iodine oxide particles did not uptake water, evidenced by D50 measurements remaining around 115 nanometers even with changing RH. These findings are consistent with those of Jimenez et al. with HTDMA diameter ratios of 1.

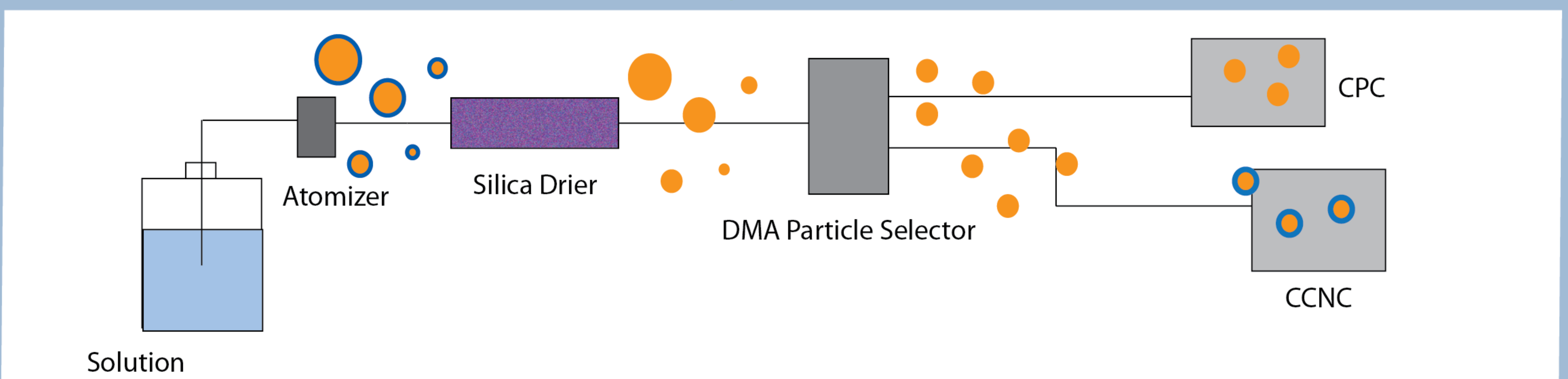


Figure 1: Traditional CPC-CCNC set-up
An atomizer generates polydisperse particles from solution. A silica drier removes excess moisture from the particles before the differential mobility analyzer (DMA) selects all dry particles of a certain diameter as dictated by varying voltage, releasing a monodisperse aerosol. A portion of the monodisperse aerosol passes to the Condensation Particle Counter (CPC) to record the total particle number. The Cloud Condensation Nuclei Counter (CCNC) creates a supersaturated environment and counts the CCN that activate to cloud droplets. The traditional method measures the amount of solute from the diameter selected in the DMA, modeling the particle as a sphere.

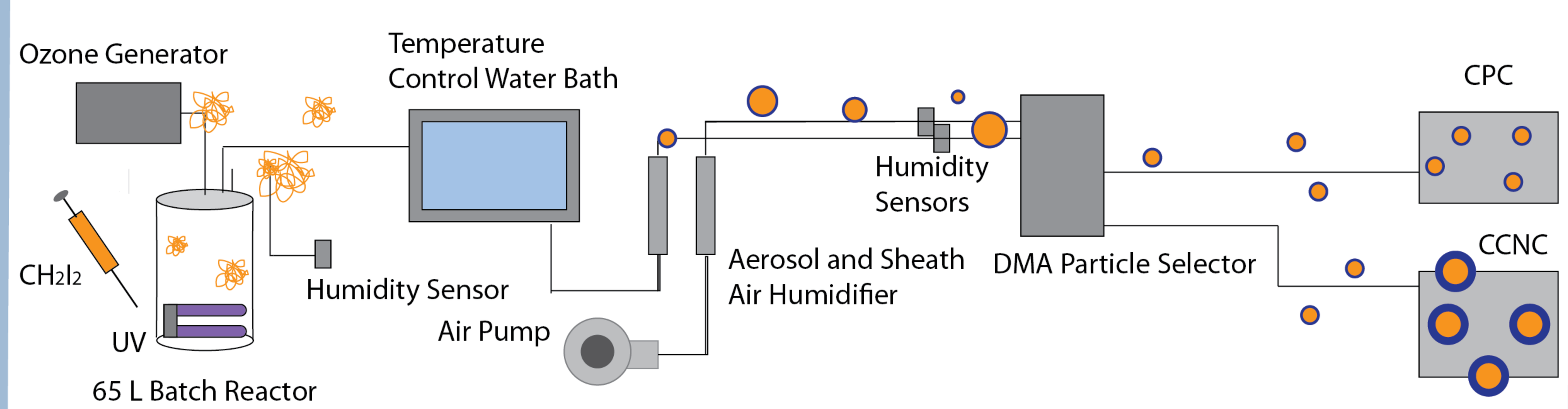


Figure 3: Wet CCN measurement for iodine oxide particles
In a closed batch reactor, ozone and iodine radicals (formed from photolysis of diiodomethane by UV) form iodine oxide particles. Fractal particles are formed in low humidity. The particles collapse once humidified. Humidity sensors record RH before the polydisperse aerosols are size selected by the DMA. Monodisperse aerosols pass to the CPC and CCNC. CPC counts particles generated and CCNC exposes particles to super-saturated conditions allowing for activation of CCN to cloud droplets.

Methods

Iodine oxide particles formed in a batch reactor with RH of <10% and 65% (Figure 3). Generated particles collapsed when exposed to higher humidity by a humidifier. Once collapsed, the particle passed through size selection in the DMA and on to CPC and CCNC as in the traditional method (Figure 1).
DMA voltage fixed selected particle diameter, the CPC counted the total number of monodisperse particles, and the CCNC counted the subset of monodisperse particles that activated to cloud droplets.
Employing κ-Kohler Theory and combining established methods for experimentally deriving κ with CPC-CCNC and Hygroscopic Tandem Differential Mobility Analyzer (HTDMA) set-ups provides a method for finding κ without measuring dry diameter as shown below:

eq. 1: dry diameter, supersaturated conditions CPC-CCNC

$$D_d = \left(\frac{4A^3}{27\kappa_{super} \ln^2 Sc}\right)^{1/3}$$

eq. 2: wet diameter, subsaturated conditions HTDMA

$$D_w = D_d\left(1 + \kappa_{sub}\frac{a_w}{1-a_w}\right)^{1/3}$$

combining eq. 1 and eq. 2 when D_{50}=D_w

$$D_{50} = \left(\frac{4A^3}{27\kappa_{super} \ln^2 Sc}\right)^{1/3}\left(1 + \kappa_{sub}\frac{a_w}{1-a_w}\right)^{1/3}$$

With measured diameter (D), water activity (aw) and saturation ratio (Sc) κ can be solved directly or curve fitted without taking dry diameter measurements.

Results

- Particles generated for RH<10% showed collapse of fractal particles. Traditional method of CCN measurement overestimated the amount of iodine oxide solute present and thus underestimated κ. We believe the collapsed particle κ of 0.5-0.7 represents the best estimate of hygroscopicity for these compounds and could not be observed using the traditional approach.
- Particles generated at RH>65% showed no uptake of water, consistent with the findings in Jimenez et al. 2003. The compounds produced via gas phase oxidation in the presence of water vapor apparently condense into particles with a very low affinity for water, which can be expressed as κ≈0.
- Further study is needed to confirm that the reaction products formed under dry and humid oxidation conditions are indeed chemically distinct and to investigate the threshold RH to observe these two distinct hygroscopic behaviors.

Summary

- Iodine oxides generated in dry (RH<10%) conditions are fractal particles whose geometry causes traditional methods to overestimate the amount of solute present and underestimate hygroscopicity.
- The new approach of wet CCN measurement is successfully applied to iodine oxides by collapsing the fractal particle and accurately measuring the amount of solute present and shows potential for application to other irregular particles
- Iodine oxides formed in humid conditions generated particles with κ≈0. The different hygroscopic behavior suggests the species generated with varied humidity are chemically distinct and is a subject for further study.