

## ***Response to Anonymous Referee #2***

We thank the reviewer for the constructive suggestions/comments. Below we provide a point-by-point response to individual comments (Reviewer comments in italics, responses in plain font; page numbers refer to the AMTD version; figures used in the response are labeled as Fig. R1, Fig. R2,...)

### ***Comments and suggestions:***

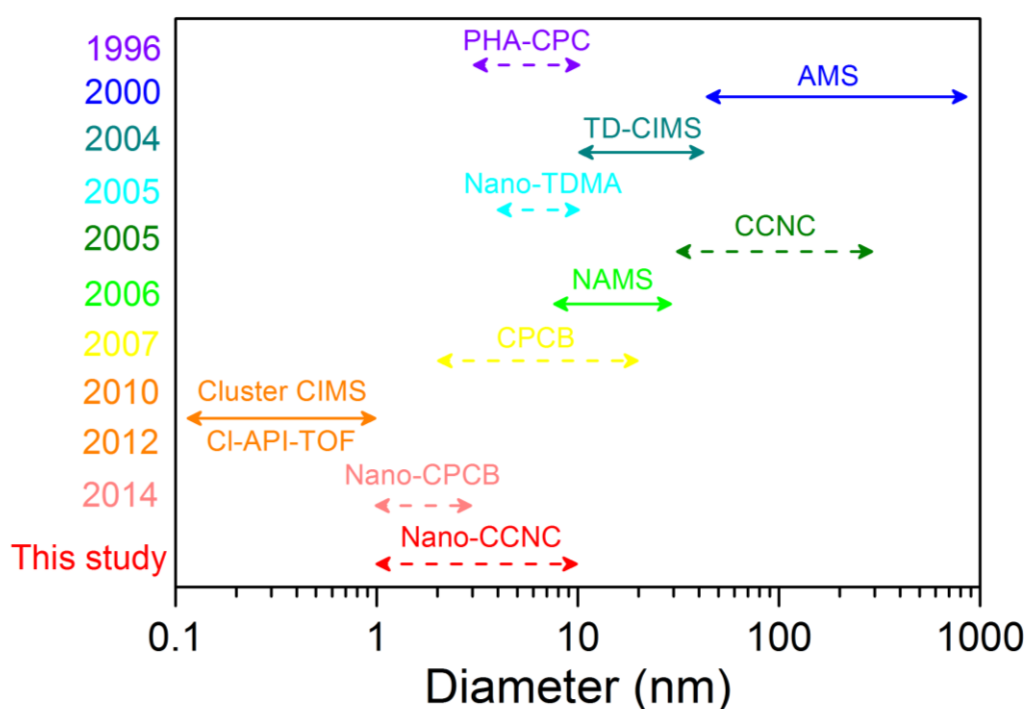
*Page 11138, line 25: To be absolutely transparent, the instruments listed in Figure 1 are representative, rather than exhaustive of the aerosol instruments that provide composition information. Please clarify this. There are a number of other studies/instruments that provide size-resolved composition information (indirect). For instance, the Nano-TDMA provides indirect composition information (analogous to this nano-CCNC) down to 4 nm (Sakurai et al. 2005), and the nano CPC battery provides size-resolved indirect composition information from 1 to 3 nm (Kangasluoma et al. 2014).*

### **Responses and Revisions:**

Good suggestion. We have revised Figure 1 (as Fig. R1) and included a new paragraph (in the introduction) to address the indirect methods:

“... A number of apparatuses based on mass spectrometry have been performed to analyze the chemical compositions of ultrafine particles (Fig. 1). A number of apparatuses based on mass spectrometry have been performed to analyze the chemical compositions of ultrafine particles (Fig. 1). Aerosol mass spectrometer (AMS) can measure particles with diameters down to ~40 nm (Jayne et al., 2000 and updated references on <http://cires.colorado.edu/jimenez/ams-papers.html>). Thermal desorption chemical ionization mass spectrometer (TDCIMS; Smith et al., 2004) and nano aerosol mass spectrometer (NAMS; Wang and Johnston, 2006) are commonly used at 10-30 nm particles. Analysis of molecular clusters with diameter up to ~1 nm has been achieved by cluster chemical ionization mass spectrometry (Cluster-CIMS; Zhao et al., 2010; Jiang et al., 2011) and chemical ionization with the atmospheric pressure

interface time-of-flight mass spectrometer (CI-API-TOF; Jokinen et al., 2012). However, direct chemical composition measurement of sub-10 nm particles is still difficult due to its relatively low transmission efficiency and mass concentration (Kulkarni et al., 2011). Therefore, alternative indirect methods have been developed, which infer the chemical composition information of nanoparticles through measurements of physical properties (such as hygroscopicity, volatility and solvent affinity), such as nano tandem differential mobility analyzer (Nano-TDMA; Sakurai et al., 2005; Ehn et al., 2007), pulse-height condensation particle counter (PH-CPC; Marti et al., 1996; Saros et al., 1996; Weber et al., 1998; O'Dowd et al., 2002; O'Dowd et al., 2004; Sipilä et al., 2009) and CPC Battery (CPCB; Kulmala et al., 2007; Riipinen et al., 2009; Kangasluoma et al., 2014).



**Figure R1:** Size ranges of representative measurement instruments in atmospheric aerosol research (modified from Kulmala et al., 2012). The year when each technique was first reported is indicated on the left-hand side. The solid arrowheads indicate the direct measurements, whereas dashed arrowheads represent the indirect measurements. The use of scanning supersaturation CPC as nano-CCNC introduced in this study mainly focus on the size range of 1-10 nm.

**Comments and suggestions:**

*Page 11139, line 16: Please amend “particle sizes” to “particle activation sizes.*

**Responses and Revisions:**

Corrected.

**Comments and suggestions:**

*Page 11140, line 7: When first describing the water CPC, please include a reference to (Hering et al. 2005).*

**Responses and Revisions:**

We have added this reference in the revised manuscript.

**Comments and suggestions:**

*Page 11140, line 11: It is rather vague to state that the curve of the CPC is the same as the curve of the CCNC. Please be more specific – same in what ways? In composition dependent response? In sharpness of the activation curve? Also, to be clear, are the efficiency data plotted in Figure 3 corrected for transport losses? If they have not been corrected for transport losses, then the efficiency data are more accurately referred to as detection efficiencies rather than activation efficiencies, since the impact of size-dependent particle diffusional losses have not been removed. Furthermore, aerosol transport losses will have the effect of broadening the resulting detection efficiency curve – this will be referenced later in this review.*

*Page 11142, line 28: Were the efficiency presented in Figure 3 corrected for aerosol transport losses in each system? The impact of size-dependent nanoparticle diffusional losses will also act to make a step function more broad, along with the impacts of diffusion and the finite dimensions of the sample capillary in the water CPC. Please clarify this in Figure 3 and in the text.*

**Responses and Revisions:**

The referee was right. The counting efficiency curve of the CPC (Fig. 3) hasn't been corrected for transport losses. The diffusional transport and broadening effect happens in both systems but only becomes significant in the CPC. We have adopted more precise wording and specified their similarity in the revised manuscript.

Page 5, line 102

“...the counting efficiency curve of the CPC reflects the same composition dependence of aerosol particles as in the activation curve of the CCNC, but being extended to smaller size ranges”.

To avoid distracting, we don't immediately discuss the losses and broadening effect in Section 2.1 but address them later in Section 2.3.

We thank the referee for pointing out the other factors, which have been included in the revised manuscript:

Page 8, line 170,

“In the aerosol activation unit (growth tube, Fig. 5a),  $S$  is not evenly distributed ( $S$  has a maximum in the centerline and a zero value at the wall, Fig. 5b). Due to finite dimensions of the sample capillary, particle dispersions and its size dependence (Stolzenburg and McMurry, 1991), aerosol particles in the growth tube are not uniformly distributed as well. By overlaying the spatial distribution of  $S$  with that of aerosol particles, we can determine  $H(S)$ , i.e., the cumulative supersaturation distribution of  $S$  that aerosol particles have been exposed to in the growth tube.”

### ***Comments and suggestions:***

*Page 11140, line 14: It is not accurate to state that the CPC is mainly used for accurate particle counting (where the detection efficiency is  $\sim 1$ ). For the scenario that the CPC is the particle detector in an SMPS (which is nearly almost always the case for an SMPS), it is absolutely critical to know the detection efficiency curve in the cut-off region ( $< 1$ ). Please revise.*

### **Responses and Revisions:**

Our point is that the detection efficiency in the cut-off region is composition-dependent. The particle counting in this regions is subject to larger uncertainties compared with the region of  $F_{\text{act}}=1$ . Therefore, we stated that “ideally operated at size ranges with activation fractions equal to 1.”

### ***Comments and suggestions:***

*Page 11141, line 14: The statement that  $S$  can be scanned by scanning the aerosol flow rate of the CPC is not entirely accurate. In Gallar et al, it is not the aerosol flow rate that is scanned, but the mixing ratio of dilution air and saturated air (as you proceed to describe later in the text). The aerosol (sample) flow rate was fixed in that study. In Wimmer et al, the CPC that could scan  $S$  was a turbulent mixing type CPC, fundamentally different than the laminar flow type CPC used in this study. In the turbulent mixing type CPC, it is the saturator flow that is scanned (not the aerosol flow) to scan  $S$ . Please revise.*

### **Responses and Revisions:**

We have clarified this in the revised manuscript:

“The scan of  $S$  can be achieved by: (1) scanning the temperature gradient between the saturator and growth tube (by changing the saturator or growth tube temperature; Mordas et al., 2008; Kupc et al., 2013); (2) scanning the mixing ratio of saturator air and dilution air (Gallar et al., 2006) or saturator flow and aerosol flow (Vanhanen et al., 2011; Wimmer et al., 2013; Lehtipalo et al., 2014).”

### **Comments and suggestions:**

*Page 11142, line 12: It is not accurate to state that particle diffusion causes nonuniformity of exposed  $S$ . First, the spatial distribution of  $S$  is non-uniform due to the effects of simultaneous heat and mass transfer in a laminar flow system. While radial diffusion will lead to some degree of particle exposure to different values of  $S$ , the fact that there is a non-negligible cross section of the sample capillary will lead to the introduction of nanoparticles into the growth tube across the width of the capillary leading also to exposure to different values of  $S$ . Please revise.*

*Page 11142, line 24: As mentioned earlier, there is dispersion of the aerosol sample already due to the finite width of the sample capillary that introduces the aerosol into the laminar growth tube.*

### **Responses and Revisions:**

Thank you for pointing that out. We have included this in the revised manuscript:

In the aerosol activation unit (growth tube, Fig. 5a),  $S$  is not evenly distributed ( $S$  has a maximum in the centerline and a zero value at the wall, Fig. 5b). Due to finite dimensions of the sample capillary, particle dispersions and its size dependence (Stolzenburg and McMurry, 1991), aerosol particles in the growth tube are not uniformly distributed as well. By overlaying the spatial distribution of  $S$  with that of aerosol particles, we can determine  $H(S)$ , i.e., the cumulative supersaturation distribution of  $S$  that aerosol particles have been exposed to in the growth tube. Fig. 5b suggests that  $H(S)$  turns out to be a broad distribution instead of a step function. As a mapping of  $H(S)$ , the activation curve  $F_{\text{act}}(D_d)$  will also be a broad distribution. The conversion between  $H(S)$  and  $F_{\text{act}}(D_d)$  is given in the following discussion.”

### **Comments and suggestions:**

*Page 11145, line 17: What was the reasoning for using the  $\text{WO}_x$  data to determine  $H(S)$ ? With the right assumptions, are the  $H(S)$  calculated from ammonium sulfate,*

sucrose, and sodium chloride data consistent with each other? Please provide an explanation.

### Responses and Revisions:

The WOx was used because the WOx generator is portable and convenient for application in the field measurement. As the referee suggested, we compared the  $H(S)$  calculated from ammonium sulfate, sucrose, and WOx data. On average, WOx shows < 5% difference in  $S$  compared to sucrose and ammonium sulfate. It means that using calibration curves of sucrose and ammonium sulfate will result in a shift of < 5% in the retrieved  $S_{\text{cri}}$  but will not change the relative order of  $S_{\text{cri}}$  of different compounds (if  $S_{\text{cri}}$  of compound A >  $S_{\text{cri}}$  of compound B holds for WOx calibrated  $H(S)$ , it also holds for sucrose/AS calibrated  $H(S)$ ).

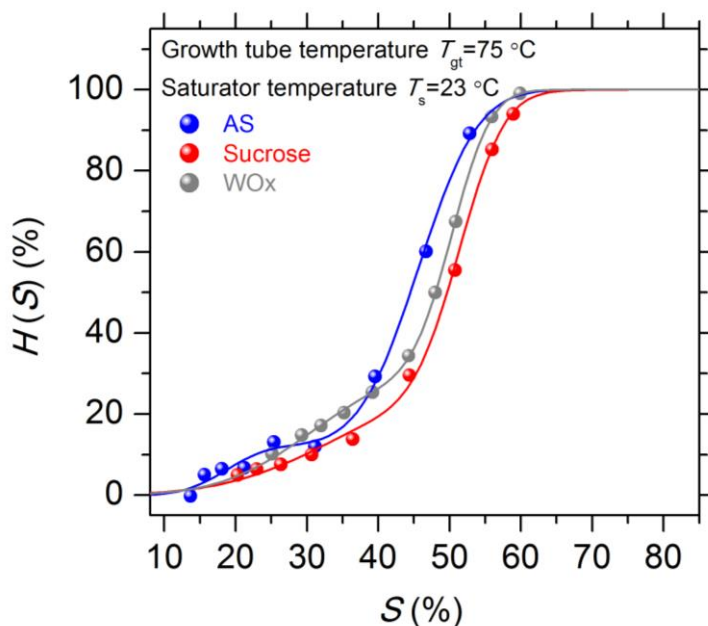


Figure R2: The distribution of  $S$  that nanoparticles have been exposed to inside CPC retrieved from the various chemical compositions.

### Comments and suggestions:

Page 11149, line 19: The instrument characterization presented in Kangasluoma et al. does include the size-resolved response of a nano CPC battery to aerosol of various composition to different working fluids. Please revise to reflect this.

### Responses and Revisions:

We have reorganized this sentence in the revised manuscript:

“The existing CPCB systems (Kulmala et al., 2007; Riipinen et al., 2009; Kangasluoma et al., 2014) can be readily extended to a SS-CPCB system and produce multiple dimensional solvoscopicity matrix.”

***Comments and suggestions:***

*Page 11163, Figure 5: In caption d, please revise “dimensions of activated particles” to “radial distribution of activated particles”. “Dimensions of activated particles” is awkward phrasing.*

**Responses and Revisions:**

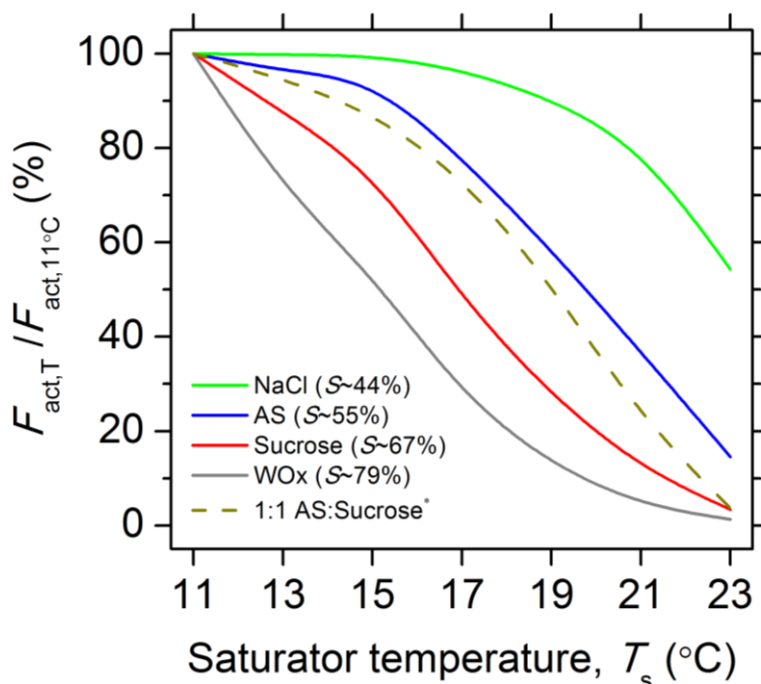
Corrected.

***Comments and suggestions:***

*Page 11167, Figure 9: What is meant by “in the range of 57 to 75%, during which is indicative of ambient nanoparticles”? Were ambient nanoparticles actually sampled with this system?*

**Responses and Revisions:**

We have not applied our nano-CCNC system in the ambient measurement. Previous studies (Kulmala et al., 2014, and references therein) have demonstrated that both the ammonium sulfate and organics contribute to the subsequent growth of newly formed particles. Hence we assumed that the critical supersaturation of ambient nanoparticles should be located between 55% (AS) and 75% (WO<sub>x</sub>). To exclude the ambiguous expression, we have removed these lines in the revised Fig. 9 (as Fig. R3):



**Figure R3:** Profiles of relative activation ratio as a function of saturator temperature. The critical supersaturations for NaCl, AS, sucrose and WOx are average values at seven saturator temperatures. The dash line represents the mixed AS and sucrose aerosols with mass ratio of 1:1.

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