We thank the reviewers for careful reading and a number of valuable suggestions.

Review by Dr. Jurányi:

This is an interesting paper introducing a method how particles' hygroscopicity can be determined if not the dry but a wet diameter (at a known relative humidity) of the particles is measured/selected during a CCNC measurement. In some cases this method can be really useful, especially if the dry mobility diameter measurement fails to sufficiently predict the volume of the solute. The "CCN state space" analysis is a good idea, but it is not completely new. An HTDMA (Hygroscopicity Tandem Differential Mobility Analyser) humidogram (widely known and applied) measurement contains the same information and is very similar. The wet CCN approach is accompanied with nice examples, but the interpretations are not always correct. I can recommend the manuscript for publication in AMT, however it needs significant improvement. Please find my comments below.

> Response:
> We agree that the CCN state space is similar to a humidogram. The key advantage of the WetCCN method is no explicit requirement of "dry diameter"; instead, CCN and RH measurement serve as constraints. This point is emphasized in section 3.3.

Major comments:

1. Section 2: You state, that the theory for wet CCN approach will be described first for the "traditional" Köhler theory, then for the kappa Köhler theory. 2.1. includes the "traditional" Köhler theory and then some equations in case of an ideal solution. This is not a theoretical description of the wet CCN approach. A significant improvement and clarification is needed here. Section 2.2 includes the description of the kappa Köhler theory, but not the derivation of the hygroscopicity parameter from the wet diameter and critical supersaturation measurement (which should be the main focus here). Eq. 7-9 contain this, please move the discussion of these equations to section 2.2, using one common kappa for both instruments. And modify eq. 9 such that it contains the RH and not the water activity because you measure the RH and not the aw, and the wet diameter is needed to derive the aw from the RH. You could also include the equation how the volume equivalent solute diameter (dry diameter) can be calculated.

> Response:
> Following the suggestions, we reworked section 2. The revised section shows how the hygroscopicity parameter can be determined from the wet diameter (D), saturation ratio (S), and critical supersaturation (s_c).
>
> In addition, we added a reference to a previous study (Snider et al., 2006) which employed a similar concept for characterizing the sphere-equivalent dry size of non-spherical CCN.

2. Section 2.3: most of this section belongs to section 2.2 and it does not contain a real discussion and error estimation what happens if the kappa values below and above saturation do not agree. The hygroscopicity parameter is derived from a single wet diameter and critical supersaturation measurement using the kappa Köhler theory and this part should definitely go to Section 2.2. Please Investigate here, that in how much error will it result if a certain difference in the kappa at sub and supersaturation exists. Please investigate how much does this error depend on the RH where the wet diameter is selected and on the particle's dry size.

Response:
We revised the description in section 2. The error is discussed in detail in the error analysis section (3.2). Since the error in κ measurement depends on both RH and D, the relative error ($\Delta\kappa/\kappa$) is shown as a contour plot (Fig.5).

3. Section 3.3: emphasize more, that the "CCN state space" is a good tool, if kappa (for some reasons) changes significantly with the saturation ratio otherwise one wet measurement is enough to derive the kappa value.

Response:
The description of the CCN state space is revised to be consistent with the new error analysis. We emphasize that if the change of kappa is bigger than the uncertainty (e.g., ~±20% for κ~0.3), the CCN state space is a good tool for inferring physical state of CCN.

4. You discuss nicely in details how the particles in the "CCN state space" behave if kappa is not constant, if efflorescence is present or if the particle is not spherical and collapses during water uptake. However these effects can also influence the shape of the activation curve and in some cases it might cause error in the D50 derivation, dependent on how D50 is determined. Please add a discussion about this to the text including how your D50 was exactly derived, and please estimate the error as well which is associated with D50. Include error bars on figures 8 and 9.

Response:

The explanation for how D50 is determined is added in the experimental section (3.1). D50 is determined in the same manner as in Petters et al. (2009). Contributions from multiply-charged particles to the activation curve was removed by using an inversion matrix. The activation curve was fit by a two parameter cumulative Gaussian function. D50 is determined by the diameter at which 50% particles were activated.

The reviewer pointed out "these effects can also influence the shape of the activation curve…". We interpret that the comment refers to the following four possibilities: 1) change in kappa (in response to S), 2) efflorescence, 3) non-sphericity, and 4) collapsing during water uptake. We conclude that these effects on the activation curve are properly described in the CCN state space. The following is the response to each possibility:

1) change in kappa
   The change in kappa in this method would results in a change in D50 (Eq. 11, at a given S and S_c). Even if the *shape* of activation curve changes (e.g., broadening or sharpening), the impact on D50 measurement would be minor.

2) efflorescence
   If efflorescence occurs in the entire size range, the shape of activation curve would not be affected (shift to small size). If only a fraction of the particle distribution effloresces, then the aerosol during activation can be an external mixture (wet and dry), and the activation curve will not be smooth. Such an effect might appear in the CCN state space as a gradual change from wet to dry state, although we consider it is unlikely to be significant. At least for ammonium sulfate, the efflorescence resulted in a sharp shift in the activation curve.

3) non-sphericity
   Non-sphericity leads to overestimation of D50 when a shape factor, χ, is not available, which is one of the motivations for the Wet CCN method. If there is a strong size-dependence in the shape factor, shape analysis (Eq. 13 in the revised manuscript) may be performed at several s_c (and D_{dry}) to probe χ variation as a function of size.

4) Collapsing
   We would like to clarify that in the WetCCN method, collapsing (if any) would occur prior to the DMA size selection because particles pass through a Nafion humidifier (at RH ~ 100%) upstream of the DMA. Therefore, the WetCCN method does not observe the moment of collapsing (particles are already collapsed); instead, the effect of collapsing appears as a gap between the WetCCN measurement and the conventional Dry CCN method. Therefore, the same argument as used to describe impacts of non-sphericity applies. The impact of non-sphericity (or collapsing) appears as an overestimation of D50, which is manifested in the CCN state space.

Instead of using error bars for each data point, error is shown as the range of the fitted κ value (e.g., ammonium oxalate $\kappa = 0.43 \pm 0.11$).

5. Some of the measurements are interpreted strangely. Some very strong conclusions are drawn that (even if they are expected) are in my opinion not viewable. These are: Page 270, L 7-8: This sentence states that your observations for ammonium sulphate agreed well with the E-AIM theory. It is true, that the agreement is not bad, but if I look at the

graph the points agree better with the kappa=0.5 isoline than with the E-AIM. Page 270, L 23-24: The statement about the non-spherical into droplet transition is far too strong. The “diameter gap” between the 5-6 points at the lowest saturations and the rest of the points is not higher than the difference between the neighboring points (which is probably measurement noise). With this you only cannot exclude that a small effect of particle restructuring occurs, but for sure figure 8 does not suggest it strongly, even if it is expected. Anyway, if the dynamic shape factor is known for ammonium oxalate you could estimate how big "the jump" in the mobility diameter is expected to be.

> Response:
> We followed the suggestions and evaluated the error in detail in the revised manuscript (3.3). We agree that the error in the ammonium sulfate measurements should be better quantified. Therefore, we evaluated the error in terms of the experimental error (±4% uncertainty in D) and uncertainty in κ_{gf}/κ_{CCN} (±50% uncertainty as a reasonable range). Following the quantification procedure outlined in section 3.3 (curve fit between 30% ~ 60% RH, and then estimation of error using κ value), κ of ammonium oxalate was determined to be 0.43 ± 0.11. We toned downed the original statement regarding this compound, now pointing out that the Wet CCN analysis suggests that the behavior of ammonium oxalate was similar to ammonium sulfate at RH>40%. The previous study reporting efflorescence of ammonium oxalate is consistent with our observations, although additional measurements are needed to determine particle physical state unequivocally.

Page 271, L 11: I don’t see here any efflorescence. Again, the measurement noise is too high to make such strong statements.

> Response:
> We toned downed the statement suggesting efflorescence as a possible interpretation.

Page 272, L 17: it is not sure, that the particles are nearly non-hygroscopic. It can very well be, that the humid reaction IOP have highly non-spherical shape with a high deliquescence point. In this case your mobility diameter does not agree with the volume equivalent diameter of the solute (not even at the highest measured RH if the particle is still not deliquesced), and therefore your derived kappa does not represent the real hygroscopicity of the particles. Please modify the discussion about the possible compositional differences between the wet and dry reaction as well, taking this into account.

> Response:
> Following the suggestion, we pointed out that the κ value may be underestimated if particles are non-spherical. Since there is no direct observation of particle shape, we cannot determine volume equivalent diameter of this particle.

Minor comments:
Page 261, L21: I think "May impact“ should be change to “Impact”

Response:
Entire section 2 is revised.

Page 262, L 17: “A” is not defined in eq. 6!

Response:
Done

Page 263, L 23: Sentence starting with “Similarly” is awkward, because the water activity still includes the wet diameter, if it is converted to RH

Response:
Entire section 2 is revised.

Page 265, L 6: please add details about the precision of the hygroclips and how they were calibrated

The text is modified as follows:
The relative humidities in both flows were measured by humidity sensors (Rotronic, Hygroclip, HC2-S, ±0.8% RH / ±0.1 K accuracy at 23 ± 5°C, valid at 10, 35, 80% RH, *calibrated by RH Systems / MBW 97, s/n 06-0808).*

Page 265, L 18-21: the kappa value of ammonium sulphate at the point of activation changes with the dry diameter, but you used a constant single value of 0.6. It is unnecessary to introduce such an error to the CCNC calibration even if it is small. Later on you show E-AIM data in the results section for ammonium sulphate, you should use the same for the calibration as well.

We regret our original description was not clear enough; the method described by the review was in fact used for calibration. The description of the calibration is now modified as follows (section 3.1):
“The calibration and analysis of activation curves were described in detail by Petters et al. (2009). The contribution from multiply-charged particles to the activation curves were removed by an inversion matrix (Petters et al., 2009). The activation curves were fitted to a cumulative Gaussian function and the diameter at which 50% particles activated was used as Ddry. The supersaturation was calibrated against ammonium sulfate (Fisher Scientific, >99%, A702), based on Köhler theory (Eq. 1) and E-AIM (Wexler and Clegg, 2002), in which the mole fraction of water in ammonium sulfate solution was calculated for varied relative humidity (aw for a bulk solution), and Sc was determined by searching for the maximum in S (accounting for Kelvin effect) for the experimentally determined

Ddry. For the range of Sc investigated in this study (1.0025 ~ 1.0040), κ ranges from 0.61 to 0.59."

Page 266, L 12: carried out*

Response:
Done

Page 267, L 1: kappa isoline

Response:
Done

Page 267, L 2: the curve fitting is not a good option if kappa is continuously changing with increasing saturation ratio. It can only be done if the kappa jumps from a kappa_gf value at sub-saturation to a kappa_ccn value at the point of activation. This is usually not the case. One needs several measurement points for a sufficient curve fit, and these have to be made at different RHs. If the kappa_gf is changing with the RH then the fit assuming a constant one will most probably not work. Please comment on this.

Response:
We agree that assigning constant kappa_gf over a wide range of RH is not a good option. As discussed in the new error analysis section (3.3), we would like to suggest RH 30 – 60% as the optimum range for quantification due to relatively large error at higher RH (>60%).

Page 267, L 15-17: the sentence is only true if the kappa is not changing with the saturation ratio. Add this to the sentence please!

Response:
Done

Page 270, L 13: The efflorescence looks to be a bit higher than 35% on figure 8.

Response:
The value is 37.7%. The agreement with previously measurement range, 35 ± 2 % (Martin et al., 2000) is reasonable. A minute amount of impurity in the prepared solution may enhance efflorescence RH by acting as a nucleus for crystallization (Martin et al., 2000), which would not impact kappa significantly. This discussion is added in the error analysis section (3.3).

Page 270, L 14: Why don't you give a precise kappa value for glucose? Why only an approximately value, it can be clearly seen that the measurement points lie on a kappa line which is a bit lower than 0.2

Response:
Kappa for glucose was 0.17 ± 0.03, in agreement with a previous study, 0.165 ± 0.033 (Ruehl et al., 2010). This is added to the manuscript.

Page 270, L 17-18: "unpublished data" is not a reference. Please cite at least a paper which is in preparation. Page 270, L 20: is it possible to give some info on how much those particle are nonspherical?

Response:
Ruehl et al. (2010) is cited instead. The good agreement of the measured κ (Wet CCN and HTDMA) and κ_{Raoult} suggests that glucose particles can be treated as spherical.

Page 270, L 25-27: This sentence has to be reformulated, such that it makes clear that the dry CCN measurement gives most probably false kappa values because the true solute volume cannot be calculated from the dry mobility diameter. The sentence suggests now that the difference in the kappa between the dry and wet CCN measurement exists due to some kind of limited dissolution of the particle.

Response:
The paragraph was rewritten to address the major comments.

Page 271, L 13-15: please use another verb instead of "narrow down", your kappa value is out-side of the range of the previous measurements.

Response:
The paragraph was rewritten to address the major comments.

Page 271, L 23: please change the term "fully dissolved" to collapsed or restructured.

Response:
Done

Page 271, L 24: please comment on the point at around 70% relative humidity having significantly lower kappa

Response:

Now the quantitative analysis is limited to RH range 30~60%. Therefore the outlier around 70% does not affect the quantification.

Page 272, L 18: if I understood correctly during the generation of IOP, the particles did not experience higher RH than 65%, and with this you have to talk about deliquescence here and not efflorescence.

Response:
Since particles are passed through a Nafion at RH~100% prior to size selection, we must consider efflorescence, not deliquescence.

Page 274, L 12-13: The evaporation is strongly dependent on the temperature. The temperature in the DMT CCNC depends on the applied supersaturation (temperature gradient in the activation column) and on the ambient temperature. Comparing the "extent of the gap" to the Romakkaniemi et al., 2013 study makes only sense if the temperatures were similar in the two DMT CCNCs.

Response:
The comparison is done at the same s_c (0.40%) (at room temperature) to be comparable.

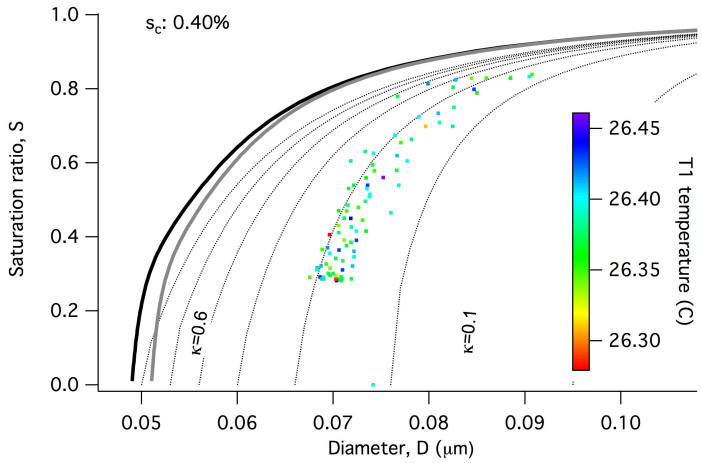
Figure 6. I find this figure unnecessary. If you still decide to keep it in the manuscript, please correct it, you cannot be sure, that IOP is spherical after wetting (it is even suggested by your humid IOP results, that they are not).

Response:
The figure is removed.

Figure 10. It would be nice to investigate whether the spread in the data points have something to do with the temperature in the CCNC or if it is just measurement noise. You could colour the points after the CCNC's temperature and if there is a trend then include it in the manuscript and discuss it.

Response:

The CCNC temperature was very stable within ~0.15C, and thus there was no correlation with CCNC temperature with the noise in S vs. D50 space. The column top temperature (T1) is shown in the graph. Other recorded temperatures (sample inlet temperature, etc.) did not show any obvious trend.



Review by anonymous referee #3:

The manuscript "Droplet Activation of Wet Particles: Development of the Wet CCN Approach" describes a new approach to quantify aerosol hygroscopicity based on CCN measurements. Measurements of critical supersaturation are combined with measurements of wet diameter at a range of saturation ratios, instead of measurements of dry particle diameter. The authors demonstrate that this technique is preferable to the traditional dry diameter approach for some chemical systems, and that new, relevant information about these systems can be obtained. This technique represents an advance in CCN measurements, and will be of interest to Atmospheric Measurement Techniques readers. I recommend publication after the following minor issues have been addressed.

> Response:
> We thank the referee for the positive assessment of our manuscript.

General:

One thing I think is missing from the discussion is the fact that growth factor measurements become more useful in predicting CCN activity at high S. This is implied in the caption for Fig. 3 – "especially at higher RH (above ~ 70%)" - as well as associated discussion in the text, but never stated explicitly or quantified. This seems like a critical feature of the Wet CCN approach, and so I suggest the authors discuss it briefly.

> Response:
> Although growth factor are more sensitive at high S, the Wet CCN approach unfortunately loses sensitivity at high S. This effect is discussed in detail in the error analysis section. One can convert the Wet CCN measurement to conventional growth factor when D_{dry} is available, but that will reintroduce the need for D_{dry}, and is hence not pursued in this study.

Specific:
P 258, L 7-8: “The new approach directly measures Köhler curves under sub-saturated conditions.” This is somewhat confusing because it implies that an entire Köhler curve could be draw under subsaturated conditions - but then it would no longer be a Köhler curve. I recommend referring to “the subsaturated portion of the Köhler curve”.

Response:
Done

Pg 262, Eq. 6: define A (currently defined for Eq. 8)

Response:
Done

P 263, L 14-16: The phrase “The possible causes include” suggests that “non-ideality” and “solubility” are the only possible causes. This suggests that surface tension variability is not a possible cause - is this the author’s intent? If not, please remove the word “The”.

Response:
Done

P 264, L12: Either state that Fig. 3 is an S vs. D curve, or change “D-axis” to “x-axis.” Somewhat confusing to refer to an unfamiliar “D-axis” without any explanation.

Response:
Changed to x-axis

P 265, L 18-20: “Calibration of supersaturation was carried out by observing activation of ammonium sulfate and using $\kappa = 0.6$ based on E-AIM calculation.” If E-AIM is used, doesn’t κ vary slightly, and can’t κ be calculated more precisely? Or are the authors suggesting that AS $\kappa = 0.6$ is adequately precise to calibrate the CCN instrument? Please explain.

Response:
The variability of κ when calibrating with E-AIM is now described more completely in the revised manuscript.

P 267, L 1-2: “When a trajectory of data points deviates from an isoline, gf and CCN may be acquired separately by curve fitting as discussed above (Sect. 2.3).” I would say the authors mentioned this but did not really discuss it in 2.3. If the authors would like to add an example of separate gf and CCN curve fitting, that would be helpful. This is not in my opinion necessary for publication.

Response:
Following Dr. Jurányi's suggestion, we acknowledged the difficulty of assigning constant gf for a range of RH, and changed the sentence.

P 267, L 23, 26: Please indicate when in the experimental procedure this collapse and/or efflorescence is occurring. I think this will make the discussion more clear.

Response:
The following sentence is added:
"More specifically, collapse of particles can occur within the Nafion humidifier (when exposed to RH ~ 100%); efflorescence can occur immediately after the humidifier when sample temperature increase from dew point (set by the humidifier) to the room temperature."

P 268, L 15-16: I don't understand why irreversible evaporation before size selection by the DMA would cause any deviation. It would cause the particle to shrink immediately after generation, but you would still have the same particle size in the DMA and the CCNC. Please explain the difference between upstream vs. downstream partitioning shifts (L12-13) more clearly.

Response:
The reviewer's comment is right for single-component particle. We meant to argue selective loss of water-soluble semi-volatile species, resulting in changes in κ. The following paragraph is added to describe this point:
For example, "Change in κ" scenario in Fig. 7 illustrates the case where evaporation of semi-volatiles – water-soluble compounds (in green) occurs upstream of the DMA (e.g., during humidification in a Nafion tube) irreversibly, which may be possible if the partitioning of semi-volatile compounds was mediated by water (Topping and McFiggans, 2012). In this case, D50 will deviate from a κ isoline because of the change in particle composition.

P 268, L 18-19: "...parameters other than particle composition (e.g., non-ideality, solubility)..." Wouldn't it be better to refer to "particle molar volume?" "[C]omposition" can be used to predict solubility or non-ideality, but molar volume is a distinct parameter.

Response:
The sentence is removed to be consistent with the new error analysis.

P 268, L 26: Raoult's Law is typically used for solution components in relatively high concentrations, which at high RH applies only to water (i.e., the solvent). It is potentially confusing to use it as is done here to refer to lowering of solute activity. Please remove or clarify.

Response:

Raoult's law would apply to the solute at low-mid RH, but would not be appropriate for high RH as the reviewer pointed out. Instead, a relevant paper is cited to refer to the effect of water on semi-volatile partitioning (Topping and McFiggans, 2012).

P 270, L 14-18: You could also cite κglucose of 0.165 determined at RH~ 99% by Ruehl et al. (ACP, 2010).

Response:
Done

P 270, L 22: is that κCCN or κgf? Seems relevant to the current topic.

Response:
Now it specifies the κ value as κ_{CCN}.

P 271, Eq 10: fw is used for the molar volume of water, but Eq. (1) uses a different symbol for the "partial" molar volume of water. I assume this is not a relevant distinction, and therefore the same symbol should be used in both equations.

Response:
Now Eq. 5 describes the molar volume.

P 271, L 13-15: "The effective κ of ammonium oxalate particles reported here for the Wet CCN technique narrowed down the previously large range in estimates." What κ does this refer to? 0.6? Please give that number here.

Response: 0.43 ± 0.11

P 272, L 17-18: Looking at Fig. 9, it appears that efflorescence occurs as high as RH~ 90%. This seems unusually high and worth of further comment. Has the efflorescence RH for this system been measured previously?

Response:
ERH for this system has not been measured previously to our knowledge.

P 275, L 20-21: Again, I don't understand how "Raoult's Effect" would suppress evaporative loss of a dilute solute.

Response:
Instead, we cited Topping and McFiggans et al. (2012)

Fig. 3 - Caption does not fully explain figure. Label what panels (a) and (b) are in caption, and I believe this will suffice.

Response:
The caption is modified as follows:
Figure 6. Illustration of the impact of κ_{gf} : κ_{CCN} on the Wet CCN analysis (s_c: 0.25%). (a) predicted trajectories for different κ_{gf}, (b) Inferred κ values for different κ_{gf}. The impact of κ_{gf} : κ_{CCN} on the observed κ value increases at higher RH (above ~60%).

Fig. 7 - I suggest you add arrows to the processes (efflores., collapse, etc.) to indicate the direction in "Wet CCN space" that each process proceeds.

Response:
Done

References:
Ruehl, C. R., Chuang, P. Y., and Nenes, A.: Aerosol hygroscopicity at high (99 to 100%) relative humidities, Atmos. Chem. Phys., 10, 1329-1344, doi:10.5194/acp-10-1329-2010, 2010.

Reference

Ruehl, C. R., Chuang, P. Y., and Nenes, A.: Aerosol hygroscopicity at high (99 to 100%) relative humidities, Atmos. Chem. Phys., 10, 1329-1344, 2010.

Snider, J. R., Petters, M. D., Wechsler, P., and Liu, P. S. K.: Supersaturation in the Wyoming CCN Instrument, Journal of Atmospheric and Oceanic Technology, 23, 1323-1339, 2006.

Topping, D. O., and McFiggans, G.: Tight coupling of particle size, number and composition in atmospheric cloud droplet activation, Atmos. Chem. Phys., 12, 3253-3260, 2012.