**Atmospheric
Measurement
Techniques
Discussions**

Interactive comment on "Droplet activation, separation, and compositional analysis: laboratory studies and atmospheric measurements" *by* N. Hiranuma et al.

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General Comments:

Hiranuma, et al. present a new method for operating a DMT CCN counter coupled with a pumped-CVI, a PALMS instrument, and an AMS to study the chemical composition of CCN droplet residuals. This is important because atmospheric aerosols are chemically-complex, and the CCN-active fraction of particles can be either internally- or externally-mixed. Comparing the composition of the droplet residuals to the overall aerosol mass distribution is able to constrain this mixing state, which would likely improve CCN closure estimates. While a similar companion paper (Slowik et al., AMTD,

2011) has also been published that uses a different, custom-built CCN counter to look at ambient aerosols in Canada, Hiranuma, et al., intend to provide a detailed laboratory validation of the technique using a commercially-available CCN counter that has become widely-used by the community in recent years. While I believe that the technique is a good one, the present manuscript does not convince me that it could be successfully used to obtain quantitative composition information. I would like to see a number of major issues addressed before this manuscript is published, as detailed below.

Specific Comments:

1) The major limitation with the current study is the extemely low transmission factor of the CCN residuals (only 3%!). Consequently, large CCN concentrations ($\sim$ 9000 cmˆ-3) are required to obtain merely qualitative composition results. The organic and inorganic mass loadings for ambient aerosol shown in Figure 6-II have extrememly low signal-to-noise, which makes drawing any compositional conclusions difficult. It may be unreasonable to expect this technique to perform well in very clean, pristine environments, but certainly it should work with total CCN concentrations as low as 500-1000 cmˆ-3. I think this is achievable and suggest the following (and highlight some potential problems with each suggestion that should be discussed in the manuscript):

A) The manuscript references a DMT Model 200 instrument, so I'm assuming that this is a dual-column design. If possible, I would suggest using both columns in the dual-column CCNC (operating at the same supersaturation) to feed the inlet to the pumped-CVI, thereby reducing the particle-free supplemental flow needed. This will introduce some supersaturation uncertainty because of slight differences between the two columns, but I would expect these differences to be minor for a well-calibrated system.

B) Increase the total CCN flow rate to, e.g., 1 lpm. This will reduce the outlet droplet size because the particle residence time will decrease from $\sim$25 seconds to $\sim$12 seconds. Depending on how much this decreases the droplet size, the minimum supersaturation

required to produce droplets large enough to penetrate the pumped-CVI may increase. While a supersaturation of, say, 0.6% or greater may be unrealistic for many weakly-forced clouds, the technique would still be useful in assessing aerosol mixing state and the composition of water-soluble species in the aerosols feeding these clouds.

C) Decrease the CCNC Sheath:Aerosol flow ratio. Currently, the manuscript uses a Sheath:Aerosol flow ratio of 10:1, but this could be decreased to 5:1 or even lower with modest broadening of the CCN-supersaturation transfer function. I would think that the beneficial gain in counting statistics would more than outweigh the increased supersaturation uncertainty.

D) Modify the pumped-CVI design to the achieve the same droplet size cutoff but with lower flow rates. I suspect that this would require a large amount of work reengineering the design and constructing a new pumped-CVI, which would be unreasonable to request of the authors for this manuscript. However, I would like to see some discussion in the manuscript on the feasibility of this approach in improving instrument performance, which could then motivate future work/studies with this technique.

E) Decrease the pumped-CVI sample flow to the CPC/PALMS/AMS, if possible, to increase the enhancement factor.

Adopting suggestions A-C: Operating both columns at 1 lpm (CCNC Sheath:Aerosol = 4:1) and combining their flows yields a CCNC output flow of 2 lpm. Only 8 lpm of supplemental flow is then required.

Let $T = (Q_{aerosol}/Q_{CCNC})*(Q_{CCNC}/Q_{PCVI})*eta*R_e$

where

$Q_{aerosol}$ is the CCNC sample aerosol flow (0.4 lpm from combined columns)

Q_{CCNC} is the CCNC flow (2 lpm from combined columns)

Q_{PCVI} is the pumped-CVI inlet flow (10 lpm)

eta is the pumped-CVI efficiency (0.75)

R_e is the pumped-CVI enhancement ratio (10)

So $T = 0.3$, which is a ten-fold improvement over the previous transmission factor of 0.03.

2) The purported goal of this study is to validate the CCN-PCVI-AMS/PALMS technique using laboratory studies (p. 695, lines 2-4), and this is accomplished using an external mixture of ammonium sulfate and PSL aerosols. Sulfate peaks are used to show that the ammonium sulfate aerosols are CCN-active, while the missing (organic?) peak at m/z 104 is used to show that PSL aerosols are not CCN-active. Probably due to the low transmission efficiencies discussed previously in this review, only qualitative composition information is presented (i.e., sulfate is present, PSL is not). While this nicely shows that the pumped-CVI is able to separate the CCNC droplets from the interstitial aerosols, I would like to see a more thorough validation that shows quantitative compositions of the CCN droplet residuals. Quantitative compositions are important and will really unlock the potential of this technique in elucidating water-soluble aerosol composition and mixing state.

Additionally, while some organics are not CCN-active, many are, and I would like to see the authors use a soluble organic compound as well to validate the technique. A low-molar-mass dicarboxylic acid (C2-C6) or similar compound would seem to be preferable given that the hygroscopicities of these compounds have been previously published. In addition to the experiments currently presented in the manuscript, I suggest the following to validate the technique:

A) CCN concentrations should not be greater than ~500-1000 cm^-3, which is more reasonable for many ambient environments. Furthermore, Lathem and Nenes (2011) have shown that high CCN loadings in the CCNC can deplete enough water vapor to affect the instrument supersaturation and outlet droplet sizes. They find this effect starts to become important around 1000-2000 CCN cm^-3 and exceeds experimental

uncertainty above 5000 CCN cmˆ-3. Keeping CCN concentrations below 2000 cmˆ-3 (and preferably below 1000 cmˆ-3) avoids this issue.

B) Provide quantitative sulfate and organic mass loadings for an internally-mixed, equimass mixture of ammonium sulfate and a soluble organic. Does the AMS mass fraction of the droplet residuals agree with the mass fractions of each component in the atomizer solution?

C) Use single-particle PALMS spectra to classify particles in an externally-mixed aerosol population containing ammonium sulfate particles and soluble organic particles. Is the external mixture detectable by the PALMS downstream of the CCNC-PCVI?

3) The experimental setup in Figure 1 and associated discussion in the text nicely shows the overall experimental setup; however, more detail should be included that shows:

A) The details of the CCNC and PCVI connection. Since the DMT Model 200 is referenced, it sounds like only one of two columns is currently being used. Where is the connection to PCVI made? After traversing the column, the aerosol flow passes through the OPC and is then sent to a chiller and pump. Presumably, the connection is made after the OPC and prior to the chiller and pump, and investigators wishing to adopt this technique would need to make this minor modification to the CCNC. Also, what is the length of the transfer tube from the CCNC OPC to the PCVI? Are there any special concerns with regard to wall losses, accumulation of water on tube walls, and droplet coalescence? A more detailed schematic of the CCNC (similar to Moore et al., 2010) and the PCVI (similar to that of Slowik et al., 2011) showing these connections seems warranted. Additional details of the inner workings of the atomizers, DMAs, CPC, AMS, and PALMS are probably unnecessary as presumably they are unmodified.

B) The locations of pumps, blowers, gas cylinders, valves, critical orifices, filters, etc. It's unclear how the flow is driven through the CCNC since, presumably, the internal

C548

pump has been bypassed.

4) While Figure 2 succeeds in showing that ammonium sulfate aerosols are CCN-active and PSL aerosols are not, I find the comparison between measured and modeled curves to be confusing. This is because the model is not described in the text (other than to say that kappa_AS = 0.61) and because the shapes of the measured and modeled curves look dissimilar. Presumably the shape of the modeled curves comes from the DMA transfer function, which creates the doubly-charged hump and the slope of the curve, but this should be explained more clearly. Also, the fraction of doubly-charged particles should not be invariant with size. The authors may also wish to dispense with having the separate modeled curve and just correct the data for the multiply-charged particles, fit the the curve with a sigmoidal function, and compare the inflection point to that expected from Kohler theory. Finally, it would be good to have the range of supersaturations in Figure 2 correspond to the range of supersaturations in Figures 3-4 (i.e., up to 0.75%) to show that PSL do not act as CCN even at the largest supersaturations.

Also, please clarify in the text how the instrument superaturation was calibrated (e.g., using the thermal-resistance model of Lance et al., 2006, following one of the empirical methods detailed in Rose et al., 2008, or some other method).

5) While this is the first time that a pumped-CVI has been coupled to a commercial CCN instrument to study water-soluble component of aerosol, there is past work in this area that should be referenced in the introduction. Ji et al. (1998) developed a "CCN Remover" to study interstitial aerosols that did not act as CCN. In the design, aerosols are exposed to a specified supersaturation in a thermal diffusion chamber, and particles that form droplets gravitationally settle out of the fluid streamline and are deposited to the bottom wall, which enables subsequent characterization of the interstitial aerosol. Osborn et al. (2008) extended the design of Ji et al. by incorporating a second chamber with a slightly higher supersaturation where particles not removed in the first chamber could activate to form droplets and be separated to a different streamline. Called the

C549

"Differential Activation Separator", this design of Osborn et al. enables characterization of both the interstitial aerosol and the cloud droplet residuals, and seems very relevant for this work. Finally, the introduction should clearly differentiate this study from that of Slowik et al. (2011) beyond the mere substitution of the DMT CCNC for the thermal-gradient diffusion chamber.

Specific and Technical Comments (by line number):

p. 693, lines 8-10: The statement "The vapor pressure over a small droplet is always larger than that over a planar water surface due to its curvature..." is incorrect because of the solute effects discussed in the next sentence. This statement is true only for pure water droplets, which do not exist in the atmosphere.

p. 693, line 10: Replace "Nascent" with "Atmospherically occuring" or something similar

p. 693, line 16: Please cite the original paper instead: Kohler, 1936.

p. 693, lines 25-27: These techniques are not necessarily limited to laboratory studies. Also, in addition to Moore et al., 2010, I would suggest citing Petters et al., J. Geophys. Res., 2009, who used a coupled CCN-DMA and a stepping-DMA-voltage technique to study size-resolved CCN activation.

p. 694, lines 19-21: Please add example citations for the studies referred to

p. 694, line 26: Insert "commercially-available" before "CCNC". The fact that this study employs a widely-used, commercial-available CCNC makes it more relevant for many in the community and this should be emphasized.

p. 694, line 29: Suggest replacing "the aerosol particle which formed the droplets" with "the CCNC droplet residuals"

p. 695, line 1: Is the AMS a HR-ToF-AMS as stated later? The AMS acronyms seem somewhat inconsistent through the manuscript.

p. 695, lines 2-3: "Laboratory studies...to validate the technique" Good summary statement, but I'd like to see a more extensive validation as described under General Comments.

p. 695, lines 7-8: No indication is given that this is a dual-column CCNC design except for the model number.

p. 695, line 17: Assuming column dimensions given by Lance et al., 2006 (R_inner = 1.15 cm, L = 50 cm) and the reported flow rate of 500 cmˆ3 minˆ-1, yields a column residence time of ∼25 seconds, not 10 seconds. I'm not familiar with the dimensions of the dual column design, but was under the impression that they are the same as the single-column design used by Lance et al.

p. 695, line 20: Note that the integrated OPC is in the CCNC

p. 695, lines 21-22: What is the difference between the "CVI" and the "pumped CVI"?

p. 696, lines 5-6: How was the cut-size set? Is this cut-size adjustable within the current experimental setup? If so, how?

p. 696, line 6: Remove the word "thus"

p. 696, lines 9-13: Why are such large flow rates required? I suspect this is an "off-the-shelf" PCVI, but could it be reengineered to accommodate lower flow rates?

p. 696, line 13: How was the CCNC modified to divert the flow? See general comment about clarity of experimental setup, instrument modifications.

p. 696, line 20: This is the first instance of this acronym, so spell out high-resolution, time-of-flight aerosol mass spectrometer. Perhaps move this definition to p. 695, line 1.

p. 696, line 26: Is it an oven or a plate?

p. 697, line 3: Change "electron impact" to "electron impaction"

p. 697, line 5: Can high-resolution mass spectra still be obtained in "V" versus "W" mode?

p. 697, line 10-11: Please explain what is meant by treating the PSL as a nitrate equivalent mass?

p. 697, line 16: The laser also ionizes the components?

p. 697, line 19: Hyphenate "in-situ"

p. 697, line 21: Remove "respectively"

p. 697, lines 20-21: PSLs do not act as CCN, within uncertainty, based on Figure 2.

p. 699, lines 1-5, Eqn. 1: First, I would suggest using T as a transmission factor (i.e. remove CCN). Second, please replace all numbers in this equation with variables, as T will change with different operating conditions. Ways to optimize T to achieve better performance should be explored more fully as discussed under General Comments.

p. 699, line 18: I'm not sure that I understand "sputtering". Do some droplets shatter into smaller droplets when they hit the counterflow? Are there ways to avoid this problem (i.e., different flow rates)? As you say, the AMS does not detect these small particles, so perhaps it is not really a problem.

p. 701-702, lines 28-4: What is the meaning of ion current used in the context of Figure 7? Does it give a feel for the total fraction of these species across the entire aerosol population or within individual particles?

p. 703, lines 3-7: This is the major limitation of the technique, but one which I think could be overcome by adjusting the operating parameters to achieve a higher transmission factor or by increasing the sample averaging time to improve statistics. The goal should be not to merely "chemical differentiate" particles, but rather to quantify the chemical composition using the HR-ToF-AMS.

Figure 7b: The PALMS data for periods I and III show greater ion current for nitrate

and sulfate than for organics. Meanswhile the AMS data from the day before show low sulfate loadings with most of the aerosol mass as organics and nitrate. Are these inconsistent with each other?

References Cited In This Review:

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Slowik. J.G., D.J. Cziczo, and J.P.D. Abbatt (2011) "Analysis of cloud condensation nuclei composition and growth kinetics using a pumped counterflow virtual impactor and aerosol mass spectrometer." Atmos. Meas. Tech. Discuss., 4, 285-313.

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C554