Response to Anonymous Referee #1

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:

In the introduction and figure 1, you should clearly distinguish between direct and indirect methods to measure chemical composition of nano-particles.
Your work is definitely not the first attempt to close the gap between ~1-10nm. The introduction and figure 1 should include previous work done to get indirect information of the composition, e.g. using CPC batteries, HTDMAs, volatility-DMPS, pulse-height analysis etc. You do refer to these later in the text (with relevant articles cited), but there should be a chapter also in the introduction, so that the reader can put your work into right context.

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).

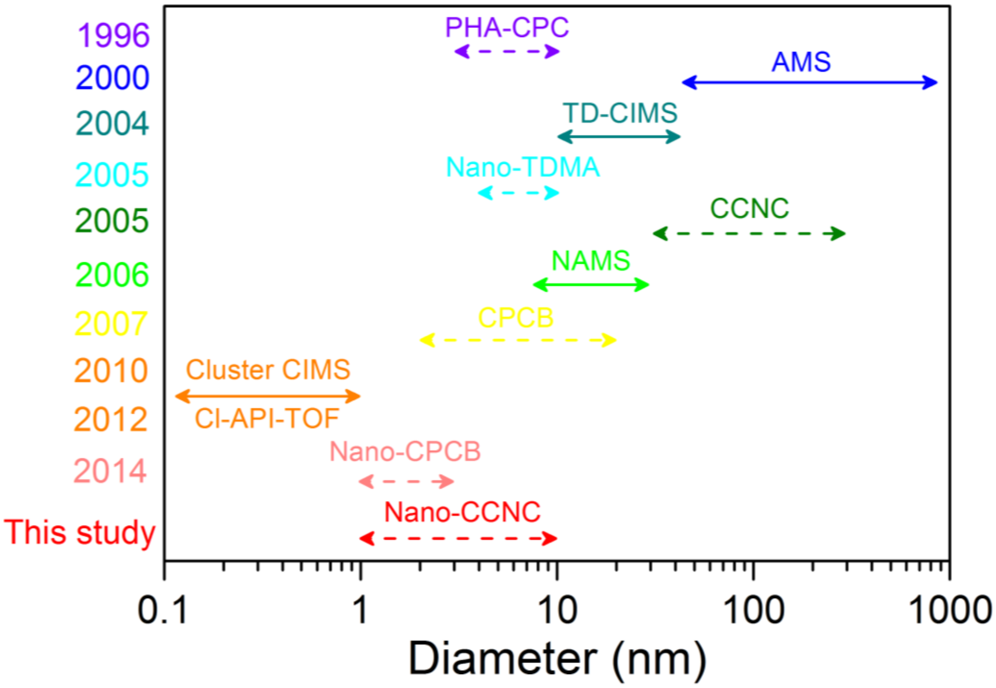

Figure R1: Size ranges of representative measurement instruments in atmospheric aerosol research (modified from Kulmala et al., 2012). The year when each technique was first reported is indicated on the left-hand side. The solid arrowheads indicate the direct measurements, whereas dashed arrowheads represent 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:

There is also another scanning supersaturation CPC system (Airmodus A11 or its previous models), which is currently widely in use (see e.g. Vanhanen et al., 2011, Kulmala et al. 2012, Lehtipalo et al., 2014). This should be discussed in chapter 2.2., when you introduce the principle of scanning supersaturation CPC. You should take this into account also in chapter 3.3. & conclusions, where you propose using the same principle also with other working fluids (which is, in fact, already done).

Responses and Revisions:

We included the relevant work in section 2.2:

"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)"

and section 3.3:

"The concept of scanning supersaturation (SS) is not limited to water-based CPCs, and may also work for CPCs with other working fluids, such as butanol, perfluorotributylamine (Gallar et al., 2006) as well as diethylene glycol (DEG; Vanhanen et al., 2011;Wimmer et al., 2013)."

Comments and suggestions:

Chapter 2.3 and figure 4 are poorly connected. The sub-figures in 4b are too small to read, and they do not help me in understanding the text, and what was done to the data. On the other hand, the text does not help me in understanding the figures although there is a reference to chapter 2.3. in the figure caption!

Responses and Revisions:

We agree that Figure 4 do not help understand the text and have removed it in the revised manuscript. We have included a new section 2.3.4 for better explanation of the data analysis procedure.

"In brief, the data analysis procedure can be summarized as follows:

(1) The first step is to determine the size-resolved activation fraction of calibration particles with known hygroscopicity properties, $F_{\mathrm{act}}(D_{\mathrm{d}})= N_{\mathrm{act}}/N_{\mathrm{tot}}$. A

nano-DMA can be used for the sizing, N_{act} can be determined by a nano-CCNC and N_{tot} can be determined by an electrometer or a particle counter that is able to count all particles (e.g., CPC with a lower cutoff size).

(2) The second step is to determine $H(S_{cri})$, the cumulative supersaturation distribution that nanoparticles are exposed to in the nano-CCNC, and its inverse function. $H(S_{cri})$ can be calculated from measured $F_{act}(D_d)$ by $H(S_{cri})=1-F_{act}(D_d)$ (Eq.2) in which S_{cri} can be calculated based on the Köhler theory. Once $H(S_{cri})$ is determined, we can calculate its inverse function $S_{cri}=f^{-1}(H)$ (Eq.3).

(3) The last step is to determine the critical supersaturation and corresponding hygroscopicity parameter (e.g.,κ) of unknown nanoparticles. Similar to step 1, size-resolved $F_{act}(D_d)$ can be measured for other kinds of nanoparticles. Their critical supersaturation at D_d can be directly calculated by $S_{cri}(D_d)=f^{-1}(1-F_{act}(D_d))$, and κ can be determined from S_{cri} and D_d by Eq. (4)."

Comments and suggestions:

Some details of the measurement setup are given in beginning of chapter 3.1. (instead of 2.3., where I would logically search for it), but a lot of information are missing. What was the polarity (positive/negative) of the size selected particles used for calibrations? What was used as the carrier gas? These things matter for the results (activation of particles in a CPC) especially in the sizes near or below 3 nm (see e.g. Winkler et al., 2008; Kangasluoma et al. 2013).
What is the model of your CPC? Include this information is chapter 2.2. A schematic picture of the whole nano-CCN instrument would also be helpful.

Responses and Revisions:

We have included detailed descriptions of our instrument setup in Section 2.4 along with a schematic picture:

"To demonstrate nano-CCNC, we used a WOx generator (Grimm Aerosol Technik, model 7.860; Steiner, 2006) to produce calibration tungsten oxide particles, and use an electrospray aerosol generator (TSI model 3480) to generate test nanoparticles (sodium chloride, ammonium sulfate and sucrose). The compress air and N_2 were used as the carrier gases for the WOx generator and electrospray, respectively. The salt and sucrose solutions were prepared in a standard 20 mM ammonium acetate buffer solution with a conductivity of 0.2 S m^{-1} (siemens per meter; Chen et al., 1995;Kupc et al., 2013).

As demonstrated in Fig. 4, the generated particles were passed through a neutralizer (Kr85, TSI model 3077), and a TSI nano-DMA (model 3085) was used to select positively charged monodisperse particles. A water-based CPC (TSI model 3788) was used as a nano-CCNC to measure N_{act} and a Faraday Cup Electrometer (Grimm Aerosol Technik, model 5.705) was used to measure N_{tot}. The variation of S distribution was achieved by varying the saturator temperature (T_s) from 284 to 296 K, while the growth tube temperature (T_{gt}) was fixed at 348 K. In total, seven $H(S)$ distributions were measured and each temperature adjustment takes 150 seconds for stabilization. ”

In addition, Figure 4 (as Figure R2) was added to show the schematic picture of the nano-CCNC system:

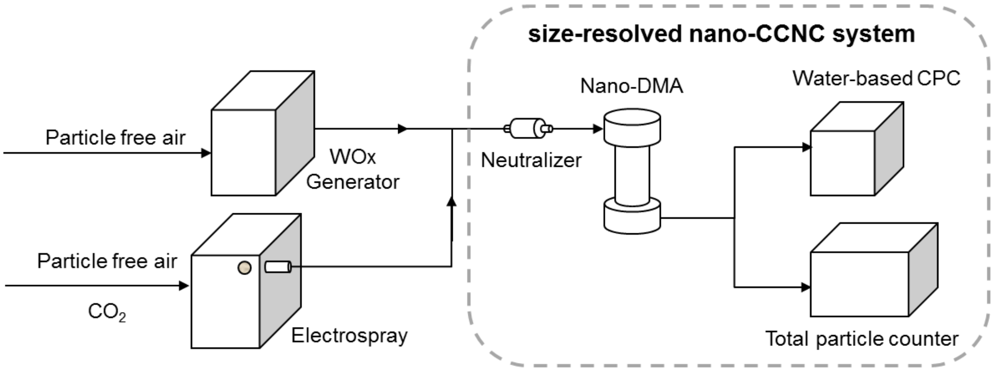

Figure R2: Schematic of the laboratory calibration. The proposed size-resolved nano-CCNC system is highlighted with square box.

Comments and suggestions:

Chapter 2.3.1. A 4th explanation of the broadening of the activation curves is that your sample is not clean (i.e. there is impurities coming from the tubing/neutralizer/sample which interfere with the results as the impurities have different activation properties than pure sample). This is a big issue in sizes below 3 nm (see Kangasluoma et al., 2013). Did you measure the composition of your sample (with a mass spectrometer)? As you do not describe the setup in enough detail, I cannot evaluate if this is an issue, but impurities could easily explain why you observe *a bi-modal distribution with the WOx (currently no explanation is given in chapter 3.1).*

Responses and Revisions:

We would like to thank the referee for the nice suggestion. The impurity might indeed be an explanation for the broadening of the activation curve. To address this issue, we performed additional measurements of activation curves for ammonium sulfate (AS), sucrose and WOx. As shown in Fig. R3, the calculated distributions of exposed supersaturation, *H*(*S*), show similar degrees of broadening for different chemical compounds (AS, sucrose and WOx) and different type of generators (electrospray generator and WOx burner generator). It is thus very likely that the impurity is not the major driving force for the broadening. We would like but unfortunately not able to measure the chemical composition with a mass spectrometer at this size range.

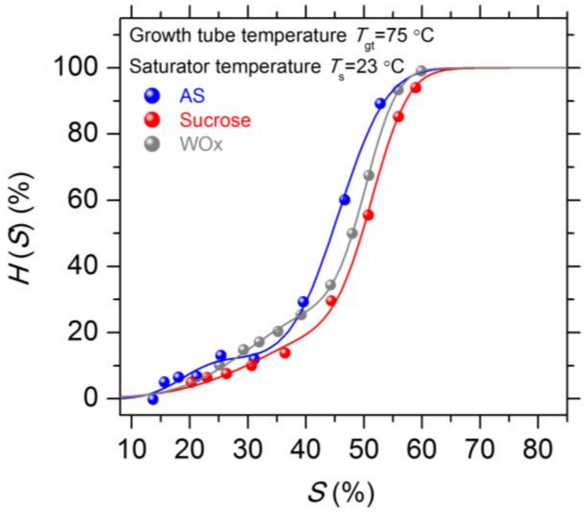

Figure R3: The distribution of *S* that nanoparticles have been exposed to inside CPC retrieved from the various chemical compositions.

Comments and suggestions:

What is the difference between solubility and solvoscopicity in this context? (There is a lot of references stating that particles soluble to the working fluid are activating in a CPC easier than insoluble ones). Can you compare the information you get from your systems, to the information from a HTDMA? You could discuss these issues in the conclusions and outlook chapter, which is currently quite restricted.

Responses and Revisions:

Solubility is the property of solute to dissolve in solvent to form a homogeneous solution while solvoscopicty is the ability of a substance to attract and hold solvent molecules from the gas phase. Take NaCl for example, the solubility describes the equilibrium between solid and liquid phase while hygroscopicity describes the equilibrium between gas and liquid phase. Solubility can influence the solvoscopicity but there is no one-to-one relation.

It is a very nice suggestion to compare our results with that from a nano-HTDMA. We would like to perform similar analysis as Petters and Kreidenweis (2007), in which κ values were compared between measurements of CCNC and HTDMA. We included the following discussion in the revised manuscript:

"In addition, a combination of nano-CCNC with nano-HTDMA might provide further insight into the concentration dependence of κ values at the nanosize range."

Comments and suggestions:

Abstract: I think the very first sentence should read: Knowledge on the chemical composition is essential….

Responses and Revisions:

Corrected.

Comments and suggestions:

Introduction, row 23: the sentence Chemical composition… is the key to understand… is very vague. Please be more specific. Why is it a key?

Responses and Revisions:

We have added more discussions to explain the importance of chemical composition:

"Though sulfuric acid has been confirmed essential for the particle growth, its condensation is two to four times slower than the observed growth rate for particles larger than ~1.7 nm (Kulmala et al., 2013). It is likely that low-volatility organic vapors are participating in the growth through condensation or heterogeneous reactions. Further investigation, however, is to a larger extent limited by the lack of measurement data in this size range."

Comments and suggestions:

Refer to Hering et al. (2005) when discussing water-CPCs in chapter 2.1

Responses and Revisions:

We have added this reference in the revised manuscript.

Comments and suggestions:

Figure 1 seems to be an adaptation of Kulmala et al. 2012 (Figure 1). Maybe there should be reference?

Responses and Revisions:

We have added this reference in the figure caption.

Comments and suggestions:

In chapter 2.2 you discuss different ways of scanning supersaturation. You should clearly mention which method was used in this study and the stabilization time of your system.

Responses and Revisions:

This information was included in section 2.4:

"The variation of S distribution was achieved by varying the saturator temperature (T_s) from 284 to 296 K, while the growth tube temperature (T_{gt}) was fixed at 348 K. In total, seven $H(S)$ distributions were measured and each temperature adjustment takes 150 seconds for stabilization."

Comments and suggestions:

Chapter 3.1. Wimmer et al. 2013 is surely not a correct reference for the WOx generator.

Responses and Revisions:

We added the correct reference for the WOx generator (Steiner, 2006).

References

Chen, D.-R., Pui, D. Y. H., and Kaufman, S. L.: Electrospraying of conducting liquids for monodisperse aerosol generation in the 4 nm to 1.8 μm diameter range, J. Aerosol Sci., 26, 963-977, http://dx.doi.org/10.1016/0021-8502(95)00027-A, 1995.

Ehn, M., Petäjä, T., Aufmhoff, H., Aalto, P., Hämeri, K., Arnold, F., Laaksonen, A., and Kulmala, M.: Hygroscopic properties of ultrafine aerosol particles in the boreal forest: diurnal variation, solubility and the influence of sulfuric acid, Atmos Chem Phys, 7, 211-222, 10.5194/acp-7-211-2007, 2007.

Gallar, C., Brock, C. A., Jimenez, J. L., and Simons, C.: A Variable Supersaturation Condensation Particle Sizer, Aerosol Sci. Technol., 40, 431-436, 10.1080/02786820600643339, 2006.

Jayne, J. T., Leard, D. C., Zhang, X., Davidovits, P., Smith, K. A., Kolb, C. E., and Worsnop, D. R.: Development of an Aerosol Mass Spectrometer for Size and Composition Analysis of Submicron Particles, Aerosol Sci. Technol., 33, 49-70, 10.1080/027868200410840, 2000.

Jiang, J., Zhao, J., Chen, M., Eisele, F. L., Scheckman, J., Williams, B. J., Kuang, C., and McMurry, P. H.: First Measurements of Neutral Atmospheric Cluster and 1–2 nm Particle Number Size Distributions During Nucleation Events, Aerosol Sci. Technol., 45, ii-v, 10.1080/02786826.2010.546817, 2011.

Jokinen, T., Sipilä, M., Junninen, H., Ehn, M., Lönn, G., Hakala, J., Petäjä, T., Mauldin Iii, R. L., Kulmala, M., and Worsnop, D. R.: Atmospheric sulphuric acid and neutral cluster measurements using CI-APi-TOF, Atmos Chem Phys, 12, 4117-4125, 10.5194/acp-12-4117-2012, 2012.

Kangasluoma, J., Kuang, C., Wimmer, D., Rissanen, M. P., Lehtipalo, K., Ehn, M., Worsnop, D. R., Wang, J., Kulmala, M., and Petäjä, T.: Sub-3 nm particle size and composition dependent response of a nano-CPC battery, Atmos. Meas. Tech., 7, 689-700, 10.5194/amt-7-689-2014, 2014.

Kulkarni, P., Baron, P. A., and Willeke, K.: Aerosol Measurement: Principles, Techniques, and Applications, 3rd Edition, John Wiley & Sons, Inc, Hoboken, New Jersey, 2011.

Kulmala, M., Mordas, G., Petäjä, T., Grönholm, T., Aalto, P. P., Vehkamäki, H., Hienola, A. I., Herrmann, E., Sipilä, M., Riipinen, I., Manninen, H. E., Hämeri, K., Stratmann, F., Bilde, M., Winkler, P. M., Birmili, W., and Wagner, P. E.: The condensation particle counter battery (CPCB): A new tool to investigate the activation properties of nanoparticles, J. Aerosol Sci., 38, 289-304, http://dx.doi.org/10.1016/j.jaerosci.2006.11.008, 2007.

Kulmala, M., Petäjä, T., Nieminen, T., Sipilä, M., Manninen, H. E., Lehtipalo, K., Dal Maso, M., Aalto, P. P., Junninen, H., Paasonen, P., Riipinen, I., Lehtinen, K. E. J., Laaksonen, A., and Kerminen, V.-M.: Measurement of the nucleation of atmospheric aerosol particles, Nat. Protocols, 7, 1651-1667, 10.1038/nprot.2012.091, 2012.

Kulmala, M., Kontkanen, J., Junninen, H., Lehtipalo, K., Manninen, H. E., Nieminen, T., Petäjä, T., Sipilä, M., Schobesberger, S., Rantala, P., Franchin, A., Jokinen, T., Järvinen, E., Äijälä, M., Kangasluoma, J., Hakala, J., Aalto, P. P., Paasonen, P., Mikkilä, J., Vanhanen, J., Aalto, J., Hakola, H., Makkonen, U., Ruuskanen, T., Mauldin, R. L., Duplissy, J., Vehkamäki, H., Bäck, J., Kortelainen, A., Riipinen, I., Kurtén, T., Johnston, M. V., Smith, J. N., Ehn, M., Mentel, T. F., Lehtinen, K. E. J., Laaksonen, A., Kerminen, V.-M., and Worsnop, D. R.: Direct Observations of Atmospheric Aerosol Nucleation, Science, 339, 943-946, 10.1126/science.1227385, 2013.

Kupc, A., Bischof, O., Tritscher, T., Beeston, M., Krinke, T., and Wagner, P. E.: Laboratory Characterization of a New Nano-Water-Based CPC 3788 and Performance Comparison to an Ultrafine Butanol-Based CPC 3776, Aerosol Sci. Technol., 47, 183-191, 10.1080/02786826.2012.738317, 2013.

Lehtipalo, K., Leppä, J., Kontkanen, J., Kangasluoma, J., Franchin, A., Wimmer, D., Schobesberger, S., Junninen, H., Petäjä, T., Sipilä, M., Mikkilä, J., Vanhanen, J., Worsnop, D. R., and Kulmala, M.: Methods for determining particle size distribution and growth rates between 1 and 3 nm using the Particle Size Magnifier, Boreal Environ Res, 19 (suppl. B), 215–236, 2014.

Marti, J. J., Weber, R. J., Saros, M. T., Vasiliou, J. G., and McMurry, P. H.: Modification of the TSI 3025 Condensation Particle Counter for Pulse Height Analysis, Aerosol Sci. Technol., 25, 214-218, 10.1080/02786829608965392, 1996.

Mordas, G., Manninen, H. E., Petäjä, T., Aalto, P. P., Hämeri, K., and Kulmala, M.: On Operation of the Ultra-Fine Water-Based CPC TSI 3786 and Comparison with Other TSI Models (TSI 3776, TSI 3772, TSI 3025, TSI 3010, TSI 3007), Aerosol Sci. Technol., 42, 152-158, 10.1080/02786820701846252, 2008.

O'Dowd, C. D., Aalto, P., Hmeri, K., Kulmala, M., and Hoffmann, T.: Aerosol formation: Atmospheric particles from organic vapours, Nature, 416, 497-498, 2002.

O'Dowd, C. D., Aalto, P. P., Yoon, Y. J., and Hämeri, K.: The use of the pulse height analyser ultrafine condensation particle counter (PHA-UCPC) technique applied to sizing of nucleation mode particles of differing chemical composition, J. Aerosol Sci., 35, 205-216, http://dx.doi.org/10.1016/j.jaerosci.2003.08.003, 2004.

Petters, M. D., and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, Atmos Chem Phys, 7, 1961-1971, 10.5194/acp-7-1961-2007, 2007.

Riipinen, I., Manninen, H. E., Yli-Juuti, T., Boy, M., Sipilä, M., Ehn, M., Junninen, H., Petäjä, T., and Kulmala, M.: Applying the Condensation Particle Counter Battery (CPCB) to study the water-affinity of freshly-formed 2–9 nm particles in boreal forest, Atmos Chem Phys, 9, 3317-3330, 10.5194/acp-9-3317-2009, 2009.

Sakurai, H., Fink, M. A., McMurry, P. H., Mauldin, L., Moore, K. F., Smith, J. N., and Eisele, F. L.: Hygroscopicity and volatility of 4-10 nm particles during summertime atmospheric nucleation events in urban Atlanta, J Geophys Res-Atmos, 110, D22S04, Artn D22s04
Doi 10.1029/2005jd005918, 2005.

Saros, M. T., Weber, R. J., Marti, J. J., and McMurry, P. H.: Ultrafine Aerosol Measurement Using a Condensation Nucleus Counter with Pulse Height Analysis, Aerosol Sci. Technol., 25, 200-213, 10.1080/02786829608965391, 1996.

Sipilä, M., Lehtipalo, K., Attoui, M., Neitola, K., Petäjä, T., Aalto, P. P., O'Dowd, C. D., and Kulmala, M.: Laboratory Verification of PH-CPC's Ability to Monitor Atmospheric Sub-3 nm Clusters, Aerosol Sci. Technol., 43, 126-135, 10.1080/02786820802506227, 2009.

Smith, J. N., Moore, K. F., McMurry, P. H., and Eisele, F. L.: Atmospheric measurements of sub-20 nm diameter particle chemical composition by thermal desorption chemical ionization mass spectrometry, Aerosol Sci. Technol., 38, 100-110, Doi 10.1080/02786820490249036, 2004.

Steiner, G.: Generierung von Nanopartikeln - Über die Konstruktion eines Heizdraht-Wolframoxidgenerators, Master Thesis, Faculty of Physics, University of Vienna, 2006.

Vanhanen, J., Mikkilä, J., Lehtipalo, K., Sipilä, M., Manninen, H. E., Siivola, E., Petäjä, T., and Kulmala, M.: Particle Size Magnifier for Nano-CN Detection, Aerosol Sci. Technol., 45, 533-542, 10.1080/02786826.2010.547889, 2011.

Wang, S., and Johnston, M. V.: Airborne nanoparticle characterization with a digital ion trap–reflectron time of flight mass spectrometer, Int. J. Mass Spectrom., 258, 50-57, http://dx.doi.org/10.1016/j.ijms.2006.07.001, 2006.

Weber, R. J., Stolzenburg, M. R., Pandis, S. N., and McMurry, P. H.: Inversion of ultrafine condensation nucleus counter pulse height distributions to obtain nanoparticle (~3–10 nm) size distributions, J. Aerosol Sci., 29, 601-615, http://dx.doi.org/10.1016/S0021-8502(97)10026-X, 1998.

Wimmer, D., Lehtipalo, K., Franchin, A., Kangasluoma, J., Kreissl, F., Kürten, A., Kupc, A., Metzger, A., Mikkilä, J., Petäjä, T., Riccobono, F., Vanhanen, J., Kulmala, M., and Curtius, J.: Performance of diethylene glycol-based particle counters in the sub-3 nm size range, Atmos. Meas. Tech., 6, 1793-1804, 10.5194/amt-6-1793-2013, 2013.

Zhao, J., Eisele, F. L., Titcombe, M., Kuang, C., and McMurry, P. H.: Chemical ionization mass spectrometric measurements of atmospheric neutral clusters using the cluster-CIMS, J Geophys Res-Atmos, 115, D08205, 10.1029/2009jd012606, 2010.