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Generation, characterization and sizing of sub-3 nm nanoparticles and molecular clusters

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Academic dissertation

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Abstract

Atmospheric aerosols exhibit the largest uncertainties in the radiative forcings of the Earth's climate. A large fraction of the uncertainties originates from the aerosol-cloud interactions, a process which is not understood completely. Understanding the processes related to aerosol formation and growth will help to narrow down these uncertainties and understand the anthropogenic fraction of the radiative forcings.

Atmospheric new particle formation creates a large fraction of the particles present in the atmosphere. To understand the process thoroughly, direct measurements of the particle concentration and chemical composition are needed. This need has pushed the instrument development forward, allowing measurements which were not possible five years ago: a direct measurement of the concentration and composition of sub-3 nm particles.

The purpose of this thesis was to develop methods to calibrate the instruments to reliably measure sub-3 nm particles. We developed an experimental setup to reproducibly generate well-characterized sub-3 nm particles in the laboratory, with the particular aim to characterize particle counters. During the course of the work the particle generation methods were modified to provide test aerosols smaller than 3 nm, of which chemical composition was monitored simultaneously with a mass spectrometer. Together with the modification of the generators, commercial fine particle counters were shown to be capable of sub-2 nm particle detection

Controlling the properties of the generated particles was found to be extremely important in the measurement of sub-3 nm particles. With the various test particles we studied the importance of the particle size, charging state and chemical composition on their detection, as well as the importance of the particle counter working fluid on the detection. The chemical composition of the particles was the most important factor determining the smallest detectable size in the sub-3 nm size range.

One of the particle counters, the Particle Size Magnifier (PSM) was characterized more in depth at low pressure conditions and various operation temperatures, providing in depth understanding on the instrument operation. The results provided key aspects on how the instrument should be operated in field experiments in order to obtain reliable data. In laboratory conditions the inversion routine of the particle PSM was experimentally verified against a high resolution differential mobility analyzer and an electrometer.

The results of this thesis provide basic knowledge on sub-3 nm particle generation and detection. The utilization of several generation techniques and test aerosols of different chemical composition, the operation of sub-3 nm particle detectors was improved along with a more in-depth understanding on the parameters governing the particle - vapor interactions. The laboratory instrumentation used in this thesis offer tools for chemical (composition) and physical (electrical mobility, charging state) characterization of the sub-3 nm particles. Overall this thesis improved the methods dealing with sub-3 nm particles from their generation to characterization, and to their detection. The methods are directly applicable to other fields of nanomaterial production and characterization, as well as environmental and industrial nanoparticle monitoring.

Keywords: sub-3 nm, cluster generation, particle counting, heterogeneous nucleation

Contents

List of publications

This thesis consists of an introductory review, followed by 5 research articles. In the introductory part, the papers are cited according to their roman numerals.

I   Kangasluoma, J., Junninen, H., Lehtipalo, K., Mikkilä, J., Vanhanen, J., Attoui, M., Sipilä, M., Worsnop, D., Kulmala, M., and Petäjä, T. (2013) Remarks on Ion Generation for CPC Detection Efficiency Studies in Sub-3-nm Size Range, *Aerosol Sci. Technol.,* 47, 556-563, Copyright 2013. Mount Laurel, NJ. Reprinted with permission.

II   Kangasluoma, J., Attoui, M., Junninen, J., Lehtipalo, K., Samodurov, A., Korhonen, F., Sarnela, S., Schmidt-Ott, A., Worsnop, D., Kulmala, M., Petäjä, T. (2015) Sizing of neutral sub 3 nm tungsten oxide clusters using Airmodus Particle Size Magnifier, *J. Aerosol Sci.*, 87, 53-62. Reprinted with permission.

III Kangasluoma, J., Ahonen, L., Attoui, M., Vuollekoski, H., Kulmala, M., Petäjä, T., (2015) Sub-3 nm particle detection with commercial condenser TSI 3772 and Airmodus A20 fine condensation particle counters, *Aerosol Sci. Technol*., 49, 674-681, Copyright 2015. Mount Laurel, NJ. Reprinted with permission.

IV Kangasluoma, J., Kuang, C., Wimmer, D., Rissanen, M. P., Lehtipalo, K., Ehn, M., Worsnop, D. R., Wang, J., Kulmala, M., and Petäjä, T. (2014) Sub-3 nm particle size and composition dependent response of a nano-CPC battery, *Atmos. Meas. Technol.*, 7, 689-700. Reprinted under Creative Commons licence.

V   Kangasluoma, J., Franchin, A., Duplissy, J., Ahonen, L., Korhonen, F., Attoui, M., Mikkilä, J., Lehtipalo, K., Vanhanen, J., Kulmala, M., Petäjä, T. (2015) Operation of the Airmodus A11 nano Condensation Nucleus Counter at various inlet pressures, various operation temperatures and design of a new inlet system, *Atmos. Meas. Technol. Discuss.*, 8, 8483-8508, Reprinted under Creative Commons licence.

1 Introduction

In the broadest context, the motivation for this thesis comes from the need to understand our atmosphere, its connections to the biosphere and human actions, and need to be able to predict how the atmosphere is going to change in the future based on the observations. The climate of the Earth has varied through the history as long as it can be tracked back to (Hansen et al., 2007), but during that time nothing like human species has existed on Earth (Steffen et al., 2007). During the past 400 000 years, the atmospheric CO_2 concentration has correlated relatively well with the surface temperature (Barnola et al., 2003). However, within the last century or so, the CO_2 concentration has increased dramatically due to the anthropogenic emissions, although the surface temperature has not risen as much as one could expect from the historical CO_2 and temperature time series (IPCC, 2014).

The radiative forcing of the Earth describes the balance, or usually imbalance, of the incoming and outgoing energy to and from the Earth due to greenhouse gases in the atmosphere. CO_2 contributes to the radiative forcing by absorbing the outgoing long wave radiation and trapping heat into the atmosphere. Therefore, an increase in the CO_2 concentration will cause a positive radiative forcing to which the atmosphere responds by warming up. Aerosol particles (termed simply aerosols hereafter), which are solid or liquid particles suspended in the surrounding gas, are known to contribute to the radiative forcing of the Earth by directly scattering the incoming solar radiation back to the space, or through aerosol-cloud interactions. While being able to contribute to the climate system, especially anthropogenic aerosols have adverse effects on human health, for example by lowering, the life expectancy of Chinese people by more than 5 years in certain areas (Chen et al., 2013).

Both radiative forcing mechanisms of aerosols most probably cause a net negative radiative forcing, i.e. a cooling effect. However, the current sum of all radiative forcings, mostly due to greenhouse gases, is positive, leading to the warming of the climate. The highest relative and absolute uncertainties in the radiative forcings are for aerosol radiative forcings (IPCC, 2014). Understanding and narrowing down these uncertainties is a task worth doing, since if the true forcing of aerosols is close to zero, then the human caused temperature increase is likely to stay rather small. On the other hand, the larger the aerosols' role in the prevention of the temperature increase, the larger the climate change will be in the future, when human starts to appreciate, and reduce, the health problems caused by anthropogenic aerosols.

Aerosols in the atmosphere are from primary and secondary sources. Primary sources include particles coming from volcanic emissions, industry, traffic, wood burning and so on (McCormick et al., 1995;Hildemann et al., 1991;Weckwerth, 2001;Kleeman et al., 1999;Andreae and Rosenfeld, 2008;Wang et al., 2005;Koulouri et al., 2008). Secondary particle formation means formation of particles from gaseous compounds in the atmosphere. Nearly half of the observed atmospheric aerosols in the troposphere are estimated to originate from the secondary aerosol formation processes (Spracklen et al., 2010).

In suitable conditions, a small subset of gas phase compounds can form small clusters of molecules. These clusters can subsequently grow by vapor condensation to sizes large enough to affect the radiative forcing of the Earth (Kulmala et al., 2004;Pöschl et al., 2010;Ehn et al., 2014;Laaksonen et al., 2005). The incomplete understanding of the secondary particle formation from the first molecules and molecular clusters, their growth and optical properties, as well as their interaction with water, is a substantial source of uncer-

tainty in the radiative forcing components of the atmosphere. In this thesis, we aim to provide understanding on the instrumentation to measure the number concentration of molecular clusters, and to probe their interactions with three different vapors.

Measuring the smallest molecular clusters is not a straightforward task. Current methods to measure the number concentration of nanoparticles are often based on condensational growth of the particles, followed by an optical detection (McMurry, 2000b). To begin the condensational growth, a high enough supersaturation of a vapor must be created around particles. Technology for growing and optically detecting the particles exists (McMurry, 2000a), but knowledge on surface – vapor interactions at very curved surfaces, such as the surfaces of the molecular clusters, is far from complete. Instruments based on measuring the electric current induced by the charge of particles are not well suited for atmospheric measurements in the sub-3 nm particle diameter range due to the low signal-to-noise ratio.

In laboratory, the first measurements utilizing the condensational growth of 3 nm ions in their detection were made by Bartz et al. (1985) and Scheibel and Porstendorfer (1986) with the low resolution instruments of that time. Later, more precise understanding of the quantities affecting the particle detection regarding the instrument design was shown by Stolzenburg and McMurry (1991), together with a design of the first commercial ultrafine Condensation Particle Counter (CPC). They demonstrated the importance of the particle sampling design in minimizing the diffusion losses of the particles, as well as how the volume and flows where the particle growth takes place should be designed. Seto et al. (1997) reported the first experiments on condensational growth of ions of approximately 1 nm in diameter. This observation led to further instrument designs and improvements, and research on growing small ions by condensation of vapor (Gamero-Castano and de la Mora, 2000;Kim et al., 2003). In the laboratory, with control over all the parameters governing the growth process, research has been conducted to understand the effect of particle composition (O'Dowd et al., 2004), condensing vapor composition (Iida et al., 2009), pressure (Hermann and Wiedensohler, 2001), ambient temperature (Quant et al., 1992) and relative humidity (Kangasluoma et al., 2013) on the operation of instruments able to detect sub-3 nm particles.

One of the first attempts to measure atmospheric sub-3 nm particle and cluster concentration was made by Kulmala et al. (2007b) with a combination of neutral air ion spectrometer (Manninen et al., 2009) and UF-proto CPC (Mordas et al., 2005). Later, similar research was published by Jiang et al. (2011b), who utilized a diethylene glycol CPC (Jiang et al., 2011a) in the same task together with a mass spectrometer, and by Sipilä et al. (2010) utilizing a particle size magnifier (PSM) (Vanhanen et al., 2011) in the detection of the sub-3 nm particles. After the work of Jiang et al. (2011b) and Sipilä et al. (2010), practically all atmospheric research on the sub-3 nm particle detection has been conducted with the instruments described by Vanhanen et al. (2011) and Jiang et al. (2011a), or a similar modification.

As noted for example by Iida et al. (2009) together with many others, the chemical composition of the particles must be taken into account when interpreting the data from sub-3 nm particle counters. This is due to the fact that the particle detection in a CPC strongly depends on the particle composition. They also noted that changes in the sample air relative humidity can affect the sub-3 nm particle detection with counters utilizing diethylene glycol.

After the pioneering experiments with the new generation of the particle counters, a significant amount of high profile research has been published (Kirkby et al., 2011;Almeida et al., 2013;Schobesberger et al., 2013a;Riccobono et al., 2014;Kulmala et

al., 2013;Ehn et al., 2014;Kulmala et al., 2012;Yu et al., 2012) on particle formation in the sub-3 nm size range, even if the exact calibration of the particle counters remains to be done. The uncertainties to be quantified are the effect of the particle chemical composition, charging state and sample flow relative humidity on the CPC activation efficiency, which should be solved for each experiment separately. Currently, the main obstacle in performing the CPC calibration is that the particle generation methods are insufficient. Even with a proper calibration of the CPC, uncertainties still remain in the data inversion (Lehtipalo et al., 2014), as no reference exists for the concentration measurement of neutral sub-3 nm nanoparticles.

In order to tackle the list of challenges presented above, the main objectives of this thesis are:
1) to build an experimental setup to generate sub-3 nm molecular clusters with a known composition, and without impurities, in a reproductive manner in atmospheric pressure (papers I, IV),
2) to verify sub-3 nm particle counters with the setup, and to understand the particle-vapor interactions as a function of particle properties (size, composition, charge state) and vapor composition (papers I, II, III, IV), and
3) to utilize this knowledge to enhance the capabilities of the current CPCs in the measurement of sub-3 nm particles (all papers).

2 Experimental methods

In this thesis, all particle sizes are given as electrical mobility equivalent diameters. This is due to the fact that the differential mobility analyzer (DMA) is the only viable tool for mobility classifying and further analyzing the particles at the sub-3 nm size range. Electrical mobility is essentially given by the ability of a charged particle to move in an electric field in some medium. In our case, the electrical mobility of a particle is defined by its shape and charging state, as the pressure of the surrounding gas is assumed to be constant and the particle inertia insignificant. Therefore, an electrical mobility measurement does not include the particle mass. If the measured particle is an ideal sphere, the obtained electrical mobility diameter is equivalent to the geometric diameter. For sphere-like big particles this assumption is valid, but for small sub-3 nm particles it is not. The difference between mass and mobility diameter has been studied, for example, by Larriba et al. (2011). In our case, we limit our analysis to the electrical mobility equivalent diameter, on which the particle size classification is based on. This should be noted when interpreting, for example, the experiments on CPC particle detection efficiency as a function of size and chemical composition.

In the CPCs particles are exposed to a high supersaturation of vapor, and condensation of vapor onto the surface of the particles occurs. This process is called heterogeneous nucleation, or particle activation. Homogeneous nucleation of vapor occurs when supersaturated vapor forms liquid droplets without the presence of seed particles. Often in experiments, the variable of interest is the heterogeneous nucleation probability, or the activation efficiency, which are defined as the ratio of the grown particles and the total number of particles. Due to the efficient diffusion of the smallest particles, a fraction of the particles entering the instrument is lost to the inlet walls before reaching the volume of a high supersaturation. Likewise, the optical detector of a CPC might not count all the grown particles. By combining the sampling losses, activation efficiency and counting efficiency of the optical detector, one obtains the detection efficiency of an instrument. Detection efficiency is the parameter of interest in a CPC calibration.

When the detection efficiency is measured as function of the particle size, one obtains a cut-off curve for a CPC, where the cut-off diameter is defined as the diameter of a particle for which the detection efficiency is 50%. If the cut-curve was measured in a traceable manner, which includes traceable flow and current measurement in the reference electrometer, one would obtain a CPC calibration (Yli-Ojanperä et al., 2010).

The research conducted in the papers of this thesis utilized various methods in the generation, characterization and detection of small nanoparticles. These methods will be presented briefly in this section, which is divided into generation, sizing and particle detection sections. All the utilized instruments are known from the previous literature, but some of them have been modified, or have been operated under conditions different from the factory settings in order to optimize their operation at the sub-3 nm sizes. A general experimental setup is presented in Figure 1, with the color labeling how the papers of this thesis are related to the experimental setup. In the experiments of this thesis, the generated aerosol is charged if needed, size selected with a differential mobility analyzer, and finally the charged size-selected nanoparticles are detected and counted with some combination of the detectors.
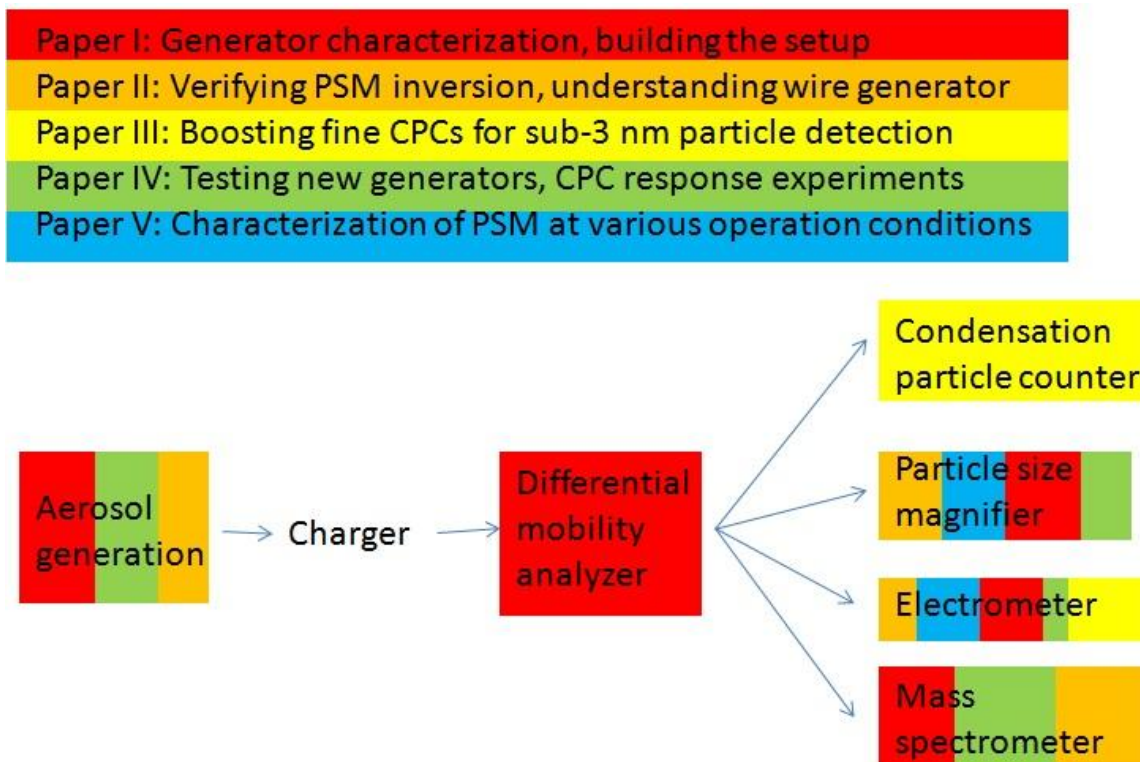
Figure 1. A generalized experimental setup used in this thesis.

2.1 Aerosol generation

2.1.1 Tube furnace

Tube furnace as an aerosol generator has been introduced by Scheibel and Porstendörfer (1983). Compressed dry air or N_2 flows through a ceramic tube, which is heated up. The sample is placed on a ceramic boat, which is inside the tube, and the sample is thermally vaporized to the gas stream. The sample melting temperature defines the furnace temperature, which is often set to some degrees below the melting point, depending on the other experimental conditions. The gas cools down when the flow exits the furnace, and supersaturation of a vapor takes place and nanoparticles are formed.

Practically, it is possible to aerosolize almost any solid sample with this method. The starting materials used in this thesis were ammonium sulfate (papers I, IV and V), sodium chloride (papers I and IV) and silver (Paper I), commonly used samples in CPC calibrations (Wiedensohler et al., 1997;Petäjä et al., 2006;Jiang et al., 2011a;Wimmer et al., 2013). When the furnace was used to generate sub-3 nm particles, the only difference in the operation was that the flow rate inside the tube was 10 – 15 liters per minute (lpm), compared to the conventional flow of 1 – 5 lpm. A water bath was placed immediately downstream of the furnace tube to facilitate the phase transition from the gas phase to the solid phase. The purity of the samples and tube inner surface was an important factor in determining the final particle composition. Nitrate and organic contaminants were found to be clustered with the formed particles, by means of mass spectrometry, if the tube of the furnace was not cleaned well before use. Cleaning the tube with acetone, methanol and Milli-Q water, and heating it up to 1200 ºC for several hours, resulted in the cleanest final particle composition.

2.1.2 Wire generator

A hot wire as nanoparticle source was introduced by Schmidt-Ott et al. (1980). A spring of thin metal wire, which is resistively heated up with high electric current, is placed into a hollow metal cross where gas stream passes by the wire. The hot surface of the wire emits vapor that rapidly cools down and forms nanoparticles into the surrounding gas. The only metal wire used in the experiments of this thesis was a tungsten wire (all papers). The restricting factor in choosing the wire material is vapor evaporation rate at the melting temperature of a particular metal, which is why, for example, gold is difficult to generate with this method. Successful experiments have been done at least with Ag, Fe, Be, Ni, Pt, Pd, W, Nb, Co and Zr wires (Peineke et al., 2006). The wire generator was selected as the particle source in paper II, since it provides a very stable source of sub-3 nm particles, part of which are self-charged. The formation of self-charged particles has already proven to be useful in the generation of charged sub-3 nm particles in the field conditions, enabling robust instrument verification at the sampling location. In paper II we studied the formation of self-charged clusters more deeply and provided an alternative explanation given earlier by Peineke and Schmidt-Ott (2008). They suggest electron emission from the wire surface as the provider of negative charge. Similarly, emission of K+ from the wire surface, which clusters with the neutral particles, provides positive charge for the particles. The formation of self-charged clusters is discussed more in section 3.1.1.

2.1.3 Electrospray

Electrospray is an instrument in which a sample is dissolved into a liquid, which is pushed at a high potential through a capillary needle. After exiting the capillary into a chamber, the liquid forms highly charged unipolar droplets in the surrounding electric field. Immediately after formation, solvent molecules start to evaporate from the droplets. Formation of charged sample molecules takes place via two mechanisms: after complete evaporation of the solvent charged residue of the sample is left or the charged sample molecules are emitted from the evaporating droplet.

Electrospray, together with a mass spectrometer, is a widely used tool in the field of chemistry. The basic requirements for successful ion generation with the electrospray are: the solvent liquid must be electrically conductive, and the sample must be dissolvable to the solvent. Common solvents include methanol, acetonitrile and 50/50 water and methanol. For his research on electrospray ionization combined to mass spectrometry, John Fenn was awarded the Nobel Prize (2002).

In this thesis, a home-made electrospray source was built, which was used in all the papers for generating big molecules of a known electrical mobility, especially tetraheptylammonium bromide (THABr (Ude and de la Mora, 2005)) positive monomer, $C_{28}H_{60}N+$ or THA+. This molecule was used to relate one DMA central electrode voltage to a known mobility, allowing the translation of the whole voltage range to electrical mobilities and electrical mobility equivalent diameters. In paper I, the electrosprayed ions were used to study the PSM detection efficiency. The utilized samples were other alkylhalides similar to THABr, and ionic liquids like 1-ethyl-3-methyl imidazolium tetraborofluoride (EMIBF$_4$, (Hogan and de la Mora, 2009)). In paper IV, electrospray was utilized to generate sucrose particles to provide another chemical composition of nanoparticles.

2.2 Differential mobility analyzer

Before any differential mobility analyzers (DMAs) existed, research on ions was mostly focused on mobilities of ions produced by X-rays (Thomson and Rutherford, 1896;Zeleny, 1898). Various innovative instruments were used to characterize and detect small air ions, as summarized by Flagan (1998). One of the many instrument designs, that by Zeleny (1900) already more than one hundred years ago, was close to the design of current mobility analyzers. It consisted of a cylindrical inner and outer electrode, of which the inner electrode was made of two separate pieces, the latter one being connected to an electrometer. With the instrument, Zeleny was able to measure mobilities of ions produced by X-rays. The main difference of Zeleny's instrument to the current DMAs was the second part of the inner electrode, which did not allow subsequent use and analysis of the ions. In 1921 Erikson (1921) presented the first true differential mobility analyzer. The geometry of the instrument was that of a parallel plate, where the bottom plate was divided into three sections and an electrometer was connected to the middle one. A polonium source was placed upstream of the electrometer, and the instrument was used to study ion aging.

The instrument of Erikson was modified for other experiments on air ions, and it took until 1957 when Hewitt (1957) published the first mobility analyzer, which closely resembles the current DMAs (schematic figure given in Figure 2): a flow with polydisperse particle population enters a gas stream from the edge of the outer electrode, and the charged particles start drifting according to their electrical mobility toward the inner electrode, as in Erikson's device. The major invention in the design of Hewitt was that a thin slit was placed at the end of the inner electrode, into which some of the charged particles drifted and were taken away as a monodisperse sample flow. Charged particles with too high electrical mobility drift too fast from the outer electrode to the inner one, and hit the central electrode before reaching the slit. Vice versa, the larger charged particles do not reach the slit, and are swept away by the sheath air flow. The charged particles of opposite electrical charge will be scavenged to the outer electrode. The instrument allowed for the first time subsequent analysis of size selected charged particles.

Later, another design of a DMA was built by Whitby (1966), which was accompanied with a charger and a detector to measure size distributions of atmospheric particles. It, however, did not have a slit at the end of the central electrode, but instead a collecting grid, which counted all particles being able to avoid hitting the central electrode. The instrument was thereby used to measure cumulative size distributions. The design became later the TSI model 3000 Whitby Aerosol Analyzer, with one downside: it weighed 182 kg. Due to its power of measuring size distributions, Liu et al. (1974) developed the next version with a weight of only 24 kg, but with the same functionalities, sold by TSI as the model 3030 Electrical Aerosol Analyzer. A year later Knutson and Whitby (1975) characterized a similar DMA as designed by Hewitt, which was to become the standard way of conducting particle mobility analysis, and to be used as a tool to generate size selected particles for instrument calibrations and verifications. Together with the experimental characterization of their DMA, a sound theoretical understanding on the DMA transfer function was provided. The transfer function "*describes the probability that an aerosol particle which enters the mobility analyzer via the aerosol inlet will leave via the sampling flow, given that its mobility is Z_p*" (Knutson and Whitby, 1975). Another successful DMA based on the Hewitt design was published by Winklmayr et al. (1991), which is widely used today. In the conventional DMAs the shape of the transfer function is triangle, of which the width is determined by the ratio of the aerosol flow rate and the sheath flow rate

(Stolzenburg and McMurry, 2008). The resolution of a DMA is given as the ratio of the transfer function peak voltage and full width at half maximum of the transfer function.

Conventional DMAs operate at sheath air flow rates of $3 - 28$ lpm and aerosol flow rates of $1 - 5$ lpm (Zhang et al., 1995;Birmili et al., 1997), which is not optimal for mobility classification of sub-3 nm particles. Low flow rates and not optimized geometry of the conventional DMAs lead to a wide transfer function at the sub-3 nm size range (Stolzenburg, 1988). Therefore, in recent years, much effort has been put to develop DMAs that are optimized for sub-3 nm mobility analysis, including the designs published by Steiner et al. (2010);de la Mora and Kozlowski (2013);Santos et al. (2009);Brunelli et al. (2009) and Herrmann et al. (2000). Of these, the Herrmann-type DMA (Herrmann et al., 2000) was used in all of the papers of this thesis, and the half-mini type (de la Mora and Kozlowski, 2013) was used in paper IV.

The Herrmann-type DMA is a high resolution DMA, which utilizes extremely high sheath air flow rates (~300 - 1000 lpm) to achieve high resolution with a rather low transmission in the sub-3 nm size range. As the exact sheath air flow rate of the Herrmann type DMA is not known due to the lack of high flow rate measurement in our laboratory, the voltage axis is always converted to mobility axis by generating THA+ ion and measuring its peak voltage. Since the mobility of the generated ion is known, it allows the conversion from electrode voltage to electrical mobility. The theory of the cylindrical DMAs does not apply for the high resolution cylindrical DMAs, since the flow profile is not parabolic as in conventional low flow rate DMAs.

Achieving the high resolution with the low transmission is a reasonable trade-off in laboratory experiments, since usually the particle generators produce high enough particle concentration to be detected downstream of the DMA. From some samples, the high resolution allows selection of perfectly monomobile particles, like for example the DMA calibration ion THA+. Monodisperse particles further allow particle detector characterizations as a function of size, such as measurement of transmission, detection probability, particle fragmentation inside the instruments, and so on.

In this thesis an air-tight, closed sheath flow loop high resolution DMA setup was built around the Herrmann type DMA. It is presented in Figure 3, which is adopted from paper I. By closing the loop of the DMA, the sheath air flow recirculates and is eventually replaced by the entering gas (Jokinen and Mäkelä, 1997). A high-efficiency particulate arrestance (HEPA) filter connected to the sheath air loop removes all particles from the sheath air flow, and the flow is kept at the room temperature with a heat exchanger. Importantly, the closed loop keeps the relative humidity of the sheath air flow, and the outgoing sample flow, at the same level as of the aerosol flow, which is challenging to accomplish with an open loop sheath air flow. Since the relative humidity of the aerosol flow often in the laboratory experiments is close to zero, also the monodisperse sample flow is dry. The effect of the relative humidity on the particle detection is discussed in later sections. The closed loop DMA setup was built on a table with wheels, which helped in the construction and modification of the experimental setups. Overall, the high resolution DMA was as important part of the thesis as the particle generators and detectors.
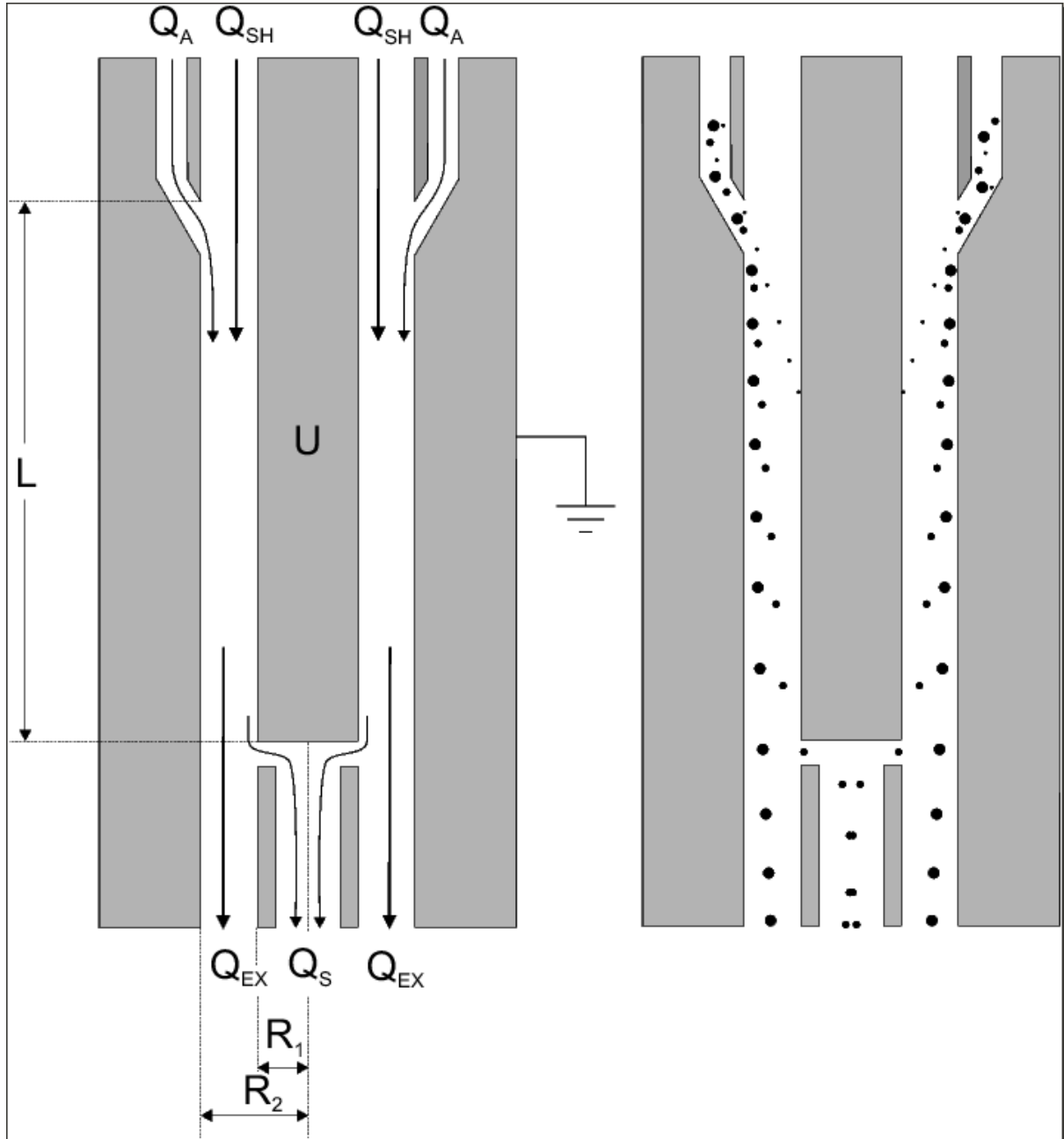
Figure 2. Schematic figure of a differential mobility analyzer. Aerosol flow (Q_a) enters the DMA from the edge of the grounded outer electrode parallel to the sheath flow (Q_s). In the size selection regime of length L and width R_2-R_1, the negative/positive particles drift toward the inner electrode at potential +/-U. Particles of a certain electrical mobility will exit the DMA together with the sample flow (Q_s). The rest of the flow exits the DMA as exhaust flow (Q_{ex}).
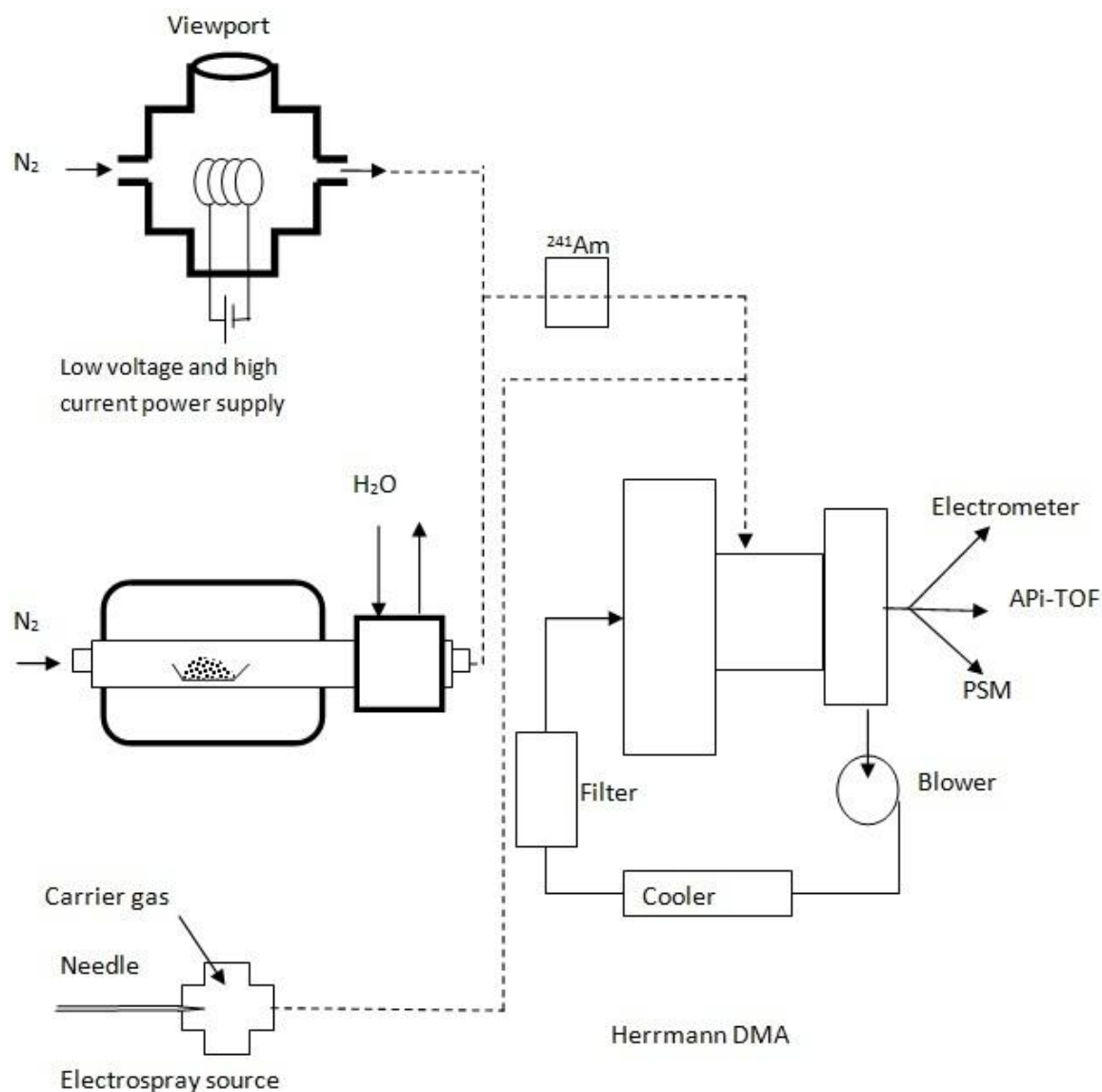
Figure 3. The experimental setup presented in paper I. Three different aerosol generators were used: a wire generator (top), a tube furnace (middle) and an electrospray (bottom). The generated particles were charged before entering the high resolution Herrmann type DMA. The closed sheath air flow loop DMA was built around the Herrmann DMA. From the DMA the sample was split to the electrometer, the APi-TOF and the PSM. The PSM detection efficiency as a function of test aerosol chemical composition was studied.

2.3 Particle detectors

Particle detectors used in this thesis can be separated into a mass spectrometer (Junninen et al., 2010) and single particle counters (Vanhanen et al., 2011;Kuang et al., 2012;Iida et al., 2008;Stolzenburg and McMurry, 1991).

2.3.1 CPC and PSM

Condensation particle counters (CPCs) are the backbone of aerosol research. History of the CPCs is given by McMurry (2000a), and another historical review on the work of Coulier and Aitken is given by Spurny (2000). In our review, we examine the work related to development of CPCs, which are capable of detecting particles smaller than 3 nm. In the review we refer to a CPC as often done nowadays, even if at the time of the research was conducted, the instruments had many different acronyms.

The first CPC experiments were conducted by Coulier (Coulier, 1875a, b) and Aitken (Aitken, 1880b, a), and further continued by Wilson (Wilson, 1897). These first CPCs were expansion type instruments always operated with the water vapor of the sample flow. In the expansion type instruments, a known volume is expanded to achieve supersaturation of working fluid. The grown droplets were detected with naked eye due to lack of optical technology. Already the first expansion type CPCs were able to detect sub-3 nm particles, since they were able to activate and grow ions produced by the X-rays, as well as produce homogeneously formed droplets from water. However, due to the lack of a proper 3 nm particle source, Kurten et al. (2005) were the first to show 3 nm particle detection with an expansion type CPC. Another commonly used method for creating supersaturation, mixing of warm flow that is saturated with vapor with another cooler flow, was invented in Russia by Kogan and Burnasheva (1960). The method was initially used to produce homogeneously formed droplets. Kousaka et al. (1982) built probably the first mixing CPC capable of sub-3 nm particle detection, however, with experiments only down to 6 nm. After Okuyama brought the mixing CPC technology to America and Yale, de la Mora and his coworkers focused their research on small ion activation and various designs of the PSM. The latest push to commercialize and make the mixing CPC technology, and the PSM as research instrument available for everyone, was made in Finland. The work of Bricard et al. (1976) showed the first laminar type diffusion based CPC that operated with an alcohol as condensing liquid. The design of their instrument is still in use in current laminar CPCs. It took until 1991, when Stolzenburg and McMurry (1991) optimized a laminar CPC down to sub-3 nm particle detection with a proper calibration setup, data analysis and inversion.

Many reviews and reports on calibration workshop results have been published during the last 20 years. Bartz et al. (1985) report results from the first CPC workshop where the smallest possible particles were tried to be detected. Wiedensohler et al. (1994) report a comparison of four ultrafine particle sizing systems: ultrafine DMPS, ultrafine diffusion battery, pulse height ultrafine CPC and temperature scanning by an ultrafine CPC. Sem (2002) gives an extensive review on the TSI butanol CPCs 3010, 3020 and 3025, in which results from many different experiments are collected. Hermann et al. (2007) show results on a TSI CPC calibration workshop, where most of the TSI CPC models are calibrated. Similar TSI CPC comparison is given by Mordas et al. (2008). Wimmer et al. (2013) and Kangasluoma et al. (2014) give the latest results of ultrafine of CPC calibration workshops. As part of this thesis, a broader review of sub-3 nm particle detection is given.

Before aerosol sizing instrumentation was available, most CPC calibration experiments were conducted against the Pollak counter (Pollak and Daly, 1957), which was thought to give a reliable number concentration measurement. Many experiments were focused to measure atmospheric particle number concentration, whereas laboratory experiments were made at the limit of homogeneous droplet formation or ion induced nucleation. Therefore, it may have been thought that the counters can count all the particles above the Kelvin diameter at the supersaturation slightly below the limit of homogeneous

nucleation. The Kelvin diameter gives the theoretical prediction for the smallest particle size that can be grown by a certain liquid without the presence of homogeneous droplet formation. The Kelvin diameter does not take into account the properties of the particle, like its solubility. For most of the liquids that can be considered as a CPC working liquid, the Kelvin diameter is from 2 to 4 nm (Iida et al., 2009).

The first note on the size dependency of a CPC detection efficiency was published by Liu and Kim (1977), and a year later by Porstendörfer and Soderholm (1978). Liu and Kim calibrated their GE CPC against an electrometer with atomized and heated NaCl particles, which were size classified by a DMA. Porstendörfer and Söderholm generated small fairly monodisperse silver and gold particles with a boiler, and size selected them with a diffusion battery. A clear size dependency was found in the detection efficiency between particles of 10 nm and 30 nm, and the obtained values were much lower than for an atmospheric particle sample. Both groups concluded that it is difficult to use a CPC to measure the particle concentration of an unknown size distribution.

The finding of Porstendörfer and Soderholm (1978) and Liu and Kim (1977) initiated research deeper into the operation and design of various CPCs. Thanks to the introduction of a DMA and an electrometer, a standard calibration setup for a CPC (Knutson and Whitby, 1975) it was possible probe and optimize various parameters of the CPCs. The key inventions in the calibration setup were two methods to generate ultrafine particles, which were heating of material in a tubular furnace (Scheibel and Porstendörfer, 1983), and atomization of material and subsequent evaporation and condensation (Bartz et al., 1987), as well as the first DMA to size select particles (Liu and Pui 1975, Knutson and Whitby 1975).

These tools were put to work by Bartz et al. (1985), who published the first results from an ultrafine CPC calibration workshop, in which four different CPCs (expansion CPC by Niesser, TSI 3020 by Argaval, CCU CPC by Stolzenburg and McMurry and MTU CPC by Kousaka) were optimized for ultrafine particle detection. The MTU and CCU CPCs showed the detection efficiency of 0.6 and 0.83, respectively, for 3 nm sodium chloride particles. The workshop clearly demonstrated the importance of the instrument design in sampling and detection of sub-3 nm particles. In 1984, another significant instrument design was published, when Okuyama et al. (1984) published their design of a mixing type CPC, a particle size magnifier (PSM), and its activation of particles down to 6 nm. Lack of suitable calibration setup, however, hindered the success of the Okuyama PSM, until the year of 1997.

Probably the main milestone in the detection of sub-3 nm particles was reached in 1991, when Stolzenburg and McMurry (1991) published their ultrafine CPC, modified from the TSI 3020. It was the prototype of the ultrafine CPCs TSI 3025A and 3776. The instrument design included various improvements to the previous laminar CPCs, including optimized inlet with two core sampling probes together with a condenser with sheath air flow, which was originally introduced by Wilson et al. (1983). The inlet has a high transport flow of 1.5 lpm, from which 0.3 lpm is extracted by core sampling. The flow is subsequently brought into a small capillary leading to the condenser, which extracts another 0.03 lpm (in 3025A) from the middle of the flow. The rest is filtered and taken to the saturator, and finally brought back to the condenser around the capillary as the sheath air flow. A major fraction of the diffusion losses, which can be determined theoretically, occur in the capillary needle. The condenser design takes advantage of the fact that the peak supersaturation is located in the middle of the condenser by feeding the sample to the center line. Other milestones of their research were the reasonable agreement of a theoretical

model of the CPC detection efficiency in comparison to the experiments, and detailed handling of the data, leading to the final detection efficiency values.

Soon after the publication of the ultrafine CPC, an independent calibration of the TSI 3025A with similar results as Stolzenburg and McMurry (1991) was published by Kesten et al. (1991). The first modification to the 3025A was published during the same year, when McDermott et al. (1991) showed the operation of the CPC with a fluorinated liquid, optimized flow configuration and condenser design. The modification resulted in detection efficiencies closer to unity compared with the previous operation conditions. Additionally, McDermott et al. (1991) showed the particle sizing capability of the modified CPC between 3 and 10 nm by scanning the condenser temperature.

The method of McDermott, and other methods for sizing low concentrations of ultrafine particles, was compared by Wiedensohler et al. (1994). The comparison included the modified 3025A with white light optics for the pulse height analysis of the final droplet size, published later by Saros et al. (1996). The pulse height analysis relies on the fact that the final droplet diameter of a grown particle is dependent on the initial particles size. The smaller the particle, the closer towards the end of the 3025A condenser it activates and starts to grow, therefore has less time to grow. This results in an observation that the smaller the initial particle, the smaller the final droplet will be. The white light scattered from the droplets is dependent on the droplet size, allowing thereby the sizing of the initial particle size. Saros et al. (1996) concluded that the pulse height analysis is applicable for various operation conditions and particle compositions, as long as a pulse height reference from the bigger ambient particles is available. Weber et al. (1998) presented data inversion for the pulse height distributions.

After the work of Stolzenburg and McMurry (1991), the next improvement in the operation of laminar type CPCs toward sub-3 nm particle detection was made by Mertes et al. (1995) and Wiedensohler et al. (1997). They showed that by increasing the temperature difference between the condenser and the saturator of the TSI 3010, it is possible to detected particles down to 4 nm and 2.5 nm, respectively. These results showed that even the conventional fine CPCs are capable of detecting very small particles. The particle detection is mostly limited by sampling losses, non-uniform saturation field and, at that time, by the lack of suitable sub-3 nm particle generation setups. With a reasonable sub-3 nm particle source, Kangasluoma et al. (2015a) showed that the commercial fine CPCs are capable of even sub-1.5 nm particle detection.

The first time when a CPC capable of detecting sub-2 nm ions met a high resolution DMA with an appropriate particle generator (electrospray) was when the PSM of Okuyama was applied by Seto et al. (1997). The working fluid of the PSM used by Seto was dibutyl phthalate (DBP). The experimental setup was applied for investigating the ion induced nucleation, especially the sign preference, as DPB was found to favor the activation of positive ions only. A similar sign preference has also been found by Okuyama et al. (1991) and Adachi et al. (1992) for DBP. The author of this thesis remarks that in the experimental research of that time, not much attention was paid to the chemical composition of the ions, which was later shown to tremendously affect the activation of small ions (O'Dowd et al., 2004;Petäjä et al., 2006;Kangasluoma et al., 2014).

Further improvement to the PSM design from Yale University was made by Gamero-Castano and de la Mora (2000, 2002), accompanied with a calibration setup consisting of an electrospray and a high resolution DMA. Their improvement included a reheater of the saturator flow between the saturator and the mixing section, which minimized the working fluid loss before the mixing section and, therefore, allowed more accurate estimation of the fluid supersaturation in the mixing zone. The reheater also prevented

the working fluid from nucleating homogeneously before the mixing section, further allowing most of the vapor to condense heterogeneously onto the sample particles in the mixing section. The experimental setup of Gamero (Gamero-Castano and de la Mora, 2000) provided a setup to investigate the activation of various ions by DBP. They showed that when the sample particles are small enough, the activation probability does not depend on the particle size anymore. This feature has been predicted by the theory (de la Mora, 2011), but to date still has not been confirmed by other experimental researchers. Gamero also illustrates how the PSM can be used at different levels of supersaturation to obtain insights on heterogeneous nucleation.

Kim et al. (2002) presents another version of the PSM, which was conveniently able to detect 3 nm particles activated by ethylene glycol. Ethylene glycol was selected as the working fluid based on its low vapor pressure and harmlessness. New in their work was the extensive probing of the PSM operation below normal atmospheric pressure. The performance was found not to change dramatically at pressures down to 200 torr, enabling the PSM design to be used at high altitudes. Kim et al. (2003) published another version of the PSM, which was based on the modifications made by Sgro and de la Mora (2004). It is the simplest version of the PSMs published so far, with only one aerosol injection tube and T-shaped mixing chamber. This PSM was characterized to detect sub-2 nm particles, with remarks on ion induced nucleation. Ethylene glycol was found to prefer nucleation on negative ions. One year later Sgro and de la Mora (2004) published their version of the PSM, in which the new aerosol injection design improved the penetration of the smallest particles. This PSM was found to be capable of activating 1.7 nm (electrical equivalent mobility diameter) ions at 100% efficiency.

The aim of the previous mixing CPCs was to detect particles as small as possible. For measurements where the sample concentration varies rapidly, the response time of the CPC is an important factor. The response time was optimized by Wang et al. (2002) in their fast mixing CPC. By having a 0.65 lpm flow through the detector with fast response time, the CPC is an ideal detector in particle sizing systems with scan time even down to 1 s.

Three more independently developed mixing CPCs are by Mavliev and Wang (2000) and Mavliev (2002), which operated with DBP as working fluid and was capable of activating 3 nm particles. Ito et al. (2011) published a PSM which was operated with ethylene glycol as working fluid, and Kim et al. (2015) studied the temperature dependence of heterogeneous nucleation with their PSM operated with DEG as working fluid.

The first water based laminar CPC was designed by Hering et al. (2005). It exploits the high diffusivity of water by first cooling down the sample flow and subsequently heating it up in the condenser with water wetted walls. This design was commercialized as the TSI model 3785 fine particle counter, with cut-off diameter somewhere between 4 to 30 nm depending on the test aerosol composition (Petäjä et al., 2006). Later, the water CPC was modified by adding a similar condenser sheath flow design as in the 3025A. The design of the ultrafine water CPC was characterized by Iida et al. (2008) and Mordas et al. (2008).

The work with the water CPCs showed that the CPC response is sensitive to the composition of the sampled aerosol particles. Similarly, as noted by O'Dowd et al. (2004), the chemical composition of the test aerosol will affect the pulse height distributions of the droplets grown by butanol. Therefore, it became evident that the composition of the test particles will have a significant effect on the CPC cut-off diameter. Indeed, the composition dependent cut-off diameter has been used in instruments, the purpose of which is to infer information about the chemical composition of atmospheric aerosol (Kulmala et al.,

2007a;Kangasluoma et al., 2014). The idea is based on the fact that two CPCs with two different working fluids can be tuned for identical performance in activating insoluble calibration aerosol particles, while the other CPC being able to activate smaller particles, which are soluble to its working fluid. Practically, for example when a butanol and a water based CPC are tuned to exhibit a similar cut-off curve for insoluble silver particles, the water based CPC can activate smaller particles of NaCl than the butanol CPC due to solubility effects.

In 2005 an expansion CPC was developed, which was the first time when the detection efficiency of an expansion CPC was characterized down to 3 nm by Kurten et al. (2005). Their CPC utilized an optical detector based on Mie scattering developed by Wagner (1985), which follows the size evolution of the growing droplets with a high time resolution. The detection method provides information on the supersaturation, and is an absolute concentration measurement. Furthermore, it allows separation of homogeneous and heterogeneous nucleation. An expansion CPC built by the Vienna group, the so-called size analyzing nuclei counter (SANC), utilizes the same sophisticated optics by Wagner (1985). Starting from the year 2008, the Vienna group has published a variety of experimental studies on heterogeneous nucleation. Winkler et al. (2008b) showed that CPCs can be made sensitive to 1.4 nm particles without the presence of homogeneous nucleation when operated with n-propanol. They further used their expansion CPC to show that n-propanol prefers the activation of negative ions over positive ions, for the first time taking into account also the size selected neutral particles (Winkler et al., 2008a). Other notable research by the Vienna group are their findings on the critical cluster size (Winkler et al., 2012), building of the mobile SANC (Pinterich, 2015) and other publications on heterogeneous nucleation (Winkler et al., 2011;Kupc et al., 2013).

After the high resolution DMA technology reached the groups of Helsinki and Minneapolis, the next steps of sub-3 nm CPC development were taken in the development of the laminar CPCs. Sipilä et al. (2008) and Sipilä et al. (2009) modified their version of a pulse height CPC from the TSI 3025A, which was operated at supersaturation high enough to produce homogeneously formed droplets. They noticed that homogeneously formed droplets grow to smaller final droplet sizes than heterogeneously formed, which can be separated in the pulse height analysis. Sipilä and coworkers applied this technology to measure small neutral ambient clusters. Their interest in atmospheric new particle formation soon after led to another design of the Okuyama PSM, the design again close to the one made by Sgro and de la Mora (2004). The PSM was for the first time applied in chamber measurements in Leipzig together with the pulse height CPC (Sipilä et al., 2010), and commercialized by Airmodus (Vanhanen et al., 2011) (Figure 4), sold today as the Airmodus A11 nano Condensation Nuclei Counter (nCNC).

Meanwhile, the group of Minneapolis began their second wave of sub-3 nm CPC development with the work of Iida et al. (2009), who theoretically studied hundreds of different liquids, and concluded that diethylene glycol was the best one to be used as a CPC working fluid. This was due to the low vapor pressure and high surface tension, together with the fact that it is odorless and harmless. Their theoretical prediction was in a sound agreement with the experiments, which were conducted with a modified TSI 3025A. The main modification to the CPC was that the optical counter was removed, and another TSI fine CPC was placed instead to count the particles that did not grow inside the 3025A to optically detectable sizes. Based on the work of Iida et al. (2009), Jiang et al. (2011a) used the modified TSI 3025A, operated with DEG, as a detector in a particle sizing system to observe atmospheric new particle formation (Jiang et al., 2011b). With similar modifications to the 3025A, Kuang et al. (2012) boosted their DEG 3025A further by

modifying the flow configuration, mainly by changing the aerosol and condenser flow rates. Wimmer et al. (2013) modified two TSI 3025As in similar fashion as Jiang et al. (2011a) and Kuang et al. (2012), and verified the instruments together with the two first PSMs by Airmodus. All these modified DEG CPCs were shown to have the cut-off diameter below 2 nm for negative sodium chloride particles and other substances, without the presence of homogeneously formed droplets(Jiang et al., 2011a;Kuang et al., 2012).

The most recent work on understanding and extending the operation of the CPCs was conducted as a part of this thesis, first by applying a mass spectrometer to measure the composition of the test particles, as well as showing more accurately the sample flow humidity dependence of the heterogeneous nucleation by DEG (Kangasluoma et al., 2013) (Paper I). We explained the apparent sign preference of DEG to negatively charged particles, as often positively charged particles were contaminated by organic molecules (Paper II). These conclusions were further supported in the following paper (Kangasluoma et al., 2014) (Paper IV), where four different ultrafine CPCs were boosted to the limit of homogeneous nucleation, and verified with seven different test particles. DEG and water activated more easily inorganic salt particles than organic particles. Furthermore, our research contributes to the size distribution measurements of neutral sub-3 nm particles by showing the accuracy of the PSM measurement and inversion against a high resolution DMA and electrometer (Kangasluoma et al., 2015b) (Paper II). In spite of the strong composition dependency of the PSM detection efficiency, with a sound calibration it was shown to reliably measure size distributions of neutral sub-3 nm tungsten oxide clusters. Our next paper continued the work of Mertes et al. (1995) and Wiedensohler et al. (1997) by boosting two fine CPCs to their maximum supersaturation and showing their capability of detecting sub-1.5 nm charged particles with an efficiency comparable to the ultrafine TSI 3776 (Kangasluoma et al., 2015a) (Paper III). Finally, in the last paper of this thesis, we inspected technical details of the PSM of Vanhanen, namely its response to various inlet pressures, various inlet temperatures, the effect of temperature settings on the whole operation of the instrument, as well as we present an inlet line system optimized for sub-3 nm particle sampling (Kangasluoma et al., 2015c) (Paper V).

The PSM (Airmodus A10) used in this thesis is shown in Figure 4. The flow through the saturator (0.1 – 1 lpm) is saturated with DEG. A 2.5 lpm sample flow is mixed with the saturator flow in the mixing section, and subsequently brought to the growth tube. The temperature of the saturator is usually between 70 ℃ and 90 ℃, the inlet temperature is between 0 ℃ and 40 ℃, and the growth tube temperature is between 0 ℃ and 10 ℃, depending on the experiment. The particles grow up to approximately 90 nm in the growth tube, and are subsequently detected with another fine CPC. This arrangement of the Airmodus A10 PSM and A20 CPC is the A11 nCNC.
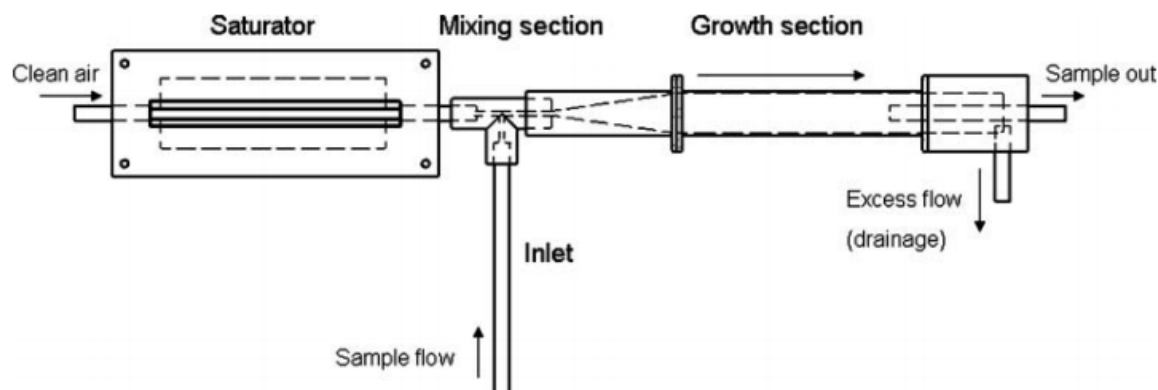
Figure 4. A schematic figure of the Airmodus A10 Particle Size Magnifier (from Vanhanen et al. 2011). The grown particles which exit the PSM are counted with the Airmodus A20 butanol CPC. The combination of the A10 PSM and A20 CPC is called Airmodus A11 nCNC.

2.3.2 APi-TOF

Particle chemical composition is an important parameter determining heterogeneous nucleation probability. In this work, the mass and chemical composition of the sub-3 nm particles was measured with an Atmospheric Pressure interface Time Of Flight mass spectrometer, APi-TOF (Junninen et al., 2010). The instrument is ideal for the experiments, since the sample particles can be generated and fed to the mass spectrometer directly from the atmospheric pressure. The pressure is reduced in four sections from the ambient pressure down to ~$10e^{-6}$ mbar. The ions are guided with two quadrupoles and ion lenses to the time of flight chamber (Figure 5). In the time of flight chamber, all ions receive an equal kinetic energy from a high frequency electric field. Since the kinetic energy is proportional to the mass and square of the velocity, particles of different mass obtain different velocities. The flight distance is known in the chamber; therefore the measured flight time of a charged particle can be converted to a mass-to-charge ratio.

The design of the instrument allows an approximate transmission between 0.1% and 0.5% depending on the inlet tuning, and mass resolution of 5000 (Junninen et al., 2010). This mass resolution is sufficient for separating molecules of the same integer mass but different exact mass, the difference being termed as mass defect. Due to the binding energies in the core of the atoms, for example tungsten oxide charged with OH-, WO_3OH-, exhibits an exact mass of 248.939 atomic mass units (amu) giving the mass defect 248.939 amu - 249 amu = - 0.061 amu. At 249 amu the full width at half maximum (FWHM) with resolution 5000 is 0.05 amu, allowing clear separation of the tungsten oxide clusters from others. Combined with the mass defect, the isotopic pattern of the particles reveal in most cases the exact molecular formula of the observed peaks in the mass spectrum. In papers I, II and IV, the APi-TOF played a crucial role in verifying the sample aerosol composition and in the development of particle generators.
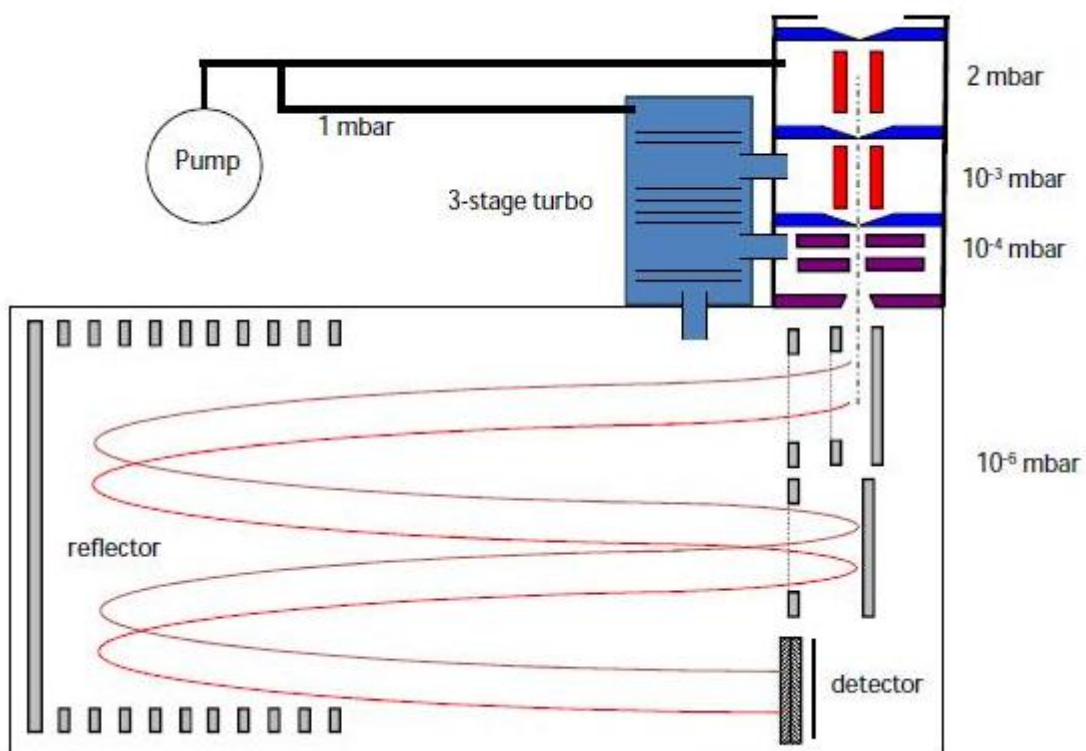
Figure 5. A schematic figure of the Atmospheric Pressure interface Time Of Flight mass spectrometer (taken from Junninen et al. (2010)).

3 Results and discussion

3.1 Generation of aerosol particles for instrument calibrations in sizes below 3 nm

3.1.1 Characterization of charged particles

Since sulfuric acid is known to be an important part of atmospheric new particle formation (Sipilä et al., 2010;Kuang et al., 2008;Lovejoy et al., 2004), ammonium sulfate was selected as a starting material for the first experiments with the tube furnace. The composition of the formed, and subsequently charged, clusters was found to be mostly bisulfate in the smallest negative clusters. The composition of the formed clusters and particles was given by the formula $(HSO_4)_x(NH_3)_ySO_4-$ (Figure 6). Bisulfate tetramer was the first cluster where ammonia was observed, and in the 10-mer the maximum signal was observed for a cluster with 2 ammonia molecules. In positive clusters, however, the x/y ratio was close to unity and the charge giving molecule was NH_4+. An example of a positive ammonium bisulfate cluster is $(HSO_4)_5(NH_3)_5NH_4+$. Ammonium bisulfate particles produced in the furnace were found to be a usable source of clusters, with a reasonable stability and reproducibility for the calibration experiments. In similar way, sodium chloride particles were generated from the furnace, exhibiting the cluster composition of $(NaCl)_x(C_4H_{10}O_3)_{0-1}Cl-$ in the negative polarity, and the composition of $(NaCl)_x(C_4H_{10}O_3)_{0-6}Na+$ in the positive polarity. The larger number of impurities in the positive polarity could explain some of the differences in the observed activation efficiencies reported previously by Kuang et al. (2012).

A spring made of tungsten wire heated up with high electric current produced negative self-charged particles given by the formula $(WO_3)_xOH-$, with possibly some organic impurities in the clusters. The wire generator was the most convenient source of sub-3 nm particles used in this thesis, since it produced self-charged particles with a single charge, and well-defined and easily reproducible particle chemical composition with the size range starting from 1 nm in mobility diameter up to tens of nanometers. In paper II we studied the mechanism of self-charging, which was found to be the formation of OH- radicals in the system (Peineke and Schmidt-Ott, 2008). This conclusion was drawn from the fact that most of the neutral WO_3 clusters were charged with OH-. Most probably the heat of the wire decomposes some impurities of the carrier gas, which leads to the formation of OH- radicals and other positive yet not identified ions. These positive ions are in fact observed already before any tungsten oxide forms as positive self-charged (contaminant) ions. Figure 6 compiles the mass and mobility spectrum of the three samples used in paper I.

Silver particles were generated with the furnace, as silver is a very common test aerosol in CPC calibrations (Scheibel and Porstendörfer, 1983;Wiedensohler et al., 1997;Sipilä et al., 2009;Iida et al., 2009). Some clean silver clusters were observed, for example $Ag_{17}-$ and $Ag_{19}-$, but most of the clusters were silver clustered with some unidentified organic molecules. With the current instrumentation, there is room for improvement in generating pure silver clusters. In other experiments not reported here, the generation of silver clusters was attempted with the wire generator and spark generator without success.
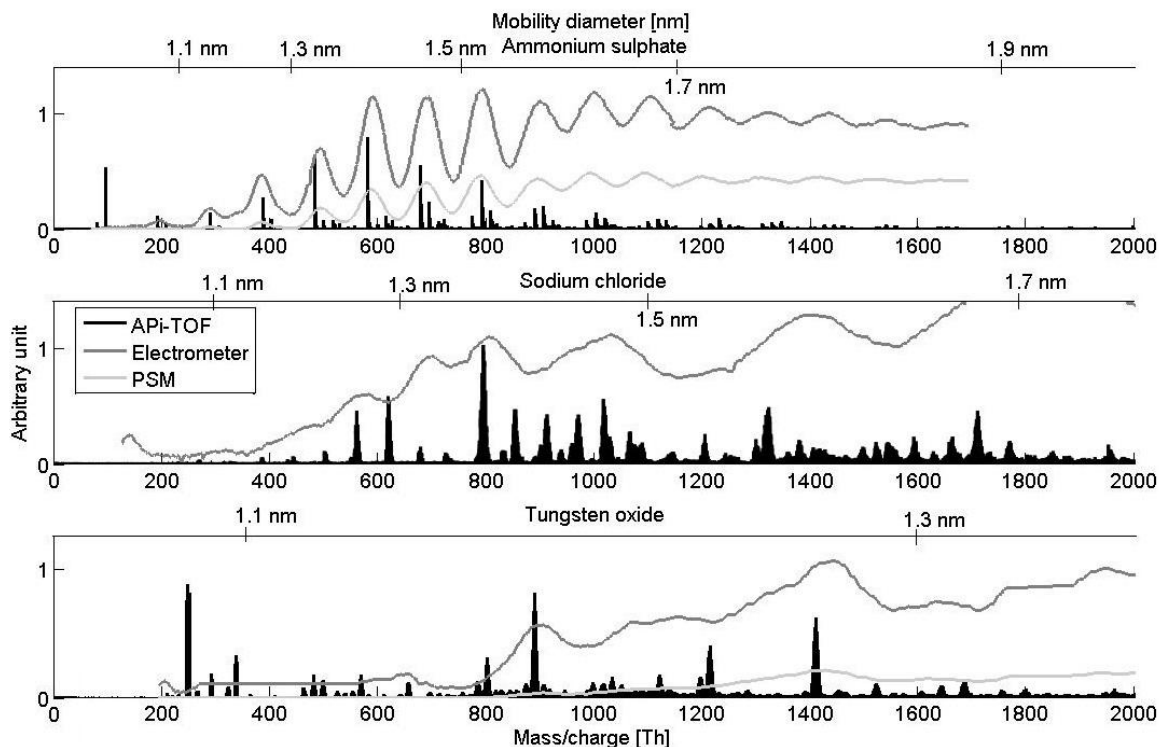
Figure 6. Combined mass and mobility spectrum of three samples generated in paper I.

3.1.2 Characterization of neutral particles

The composition of the neutral clusters produced with the wire generator and tungsten wire was probed by charging the neutral clusters with a [241]Am source or nitrate chemical ionization inlet in front of the APi-TOF. Tungsten oxide was found to cluster with various negative ions, the most abundant being tungsten oxide clustered with nitrate monomer (NO_3-) or dimer (HNO_3NO_3-). The overall conclusion was that tungsten oxide was almost always observed (WO_3- was observed too) to be clustered with some other ion, which gives the charge in negative polarity, strongly suggesting that the neutral clusters are made of pure tungsten oxide (Paper II).

3.2 Parameters affecting the CPC detection efficiency

The vapor pressure over a flat surface is different from the vapor pressure over a curved surface, which is described by the Kelvin equation (Thomson, 1871):

$$ln\frac{p}{p_0} = \frac{2\gamma V}{rRT}.$$

Here p is the vapor pressure, p_o is the saturation vapor pressure, γ is the surface tension, V is the molar volume of the liquid, R is the universal gas constant, r is the radius of the droplet, and T is temperature. In practice the equation implies that the smaller the particle, the higher the supersaturation, which is required to condense vapor onto the surface of the particle. The critical vapor pressure is defined as the vapor pressure at which homogeneous nucleation of vapor starts to occur. By limiting the vapor pressure to the critical vapor

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pressure, one obtains the Kelvin diameter from the Kelvin equation. The Kelvin diameter is the smallest particle diameter that can be activated without homogeneous nucleation of the vapor taking place, according to the Kelvin equation.

In a laminar type CPC, the sample flow is saturated with a working fluid in the saturator. Since the saturation vapor pressure is a function of the temperature, the sample flow becomes supersaturated after being cooled in the condenser. Other methods to supersaturate a gas flow have been discussed in the previous sections. The larger the temperature difference between the temperature where sample flow saturation and cooling down occurs, the smaller the particle size which can be grown to optically detectable sizes. It is known, that particle activation can happen below the Kelvin diameter. Winkler et al. (2012) suggest that particles adsorb vapor onto their surface enough to grow to the Kelvin limit, after which condensational growth of the particles occur.

The absolute pressure in a CPC can affect the activation efficiency. By lowering the pressure in the condenser, the thermal cooling is increased, but at the same time the vapor depletion onto the walls is increased, as shown by Zhang and Liu (1990). This feature has been experimentally confirmed by Hermann and Wiedensohler (2001): the decreasing pressure improves the performance of a CPC by lowering the cut-off size. At pressure around 20 kPa and lower pressures, the cut-off size starts to increase again.

The particle chemical composition has been shown to influence the CPC cut-off diameter. In the heterogeneous nucleation theory (Winkler et al., 2008a) the only parameter describing the effect of particle chemical composition on the nucleation probability is the contact angle. The contact angle describes the angle between the particle surface and forming liquid droplet. A complete wettability is described with a contact angle of 0º and no wetting with an angle of 180º. Therefore, for example water is expected to have a small contact angle on NaCl surface. If the particle is charged, the charge will lower the critical cluster size of the forming droplet. In practice, a charged particle will activate at a smaller supersaturation than an equally-sized neutral particle (Paper II).

3.2.1   Particle size

It is known that the smaller the particle, the smaller the probability that heterogeneous nucleation of vapor onto the particle surface occurs. Activation of the sampled particles as a function of their size was measured in all the papers of this thesis, and no exceptions were found to the previous statement. The activation efficiency was observed to increase always with the increasing particle size, with constant particle chemical composition. The effect of the particle chemical composition on the activation probability will be discussed more in a later section (3.2.4).

3.2.2   Supersaturation

In paper III, we investigate how small particles the fine CPCs TSI 3772 and Airmodus A20 can detect by varying the operation temperatures and the inlet flow rate. Previously a similar CPC has been reported to be able to detect 2.5 nm particles without the presence of homogeneously nucleated droplets (Mertes et al., 1995). Similar experiments with smaller particles have been lacking, probably due to the limited access to sub-3 nm particles and the introduction of the ultrafine CPC (Stolzenburg and McMurry, 1991). With the two CPCs, we set the saturator temperatures to 46 ºC and 47 ºC, respectively, and condenser temperatures to 10 ºC. At these settings, the CPCs were at the brink of homogeneous nu-

cleation, with an operational definition as approximately 1 count min^{-1}. The response of the CPCs as a function of the particle size was measured with negative tungsten oxide particles together with the ultrafine TSI 3776 and Airmodus A11, providing a comparison (Figure 7). The performance of the fine CPCs down to 1.5 nm was reasonably good, given that they were originally not optimized for the sub-3 nm particle detection. By setting the temperature difference to the maximum allowed by the firmware, the CPCs were sensitive even to the smallest 1.1 nm clusters. The ultrafine CPCs perform better compared with the fine CPCs due to minimized losses with the instrument design.

In paper V, we show that although the PSM (Vanhanen et al. 2011) was thought to be a mixing CPC, the activation of the particles actually takes place in the growth tube, not in the mixing zone. As predicted by Vanhanen et al. (2011), the peak supersaturation should occur when the saturator flow rate is set to 0.3 lpm, in spite of the fact that their experiments showed an increasing supersaturation until saturator flow rate of 1 lpm. This discrepancy was due to the fact that the supersaturation was calculated for mixing zone, while the supersaturation was higher in the growth tube. Figures 8 and 9 present two size dependent detection efficiency experiments with the PSM operated in the mixing and in the laminar mode. In these experiments the PSM detection efficiency was measured as a function of the particle size for negative bisulfate particles with the following temperature settings: saturator temperatures were 76 °C and 85 °C, inlet temperatures were 0 °C and 35 °C, and growth tube temperatures were 40 °C and 0 °C, which are the mixing mode and laminar mode settings, respectively.

The results showed that in the mixing mode the highest particle detection and supersaturation is in the mixing zone, whereas in the laminar mode the maximum supersaturation takes place in the growth tube. When the PSM was operated in the mixing mode, the maximum detection efficiency was at the saturator flow rate that Vanhanen et al. (2011) had predicted. The shape of the detection efficiency curves in the growth tube activation mode is better suited for the data inversion, which is why the PSM should be still operated as it is now in laminar mode.
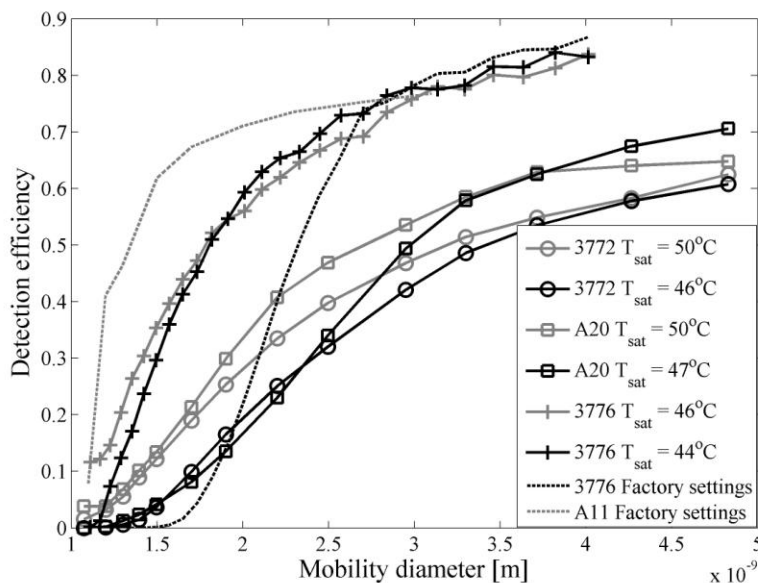

Figure 7. The detection efficiency of the TSI 3772 and Airmodus A20 with tuned temperature settings as a function of particle size for negative tungsten oxide particles. Similar measurement for the ultrafine TSI 3776 and Airmodus A11 is presented for a comparison.

Figure 8. The detection efficiency of the PSM as a function of saturator flow with mixing type temperature settings determined for negative ammonium bisulfate particles. The temperatures in the PSM were set to: saturator 76 ℃, inlet 0 ℃ and growth tube 40 ℃. The PSM operated as a mixing type CPC, since the highest supersaturation was in the mixing region, where the particle activation occurred.
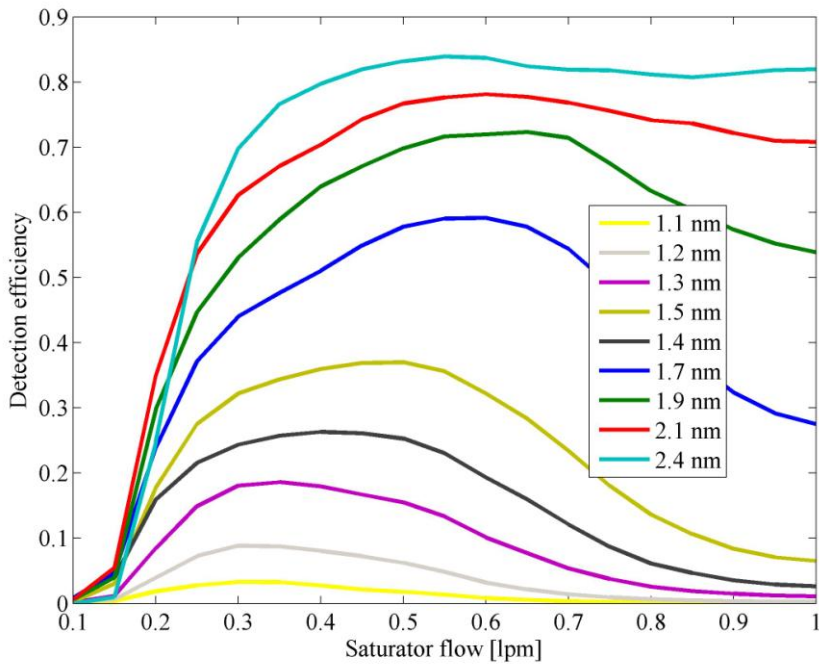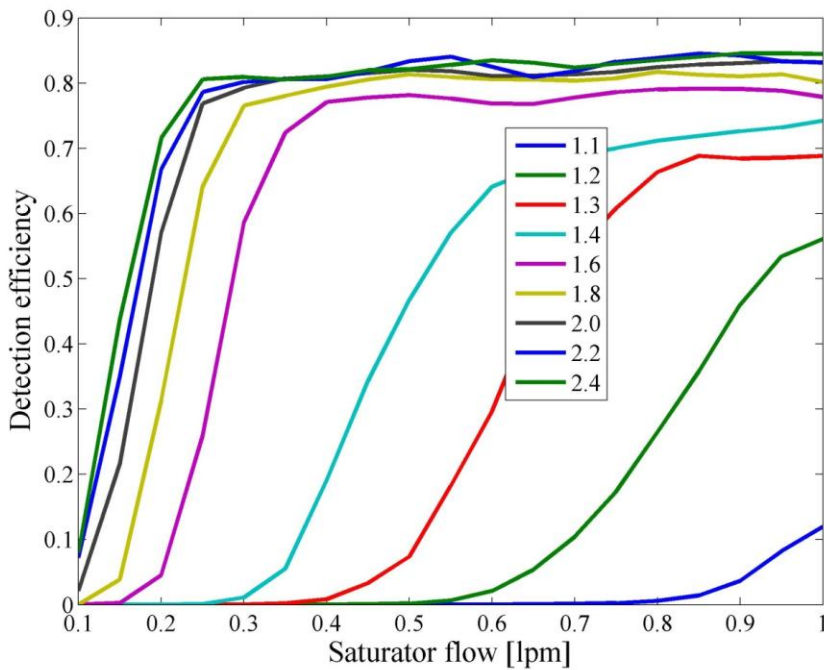

Figure 9. The detection efficiency of the PSM as a function of saturator flow with laminar type settings for negative ammonium bisulfate particles. The PSM temperatures were set to: saturator 85 ℃, inlet 35 ℃ and growth tube 0 ℃. The PSM was operated as a laminar type CPC, since the highest supersaturation was in the growth tube, where the particle activation occurred.

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3.2.3 Pressure

The PSM and the CPC with it have been operated at low pressure altitudes like mountain tops and onboard air planes (Kivekas et al., 2009;Schobesberger et al., 2013b;Andreae et al., 2004;Minikin et al., 2003). Therefore, the A11 was tested in under pressure conditions in paper V. Figure 10 shows the response of the A11 for 50 nm ammonium sulfate particles at varying inlet pressure. The dilution ratio inside the PSM does not change significantly due to the changing volume flows rates. The error in the measured concentration due to the changing dilution factor is rather small compared with the error coming from the CPC under counting at low pressure, as shown in Figure 10. The PSM cut-off, however, does not change significantly due to the changing pressure (Figure 11).
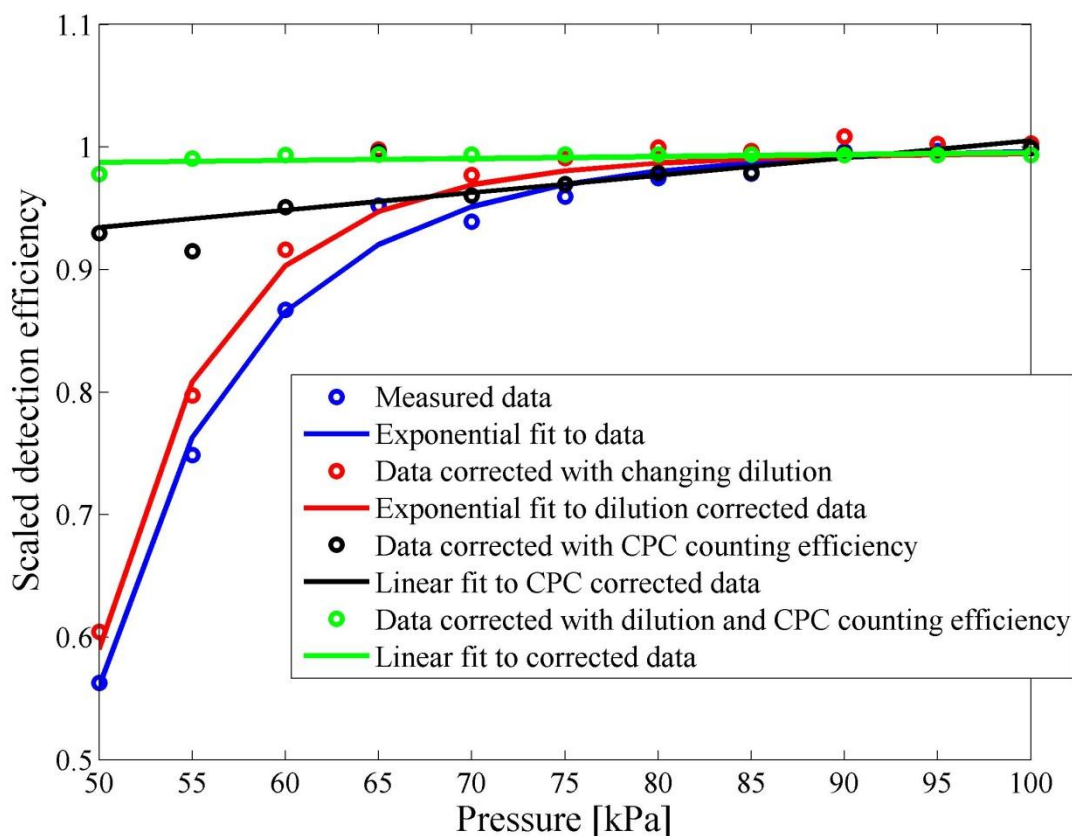

Figure 10. The response of the A11 nCNC (PSM and CPC) to 50 nm ammonium sulfate particles at various inlet pressures. All data was scaled to unity at normal pressure to only study the effect of the inlet pressure. The main source of uncertainty in the detection efficiency originates from the CPC counting efficiency.
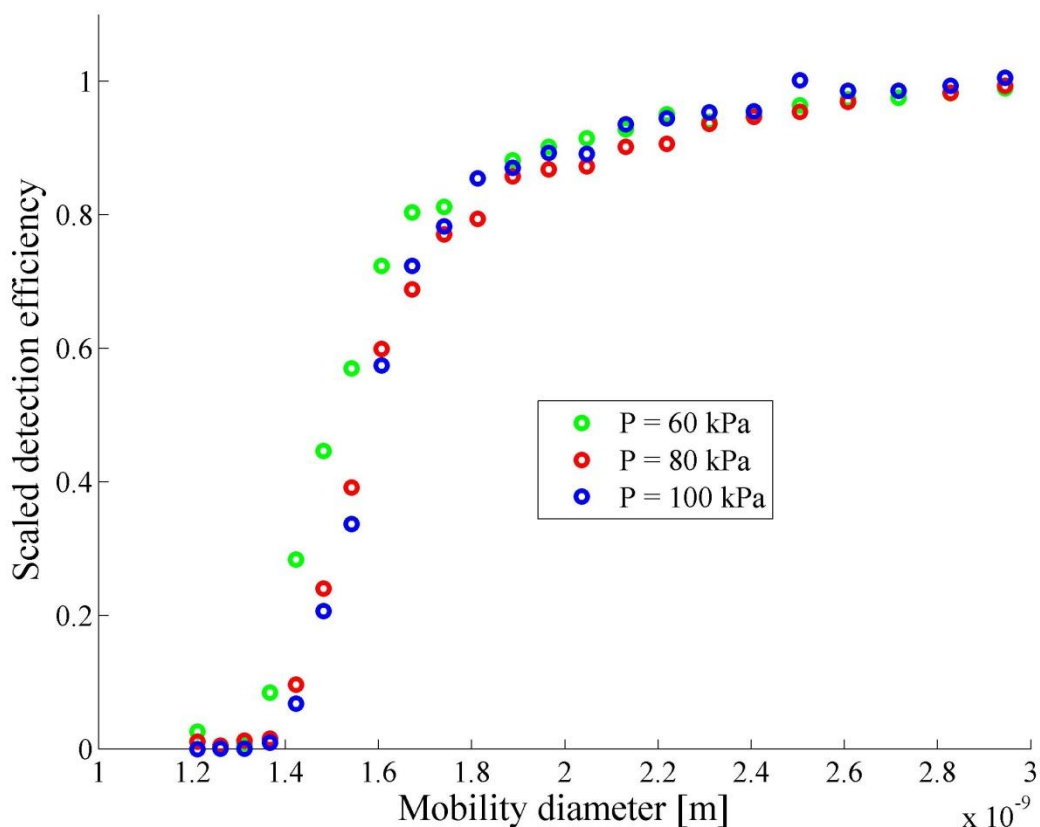
Figure 11. The change of the PSM cut-off for negative tungsten oxide due to pressure. All data was scaled to unity at normal pressure to only study the effect of changing pressure. The effect of the pressure to the PSM cut-off diameter is almost negligible.

3.2.4 Chemical composition of sample particles and condensing liquid

As found for example by Kulmala et al. (2007a) and Petäjä et al. (2006), a water CPC exhibits various cut-off diameters for particles of different chemical composition, whereas the cut-off diameter of a butanol CPC shows much smaller variation with varying particle composition (Paper IV) (Giechaskiel et al., 2011). In our paper I, we found a very similar behavior for the activation of particles by DEG vapor as compared with the water vapor: a clear affinity to ammonium sulfate and sodium chloride particles opposed to larger cut-off diameters for silver particles and other organic contaminants. Based on the mass spectrum of the silver particles, at least part of the difference in the cut-off diameter for example compared to sodium chloride is explainable by organic molecules which are clustered with silver particles.

Paper IV describes a more throughout activation efficiency experiments for four different ultrafine CPCs operated with three different working fluids. The motivation of the study was to operate all of them as detectors in a particle sizing system. All the operation temperatures of the CPCs were set to as close as possible to the limit of homogeneous nucleation to maximize the detection of the smallest particles without background counts from homogeneously formed droplets. DEG showed a similar affinity to inorganic salt particles as in paper I judged from the measured cut-off diameters, and less affinity to organic particles. Similar behavior was observed for water vapor. Particle activation with

butanol vapor, on the other hand, was the least dependent on the seed particle composition. All measured cut-off diameters from the experiments are presented in Table 1. Based on Table 1, we find approximately a 1 - 1.5 nm difference in the cut-off diameter when examining a constant condensing vapor and varying seed composition. A smaller, approximately 0.8 nm difference in the cut-off diameter was observed when having a constant seed composition but a varying working fluid. From these two numbers we can conclude that the seed particle surface plays a bigger role in the particle activation than the composition of the condensing liquid or, in the examined size range, the seed particle size. The observed dependency of the activation efficiency on the seed particle chemical composition verified the use of the four CPCs as a detector in a particle sizing system to obtain chemical information in the size range of 2 to 3 nm.

Table 1. A compilation of measured cut-off diameters (mobility diameter [nm]) for four different ultrafine CPCs in paper IV.

	DEG-CPC	PSM	3025A	3786
Ammonium bisulphate-	1.52	1.41	1.83	1.73
Ammonium bisulphate+	1.52	1.49	1.84	1.67
Sodium chloride-	1.39	1.42	1.73	1.44
Sodium chloride+	1.72	1.71	3.09	1.78
Tungsten oxide-	1.52	1.50	1.76	2.07
Tungsten oxide+	1.65	1.65	1.77	2.16
Sucrose-	1.83	1.86	1.87	2.04
Sucrose+	1.80	1.82	1.83	2.03
Limonene ozonolysis products-	2.65	2.64	2.63	2.70
Limonene ozonolysis products+	1.79	1.69	1.74	2.27
Candle flame products-	1.22	1.02	1.47	1.75
Candle flame products+	1.79	1.69	1.74	2.27

3.2.5 Charge

The role of particle charge in new particle formation and heterogeneous nucleation in the atmosphere and laboratory has remained unsolved with some contradicting publications (Kirkby et al., 2011;Kulmala et al., 2013;Winkler et al., 2008a;Yu, 2010). In our paper II

we repeated similar experiment as conducted by Winkler et al. (2008a): a particle of known size and charging state was generated, and the particle was exposed to varying supersaturation. The supersaturation was varied so that at the lowest supersaturation no activation of the test particles took place, and at the highest supersaturation 100% of the particles were activated. By comparing the 50% activation supersaturations, one can obtain insight about the role of charge of a particle during heterogeneous nucleation. For the experiment we selected 1.6 nm tungsten oxide particles.

To generate size selected neutral particles, we built an ion drift tube, from which unipolar small ions generated by a radioactive source were guided to the sample flow. The ions were guided against a 0.2 lpm counter flow with an electric field, and mixed with the sample flow in a mixing chamber. (Paper II). These small ions were observed to neutralize a fraction of the sample particles. The remaining charged particles and ions were removed with an ion filter upstream of the PSM to study only the activation of the neutral particles. The result of the experiment is presented in Figure 12. The difference in the activation efficiency between negative particles and neutralized negative particles is rather similar compared to the difference between positive particles and neutralized positive particles. The difference of $1 - 2$ ℃ in the saturator temperature translates into a charge enhancement of approximately 0.1 nm in the cut-off diameter due to the positive or negative charge. A similar result, reported by Winkler et al. (2008a), showed only one curve for neutral particles, thus not giving a complete view on the sign preference of heterogeneous nucleation, which certainly requires an experimental revision.

The particles that are multiply charged can create an artifact for a lower activation efficiency, since the electrometer counts two particles for one doubly charged particle, and their mobility is higher than the mobility of a singly charged particle. This is a possible problem when generating particles with the electrospray, since most particles are charged and the bigger ones are often multiply charged. Those large, multiply charged particles can overlap with the smaller generated ions due to a similar electrical mobility. Singly and multiply charged particles can be mixed in the detector signal, especially if the resolution of the DMA is not high enough.
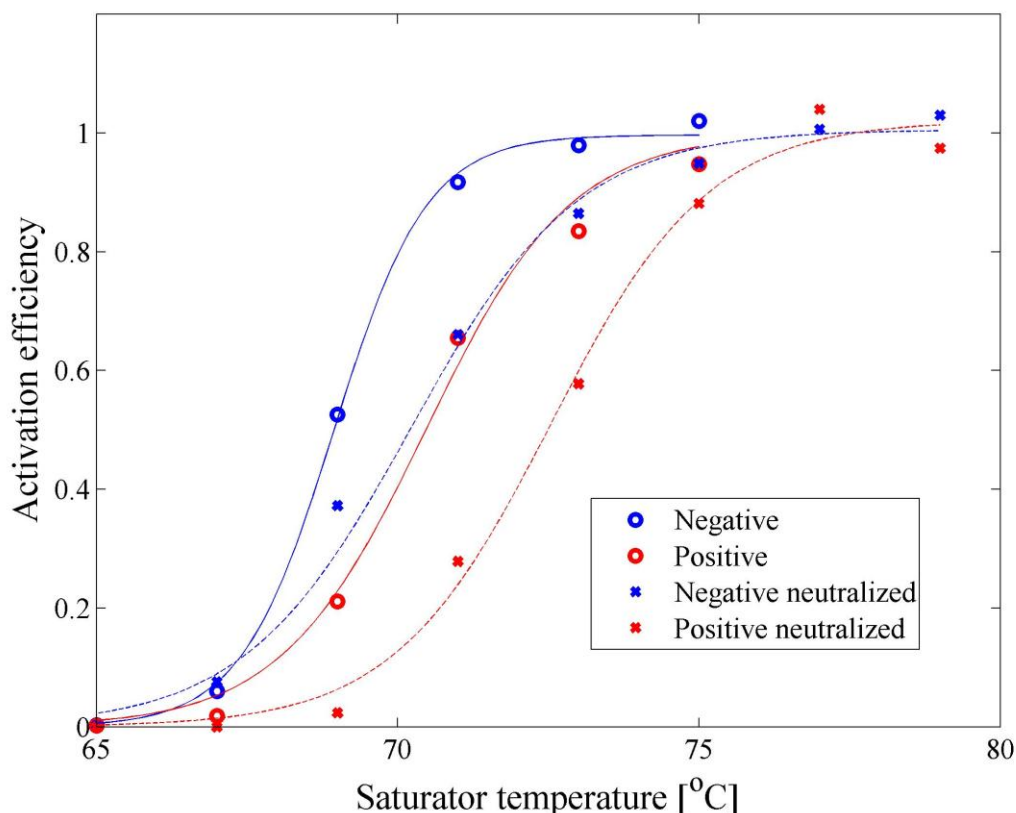
Figure 12. PSM activation efficiency for 1.6 nm tungsten oxide particles of various charge states as a function of the saturator temperature (a trace for supersaturation). The difference in the activation efficiency between the charged and neutral particles translates into approximately 0.1 nm difference in cut-off diameter.

3.2.6   Relative humidity

In paper I an experiment was conducted to probe the observed inconsistencies in the detection efficiency experiments with the open loop DMA and the PSM. The hypothesis was that the sample carrier gas composition changes the activation efficiency of the PSM via multicomponent nucleation. To test the hypothesis, the sample flow relative humidity was controlled by diluting the sample flow with another flow, of which relative humidity was controlled. The dilution was done upstream of the DMA to stabilize also the sheath flow loop into a constant relative humidity. At four different relative humidities the cut-off diameter of the PSM was measured for negative bisulfate particles. Similarly, the THABr sample flow was humidified and the detection efficiency of the PSM was probed as a function of the relative humidity. The result of this experiment is shown in Figure 13. At ambient temperature of approximately 20 ℃ when relative humidity increased from 0 to 36%, the cut-off diameter of the PSM decreased approximately from 1.5 to 1.2 nm.
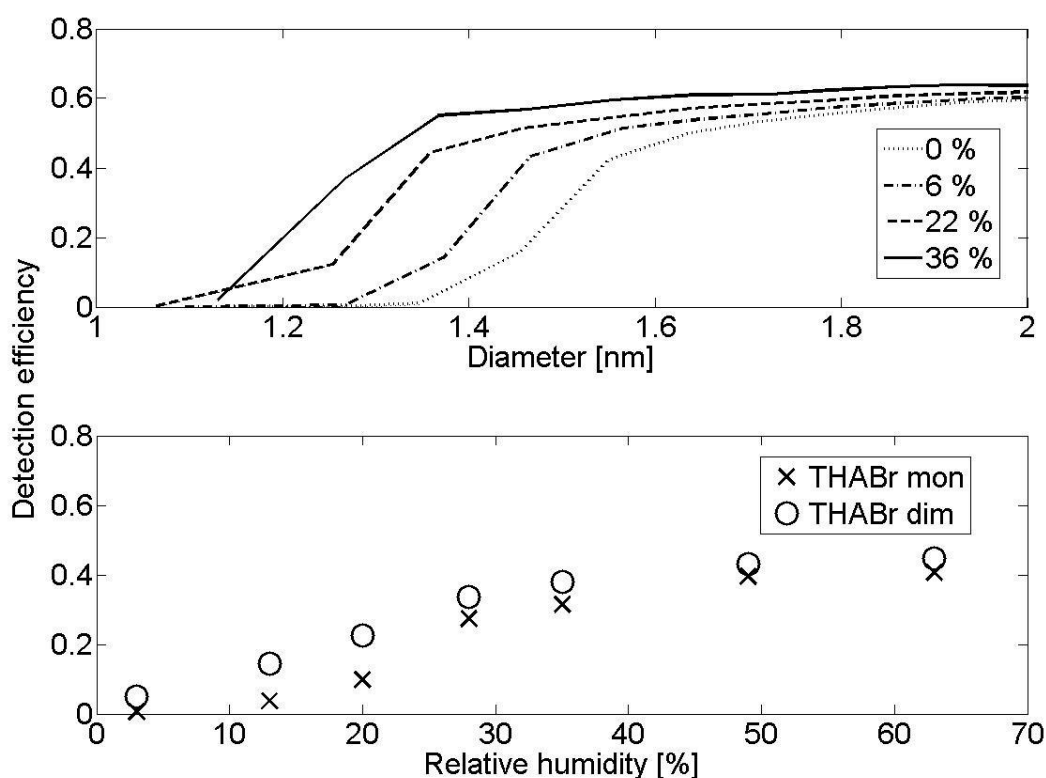
Figure 13. The PSM cut-off diameters measured for negative ammonium sulfate particles, and THABr monomer and dimer detection efficiency measured at varying sample air relative humidity. The PSM detection efficiency increases with increasing relative humidity.

3.3 Implications to field measurements

In the laboratory the wire generator provides a source of small particles with a semi-continuous size distribution to characterize and optimize the APi-TOF inlet. The wire generator has proven to be a robust enough generator to be taken to the field campaigns. It provides a stable source of sub-3 nm particles, which can be used to verify the operation of either the PSM or the APi-TOF at the field site. With some characterization on the operation of the wire generator with ambient air as carrier gas, the source would provide a nice solution to the field verification of the PSM in ambient relative humidity.

The performance of the tuned conventional CPCs does not revolutionize the atmospheric nucleation studies, but they offer a relatively cheap detector for measuring sub-3 nm particles, especially for laboratories without the ultrafine CPC. More importantly from the author's point of view, the results suggest that the performance of the CPCs is mostly limited by the particle losses inside the instrument. This observation strongly suggests that there is still room for improvement in the design of the current ultrafine CPCs.

The finding that the PSM is a laminar type CPC, and understanding the mixing type activation, explains the odd concentration data as a function of the saturator flow rate measured in some of the field campaigns. If the ingoing sample air is cold, it increases the temperature difference between the inlet and saturator, increasing also the supersaturation in the mixing zone. Since the supersaturation in the mixing zone peaks at saturator flow rate of 0.3 lpm, while the supersaturation in the growth tube peaks at saturator flow rate of

1 lpm (or higher), the scanning of the saturator flow rate from 0.1 to 1 lpm does not yield a monotonically increasing supersaturation scan. The peak in the middle of the supersaturation scan makes it challenging to invert the concentration data of that part of the scan. In practice, the previous problem can be now avoided up to some limit by increasing the inlet temperature to 40 ºC, which is the firmware maximum, setting the growth tube temperature to as small as possible (1 ºC firmware minimum), and adjusting the saturator temperature so that a suitable supersaturation is reached. With the previous method the supersaturation in the mixing zone is minimized, and the loss of data in the middle of the scan can be avoided.

The design of the sampling line described in the paper V will help to minimize the particle losses and uncertainty in the measured concentration of the PSM. The automatic zero measurement will help to follow the concentration of homogeneously nucleated droplets that is found to be a good trace for the activation efficiency of the PSM. With the automated zero measurement it is possible to remotely operate the PSM. The on/off ion filter allows the measurement of the size classified sub-3 nm charged fraction of the particles with the PSM. The results from the under pressure experiments confirm that the PSM can be operated in low pressure environments, provided that the CPC counting efficiency correction is taken into account.

In paper IV, we studied the effect of chemical composition with three different working fluids: DEG, water and butanol. The results showed the affinity of DEG to inorganic salt particles while less affinity compared to organic particles. This finding has strong implications on how the PSM (and other CPCs operated with DEG) should be operated in the field experiments. If the sample particles are expected to be freshly nucleated organic particles, the PSM should be operated at supersaturations high enough to yield a homogeneously nucleated background concentration of 10-100 cm^{-3} at largest saturator flow rate. At this high supersaturation the PSM should be capable of activating a fraction of the smallest sub-2 nm particles. On the other hand, if for example measurement of pure sulfuric acid particles is expected, the good operating supersaturation for the PSM is at the brink of the homogeneous nucleation at the highest saturator flow. Despite the efforts of this thesis, the final solution on how to operate the PSM in the field and obtain always comparable data is still lacking.

Since the decrease in the PSM cut-off diameter due to particle charge was found to be only approximately 0.1 nm, the uncertainty due to that in the measured size classified concentration is rather small compared to uncertainty due to particle composition. More generally this can be neglected, except when making laboratory experiments which require an absolute accuracy.

The fact that the relative humidity of the sample flow changes the operation of the PSM makes some of the ambient measurements complicated. The problem arises especially when the size distribution of the ambient particles has a large gradient as a function of the size, which is usually the case when atmospheric nucleation takes place. In principle, the problem is that if during one day a certain size classified concentration is measured, and on the next day lower size classified concentration is measured, then without the knowledge on the humidity effect one cannot know whether the lower concentration was due to lower real concentration or due to a lower PSM detection efficiency. In other experiments not reported here, we found that the homogeneously nucleated background concentration is a reasonable trace for the activation efficiency. The first solution to this challenge is to periodically measure the PSM background concentration, and adjust the saturator temperature so that the background concentration stays approximately constant. This way of operation has given the first consistent time series, but there is an urge to automate

it completely. Another solution could be a redesign of the instrument operation parameters, which would minimize the water content in the growth tube.

4   Review of papers and the author's contribution

Paper I In the first paper we described an experimental setup to produce sub-3 nm particles of known composition down to mobility diameter of 1 nm. The paper shows how the organic impurities in the sample particles can change the PSM detection efficiency. The importance of the closed sheath flow loop DMA in the experiments was studied by varying the relative humidity of the sample flow. The sample flow relative humidity was shown to significantly alter the detection efficiency of the PSM.

Paper II This paper presents a comparison of two independent methods to measure a size distribution of sub-3 nm neutral tungsten oxide particles. In order to do the measurement with the PSM, we probed the composition of the neutral tungsten oxide particles and measured how much the detection of charged 1.6 nm particles differs from the detection of neutral particles of the same size. To do the measurement with a combination of a high resolution DMA and an electrometer, we measured the transmission of the DMA and the charged fraction of the unipolar sample. The two methods exhibited a reasonably good agreement.

Paper III In this paper, with experiments and a model, we studied what is the smallest particle size that a conventional fine CPC can detect. The temperature difference between the saturator and condenser was set to the maximum that does not produce homogeneously nucleated background particles. The CPCs were able to detect charged particles as small as 1.5 nm, which has not been previously shown. We compared the results to two ultrafine CPCs and found a reasonable comparison. We conclude that the main disadvantage of the conventional CPCs in detecting the smallest particles is the internal losses.

Paper IV The fourth paper of this thesis presents an extensive set of experiments for the four of the best available sub-3 nm particle counters. We generated particles of seven different chemical compositions to verify the operation of the CPCs, and explored the composition dependency of the particle activation thoroughly. A strong composition dependency was found for activation of particles by DEG and water, whereas activation of particles by butanol seemed to be relatively independent on the composition of the particles. The results offer a basis to operate the CPCs as a part of a particle sizing system in field conditions, which could give insight into the composition of approximately 2 nm atmospheric particles.

Paper V Technical aspects of the PSM are considered in the fifth paper. We tested the operation of the PSM at low pressure conditions. The paper shows how the PSM can be operated as mixing type and laminar type CPC, as well as how the PSM is capable of

scanning size the of 1 to 6 nm particles by scanning the growth tube temperature. We described and characterized a new core sampling inlet line, which minimized the diffusion losses of the smallest particles in the sampling line of the PSM.

Author's contributions:

For paper I I did most of the experiments, all analysis with the help of coauthors and wrote the paper. In paper II I did the experiments together with my coauthors, all analysis and wrote the paper. For paper III I did the experiments together with my coauthors, my coauthors built the model, and I wrote the paper. The experiments and analysis for paper IV was done together with a coauthor, and I wrote the paper. For paper V I did all the experiments, analysis and wrote the paper, while my coauthors designed the inlet.

5 Conclusions

In this thesis we have improved the measurement of sub-3 nm particles in several ways. We built a high resolution closed sheath flow loop Herrmann type DMA setup. The flexible on-a-trolley DMA provided the basis of production of size selected sub-3 nm particles for all the experiments in the thesis. With the closed sheath flow loop, we explained the observed day-to-day variations in the PSM experiments, the reason of which was that the changing sample air water content changes the PSM activation efficiency.

With the help of the high resolution DMA and a mass spectrometer, we modified the operation of the tube furnace and wire generator for sub-3 nm particle generation with control over impurities. Impurities clustered with the sample particles, originating probably from the surface of the tube or the carrier gas, were found to lower the PSM detection efficiency significantly. Control over the test aerosol composition and sample flow relative humidity is the basis for a reproducible PSM calibration.

This thesis describes laboratory calibration methods, which are currently at a sufficient level for reliable instrument comparisons. However, a sound field calibration and operation of the PSM is still lacking due to the uncertainty in the composition of the nucleated atmospheric particles and varying ambient water content. One way to solve the problem, and in fact the best way, would be to conduct the calibration in the field with the nucleated ambient particles at the ambient relative humidity. Currently the field calibration of the PSM remains technologically very challenging. The PSM was shown to be able to operate in low pressure conditions, the biggest error in the detected concentration originating from the counting efficiency of the CPC.

The source of tungsten oxide particles, the wire generator, was found to be the most stable sub-3 nm particle generator tested in this thesis. The generator was characterized in depth, beginning from the formation mechanism of the self-charged particles. Probably heat induced OH- formation from impurities of the carrier gas allows OH- to cluster with neutral $(WO_3)_x$, giving negative charge for the neutral clusters. The positive self-charged clusters form by clustering with a positive ion formed from decomposition of organic impurities of the carrier gas. Based on the experiments, the neutral particles emitted by the wire are most probably clean tungsten oxide. Based on the source characterization and characterization of the response of the PSM for tungsten oxide particles, we compared two independent methods to measure neutral sub-3 nm size distributions. The agreement between the two methods, the PSM and the combination of a high resolution DMA and an electrometer, was fairly good.

All particle generators used in this thesis were utilized to verify the operation of a battery of four ultrafine CPCs. Strong particle composition dependency in the CPC cut-offs was found for water and DEG based CPCs, whereas the butanol CPC response seemed to be relatively independent on the particle composition. The measured cut-off diameters suggest that the most important factor determining nucleation probability, at a constant mobility diameter, is the particle surface. The second most important parameter is the condensing vapor composition, and most probably the effect of the charge is almost negligible compared with the other two parameters. Experiments of the paper II, however, show that the sign preference of heterogeneous nucleation requires an experimental revision by more throughout experiments with neutral size selected seeds. These results offer a basis for operating the battery of CPCs as a detector of a DMA. By looking at the differences at observed concentrations between different CPCs, one could obtain chemical information from particles of 2 to 3 nm in size.

Finally, we showed how sub-3 nm particles can be detected with conventional fine CPCs. The performance of the fine CPCs in detecting the smallest sub-3 nm particles was found to be rather good compared to the ultrafine TSI 3776 and Airmodus A11. The results offer a tool for sub-3 nm particle detection to laboratories without an ultrafine CPC.

In this thesis, we have improved the sub-3 nm particle detection and generation in the laboratory conditions, and provided insight on the field operation of the PSM. Monitoring the chemical composition of the test particles and sample flow properties was found to be essential for obtaining reproducible results in laboratory experiments. On the other end, selecting a suitable CPC working fluid and a supersaturation was shown to be important when selecting a particle counter for a given experiment. The research of this thesis offer basic knowledge on the generation and detection of sub-3 nm particles.

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