Comments by Referees are in blue. Our replies are in black. Changes to the manuscript are highlighted in red both in here and in the revised manuscript.

Reply to Ref #3

This manuscript describes a technique for determining the mass growth factor (MGF) and deliquescence relative humidity (DRH) of compounds using a commercial vapour sorption analyser. The authors present the methodology for determining the DRH and the MGF, followed by measurements of DRHs for different compounds/temperatures intended to confirm the RH calibration of the instrument. They then present measurements of the mass hygroscopic growth of ammonium sulphate and sodium chloride at two different temperatures, followed by calcium sulphate dihydrate which is used as a mimic for a low hygroscopicity species. In Lines 94-97, the authors note that two groups have already reported measurements using a similar technique, but that the novelty of their manuscript lies in the fact that it systematically evaluates the performance of the technique which has not been done before. I believe the manuscript is suitable for publication in AMT only after the concerns regarding the rigour of this validation included in the list below are adequately addressed.

Author reply: We would like to thank Ref #3 for his/her very valuable comments, which have significantly help improve our manuscript. All the comments have been properly addressed in our revised manuscript, as detailed below.

(Line 1-2) The title of the manuscript is factually incorrect. The paper reports water adsorption and hygroscopicity of atmospherically relevant compounds, not of atmospheric particles (i.e. sampled directly from the atmosphere). This should be changed.

Author reply: We agree with the referee that our original title does not precisely reflect what we did. Although particles used in our work are not airborne, these materials, such as $(NH_4)_2SO_4$ and

NaCl, are commonly found in atmospheric particles and thus relevant for the atmosphere. In the revised manuscript we have changed the title to “Investigation of water adsorption and hygroscopicity of atmospherically relevant particles using a commercial vapor sorption analyzer”.

(Lines 67-72) The authors say the strength of the technique is the ability to make measurements on non-spherical particles, which can be problematic for some of the more commonly used techniques which make measurements on species in the aerosol phase. However, the authors do not mention any of the drawbacks of looking at the hygroscopic behaviour of particles on a hydrophilic surface, in that they will not be able to access supersaturated solute states or determine the efflorescence RH.

Author reply: The referee is right. In the revised manuscript **(line 398-404)** we have discussed the drawbacks of this technique: “We note that this technique also has a few drawbacks: 1) this technique cannot be used to examine supersaturated droplets or determine efflorescence relative humidities (ERH), due to the contact of particles with the sample pan; 2) substantial amount of particles, typically around or larger than 1 mg, are required by this technique, limiting its application to atmospheric particles even after they are collected (e.g., using a filter or an impactor plate); 3) the experiment is very time-consuming, and a typical experiment can take several hours and even a few days, depending on experimental conditions.”

(Line 155-156) The authors state that the RH can be varied between 0 and 98% with an absolute accuracy of +/- 1% as measured by a probe. Can the authors provide any details on the type of probe used here? Capacitance probes typically used for RH determination can be expected to have an accuracy of +/- 2% at RHs below 80%, but the error can climb to +/- 3% at RHs above this. These are obviously significantly larger than the quoted value.

Author reply: The referee has made a good point here. In our original manuscript we did make it very clear how to control and determine RH. In fact, high accuracy of RH control is achieved by precise control of the dry and wet flow rates. In the revised manuscript **(line 156-160)** we have added a few sentences to clarify it: "High accuracy in RH control, with a stated absolute accuracy of ±1%, is achieved by precisely controlling the dry and humidified N_2 flow rates, using mass flow controllers regularly calibrated. The accuracy of RH control is routinely checked by measurement of the DRH of NaBr, as detailed in Section 3.1 In addition, as shown in Figure 1, two capacitance RH sensors are used to check relative humidity in the chamber."

(Line 177-181) If the authors are measuring the DRH why does the experimental method involve setting the RH higher than the DRH and then lowering it slowly? If there is no lag between slowly changing the desired RH in the software and this value equilibrating in the chamber (the authors do not mention one), why can the measurement not be performed by increasing the RH slowly from a value below the DRH? This way you would get a lot more data which would actually visualise the step change in mass as the particle deliquesced.

Author reply: Indeed the method suggested by the referee has some advantage. We have also realized this after we submitted our manuscript, and DRH values have also been measured using this method, showing good agreement with those determined used the method described in our original manuscript. In the revised manuscript **(line 215-232)**, we have added one paragraph and a new figure to describe this experimental method. Please refer to our revised manuscript for further details.

Figure 2. Error bars in the RH (from the absolute accuracy of the probe stated in line 156) need adding to this plot.

Author reply: This figure shows the raw data without being processed, and therefore it is not necessary to have the error bars. However, as suggested by the referees, error bars have been added for other figures.

Table 1 and Table 2. DRH values determined from this work need an associated error originating from the probe accuracy.

Author reply: In the revised manuscript uncertainty information has been provided for these two tables.

Figure 3. Errors bars in RH are included for the DRH reference data but not for the DRH values determined in this work. These need adding to the plot.

Author reply: In the revised manuscript we have provided uncertainty information for our measured DRH values displayed in this Figure. Please note that in some cases the error bars are too smaller to be clearly visible.

Also, the authors should comment on the systematic disagreement between the data as a function of temperature which can be seen in panel b).

Author reply: It looks like that there is systematic disagreement as a function of temperature, as pointed out by the referee; however, the difference is not significant compared to uncertainties in DRH measurement. In the revised manuscript **(line 295-298)** we have added one sentence to discuss this: "It also appears that the difference between our measured and previously reported DRH of $Mg(NO_3)_2 \cdot 6H_2O$ may show a dependence on temperature; however, the difference is not significant compared to uncertainties in DRH measurement."

Figure 4. There are not enough data points on the graphs here to use them as a validation of the technique. In each panel all but one of the data points are on the flat region of the hygroscopic curve and there are no data at all either side of the deliquescence event, which is actually the region

of interest. Further data points need adding to each plot which show a clear tracing out of the deliquescence region and more data points should also be added at high RH as this is the region most relevant to activation of aerosol in the atmosphere. Error bars in the RH (from the probe) should be included.

Author reply: We agree with the referee. We have conducted additional measurements with RH increment was reduced from 30% to 10%, and the new results have been presented with error bars included. We have also expanded our discussion on comparison of our measurement with E-AIM predictions. Please refer to our revised manuscript **(line 326-345)** for more details.

The authors should also comment on the fact that the ammonium sulphate data at both temperatures deviates from E-AIM at high RH.

Author reply: As suggested, in the revised manuscript **(line 326-340)** we have added a few sentences to discuss the issue raised by the referee: "The agreement between measured and calculated growth factors is excellent for NaCl at both temperatures; for $(NH_4)_2SO_4$, the agreement is not as good as NaCl. This may be caused by two reasons. First, after $(NH_4)_2SO_4$ is deliquesced, mass hygroscopic growth factors increase sharply with RH, and therefore a small difference in RH would lead a relatively large change in measured mass hygroscopic growth factors; if taking into account the uncertainty in RH (±1 %), the difference between our measured and predicted mass hygroscopic growth factors is <15%. Second, inspection of the data in Table 2 reveals that the difference between our measured and previously reported DRH is <1% for all the other compounds except $(NH_4)_2SO_4$. This may indicate that the purity of $(NH_4)_2SO_4$ could lead to the small but yet detectable difference. In the near future we will purchase $(NH_4)_2SO_4$ with higher purity and measure its DRH and hygroscopic growth factors. Overall, it can be concluded from the comparison that our measured mass hygroscopic growth factors agree well with theoretical values for $(NH_4)_2SO_4$ and NaCl at both 5 and 25 ^{o}C. This gives us further confidence that the method developed in this work is reliable for hygroscopicity measurements of atmospheric particles."

Figure 5 panel b) The raw mass data shows frequent dips and spikes. What is the origin of this?

Author reply: Because the mass change is very small, these dips in spikes are due to random noise in mass measurement. As we stated in the original manuscript, the noise level, smaller than 0.025%, determines our detection limit in hygroscopicity measurement.

(Line 314) Is this number supposed to be 0.025%?

Author reply: The referee is right. It should be 0.025%, and we have corrected it in the revised manuscript.

(General comment) The authors say the greatest advantage of this technique is the ability to look at non-spherical particles, however they report no measurements (even preliminary ones) of non-spherical particles here. The impact of this manuscript would be much higher if some were to be included.

Author reply: The principle of our technique relies on measurements of mass change and thus particles under investigation do not need to be spherical. Our work show that for RH in the range of 95%, $CaSO_4{\cdot}2H_2O$ particles are not deliquesced and thus may exist as non-spherical particles. In the revised manuscript **(line 355-356)**, we have added one sentence to make this more clear: "This also implies that airborne $CaSO_4{\cdot}2H_2O$ particles are not deliquesced for RH up to 95% and therefore may exist as non-spherical particles."