Published in final edited form as:

Aerosol Sci Technol. 2013 ; 47(6): 645–654. doi:10.1080/02786826.2013.779629.

Minimizing Concentration Effects in Water-Based, Laminar-Flow Condensation Particle Counters

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Abstract

Concentration effects in water condensation systems, such as used in the water-based condensation particle counter, are explored through numeric modeling and direct measurements. Modeling shows that the condensation heat release and vapor depletion associated with particle activation and growth lowers the peak supersaturation. At higher number concentrations, the diameter of the droplets formed is smaller, and the threshold particle size for activation is higher. This occurs in both cylindrical and parallel plate geometries. For water-based systems we find that condensational heat release is more important than is vapor depletion. We also find that concentration effects can be minimized through use of smaller tube diameters, or more closely spaced parallel plates. Experimental measurements of droplet diameter confirm modeling results.

Introduction

Condensation particle counters (CPCs) are one of the more widely used aerosol instruments. Applications range from ambient air measurements to particle detection for mobility sizing systems, and from respirator fit testing to ultra-pure water monitoring. From the pioneering work of Aitken in the 19th century, to the nanometer detection systems developed recently (Gamero-Castano et al., 2000, Iida et al., 2009, Vanhanen et al., 2011, Kuang et al., 2012), a wide variety of condensation particle instruments have been introduced (McMurry, 2000). All use condensational growth to facilitate the detection of particles that are too small to be detected directly by optical means.

It has been long recognized that the condensational growth within these instruments can be affected by the number concentration of particles in the sampled air. Aitken, with his adiabatic expansion instrument, wrote that it was necessary to repeat measurements at multiple dilutions to obtain a consistent indication of the initial particle number concentration (Aitken, 1889). Argawal and Sem (1980), in describing the continuous, laminar-flow butanol-based condensation particle counters, showed that the size of the droplets formed decreases with increasing number concentration of activated particles. More recently Stratmann et al. (2010) present a numeric model of the first commercial, laminar-flow water-based condensation counter showing effects of concentration on activation size. For newer CPCs employing faster optics that extend single-particle counting to higher particle concentrations, it is important to understand these effects. Perhaps even more important are the effects in condensational growth systems used for particle collection or aerodynamic focusing, where there is no external constraint, analogous to the coincidence limit in counting systems, that otherwise places an upper limit on the measurement concentration.

This paper examines the role of sampled particle number concentration on instrument performance for several geometries of laminar-flow, water-based condensation systems, including those used in the commercial water-based condensation particle counters sold by TSI Inc. (WCPCs, Shoreview, MN). Our analysis includes numeric modeling of the condensational growth and experimental measurement of droplet size. The relative roles of condensational heating and vapor depletion are discussed. Moreover, we demonstrate how concentration effects can be minimized.

Laminar Flow WCPCs

Laminar flow, water-based condensation particle counters and growth systems utilize wet-walled tubes or parallel plates, the second portion of which is warmer than the first (Hering and Stolzenburg, 2005). Particle activation and condensational growth occur in the warmer portion because the diffusion of water vapor from the walls is faster than the diffusion of sensible heat. In contrast, the commonly used butanol-based CPCs use a warm saturator followed by a cold wall condenser wherein thermal diffusion dominates.

Several types of laminar-flow water condensation counters are available commercially, as described by Hering et al. (2005), Liu et al (2006), Petaja et al (2006), Iida et al (2008), Kulmala et al, (2007) and Kupc et al. (2013). The first of these, TSI Models 3781, 3785 and 3786 (Shoreview, MN) were designed using an analytical model of the heat and mass transfer of Stolzenburg and McMurry (1991). This analytical model is applicable at low concentrations; but it does not include vapor depletion or condensational heating, both of which become important at high particle concentrations. To guide the design of a second generation of WCPCs, with improved high concentration performance, we developed a numeric model that includes these concentration effects. The newest WCPCs, TSI Models 3783, 3787 and 3788, all incorporate results from this effort.

Methods

Numeric Modeling

Calculations were done for cylindrical and parallel plate growth cell geometries, with varying wall temperature profiles, cylinder diameters and plate separations. For any given calculation the cylinder bore, or parallel plate gap width, was fixed. The walls are wetted throughout, with an assumed relative humidity of 100% at the wall temperature. The initial section is a “conditioner” and has a wall temperature T_c . The second section is the “growth region”. Its entrance is modeled with a short, linear ramp in the wall temperature from T_c to $T_h > T_c$. This is followed by a longer section with constant wall temperature T_h . Model results are reported for the final, growth region.

To handle varying wall temperature profiles, and the non-idealities of condensational heating and vapor depletion, we developed code in the Igor programming environment [www.wavemetrics.com]. The model assumes a fully developed laminar flow profile, and solves the 2-D axial symmetric diffusion equations for heat and mass transfer. Upon activation, the condensational growth is calculated along each step of the trajectory by solving the coupled, quasi-static mass and energy balance relations presented by Chang and Davis (1974) and Barrett and Clement (1988), among others. Concentration effects are modeled iteratively through recalculation of the flow temperature and water vapor content at each time step to account for the loss of water vapor and the release of heat from condensation. Our growth calculations assume wettable, insoluble particles, i.e. the Kelvin effect is included but solute effects are ignored. The kinetics of particle activation were not considered. At low concentrations our model was verified against the analytical model of (Stolzenburg and McMurry, 1991). For modeled concentrations, extending up to 10^5 cm^{-3} ,

our model agrees with that of Stratmann et al. (2010). Details of the model are presented in the Supplemental Information (SI).

Several variants on our model were explored. In the simplest model, the walls of the conditioner and growth sections were held at fixed temperatures connected by a short ramp. The water vapor concentration adjacent to the wall was at 100% RH at the wall temperature. Additional complexity was added by taking into account evaporative cooling of the wick surface and the finite heat transport through the wick material. While modeling of the thermal and water transport properties of the wet wick depended on parameters that were not well known, it became clear that all the qualitative results and trends were the same as with the original boundary conditions. Moreover, one could just as easily use the simpler model with wall temperatures adjusted to achieve the same results. Evaporative cooling of the walls has a small effect on the final particle size, as most of the cooling occurs right at the entrance of the warmed section. The effect is roughly equivalent to having a slightly longer transition from the cold preconditioner to the hot condenser.

We also considered changes in flow velocity and profile from the changing temperature and relative humidity. We found that accounting for changes in the velocity field due to changes in the gas density with temperature and relative humidity, or due to the addition of water vapor mass from the walls, have relatively small effects on the modeled final particle size. These effects are roughly equivalent to the simple calculation with a small decrease in the length of the tube.

We examined changes in the diffusion constants with temperature. Since the diffusion coefficients show significant temperature dependence, one may expect that including this would significantly affect the final particle size and the vapor saturation ratio field. However saturation profiles in the WCPCs are dependent on the relative rates of thermal and vapor diffusion, and since both diffusion constants have the same dependence on temperature and concentration, the two track each other over the range of interest, and there is an insignificant effect on the model results.

Finally, we evaluated concentration effects for both monodisperse, and log-normally distributed particles. The computational time for the log-normal input size distributions was significantly longer than for monodisperse particles, but the resulting droplet sizes were similar. Qualitatively, the trends with concentration in the calculated saturation ratio profiles, the exiting droplet sizes and the activation diameters were independent of the shape or median diameter of the assumed shape of the particle size distribution.

After exploring these variations in the model assumptions, we employed the faster, “simpler” version of our model to explore effects of vapor depletion and condensational heating for a variety of geometries and operating conditions. This simpler model assumes fully saturated vapor concentration at the walls, does not account for changes in the velocity field due to the addition of water vapor to the flow, ignores the temperature dependence of the diffusion coefficients, and assumes an accommodation coefficient of 1. Calculations were done using $0.251 \text{ cm}^2\text{s}^{-1}$ for the mass diffusivity of water vapor in air, and $0.219 \text{ cm}^2\text{s}^{-1}$ for the thermal diffusivity of air.

Most of the modeling results presented assume a perfect “conditioner”, wherein the flow entering the growth region is assumed to be fully saturated at temperature of the conditioner walls. For comparison to experiments, we modeled the transport of within the preceding conditioner section as well. In both cases we allow for a short ramp in the wall temperature at the growth region entrance to account for the fact that these systems use a single tube extending from the cold conditioner into the warm supersaturator. For cylindrical geometry

our calculations assume a ramp length to flow ratio of $L_r/Q=0.08$ s/cm², or 13 mm for an airflow of 16.67 cm³s⁻¹ (1 L/min). Calculations for parallel plate geometry scale as $(z/h)(w/Q)$, where Q/w is the volumetric flow per unit plate width and h is the gap spacing. For the parallel plates we have assumed ramp length to gap spacing ratio of 12 for $Q/w=33$ cm²/s (corresponding to $(L_r/h)(w/Q)=0.36$ s/cm²). All of the droplet growth calculations presented in this paper assume a 40 nm, monodisperse aerosol at the input.

Experimental Methods

Measurements of the concentration dependence of the output droplet diameter were made for two different condensation growth systems. One of these was taken from the Model 3785 WCPC, and is a cylinder measuring 229 mm in length by 9.5 mm ID. The first half of the tube has walls at a temperature T_c and serves as the conditioner. The second half has warmer walls at a temperature T_h , and is the growth region. The second was a system built in our laboratory, consisting of three parallel tubes, each measuring 3.8 mm in diameter and 89 mm in length, with equally long conditioner and growth sections.

Exiting droplet sizes were measured using two different approaches. First we inferred the droplet size by directly coupling an impactor to the output of the growth tube and measuring the concentration-dependent particle penetration. This approach mimics the droplet transit in the WCPC, thereby minimizing bias, but provides limited data. To obtain more complete droplet size distribution data, we used an Aerodynamic Particle Sizer, the accuracy of which was assessed by comparison to the impactor approach.

For the 9.5 mm ID tube of the Model 3785 WCPC, an impaction stage was placed where the optics head would normally be mounted, with the focusing nozzle of the WCPC serving as the impaction jet. Monodisperse aerosol was introduced at the inlet, and the particle collection efficiency was measured as a function of the input particle concentration. Tests were done with several versions of this nozzle, with diameters of 0.56 mm, 0.99 mm, 1.6 mm and 2.4 mm, corresponding to cutpoints of 0.5 μm, 1.3 μm, 2.6 μm, 4.6 μm at the growth tube design flow rate of 1 L/min (calculated for a critical Stokes number of 0.22). For the data shown here the test aerosol was monodisperse, 140 nm ammonium nitrate, the flow rate was 1 L/min, the walls of the conditioner were at $T_c=2^\circ\text{C}$, and those of the growth region were at either $T_h=32^\circ\text{C}$ or $T_h=42^\circ\text{C}$. The impaction efficiency was calculated as $(1-N_{dn})/N_{up}$, where N_{dn} is the concentration measured downstream of the impactor collection stage, and N_{up} is the particle concentration entering the growth tube, as measured using a pair of WCPCs. This measurement approach was selected because the WCPC optics were not precise enough to provide droplet size information, yet the similarity in geometry ensured that the droplet size at the point of impact was the same as for the WCPC optics.

For both 9.5 mm and 3.8 mm ID growth tubes, the output droplet size distributions were examined using an Aerodynamic Particle Sizer (APS, TSI Model 3321). This was done by sampling directly into the 1 L/min APS aerosol sample flow tube. To examine the shift in droplet size with concentration, the output from the growth tube was diluted with humidified air before introduction into the APS. The same amount of dilution flow was used for all concentrations measured, so that any change in droplet size induced by the measurement process would be consistent across all concentrations. To check the accuracy of this approach, the number median droplet diameters from the APS were compared to that indicated by the impactor measurements. A variety of tests aerosols were used, including ambient laboratory aerosol, fluidized-bed generated Arizona road dust, and nebulized, polydisperse ammonium sulfate. Data reported here are for atomized (polydisperse) ammonium sulfate.

Results and Discussion

Modeling Results

Figure 1 shows the saturation profiles for the growth region calculated for the cylindrical geometry of the TSI WCPCs. These instruments operate with a conditioner wall temperature of 20°C and growth region wall temperatures of 60°C, both of which are lined by a wetted wick. Our calculations assume a “perfect conditioner” with fully saturated flow entering the growth region at the conditioner wall temperature. The growth region is modeled with a 13 mm long entrance with linearly increasing wall temperature from 20°C to 60°C, followed by a 100 mm long section with 60°C walls. Walls are wetted throughout. All profiles are shown as a function of the radial position, r , normalized with respect to the tube radius, R_0 , and the axial coordinate, z , normalized with respect to the volumetric flow rate, Q .

Figure 1a presents the saturation profiles obtained without particles present; i.e. in the absence of condensational heating and vapor depletion. Under these conditions the normalized profiles obtained from the laminar flow relations are independent of the tube diameter. Doubling the tube diameter both slows the flow and increases the diffusion distances. Under laminar conditions these two effects cancel. In wide tubes the laminar flow can be disrupted by buoyancy driven convection, an effect that scales as the Froude number, but for the dimensions of the WCPCs the Froude number is small, and forced convection dominates.

Figures 1b and 1c show the saturation profiles for two different growth tube diameters when sampling 40nm (monodisperse) particles at a concentration of $1 \times 10^5 \text{ cm}^{-3}$. The narrower of these (4.8 mm, Figure 1b) approximates that used in the newer line of WCPCs (TSI Models 3783, 3787, 3788) whereas the larger bore (9.5 mm, Figure 1c) equals that used in the first commercial WCPC (Models 3785, 3786). In both cases the peak supersaturation drops with the increased particle concentration. This decrease is more pronounced for the wider bore. When particles are not present, the peak supersaturation is achieved along the centerline. As the particle concentration increases position of maximum supersaturation shifts outward, and the extent of this shift is greater for the larger tube diameter. The largest changes in S occur along the centerline. At 10^5 cm^{-3} the peak supersaturation in the wide bore (9.5mm) tube drops from 1.78 to 1.30, and moves to a normalized radial position is near $r/R_0=0.65$. The narrower (4.8mm) tube produces a broad maximum of 1.5 extending from the centerline to $r/R_0=0.6$. A similar effect was noted by Stratmann et al. (2010).

The consequences of this decreased saturation ratio are both a decrease in the exiting droplet size, and an increase in the activation diameter. Figure 2 compares exiting droplet size distributions for both the wide and narrow bore tubes as a function of sampled particle number concentration. These calculations assume monodisperse, 40nm aerosol at the input. The spread within each droplet size distribution occurs because of differences in growth for different radial trajectories. The sharp peak in each distribution is likely a result of our assumption of a parabolic flow profile, for which the residence time near the walls approaches infinity. Results at other particle concentrations, and for polydisperse aerosols, are similar.

We find that the droplet size is a strong function of the particle number concentration. For the wide-bore tube at near-zero concentration the median diameter of the exiting droplets is a factor of 3 larger than at the highest concentration shown ($2 \times 10^5 \text{ cm}^{-3}$). The narrower tube produces nearly the same droplet size as the wide-bore tube at high concentrations, but at low concentrations its droplet size is approximately half of that from the wider tube. The result is a much narrower overall range in droplet size as a function of the number concentration of the activated particles. Additionally, for the same value of the temperature

difference $\Delta T = T_h - T_c$, the droplet size distributions are nearly independent of the initial temperature T_c , as seen by comparison of the lines in Figure 2 for $T_c = 2^\circ\text{C}$ and $T_c = 20^\circ\text{C}$.

This similarity in droplet size at high concentrations for the same ΔT is something we observed throughout our model calculations conducted over a wide range of geometries and operating conditions. This is because the dominant factor is the saturation ratio, and profiles of S depend strongly on the temperature difference between the walls and the entering flow, and only weakly on their absolute values. This is a result that can be seen in the first order solution to the series solution to the diffusion equations used by Stolzenburg and McMurry (1991). The mass transport to the droplet, absent Kelvin and solute considerations, is driven primarily by the value of S , a result that is seen from combining the mass and heat balance relations for droplet growth and applying the Clausius-Clapeyron relation for vapor pressure (see for example equation 10 of Stratmann et al., 2010 or equation 26a of Barrett and Clement, 1988). Also, the warming from condensation provides a negative feedback that slows the particle growth. At high concentrations this limits the total volume of condensate, which in turn fixes the droplet volume as a function of droplet number.

The size of the smallest particle that will be activated is also affected by the sampled particle number concentration. Absent kinetic limitations the activation size depends on the difference in Gibbs free energy between the liquid and vapor, which in turn depends properties of the vapor (surface tension, saturation ratio and temperature) as well as properties of the particle (solubility, wettability). The Kelvin equivalent diameter, defined as $4\sigma v / R_g T \ln S$ (where σ is the surface tension, v the molar volume of the liquid, and R_g is the gas constant), describes the minimum size of a water droplet that would be more likely to grow than to shrink, and characterizes much of the vapor properties important to activation. Each flow streamline has a characteristic minimum Kelvin equivalent diameter along its trajectory, from which we derive a “nominal efficiency” which is the fraction of the flow as a function of the minimum Kelvin equivalent diameter encountered.

Figure 3 shows, for two sizes of growth tubes, how this nominal efficiency shifts as a function of the number concentration of activated particles. As with the droplet diameter, the shift is more pronounced for the larger tube diameter. At higher concentrations the efficiency curves are not as sharp, with much more gradual cutpoints. This is because the saturation ratio near the centerline of the flow is most affected by the particle concentration, as shown in Figure 1.

The evolution of droplet growth along the axial direction is shown in Figure 4 for the narrower, 4.6 mm ID tube, where a 20°C saturated flow enters a growth region with a 60°C wetted walls. These calculations were done for an initial particle size of 40 nm, so essentially all particles are activated. Because we have assumed monodisperse input aerosol, the condensational growth along each trajectory is uniform, and the droplet diameter along an individual trajectory depends only on its axial position.

As shown in Figure 4, particles along different radial trajectories activate at different axial positions, and form different exiting droplet diameters. For trajectories closer to the wall, as illustrated by the trajectory along normalized radial position of $r/R_0 = 0.7$, the particle growth initiates closer to the entrance. Those particles along the centerline trajectory activate last, as the peak supersaturation occurs further downstream. For all radial positions, the growth is most rapid when the particles are first activated. The largest droplets form next to the wall, where the residence time is longest. Those particles along the centerline, with the highest peak supersaturation, grow more quickly, but do not achieve quite as large a final droplet size as those closer to the wall. In all cases the final droplet size is smaller at higher particle concentrations. The divergence in droplet size at higher particle concentrations occurs after

the droplets reach 1-2 μm . The concentration dependence shown here is not nearly as large as predicted for the wider bore tube.

Modeling of a parallel plate geometry yields similar results as those shown above for the cylindrical systems. Saturation profiles resemble those for the tubular geometry shown in Figure 1. In the limit of zero particle concentration, the maximum supersaturation occurs along the center of the flow, i.e. midway between the plates. As the particle number concentration increases, the saturation ratio drops. This decrease in saturation ratio is most pronounced in the center, and the maximum supersaturation moves toward the edges of the flow with increasing particle concentration. Analogous to the cylindrical geometry, the concentration effect is smaller when using a narrower spacing between the two parallel plates.

Figure 5 compares the number median diameter of the exiting droplet size distribution, and the activation cutpoint (defined as the minimum Kelvin equivalent diameter seen by 50% of the flow) for cylindrical and parallel plate configurations. Calculations are for two tube diameters, or gap spacings, respectively, where the overall growth length is 2.3 times the distance to reach peak supersaturation in the absence of particles. As before, results are shown for a 20°C saturated flow entering a region with 60°C wetted walls. With the parallel plate geometry, the same operating temperatures do not achieve quite as high a peak supersaturation, or quite as small a cutpoint as for the cylindrical geometry. However, both geometries exhibit similar effects for sampling at high particle concentrations.

We investigated many different operating configurations, including both upward and downward axial temperature ramps, and different starting temperatures. While the droplet size at low concentration can be varied, the fundamental result was unchanged. Those conditions that produce large droplets at low particle concentrations showed pronounced concentration effects, with large decreases in the droplet size with increasing particle concentrations. Narrower tubes, or more closely spaced plates, produce smaller droplets at low concentrations, and exhibit a smaller decrease in droplet size with increasing concentration. As a result, the droplet sizes and Kelvin equivalent diameters are less dependent on the sampled particle concentration.

Experimental Confirmation

Figure 6 shows the concentration-dependent collection efficiency of an impactor coupled to the outlet of the 9.5 mm diameter condensation growth tube of the design used in the TSI 3785. Most of the data are for operation at temperatures with $T_c=2^\circ\text{C}$ and $T_h=32^\circ\text{C}$. At fixed operating temperatures, the droplet size decreases with increasing particle concentration, as predicted by the models. For an input concentration of $8 \times 10^3 \text{ cm}^{-3}$ the droplets are all above 4.6 μm in diameter, whereas at $6 \times 10^4 \text{ cm}^{-3}$ less than 10% are this large. Throughout the concentration range studied, all droplets are larger than 1.3 μm .

Figure 6 also shows one set of data for operation at $T_c=2^\circ\text{C}$ and $T_h=42^\circ\text{C}$. This shows higher collection efficiencies for the same particle number concentration than obtained at $T_h-T_c=30^\circ\text{C}$, indicating a shift to larger droplet diameters when the same growth tube is operated at a larger temperature difference. This is consistent with the modeling which shows that the larger temperature difference produces higher supersaturations, and greater droplet growth.

Figures 7 shows the droplet size distributions obtained with the APS for two systems, employing growth tube diameters of 9.5 mm and 3.8 mm, respectively. These data were obtained with $T_c=2^\circ\text{C}$ and $T_h=42^\circ\text{C}$, for which the modeling predicts the same droplet sizes as for the normal operating conditions of $T_c=20^\circ\text{C}$ and $T_h=60^\circ\text{C}$ (see Figure 2). For the

wide-bore tube, the number median diameter of the exiting droplets is $7.4\text{ }\mu\text{m}$ at low particle concentrations. This decreases to $1.6\text{ }\mu\text{m}$ at $5\times 10^5\text{ cm}^{-3}$. With the narrower tube, the droplet number median diameter shifts from $3.5\text{ }\mu\text{m}$ at low concentration to $1.4\text{ }\mu\text{m}$ at $5\times 10^5\text{ cm}^{-3}$. While the results are similar at high concentrations, the overall range in droplet size is smaller for the narrower tube.

To check the accuracy of the APS measurements of the droplet size, we compare these data to the impactor efficiency measurements of Figure 6. We note that for input particle number concentrations that yield a collection efficiency of 50%, the number median diameter of the droplet size distribution is approximately equal to the impactor cutpoint. For operation at the same temperatures as the APS measurements ($T_c=2^\circ\text{C}$, $T_h=42^\circ\text{C}$), impactor collection efficiency data show that the number median droplet diameter is $4.6\text{ }\mu\text{m}$ at a concentration of $4.8\times 10^4\text{ cm}^{-3}$. Interpolation of the complete set of APS data for this growth tube (only some of which is shown in Figure 7) yields a number median diameter of $4.6 \pm 0.3\text{ }\mu\text{m}$ at this concentration, where the precision in the measurements was derived from replicate data at similar concentrations. Within this precision, we see no systematic bias in the droplet sizing from the APS.

Figure 8 compares the number median diameters (NMD) measured with the APS with those calculated by our model. To better mimic the experimental conditions, the model calculations were done for a 25°C , dry air flow entering a 2°C wet-walled conditioner, followed by a 42°C growth section. Calculations were done with the dimensions of the growth tubes employed for the measurements (with 9.5cm and 3.8cm ID). Because the conditioner was operated at below ambient temperature, the flow did not fully cool to the conditioner wall temperature before entering the growth section, resulting in lower peak supersaturations than in the model results presented above. While the model tends to over-predict the measured droplet size, there is qualitative agreement with the trends observed for variations in particle concentration and tube diameter.

Several important points should be noted regarding these concentration effects. Decreasing the tube diameter does not affect the temperature and saturation profiles at low particle concentrations; however it does lower the transit time. At low particle concentrations the droplet size is controlled by this residence time, and thus the narrower tube produces smaller droplets. At high concentrations, the growth of the surrounding particles decreases the degree of supersaturation, and limits the growth for both tube geometries. The concentration at which the transition between these two regimes occurs depends on the growth tube geometry. The limitation imposed by the residence time is more pronounced in the smaller diameter tube. As a result, there is less dependence of the droplet size on the input aerosol concentration.

Source of the Concentration Effect

There are two mechanisms that account for the reduction in the flow supersaturation: (1) the depletion of water vapor due to the uptake by the droplets, and (2) the increase in the equilibrium vapor pressure due to warming of the flow from condensational heat release. The relative impacts of condensational heat release and vapor depletion on the saturation ratio are presented in Figure 9. Shown is the saturation ratio S at a particle number concentration of 10^5 cm^{-3} calculated (a) including vapor depletion while ignoring condensational heating, (b) including condensational heating without vapor depletion, and (c) including both terms. Values are shown along the centerline and at $r=0.7R_0$ for the 4.8 mm diameter tube, and are compared to S calculated at 0 cm^{-3} . For both trajectories the vapor depletion has a relatively small effect compared to the condensational heating.

The WCPC operates at relatively high water vapor concentrations, and thus the fraction of water vapor lost to condensation is small. However, the condensational heat release raises the flow temperature, increasing the equilibrium vapor concentration and decreasing S . Even though water has a similar molar latent heat as does butanol, its molar volume is smaller, and hence more moles of water vapor must condense to produce the same size droplet. For WCPCs, condensational heat release is the dominant factor contributing to lower the saturation ratios at higher particle number concentrations. While the role of condensational heating is considered in discussions of low water vapor supersaturation conditions, such as are prevalent in cloud formation (eg Barrett and Clement, 1988), its importance to CPC performance has not been generally recognized.

In the Supplemental Information we present a “box model” of the concentration effects, wherein we examine the heating and vapor depletion associated with condensation in a closed system. This simple model provides insights into the relative roles of operating temperatures, molar volume, and latent heat in these concentration effects. The box model confirms that condensational heating is the primary source of the concentration effects in the WCPC, while for butanol systems, condensational heating and vapor depletion are comparable.

Summary

As in other laminar flow condensation systems discussed in the literature, water-based systems exhibit smaller final droplet sizes and larger critical Kelvin equivalent diameters with increasing particle number concentrations. For water condensation systems, this concentration effect is primarily associated with condensational heat release. Vapor depletion is a minor contributor. Modeling and experimental measurements show that narrower growth tubes, or closely spaced parallel plates, mitigate this concentration effect. With these smaller dimensions the growth systems produce smaller droplets because the time spent in the region of high vapor supersaturation is limited. The result is a more consistent Kelvin equivalent diameter, as well as a more consistent final droplet size, over a large range of particle concentrations.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work has been supported in part by Department of Homeland Security NBCHC070117, US Army Project 05-153, Department of Energy DE-FG02-04ER-86179 and NIH grant 1RC3ES019081. We thank Mark Stolzenburg for his advice in our development of the model of droplet growth, and Steven Speilman for his input to the “box model” presented in the Supplemental Information.

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Figure 1.

Profiles of saturation ratio obtained with the numeric model for flow at 100% RH and 20°C entering a wet-walled cylinder of radius R_0 with wall temperature of 60°C. The flow direction is upward, the flow centerline is along the left hand axis. (a): without particles present. (b) and (c): with 40 nm particles at a concentration of 10^5 cm^{-3} for tube diameters of 4.8 mm and 9.5 mm, respectively.

Figure 2.

Size distribution of droplets exiting narrow (4.8mm) and wide (9.5mm) diameter growth tubes at two sets of operating conditions for particle concentrations ranging from near zero to $2 \times 10^5 \text{ cm}^{-3}$, as indicated. T_c is the temperature of the flow entering the growth region, and T_h is the temperature of the wetted walls within the growth region. Calculations are for sampling 40nm, monodisperse aerosols.

Figure 3.

Fraction of the flow as a function of the minimum Kelvin equivalent diameter encountered for narrow (4.8mm) and wide (9.5mm) diameter growth tubes operated with $T_c=20$ and $T_h=60$, for particle concentrations ranging from zero to $2 \times 10^5 \text{ cm}^{-3}$, as indicated. When no particles are present, the curves for the two tube diameters are coincident.

Figure 4.

Droplet diameter along two flow trajectories for the narrow (4.8 mm diameter) growth tube as a function of sampled particle concentration for 40nm particles in a fully saturated 20°C flow entering a growth region with 60°C wetted walls. Trajectories are shown for the centerline ($r=0$) and for a radial position r equal to 70% of the tube radius R_0 . Concentrations (cm⁻³) are labeled for the centerline trajectory. Those for $r/R_0=0.7$ follow in the same order.

Figure 5.

Modeled droplet number median diameter and 50% Kelvin equivalent diameter cutpoints for cylindrical and parallel plate geometries of varying diameter or plate separation, respectively. Calculations assume a saturated flow at 20°C entering a growth region with 60°C walls, and an overall length equal to 2.3 times the axial position of peak supersaturation when no particles are present.

Figure 6.

Collection efficiency measurements for the 9.5 mm diameter growth tube coupled to an impactor (mounted in place of the optics head). The growth tube was operated at 1 L/min with conditioner temperature of $T_c=2^{\circ}\text{C}$ and growth region temperatures of $T_h=32^{\circ}\text{C}$ and 42°C (corresponding to temperature differences of $\Delta T=30^{\circ}\text{C}$ and $\Delta T=40^{\circ}\text{C}$, respectively). The test aerosol was 140 nm ammonium nitrate. Measurements were made with 4 different impactor jets with cutpoints of 0.5 μm , 1.3 μm , 2.6 μm , and 4.6 μm . Collection efficiencies indicate the fraction of droplets with diameters above the cutpoint.

Figure 7.

Normalized droplet size distributions exiting growth tubes with 9.5 mm and 3.8 mm diameters, as measured with an aerodynamic particle sizer. The growth tube was operated at 1 L/min with $T_c=2^\circ\text{C}$, $T_h=42^\circ\text{C}$. The input aerosol was polydisperse ammonium sulfate. Numbers indicate particle number concentration (cm^{-3}) at the growth tube inlet.

Figure 8. Comparison of the number median droplet diameters measured with the APS (see Figure 7) with model calculations.

Figure 9.

Effects of vapor depletion and condensational heating to the saturation ratio when particle concentrations are increased from 0 to 10^5 for trajectories along the centerline (top) and at 70% of the tube radius (bottom). “With vapor depletion only” are model results ingoring warming of the flow; “with condensational heating only” assumes no depletion of vapor concentration; “full model” includes both terms. Calculations are for a 4.8 mm diameter tube with a 20°C saturated flow entering a growth region with 60°C wetted walls.