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Characterization of two types of CEN-certified Condensation Particle Counters at ambient and low pressure conditions

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Abstract

The particle number concentration is one of the most important parameters when measuring aerosols. Condensation particle counters (CPCs) are the most commonly used measurement devices for measuring the number concentration of aerosol particles down to the nanometer size range. In order to enable comparability and reproducibility over different measurement facilities and measurement campaigns, the instruments have to work according to a common standard. In the field of aerosol measurements the European Committee for Standardization (CEN) specified the technical standard CEN/TS 16976:2016 for CPCs. This standard specifies certain conditions on the measurement accuracy under standard pressure and temperature, but in various real-life scenarios, these environmental conditions are not fulfilled. For example, in aircraft measurement campaigns or in measurement facilities high above sea level (e.g. in the mountains), the instruments have to work under low pressure conditions.

The aim of this thesis is to characterize the performance, i.e. the counting efficiency, of two CEN certified CPCs, namely the Grimm 5410 CEN and the TSI 3772-CEN at ambient pressure and various low pressure levels. At all measured pressure levels the CEN compliance will be examined and the performance of the two different CPC models will be compared.

The measurements showed that at ambient pressure (1000 hPa) and at 750 hPa both models fulfill the CEN requirements and deliver comparable good results. For low pressure levels of 500 hPa and below, the CEN standard can not be met. The measurements at low pressure showed the same behaviour for both CPC models: With decreasing pressure, the counting efficiency decreases. Here, the Grimm 5410 CEN showed, in general, higher counting efficiencies compared to the TSI 3772-CEN, when measuring at 500 hPa and lower. The findings can be seen as a motivation to develop a new standard which takes this pressure dependence into account, given the abundance of real-world scenarios with these low pressure conditions.

Zusammenfassung

Die Partikelanzahlkonzentration ist einer der wichtigsten Parameter bei der Messung von Aerosolen. Hierbei sind Kondensationskernzähler, kurz CPCs, die am häufigsten verwendeten Messgeräte zur Messung der Anzahlkonzentration von Aerosolpartikeln bis in den Nanometerbereich. Um Vergleichbarkeit und Reproduzierbarkeit über verschiedene Messeinrichtungen und Messkampagnen hinweg zu ermöglichen, müssen die Geräte nach einem gemeinsamen Standard arbeiten. Im Bereich der Aerosolmessungen hat das CEN die technische Norm CEN/TS 16976:2016 für CPCs festgelegt. Diese Norm legt bestimmte Bedingungen für die Messgenauigkeit unter Standarddruck und -temperatur fest. Allerdings können diese Bedingungen in zahlreichen realen Szenarien nicht erfüllt werden. So müssen beispielsweise bei Messkampagnen in Flugzeugen oder in Messeinrichtungen hoch über dem Meeresspiegel (z.B. in den Bergen) die Instrumente im Unterdruck arbeiten.

Ziel dieser Arbeit ist es, die Performance, genauer gesagt die Zähleffizienz, von CEN-zertifizierten CPCs bei Umgebungsdruck und verschiedenen Unterdruckstufen zu charakterisieren. Im Rahmen dieser Arbeit wurden die beiden Modelle Grimm 5410 CEN und TSI 3772-CEN verwendet. Bei allen gemessenen Druckstufen wird untersucht, ob der CEN-Standard eingehalten werden kann und die Performance der beiden CPC Modelle wird verglichen.

Die Messungen haben gezeigt, dass bei Umgebungsdruck (1000 hPa) und bei 750 hPa beide Modelle die CEN-Anforderungen erfüllen und vergleichbar gute Ergebnisse liefern. Für Unterdruckstufen von 500 hPa und darunter kann die CEN-Norm nicht erfüllt werden. Die Messungen bei Unterdruck zeigten für beide CPC-Modelle das gleiche Verhalten: Mit abnehmendem Druck nimmt die Zähleffizienz ab. Hier zeigte der Grimm 5410 CEN CPC bei Messungen bei 500 hPa und niedrigerem Druck im Allgemeinen eine höhere Zähleffizienz als der TSI 3772-CEN CPC. Die Ergebnisse können als Motivation für die Entwicklung einer neuen Norm gesehen werden, die diese Druckabhängigkeit berücksichtigt, da es in der Praxis eine Vielzahl von Szenarien mit diesen niedrigen Druckbedingungen gibt.

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1 Introduction

Aerosols

When discussing issues such as climate change or public health (especially in light of the current pandemic), one cannot avoid talking about aerosols. Regarding their significant influence, these microscopic particles, exactly defined as solid or liquid particles suspended in a gas (Hinds 2012), play an important role in addressing both issues. For instance, in view of their influence on the climate, aerosol particles can interact with solar radiation and thus change the energy budget of the Earth (IPCC 2013). While this describes an aerosol-radiation interaction (direct influence), aerosols can also participate in an aerosol-cloud interaction (indirect effect on climate), for example, by serving as cloud condensation nuclei and thereby changing the Earth's albedo (IPCC 2013). Due to the numerous different interactions, aerosols can cause a warming or a cooling effect locally, depending on their properties and concentration (IPCC 2013). Overall, they have a cooling effect (IPCC 2013). However, the uncertainties of the influence of aerosols are still rather large (IPCC 2013). In the domain of public health the interest in aerosols is manifold. The presence of certain aerosols can lead to infectious diseases, acute toxic effects, or allergies (Srikanth et al. 2008). Moreover, ultrafine aerosol particles can be inhaled and then be taken up by the cells in the lung, or they can penetrate circulatory systems and lodge in organs (Kennedy 2007). More recently, due to the COVID-19 pandemic, the exhaust and inhalation of aerosols with different mask-types has been studied, in order to see their effectiveness to prevent aerosol transmission (Asbach et al. 2021).

Aerosols can be divided into primary and secondary particles, where primary particles are directly introduced into the atmosphere and secondary particles are formed by chemical reactions in the atmosphere (Hinds 2012). Furthermore, aerosols can be classified according to their source where a distinction is made between natural and anthropogenic origin (Hinds 2012). Natural sources of aerosols are for example sea salt, forest fires, or soil dust, whereas anthropogenic aerosol sources are for example emissions from industry or cars (Hinds 2012).

The physical properties of aerosols are highly dependent on the size of the particles (Hinds 2012), but the size of particles in the atmosphere span over a range of four orders of magnitudes (Seinfeld et al. 2016). Based on their size it is possible to classify particles in different ways, e.g. according to their modal distribution (Lazaridis et al. 2013). Here four different modes can be distinguished: The nucleation, the Aitken, the accumulation, and the coarse mode (Lazaridis et al. 2013). Particles are assigned to the different modes according to their size, e.g., parti-

cles with a diameter below $0.1\mu\text{m}$ are in the nucleation mode (Lazaridis et al. 2013). When measuring aerosols the particle number concentration is one of the most important parameters (Takegawa et al. 2011). By measuring the number size concentration over a range of diameters a number size distribution of the aerosol particles can be determined. Aerosol distributions can also be determined with respect to other parameters such as mass or volume.

An example of different representations of aerosol distributions is shown in Fig. 1.1, which is taken from Seinfeld et al. 2016. It shows the distribution of the ambient aerosol in terms of number (upper part) and volume (lower part). The volume-size distribution is dominated by the accumulation and the coarse mode whereas the number-size distribution is dominated by the nucleation and the Aitken mode (Seinfeld et al. 2016). This work deals with particle sizes below or equal to 30 nm , which means that the particles are in the nucleation and the Aitken mode and therefore the number size distribution plays the most important role to describe the measured particles.

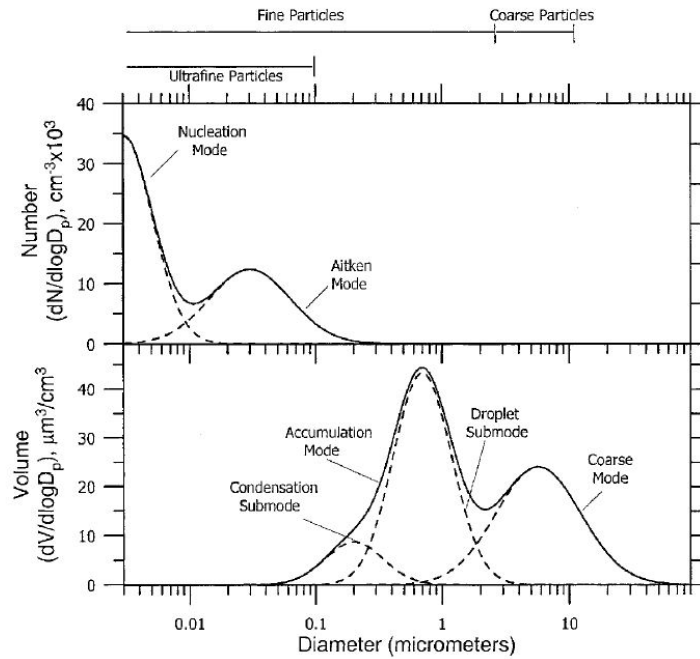


Figure 1.1: *Distribution of the ambient aerosol represented in two different ways. The upper part shows the number distribution and the lower part the volume distribution (Seinfeld et al. 2016).*

Aerosol measurement and applications

The integral particle number concentration is most commonly measured with a CPC, using ground based, airborne, and satellite-based methods (McMurry 2000). The working principle of this instrument is based on particle growth by condensation, whereby particles grow to a size that can be optically detected (Chen et al. 2013), allowing to measure ultrafine particles (Seinfeld et al. 2016). CPCs have several advantages, such as being able to detect particles as small as a few nanometers (Takegawa et al. 2011), being able to handle low particle number concentrations through individual particle counting, or being able to work as a detector in combination with other instruments, such as an electrical mobility classifier (McMurry 2000). Different CPC types can be distinguished by the way in which supersaturated conditions are achieved, for example expansion type, or conductive cooling CPCs (Kulkarni et al. 2011). In general, instruments which use condensation techniques are known since 1888 and additional to the CPC two other types of devices evolved: Cloud Condensation Nucleus Counters (CCNC) and cloud chambers (Kulkarni et al. 2011).

Due to the mentioned advantages of CPCs, they are often used for measurement campaigns on aircrafts (e.g. DABEX (Johnson et al. 2008), NMASS in ATom (Williamson et al. 2018)), or in general in measurement facilities (e.g. ACTRIS observatory platforms (ACTRIS 2021), the Nepal Climate Observatory Pyramid station (Bianchi et al. 2020)). The latter example of a measurement facility (the Nepal Climate Observatory Pyramid station) is in the Himalayas and is at 5079 m above sea level (Bianchi et al. 2020). Due to the height of the station, the ambient pressure is only about 500 hPa (Bianchi et al. 2020). For aircraft applications and for measurement station high above sea level CPCs are used under low pressure conditions. Therefore it is important, that such instruments can work at various pressure levels. Previous studies on the pressure dependent performance of CPCs (e.g., Hermann et al. 2001, Takegawa et al. 2011, Zhang et al. 1990) already showed that the counting efficiency is dependent on the pressure.

ACTRIS and CEN

One of the largest infrastructures to investigate and better understand the impact of aerosols on the climate is ACTRIS, which is the abbreviation for Aerosol, Clouds and Trace Gases Research Infrastructure. It is a pan-European research infrastructure that includes 22 countries and over 100 research performing organizations (ACTRIS 2021). In Austria alone ACTRIS has seven partners, namely five universities, the national weather service (ZAMG), and a private company called LuftBlick (ACTRIS 2021). Due to the large number of partners ACTRIS

can provide high-quality long-term atmospheric data (ACTRIS 2021). One goal of their research is to gain a better understanding of the drivers of climate change and air pollution, as well as to improve the accuracy of climate models and their sensitivity (ACTRIS 2021). To achieve this goal, a large amount of data is needed, which is provided by observatory platforms and exploratory platforms. The former are ground-based stations that regularly provide long-term data and are located in various climatic regions (ACTRIS 2021). The latter are atmospheric simulation chambers, or mobile platforms, where experiments can be performed and which provide data on atmospheric constituents (ACTRIS 2021). The instruments in the research facilities have to work on common operation standards to deliver standardized data (ACTRIS 2021).

To get standardized data the used instruments have to fulfill certain requirements. One organization that defines such requirements is called European Committee for Standardization (CEN) and is a private international non-profit organization (CEN 2021). It provides a platform for the development of European standards and other technical documents and links the National Standardization Bodies of 34 European countries (CEN 2021). By cooperating with other international standardization organizations (e.g. ISO, or IEC), the following goal is pursued: one standard, one test, accepted everywhere (CEN 2021). The requirements for condensation particle counters are defined in CEN/TS 16976:2016 at standard pressure and temperature (CEN/TS 2016). There are numerous criteria that must be met, like performance criteria and test methods.

Motivation and aim of the thesis

Currently the rooftop laboratory at the Department of Physics is being rebuilt to become the AEP Observatory (AEP stands for Aerosol Physics and Environmental Physics Group) and serve as a new measurement station for ACTRIS. Therefore, new CPCs, namely four Grimm 5410 CEN CPCs, were purchased. As already mentioned, the instruments used in ACTRIS measurement facilities have to fulfill the CEN requirements in order to ensure comparability of the measured data. For that reason it should be examined whether the new devices meet the corresponding CEN standard. Since aircraft measurements are also performed in the AEP group, not only the behavior at standard pressure, but also the behavior at lower pressure levels is of interest. Therefore, the behaviour of these CEN standardized devices under low pressure conditions will be tested. Such a characterization of two TSI 3772-CEN CPCs at low pressure conditions was performed in the master thesis of Spät 2020. The focus of Spät 2020 is on the aircraft application of the TSI CPC. In contrast to that, our focus is on the CEN compliance, which requires additional measurements. Moreover, we characterized a second CEN CPC and compared the

performance under low pressure conditions. These differences will be highlighted in more detail at the relevant positions in Section 3.2.2 and Section 4.3.2.

The aim of this thesis is to characterize the four newly purchased Grimm 5410 CEN CPCs, as well as two TSI 3772-CEN CPCs, at both ambient pressure and various low pressure levels. For this purpose, the counting efficiency and the cutoff diameter at different pressure levels will be determined, which will allow a comparison of the performance under low pressure conditions of the two models. In addition, at all measured pressure levels, it is investigated whether the CEN requirements are fulfilled and down to which pressure level the devices still are in accordance with the CEN standard.

In this thesis, a theoretical overview of condensation theory and CPCs is given in Section 2, which includes particle loss mechanisms and the pressure dependence of parameters. In addition, Section 2 gives an overview of differential mobility analysis, which contains information about electrical properties, size distributions and differential mobility analyzers (DMAs). An overview of the measurement and data evaluation methods is given in Section 3, which includes a description of the setup, particle generation, selection and detection. In Section 4 the results of the measurements are presented and discussed, and Section 5 sums up this work with some concluding remarks and an outlook for future work.

2 Theory

The presented information in this chapter is based on various books and papers, but mainly follows explanations found in Hinds 2012, Seinfeld et al. 2016, Kulkarni et al. 2011, and P.M. Winkler et al. 2022.

2.1 Condensation theory

The formation of new particles can be divided into two parts: Nucleation, where particle formation occurs, and growth by condensation (Hinds 2012). Nucleation can either occur in absence or presence of condensation nuclei, which is called homogeneous and heterogeneous nucleation, respectively (Seinfeld et al. 2016). Both types of nucleation are described below. The focus of this work is on CPCs, in which particles reach a detectable size by growth due to condensation, i.e., heterogeneous nucleation (Kulkarni et al. 2011). Thus, the focus of this section will also be more on this process.

2.1.1 Nucleation

A prerequisite for the process of nucleation, independent of type, is a supersaturated vapor (Hinds 2012). To describe saturation conditions the so called saturation ratio S with

$$S = \frac{p}{p_s(T)} \quad (2.1)$$

is used. Here, p denotes the partial vapor pressure and p_s the saturation vapor pressure where the solute is in equilibrium with its liquid phase at a certain temperature T (Seinfeld et al. 2016). The logarithm of S is proportional to the difference in the chemical potential of the vapor molecules μ_v and the chemical potential of the liquid phase μ_l , i.e.,

$$\mu_v - \mu_l = kT \ln S, \quad (2.2)$$

where k is the Boltzmann constant (P.M. Winkler et al. 2022). Three cases can be distinguished:

- **$S = 1$** : The vapor is saturated (Hinds 2012) and $\mu_v = \mu_l$. This means the system is in equilibrium and the condensation rate equals the evaporation rate (P.M. Winkler et al. 2022).
- **$S < 1$** : The vapor is unsaturated (Hinds 2012) and $\mu_v \neq \mu_l$. This means that evaporation dominates to bring the system back to equilibrium (P.M. Winkler et al. 2022).

- **S > 1** : The vapor is supersaturated (Hinds 2012) and $\mu_v \neq \mu_l$. This means that condensation dominates to bring the system back to equilibrium (P.M. Winkler et al. 2022).

Since supersaturated conditions are required for nucleation, the saturation ratio must be greater than one (P.M. Winkler et al. 2022). The saturation vapor pressure in Eq. (2.1) is generally defined for a plane liquid surface, so modifications must be made when considering a curved surface, such as a droplet (Hinds 2012). The changes due to the curved surface affect the attractive forces of the surface molecules and it follows that the smaller the droplet, the easier it gets for molecules to evaporate (Hinds 2012).

2.1.2 Homogeneous nucleation

Homogeneous nucleation, also called self-nucleation, describes particle formation without condensation nuclei (Hinds 2012) and is based on rate equations derived by gain and loss of molecules (Seinfeld et al. 2016). Thermodynamics can be used to describe the change in the Gibbs free energy ΔG as a function of the particle radius R_p (Seinfeld et al. 2016). It is described as

$$\begin{aligned}\Delta G_{hom}(R_p) &= G_{droplet} - G_{vapor} \\ &= -\frac{4\pi}{3} \frac{kT}{v_l} R_p^3 \ln S + 4\pi\sigma R_p^2,\end{aligned}\tag{2.3}$$

where T denotes the temperature, v_l the volume of a molecule of a certain species, S the saturation ratio, and σ the surface tension (Seinfeld et al. 2016). As the behavior of ΔG_{hom} depends on the saturation ratio S the following cases can be distinguished:

- **S < 1** : The logarithm is negative and therefore ΔG_{hom} will increase monotonically with the particle radius R_p (Seinfeld et al. 2016).
- **S > 1** : The logarithm is positive and therefore the cubic term in R_p is monotonically decreasing. For small R_p the quadratic term dominates the cubic term and so ΔG_{hom} will increase until a maximum ΔG_{hom}^* is reached. After this maximum the cubic term dominates the quadratic term and so ΔG_{hom} will then decrease (Seinfeld et al. 2016).
- **S = 1** : The first term in Eq. (2.3) is zero and therefore ΔG_{hom} is proportional to R_p^2 .

For illustration purposes, the behavior of ΔG_{hom} is shown in Fig. 2.1.

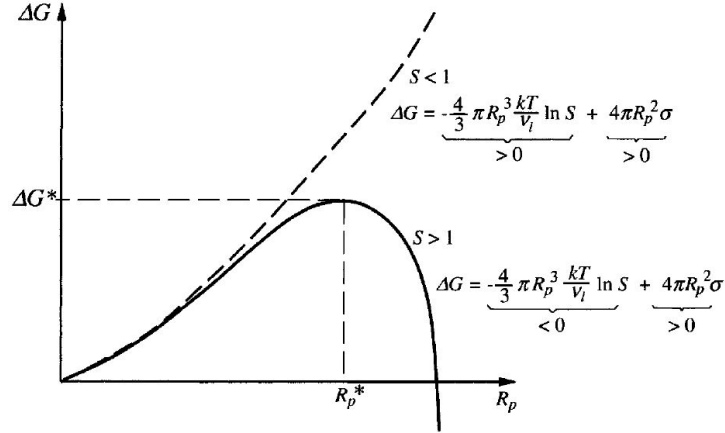


Figure 2.1: Behavior of the change of the Gibbs free energy as a function of the particle radius R_p for saturation ratios S smaller and bigger than one (Seinfeld et al. 2016).

The associated radius to the maximum of ΔG_{hom}^* is denoted as R_p^* and called critical radius (Seinfeld et al. 2016). The addition of more vapor molecules becomes more favourable and the cluster can grow by condensation (P.M. Winkler et al. 2022). The critical radius R_p^* can be obtained by setting the derivative of Eq. (2.3) to zero. This leads to the so-called Kelvin equation

$$R_p^* = \frac{2\sigma v_l}{kT \ln S}. \quad (2.4)$$

Here, σ is the surface tension, v_l the volume of a molecule, k the Boltzmann constant, and T the temperature (P.M. Winkler et al. 2022). By rearranging Eq. (2.4), one can calculate the saturation ratio S needed to maintain a mass equilibrium for a certain particle radius R_p^* (Hinds 2012). Additionally, the following observations can be made from Eq. (2.4):

- The Kelvin equation defines conditions on R_p^* and S such that particles are in equilibrium with the surrounding vapor (Thomson et al. 1934).
- For a specific particle size the proper saturation ratio can be calculated and vice versa (P.M. Winkler et al. 2022).
- The smaller the particle, the higher the saturation ratio has to be to maintain equilibrium (Seinfeld et al. 2016).

In general, for homogeneous nucleation and for a given saturation ratio a particle must reach a critical radius R_p^* before it can become a stable droplet and grow (Hinds 2012). The Kelvin equation accounts for uncharged particles, but if the particles are charged the Kelvin equation is replaced by the Kelvin-Thomson

equation which also accounts for charge effects in the equilibrium condition (P.M. Winkler et al. 2022):

$$\ln S = \frac{2\sigma}{n_l k T R_p^*} - \frac{q^2}{32\pi^2 \epsilon_0 n_l k T R_p^{*4}} \left(1 - \frac{1}{\epsilon_l}\right). \quad (2.5)$$

Here ϵ_0 denotes the electric constant, ϵ_l the relative permittivity of the liquid, and $q = i \cdot e$ the number i of elementary charges e on a seed particle (P.M. Winkler et al. 2022). The second term, also called charge term, is always positive, because of q^2 (P.M. Winkler et al. 2022). Therefore, the first term, also called Kelvin term, will be reduced by the amount of the charge term which means that for charged particles lower saturation ratios are necessary (P.M. Winkler et al. 2022).

2.1.3 Heterogeneous nucleation

The difference between homogeneous nucleation and heterogeneous nucleation is that the latter occurs in the presence of condensation nuclei and can therefore occur at a lower supersaturation (Hinds 2012). It is the primary cause for cloud formation in the atmosphere and is used in CPCs for nanoparticle detection (P.M. Winkler et al. 2008). In this case the Gibbs free energy can be expressed as

$$\begin{aligned} \Delta G &= \Delta G_{hom}^* f(m, x) \\ &= \frac{16\pi}{3} \frac{v_l^2 \sigma_{LV}^3}{(k T \ln S)^2} f(m, x), \end{aligned} \quad (2.6)$$

where v_l denotes the volume per molecule, σ_{LV} the surface tension between the embryo and the surrounding phase, and $f(m, x)$ accounts for the geometry of the embryo (Seinfeld et al. 2016). Here, m is called contact parameter and is the cosine of the contact angle θ between the nucleus and the substrate which is shown in Fig. 2.2 (Seinfeld et al. 2016). The contact angle is used to describe the wetting properties of the condensing liquid and the underlying surface, which can furthermore be used to determine the reduction of the energy barrier (P.M. Winkler et al. 2022).

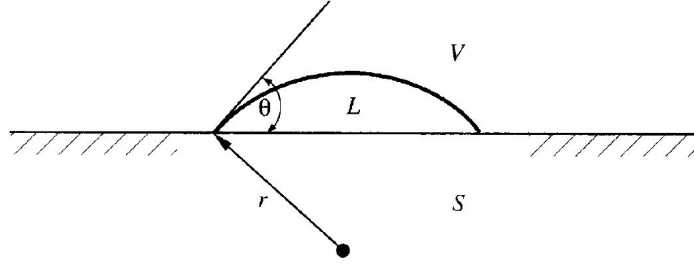


Figure 2.2: Cluster formation on a flat surface. θ is the contact angle between the nucleus and the surface (Seinfeld et al. 2016).

The contact angle is described with the so called Young equation

$$m = \cos\theta = \frac{\sigma_{SV} - \sigma_{SL}}{\sigma_{LV}}, \quad (2.7)$$

where σ describes the surface tension between two phases and the indices S , V , and L indicate the phases solid, vapor, and liquid, respectively (Seinfeld et al. 2016). Similar as for homogeneous nucleation also for heterogeneous nucleation a critical radius for an embryo can be defined:

$$R_p^* = \frac{2v_l\sigma_{LV}}{kT\ln S}. \quad (2.8)$$

This equation is equivalent to Eq. (2.4) (Seinfeld et al. 2016).

To express the number of new emerging clusters per time and unit area the nucleation rate can be defined as a function of the saturation ratio and the temperature (Seinfeld et al. 2016). Definitions and derivations of the heterogeneous, as well as the homogeneous, nucleation rate J can be found for example in Seinfeld et al. 2016 or R. McGraw et al. 2012. However, note that there is a difference between the two:

- **Homogeneous nucleation:** The nucleation rate $J_{hom}[\text{cm}^{-3}\text{s}^{-1}]$ gives the number of newly formed particles per unit volume and time. So the probability to observe it increases with observation volume and time (P.M. Winkler et al. 2022).
- **Heterogeneous nucleation:** The nucleation rate $J_{het}[\text{s}^{-1}]$ gives the rate per preexisting particle per unit time (P.M. Winkler et al. 2022).

In an experiment it is hard to measure J_{het} directly, instead the number concentration of activated particles N_{act} as a function of the saturation ratio is measured

(P.M. Winkler et al. 2022). N_{act} can be normalized to the total number concentration N_{tot} to get the heterogeneous nucleation probability

$$P = \frac{N_{act}}{N_{tot}} \quad (2.9)$$

(P.M. Winkler et al. 2022). P then describes the probability that a particle is activated (R. L. McGraw et al. 2017) and it is related to the heterogeneous nucleation rate via $P = 1 - \exp(-J_{het} \cdot t)$, where t is the nucleation time (P.M. Winkler et al. 2022).

Supersaturation at spherical particles

The geometry of nucleating clusters is more complex than described in the Young equation (Eq. (2.7)), because a flat surface was assumed there. Additionally, the geometry of nucleating clusters is more complex for heterogeneous nucleation than for homogeneous nucleation (P.M. Winkler et al. 2022). Even in the approximation that condensation nuclei are assumed to be spherical (Fletcher 1958) the critical cluster can form a special cap embryo (P.M. Winkler et al. 2022). This special cap embryo can either be attached to the seed particle or engulfed by it, depending on the seed particle size and the contact angle (P.M. Winkler et al. 2022). This situation should also be considered and Fig. 2.3 shows its geometry.

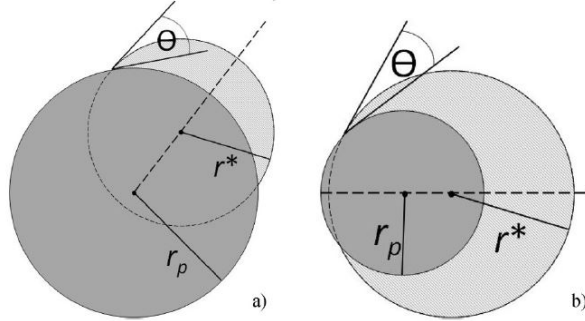


Figure 2.3: *Special cap embryo on a spherical seed particle with radius r_p . a) shows a critical cluster with radius $r^* < r_p$ and b) $r^* > r_p$. The contact angle θ is also shown (P.M. Winkler et al. 2022).*

For the above situation, x in Eq. (2.6) can be replaced by R/R_p^* , where R is the radius of the particle and R_p^* is the critical radius (Fletcher 1958). The wetting phenomena in heterogeneous nucleation can be described by the contact angle θ (P.M. Winkler et al. 2022). The influence of θ on the geometrical factor $f(x, m)$, where $x = R/R_p^*$, is shown in Fig. 2.4. It is shown that the geometrical factor $f(m, x)$ for low contact angles θ drops faster and thus the conditions for nucleation

are favored (Fletcher 1958). Note that Fig. 2.4 shows the contact parameter instead of the contact angle. With $\theta \in [0, \pi]$ and $m = \cos\theta$, a smaller θ means a higher value of m .

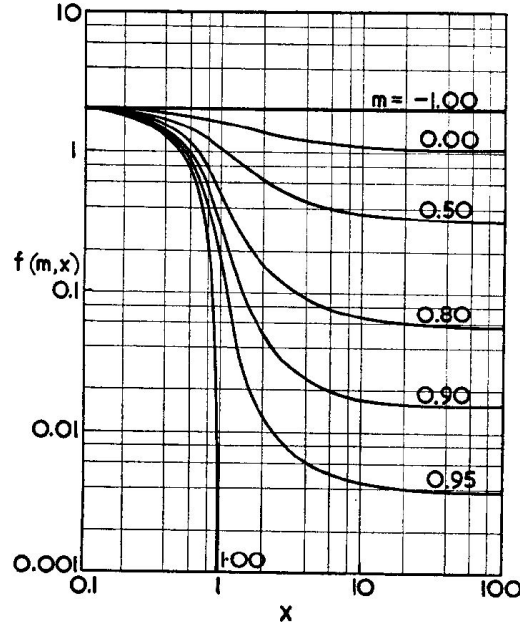


Figure 2.4: The geometrical factor $f(m, x)$ in terms of x for different $m = \cos\theta$ (Fletcher 1958).

2.1.4 Condensation particle counter

One of the most common applications of heterogeneous nucleation is the detection of nanoparticles with a CPC (P.M. Winkler et al. 2022), whose working principle is based on three processes: the supersaturation of a working fluid, particle growth by vapor condensation, and the detection of particles (Kulkarni et al. 2011). In laminar flow conductive cooling type CPCs the first two processes take place in the so-called saturator and condenser, the last step takes place in the optics block (Kulkarni et al. 2011). As the particles in the CPC are enlarged by condensation, they can be detected optically (Stolzenburg et al. 1991) by passing them through a laser beam and counting the light pulse each time a particle passes through (P.M. Winkler et al. 2022).

Particle activation and growth

Four basic types of CPCs are distinguished depending on how supersaturated conditions are achieved, namely expansion type, conductive cooling, differential

diffusion, and mixing type CPCs (Kulkarni et al. 2011). Since the devices used in our experiments are conductive cooling CPCs, this principle is described in more detail below. Following the description in Kulkarni et al. 2011 they work as follows: The aerosol particles first flow through the saturator where a working fluid, which is alcohol, is kept at a certain temperature in a reservoir. Its residence time in the saturator is long enough to be saturated with the working fluid at the set temperature (Kulkarni et al. 2011). Afterwards, the aerosol particles flow into the condenser, which is set to a lower temperature than the saturator by cooling walls. In the condenser two processes occur: on the one hand conductive cooling from the walls to the stream and on the other diffusion transport of the gas molecules to the walls (see Fig. 2.5) (Kulkarni et al. 2011). Due to the size of the alcohol molecules and their high inertia heat transport occurs faster than mass transport which leads to supersaturation (Kulkarni et al. 2011). Considering Eq. (2.1) and the temperature dependence of $p_s(T)$, it can be seen that $p_s(T)$ decreases faster than p which causes supersaturated conditions and leads to activation and condensational growth of the particles (Kulkarni et al. 2011).

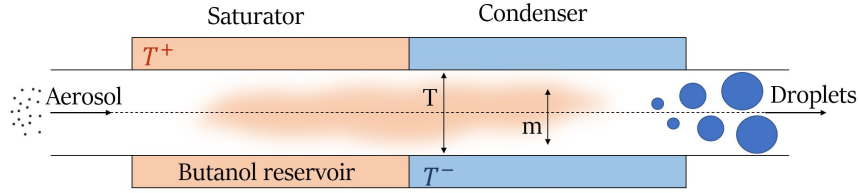


Figure 2.5: Schematic of the particle activation and growth inside the CPC. The arrows denote the temperature and mass transfer to the walls, whereas T^+ and T^- indicate the higher temperature in the saturator and the lower temperature in the condenser, respectively.

According to Hinds 2012 and Eq. (2.4), it is evident that, depending on the achieved supersaturation, the smallest particle that can be activated and thus will grow has the size R_p^* . The droplet size in condensation instruments is nearly uniform and depends on the system configuration, the operating conditions and the particle number density, but it is nearly independent on the initial particle size (Kulkarni et al. 2011). So, regardless of their initial size, particles that have been exposed to the same supersaturation for the same amount of time will grow to a near-uniform size between 2 and 15 μm (Kulkarni et al. 2011). The smaller the particles the greater the saturation ratio must be for heterogeneous nucleation, however for particles in the nanometer range the saturation ratio can be so high that homogeneous nucleation occurs, resulting in an increase of the measured number concentration above the primary aerosol particle concentration (P.M Winkler

et al. 2008). Homogeneous nucleation in the CPC should be avoided during experiments. In our experiment this was achieved by an appropriate temperature selection of saturator and condenser and was checked with a zero measurement.

Counting efficiency and cutoff

The total counting efficiency, i.e., the fraction of particles in the ambient aerosol detected by the CPC, at a given particle size is given by

$$\eta_c(D_p) = \eta_s(D_p) \cdot \eta_a(D_p) \cdot \eta_{det}(D_p), \quad (2.10)$$

where η_s denotes the sampling efficiency inside the CPC, η_a the activation efficiency, and η_{det} the detection efficiency (Stolzenburg et al. 1991). In more detail:

- η_s is given by the ratio of particles entering and exiting the instrument and therefore describes internal particle losses in the CPC (Stolzenburg et al. 1991).
- η_a is given by the fraction of particles which are activated in the condenser and is therefore influenced by the saturation ratio (Stolzenburg et al. 1991).
- η_{det} is the ratio of particles which grow to large enough droplets to be detected by the optical system (Stolzenburg et al. 1991).

The three efficiencies mentioned above can only be evaluated theoretically with simulations (such simulations can be, for example, found in (Stolzenburg et al. 1991)). To characterize the performance of a CPC, the counting efficiency curve is taken which is a function of particle size. It is given by the ratio of the particle number concentration measured with the CPC, N_{act} , to the total particle number concentration, N_{tot} , (Hermann et al. 2001) and can be calculated according to Eq. (2.9). Note that N_{act} is a function of particle size and that a reference instrument is needed to measure N_{tot} (P.M. Winkler et al. 2022). From the counting efficiency, the cutoff diameter can be determined and is defined as the diameter where the counting efficiency decreases to 50% (P.M. Winkler et al. 2022). This decrease can have different causes, namely, it can be a consequence of the limited heterogeneous nucleation and it can be affected by non-uniformities of the saturation ratio or by particle losses (P.M. Winkler et al. 2022). The cutoff diameter is also used to characterize the counting efficiency curve and to describe the lower detection limit (Hermann et al. 2001). Note that the temperature difference between saturator and condenser influences the cutoff diameter (Tuch et al. 2016).

Coincidence

Another limiting factor of CPCs is coincidence. It happens if the number concentration of the aerosol particles is too high and two or more particles are in

the sensing volume (Hinds 2012). As a result it comes to an underestimation of the particle number concentration (Hinds 2012). Depending on the used instrument the aerosol should be diluted under a certain threshold to avoid coincidence (Hinds 2012). If this is not possible the reduction of the particle concentration due to coincidence can be described as

$$\frac{N_o}{N_t} = \exp(-N_t Q \tau). \quad (2.11)$$

It describes the ratio of the observed counts N_o to the true counts N_t . Q denotes the flow rate through the sensitive volume and τ the time the particles need to traverse the beam (Hinds 2012).

2.2 Particle losses

To transport aerosol particles from a sampling location to the measuring devices, a system is needed that ideally does not change the aerosol characteristics, composition, concentration or size distribution (Weiden et al. 2009). However, in a real system various particle loss mechanisms can be found during the particle transport (Weiden et al. 2009) and according to Hinds 2012 the five most important mechanisms include the following.:

1. **Interception:** The case when a particle follows the streamline of the gas, gets too close to a wall and deposits there (Hinds 2012). Compared to other particle loss mechanisms interception has a small effect and can be neglected in most cases (Weiden et al. 2009).
2. **Inertial impaction:** If there is a bend, a contraction or an enlargement of the tubing and the gas streamline changes the direction, bigger particles can not follow and may deposit (Weiden et al. 2009). This happens because larger particles have higher inertia and thus cannot adapt quickly enough to the abrupt change in streamline (Hinds 2012).
3. **Gravitational settling:** Due to the gravitational force, which always influences the particles, deposition can occur (Hinds 2012).
4. **Diffusion:** For small particles the Brownian motion increases the probability of hitting a wall when travelling past it (Hinds 2012).
5. **Electrostatic attraction:** Happens when the aerosol particles have an opposite charge compared to the wall and are then attracted to it due to Coulomb attraction (Hinds 2012). To minimize this effect the tubing should be grounded and consist of a conductive material, so that there is no electric field inside the tube (Weiden et al. 2009).

Note that as most particle losses happen during transport the length of the tubing is important (Weiden et al. 2009). Due to the size of the particles used in our experiment, the main loss mechanisms are electrostatic attraction and diffusion losses. Diffusion losses will be discussed again in more detail.

Diffusion losses

Due to Brownian motion a net flux of particles from areas with high to areas with low concentration is created (Kulkarni et al. 2011). This mainly affects particles with a size below 100 nm (Weiden et al. 2009) and there is a net transport of particles to the walls where they deposit (Weiden et al. 2009). The transport efficiency which takes diffusion losses into account is described by Kulkarni et al. 2011 as

$$\eta_{diff}(d) = \exp\left(-\frac{\pi DL \cdot Sh}{Q}\right), \quad (2.12)$$

where Sh denotes the Sherwood number and D the particle diffusion coefficient, L the tube length, and Q the flow rate (Kulkarni et al. 2011). The Sherwood number, also called the mass transfer coefficient, is a dimensionless parameter whose definition contains the deposition velocity for diffusion (Kulkarni et al. 2011). Furthermore, it is connected with the Reynolds number Re and the Schmidt number Sc for laminar and for turbulent flow conditions (Kulkarni et al. 2011). In Eq. (2.12), different definitions of the Sherwood number are used for different flow conditions (Kulkarni et al. 2011). For laminar flow conditions the definition of the Sherwood number according to Holman 1972 is

$$Sh = 3.66 + \frac{0.2672}{\xi + 0.10079 \cdot \xi^{1/3}} \quad (2.13)$$

with $\xi = \frac{\pi DL}{Q}$. For turbulent flow conditions an experimentally obtained Sherwood number

$$Sh = 0.0118 \cdot Re^{7/8} \cdot Sc^{1/3}. \quad (2.14)$$

by Friedlander et al. 1957 is used.

2.3 Pressure dependence of CPCs

To determine the pressure dependency of a CPC, a closer look at the counting efficiency is needed. Following Barmounis et al. 2018 the counting efficiency depends mainly on the activation probability which is a function of the supersaturation and the particle diameter. Therefore the supersaturation profile of a CPC is worth a closer look and various works have already simulated the supersaturation profile of the condenser tube (e.g. Zhang et al. 1990, Stolzenburg et al. 1991). These

simulations were made by solving the heat and mass transfer equations (Barmounis et al. 2018). In Zhang et al. 1990 a study on the pressure, temperature, and flow rate dependence of the performance of a CPC is performed. There it was found that the pressure and flow rate influence the condensation process (Zhang et al. 1990). As the counting efficiency depends on the supersaturation it can be said that the counting efficiency is a function of the Reynolds number Re , the Prandtl number Pr , the Schmidt number Sc , the length to diameter ratio of the condenser, the saturator temperature T_s , and the temperature difference between the saturator and the condenser δT (Zhang et al. 1990), i.e.,

$$\eta = f \left(Re, Pr, Sc, \frac{L}{D_t}, T_s, \delta T \right). \quad (2.15)$$

Re , Pr , and Sc are dimensionless parameters which are determined by the operating parameters of the instrument and the physical properties of the carrier gas and the condensing vapor (Zhang et al. 1990). They are defined as following:

- **Reynolds number:** The Reynolds number is defined as the ratio of inertial forces to viscous forces and is used to describe the flow condition in a system (Kulkarni et al. 2011). It can be written as

$$Re = \frac{\rho U D_t}{\mu}, \quad (2.16)$$

where ρ denotes the density of the carrier gas, U the mean velocity of the flow through the condenser, D_t the inner diameter of the condenser tube, and μ the dynamic viscosity of the gas (Zhang et al. 1990).

- **Prandtl number:** The Prandtl number is the ratio of the kinematic viscosity ν to the thermal diffusivity α and can be written as (Zhang et al. 1990)

$$Pr = \frac{\nu}{\alpha}. \quad (2.17)$$

- **Schmidt number:** The Schmidt number is defined as the ratio of the kinematic viscosity ν to the diffusion coefficient D and is used to describe the diffusive transport in fluids (Kulkarni et al. 2011)

$$Sc = \frac{\nu}{D}. \quad (2.18)$$

The kinematic viscosity can be expressed as $\nu = \frac{\mu}{\rho}$ and the thermal diffusivity as $\alpha = \frac{k}{\rho c_p}$, where k is the thermal conductivity and c_p the specific heat capacity

(Zhang et al. 1990).

Following Zhang et al. 1990 the mean velocity U , the diffusion coefficient D and the density ρ of the gas can be rewritten to

$$U = U_0 \left(\frac{U}{U_0} \right) = U_0 \left(\frac{Q}{Q_0} \right) \quad (2.19)$$

$$D = D_T \left(\frac{P_0}{P} \right) \quad (2.20)$$

$$\rho = \rho_0 \left(\frac{P}{P_0} \right), \quad (2.21)$$

where U_0 denotes the mean velocity at standard sample flow rate Q_0 , D_T the diffusion coefficient at atmospheric pressure and temperature, P_0 the atmospheric pressure, and ρ_0 the density at atmospheric pressure (Zhang et al. 1990). Using Eq. (2.19)-Eq. (2.21) one can rewrite Eq. (2.16)-Eq. (2.18) and gets

$$Re = Re_0 \left(\frac{Q}{Q_0} \right) \left(\frac{P}{P_0} \right) \quad (2.22)$$

$$Pr = Pr_0 \quad (2.23)$$

$$Sc = Sc_0. \quad (2.24)$$

Here Re_0 , Pr_0 , and Sc_0 are the Reynolds, Prandtl and Schmidt number at standard operating conditions (Zhang et al. 1990). This shows that the Prandtl and the Schmidt number are independent of the pressure and that only the Reynolds number is a function of pressure and flow rate (Zhang et al. 1990). This means that a change in pressure or flow rate will lead to a change in the Reynolds number and therefore to a change in the heat and mass transfer which will lead to a change in the saturation profile inside the condenser and therefor the activation probability (Zhang et al. 1990).

2.4 Differential mobility analysis

Differential mobility analysis is one of the most common methods to measure size distributions of particles smaller than $1 \mu\text{m}$ and is thus one of the most important measurement techniques (Flagan 2008). Its working principle is that electrostatic forces and properties are used to select particles according to their electrical mobility (Hinds 2012). Differential mobility analysis consists of the combination of a particle classifier, usually referred to as differential mobility analyzer (DMA), which selects particles within a narrow size range, and a detector, which counts the particles in that size interval (Flagan 1999). In addition, a DMA can be used to produce a nearly monodisperse aerosol (Steiner et al. 2010).

2.4.1 Electrical properties

For differential mobility analysis, electrostatic forces are used to achieve high resolution division of small particles (Flagan 1999). If a particle with charge q is in an electric field it experiences the following force:

$$\vec{F} = q \cdot \vec{E}. \quad (2.25)$$

If the above equation equals the drag force and the Reynolds number is less than one an expression for the terminal electrophoretic migration velocity can be found:

$$\vec{v}_{TE} = Z \cdot \vec{E}, \quad (2.26)$$

where Z denotes the electrical mobility (Flagan 2008).

Electrical mobility

The electrical mobility Z describes the relationship between the terminal electrophoretic migration velocity $\vec{v}_{TE}$ and the applied electric field $\vec{E}$ (Hinds 2012). It can be written as

$$Z = \frac{\vec{v}_{TE}}{\vec{E}} = \frac{ieC_c(d_p)}{3\pi\eta d_p}, \quad (2.27)$$

where ie denotes the particle charge (i denotes the number of charges and e the elementary charge), d_p the particle diameter, C_c the Cunningham correction factor, and η the gas viscosity (Wiedensohler et al. 2018).

The Cunningham correction factor is needed for small particles, i.e., particles whose size is approximately equal to the mean free path λ , because noncontinuum effects become important for these particles (Seinfeld et al. 2016). It depends on the particle diameter d_p and the mean free path λ :

$$C_c(d_p) = 1 + \frac{\lambda}{d_p} \left[2.34 + 1.05 \exp \left(-0.39 \frac{d_p}{\lambda} \right) \right]. \quad (2.28)$$

From Eq. (2.27) it can be seen that the electrical mobility Z is dependent on the particle diameter and can thus be used to select specific particle diameters.

Particle charging

To measure the size distribution with differential mobility analysis the knowledge of the charging probability as a function of the particle size is needed (Flagan 2008). The charging probability indicates the capability of a particle to gain a net charge of a given polarity (Ibarra et al. 2020). There are different charging mechanisms for aerosol particles, e.g. diffusion or field charging (Hinds 2012). For

the differential mobility analysis it is necessary to change the charge state of the particles to produce a known charge distribution (Flagan 2008). The charging of aerosol particles and the resulting charge distributions are widely discussed and several approaches are developed, e.g. Fuchs distribution, Boltzmann distribution, or Wiedensohler distribution (Gerhard Steiner 2011). Wiedensohler 1988 derived an approximation formula for a bipolar charge distribution that gives the fraction of particles that carry k charges in the steady-state charge distribution (Flagan 2008):

$$f(k) = 10^{\sum_{i=0}^{i=5} \alpha_i(k)(\log D_p)^i}. \quad (2.29)$$

Here the coefficients $\alpha_i(k)$ of this Wiedensohler approximation are empirically fitted to the Fuchs solution and the appropriate values can be found for example in Flagan 2008. Based on this theory a charging probability can be determined and is shown in Fig. 2.6.

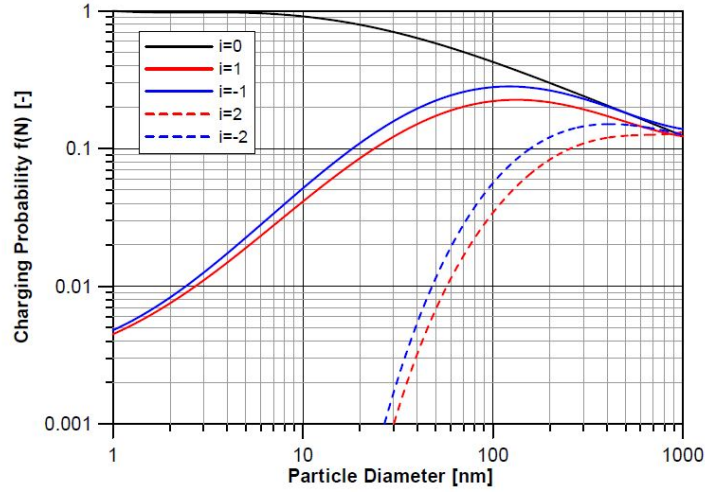


Figure 2.6: Charging probability of the Wiedensohler approximation for positive and negative singly and doubly charged particles and for particles without a charge (Gerhard Steiner 2011).

Fig. 2.6 shows that the charging probability depends on the particle diameter. The larger a particle, the higher the probability to carry a higher number of charges. It should be noted that the charging probability for more charges, i.e. $i = 3, 4, \dots$ are not shown in the figure, but still may occur. For particles with a diameter of up to nearly 30 nm, the charging probability for more than one charge is negligible and for particles with a diameter below 100 nm only few carry more than one charge (Flagan 2008).

2.4.2 Classifier: Differential mobility analyzer

Measurements of particle size distributions based on the electrical mobility have been performed since 1902, but the first so-called DMA was not presented until 1975 by Knudson and Whitby (Kulkarni et al. 2011). Since then, the design has been modified and improved to achieve better results (Kulkarni et al. 2011). One of the designs is the Vienna type DMA, which is important for the experiments and will be described in more detail below.

Instrument

The Vienna type DMA is a cylindrical capacitor whose inner electrode, unlike other types of DMAs, is shaped like a bullet (Steiner et al. 2010). A schematic cross section of the instrument is shown in Fig. 2.7.

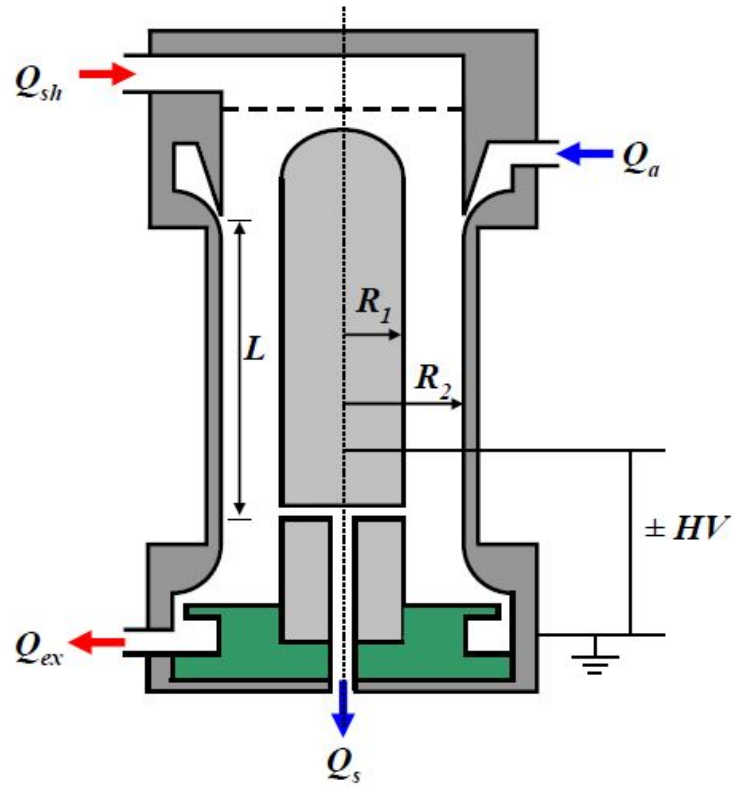


Figure 2.7: Schematic cross section of a Vienna type DMA from Gerhard Steiner 2011.

To determine the performance of a DMA two types of parameters are needed: the geometry parameters and the operating conditions as described in Reischl 1991. All of them are shown in Fig. 2.7. The geometry parameters include the outer radius of inner electrode R_1 , the inner radius of outer electrode R_2 and the distance from

the aerosol inlet to the aerosol outlet L (Reischl 1991). The operating conditions are composed of four flow rates: An incoming aerosol flow rate Q_a from which certain particles will be selected, an outgoing sample flow rate Q_s which contains only the selected particles, an incoming clean gas flow, called sheath air Q_{sh} and the outgoing excess air flow rate Q_{ex} , where all particles which are not selected leave the DMA (Steiner et al. 2010). Note that Q_{sh} and Q_{ex} are approximately equal.

Working principle

The sheath air Q_{sh} enters tangentially at the top of the DMA and just after the inlet there is a laminarization screen which ensures that the flow is laminar (Gerhard Steiner 2011). Below the sheath air, the aerosol flow Q_a is introduced, also tangentially, and the bullet shaped inner electrode causes a smooth transition of the two flows (Gerhard Steiner 2011). The particles flow between the two electrodes to which a voltage is applied (Hinds 2012). Due to the resulting electric field the particles are deflected and only particles with a certain electric mobility can flow through the gap and thus through the aerosol outlet (Q_s) (Kulkarni et al. 2011). Particles with higher mobility migrate earlier and deposit on the inner electrode, while particles with lower mobility are deflected later and deposit behind the gap (Kulkarni et al. 2011). All particles not selected exit the DMA with the excess flow Q_{ex} which is filtered and dried and then fed back into the DMA as clean sheath air (Flagan 2008). Following Flagan 2008 there are two flow ratios which characterize the performance of the DMA:

$$\delta = \frac{Q_s - Q_a}{Q_s + Q_a} \quad (2.30)$$

$$\beta = \frac{Q_a + Q_s}{Q_{sh} + Q_{ex}}. \quad (2.31)$$

δ represents the imbalance of the aerosol flows (Flagan 2008) and β indicates the limiting resolution of the DMA for balanced flows ($\delta = 0$) and no diffusion (Flagan 1999). For fixed operating conditions, the following unique relationship between the electrical mobility selected with the DMA and the applied voltage can be found (Steiner et al. 2010):

$$\begin{aligned} Z &= \frac{1}{V} \left(\frac{Q_{sh} + Q_{ex}}{2} \right) \frac{\ln(R_2/R_1)}{2\pi L} \\ &\stackrel{Q_{sh}=Q_{ex}}{=} \frac{Q_{sh}}{V} \frac{\ln(R_2/R_1)}{2\pi L}. \end{aligned} \quad (2.32)$$

Here, V denotes the applied voltage (Steiner et al. 2010). For our experiments we assume that geometry parameters and operating conditions are fixed. In reality,

not only particles with the calculated mobility are selected, but also particles with slightly higher and lower electrical mobility can be transmitted to the sample flow (Flagan 2008). If the flows are balanced the upper and lower limit can be described as (Flagan 2008)

$$\begin{aligned} Z_{min} &= Z(1 - \beta) \\ Z_{max} &= Z(1 + \beta). \end{aligned}$$

The probability that a particle with a certain electrical mobility is selected can be described with the DMA transfer function which has the form of a triangle (Wiedensohler et al. 2018). The transfer probability that a range of electrical mobilities is selected is 50% (Wiedensohler et al. 2018). In reality its shape differs slightly from a triangle due to diffusion (Wiedensohler et al. 2018).

Multiple charges

As already mentioned, particles can carry more than one elementary charge which has to be considered in the data evaluation. To find doubly charged particles which have the same electrical mobility as singly charged particles the following formula has to be solved (which can be obtained from Eq. (2.27)):

$$i_1 \cdot \frac{D_{p,2}}{C_c(D_{p,2})} = i_2 \cdot \frac{D_{p,1}}{C_c(D_{p,1})}. \quad (2.33)$$

The formula shows that $D_{p,1}$ and $D_{p,2}$ are not equal, but, as they have the same electrical mobility, can be both present if a certain voltage is applied. i_1 and i_2 denote the number of charges on the particles with diameter $D_{p,1}$ and $D_{p,2}$, respectively. Assuming $D_{p,1}$ is singly charged and $D_{p,2}$ doubly charged, $i_1 = 1$ and $i_2 = 2$. Therefore, the knowledge of the charge distribution is also important. To get the corresponding doubly charged particle sizes Eq. (2.33) must be solved numerically.

To obtain the voltage necessary to select particles of a certain diameter, Eq. (2.27) and Eq. (2.32) must be set equal. This leads to the following:

$$\begin{aligned} \frac{Q_{sh}}{V} \frac{\ln(\frac{R_2}{R_1})}{2\pi L} &= \frac{ieC_c(D_p)}{3\pi\eta D_p} \\ \Rightarrow V &= \frac{Q_{sh} \cdot \ln(\frac{R_2}{R_1})}{2\pi L} \cdot \frac{3\pi\eta D_p}{ieC_c(D_p)}. \end{aligned} \quad (2.34)$$

Here η is the dynamic viscosity of air, e the elementary charge and i the number of charges.

2.4.3 Size distribution

To measure a size distribution, one has to select voltages which span over the whole operating range of the DMA to get particle concentrations in narrow mobility bins (Flagan 2008). Due to the known relationship between the electrical mobility and the particle size, the mobility distribution can be converted into a size distribution by a numerical inversion (Wiedensohler et al. 2018). Following Reischl 1991 the formula

$$R(V) = \frac{Q_q^2}{Q_{sh}} \cdot \sum_{i=1}^{\infty} \left[\alpha(D, i) \cdot \psi(D) \cdot \frac{dN}{d \ln D_p} \right]_{D=D_i} \quad (2.35)$$

shows the response of a CPC (i.e. its counting rate) for a certain input distribution $\frac{dN}{d \ln D_p}$ (Reischl 1991). Additionally, $\alpha(D, i)$ denotes the charging probability function and $\psi(D)$ the dimensionless transfer function.

3 Experimental methods

This section describes the methods that are used to characterize the furnace size distribution and the CPCs at ambient pressure and different low pressure levels. It starts with a description of the used instruments, i.e., the instruments for aerosol particle generation, selection and detection. Then the setups for both, the characterization of the furnace size distribution and the measurements at ambient and different low pressure levels are described. Furthermore, the data evaluation will be discussed.

3.1 Instruments

The instruments that are used in the two setups (see Section 3.2) will be described in detail below. In general the instruments are classified according to their intended use in particle generation, particle selection and particle detection. Fig. 3.1 shows this classification with a simplified setup of the CPC characterization.

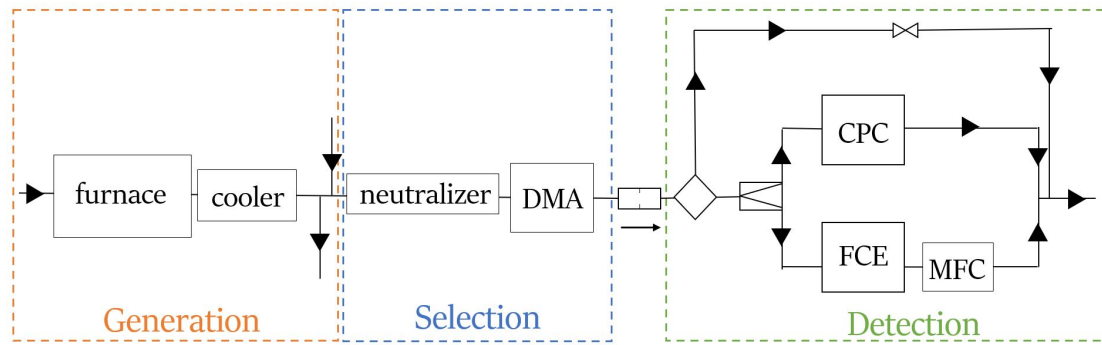


Figure 3.1: *Simplified setup for CPC characterization with the classification in particle generation, selection and detection.*

3.1.1 Particle generation

Following the CEN standard (CEN/TS 2016), particles are generated by evaporating silver in a tube furnace. In our experiments we were using a furnace built by the company Nabertherm with clean air as carrier gas. A sketch of the furnace is shown in Fig. 3.2.

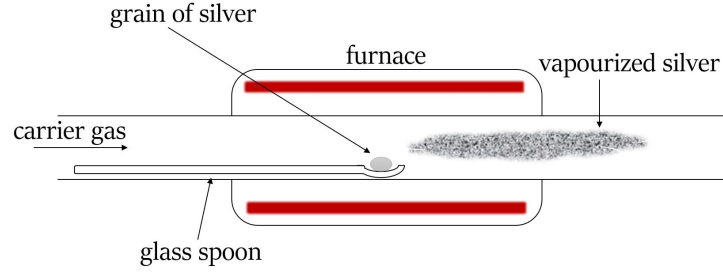


Figure 3.2: *Schematic of the furnace used for particle generation.*

In this instrument the carrier gas passes through a glass tube and the silver is placed at its central position using a glass spoon. Due to the high temperature in the furnace the silver evaporates and is carried away with the carrier gas. After the furnace, a water cooler is installed which allows the generation of aerosol particles. This happens via homogeneous evaporation and condensation of the gaseous matter (Scheibel et al. 1983).

Fig. 3.3 shows a schematic of the used setup, including operating temperatures, for the silver particle generation. For silver to evaporate, a temperature above 900°C is required in the furnace (Scheibel et al. 1983). The water cooler behind the furnace is set to 15°C with a cooling circulator. Depending on the temperature and flow within the furnace the resulting size distribution of the aerosol particles varies. This variation of the distribution is shown in Section 4.1.

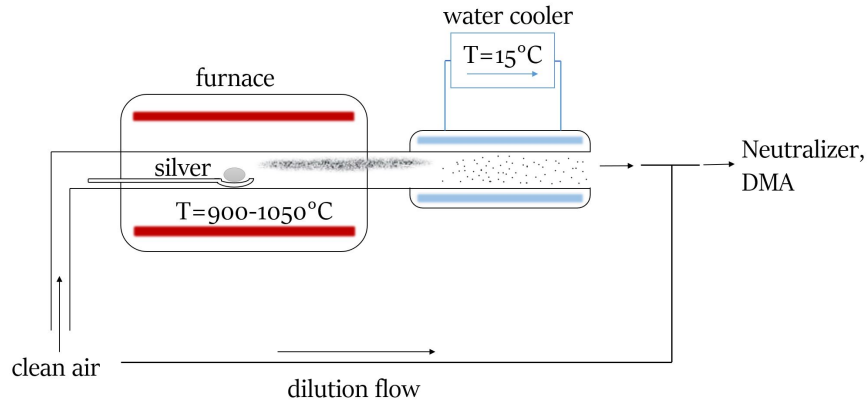


Figure 3.3: *Schematic of the setup for the silver particle generation using a furnace and a water cooler. The operation temperatures are shown for each of the devices individually.*

3.1.2 Particle selection

One of the most common methods to measure size distributions or to obtain monodisperse particles is the differential mobility analysis, presented in detail in Section 2.4. A central quantity is the electrical mobility, which depends on the charge and the size of the aerosol particle as shown in Eq. (2.27). An aerosol neutralizer was used to create a defined charge distribution. The particles are then selected, depending on their electrical mobility, with a Vienna type nano-DMA.

Neutralizer

We utilized a soft X-ray aerosol neutralizer (TSI Neutralizer model 3087) in our experiments, which is a bipolar diffusion charger (TSI Incorporated 2010). Soft X-rays are used to generate ions and creating a balanced number of positive and negative charges (TSI Incorporated 2010). Bipolar diffusion charging describes the case where both positive and negative ions are present (Kulkarni et al. 2011). Thus, due to the attachment of charges with the same polarity the magnitude of charges on a particle increases and due to the attachment of charges with opposite polarity the magnitude of charges on a particle decreases (Kulkarni et al. 2011). Diffusion charging in general describes the process when the generated ions are brought through diffusion to the particles and they then interact and exchange charges (TSI Incorporated 2010). The rate of ion attachment depends on the diffusion rate of the ions and on the migration in the electric field which is induced due to the interaction (Kulkarni et al. 2011). If a balanced ion population is used a quasi-steady charge state of the aerosol particles is reached (Kulkarni et al. 2011). Then the rate of attachment of positive ions equals the rate of attachment of negative ions (Kulkarni et al. 2011).

Fig. 3.4 shows a schematic of the used instrument. Charged particles flow in at the bottom of the neutralizer and attract air ions inside that have the opposite charge (TSI Incorporated 2010). If the residence time and the ion concentration is sufficiently high, a steady state charge distribution is reached (TSI Incorporated 2010).

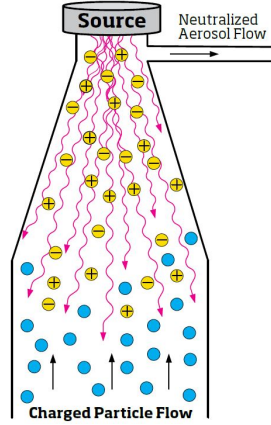


Figure 3.4: Schematic of the TSI neutralizer model 3087 (TSI Incorporated 2010).

Differential mobility analyzer

For our experiments a nano-DMA is used which is based on a Vienna-type design. The prefix nano indicates the order of magnitude in which the DMA can measure, which here is the nanometer size range (Kulkarni et al. 2011). The working principle of this instrument is explained in Section 2.4.2. Table 3.1 lists the parameters of the DMA used in the experiments.

Table 3.1: Parameters of the used DMA.

Parameter	
L	15.5 mm
R_1	17.5 mm
R_2	24 mm
Q_{sh}	24 l min^{-1}
Q_{ex}	24 l min^{-1}
Q_a	2 l min^{-1}
Q_s	2 l min^{-1}

The sheath and the excess flow were kept constant throughout the whole experiment. Furthermore, for the pressure measurements the aerosol flow was also kept constant to always have the same DMA resolution (a detailed description can be found in Section 3.2.2).

Multiple charges

The bipolar charge distribution obtained from the neutralizer may also contain multiple charges, which must be taken into account. In our experiments, measures were taken to avoid multiple charges. First, only particles up to 30 nm were measured and second, similar to Tuch et al. 2016 particles at the right flank of the furnace distribution are measured which further reduces the number of multiple charged particles. Due to these two reasons, in the measured size range only single charged particles have to be considered. Table 3.2 shows some important parameters, like the diameter of singly charged and the corresponding doubly charged particles, the appropriate DMA voltage and the charging probabilities for singly and doubly charged particles. It shows that the charging probability for doubly charged particles below 20 nm is negligible. However, even for 30 nm particles the charging probability for doubly charged particles is only 0.2% which is rather low and therefore it is rather unlikely to measure them.

Table 3.2: *Table with diameters of singly and corresponding doubly charged particles, the DMA voltage and the charging probabilities for the singly and doubly charged particles.*

$D_{p,single}$ [nm]	$D_{p,double}$ [nm]	U [V]	$\alpha(D_p, 1)$ [%]	$\alpha(D_p, 2)$ [%]
5	7.1	160.8	1.9	$1.1 \cdot 10^{-7}$
10	14.3	634.5	4.1	0.0007
15	21.6	1408.1	6.4	0.02
20	28.9	2469.1	8.5	0.08
25	36.4	3805.1	10.4	0.2
30	43.9	5404.1	12.1	0.4
50	74.6	14204.7	17.0	1.8
100	155.5	49603.7	21.4	5.7

3.1.3 Particle detection

Behind the particle generation and selection two different instrument types were used for particle detection. On the one hand two different CEN standardized CPC models and on the other hand an Faraday cup electrometer (FCE) as a reference instrument.

Condensation particle counter

Two different CPC models are used for the experiments, namely four CPCs of the model Grimm 5410 CEN (labelled ACTRIS1-ACTRIS4) and two CPCs of the

model TSI 3772-CEN (labelled TSI CPC1 and TSI CPC2). ACTRIS1-ACTRIS4 are new acquisitions at the Department of Physics and have not yet been characterized. Whereas, TSI CPC1 and TSI CPC2 are older models and were, for example, already used for measurements by Spät 2020. Both CPC models are conductive cooling CPCs which work with a continuous flow and basically consist of three blocks: the saturator, the condenser and the optics block (Kulkarni et al. 2011). Their operation principle is based on generation of supersaturation of a working fluid vapor by diffusion cooling and condensational growth of the particles (Kulkarni et al. 2011). The working principle of CPCs is described in more detail in Section 2.1.4. Fig. 3.5 shows a schematic of the TSI 3772-CEN CPC. The structure of the Grimm 5410 CEN is very similar.

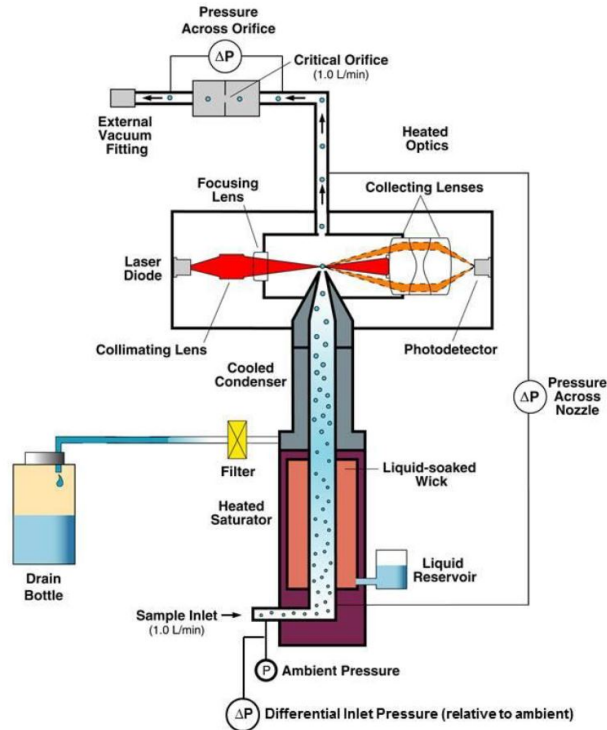


Figure 3.5: *Schematic of the TSI 3772-CEN CPC (TSI Incorporated 2016).*

Grimm 5410 CEN

The Grimm 5410 CPC is a compact instrument which uses n-butanol as a working fluid and can operate either in a single counting mode (particle concentration up to 10^5 cm^{-3}) or in a photometric mode (particle concentration up to 10^7 cm^{-3}) (Grimm 2020a). The settings of this instrument can be adjusted to be CEN compliant (Grimm 2020a). According to Grimm 2020b the working principle and

specific functions of this instrument are as follows:

- **Specific functions:** In default settings, the temperature of the saturator is 36 °C and that of the condenser is 10 °C, resulting in a cutoff diameter of 4 nm. However, for the CPC to be CEN compliant, the cutoff diameter must be 7 nm and thus, the settings of the device have to be adjusted. To get a cutoff diameter of 7 nm the temperature of the saturator must be 36 °C and the temperature of the condenser must be 17 °C. As already mentioned, this instrument has two different counting modes: the single particle counting mode detects single scattered light pulses whereas the photometric mode measures the scattered light of an aerosol cloud. While an empirical calibration is required for the photometric mode, the single counting mode is an absolute measurement. After the detection, the measured count rates are converted into number concentrations with an instrument specific calculation flow rate by the device itself. (Grimm 2020b)
- **Flow system:** The Grimm 5410 CPC operates at a flow rate of 0.6 L min⁻¹ which is controlled with a temperature stabilized critical orifice. For a constant flow rate to pass through the orifice, the pressure ratio of the upstream and downstream must be large enough and depends on the gas. E.g., for air this lower limit is approximately 2. This ratio is monitored constantly with pressure sensors. (Grimm 2020b)

TSI 3772-CEN

The TSI 3772-CEN CPC is a compact, single particle counting instrument which uses n-butanol as a working fluid and is designed to follow the CEN standard (TSI Incorporated 2016). It can detect particles down to 7 nm in a concentration range from 0 to 5 · 10⁴ cm⁻³ (TSI Incorporated 2016). Following the description in TSI Incorporated 2016 the TSI 3772-CEN CPC has the following important features.

- **Specific functions:** The temperature of the saturator is set to 39 °C and the condenser is set to 18 °C. These temperature settings result in a cutoff diameter of 7 nm. The optics block has a temperature of 40 °C to prevent condensation on the lens surfaces. The instrument operates in a single counting mode and the maximum concentration is 5 · 10⁴ cm⁻³. Moreover, up to this concentration the CPC can use a continuous, live-time coincidence correction to improve the counting accuracy. (TSI Incorporated 2016)
- **Flow system:** The TSI 3772-CEN CPC operates with a critical flow of 1 L min⁻¹. To achieve this an orifice and an external pump is used to operate at the critical pressure ratio which then provides a critical flow, which is stable and constant. This volumetric flow assures accurate concentration

measurements even with varying inlet pressures. Conversely to the Grimm CPC the manual of the TSI CPC defines an upper limit for the critical pressure ratio. Here, the pressure ratio is defined as downstream divided by upstream. For air the critical ratio has to be below 0.528 (TSI Incorporated 2016). According to Kangasluoma et al. 2015 the TSI 3772-CEN has a multitube condenser, which means that the flow is split up in 8 parts, which leads to $\frac{1}{8}$ of the inlet flow in the condenser tube, which is 0.125 L min^{-1} (Kangasluoma et al. 2015).

Comparison of the two CPC models

Now that both instruments have been described in more detail, the similarities and differences will be highlighted:

- **Similarities:** First of all, both CPCs are continuous flow conductive cooling CPCs, which means that they basically have the same working principle. Moreover, as they are both CEN compliant, their working fluid is n-butanol and the cutoff diameter can be set to 7 nm.
- **Differences:** The main differences between the models are in the flow rates and temperature settings to get a cutoff diameter of 7 nm. The temperature settings include the temperature of the saturator T_{sat} and the temperature of the condenser T_{cond} . However, the flow rates are differentiated between the flow rate of the instrument Q_i and the flow rate through the condenser Q_c . While the two are the same for the Grimm 5410 CEN, they are different for the TSI 3772-CEN. The exact values are given in Table 3.3.

Table 3.3: Differences of the two used CEN-CPCs.

	Grimm 5410 CEN	TSI 3772-CEN
Q_i [L min^{-1}]	0.6	1
Q_c [L min^{-1}]	0.6	0.125
T_{sat} [$^{\circ}\text{C}$]	36	39
T_{cond} [$^{\circ}\text{C}$]	17	18

Faraday cup electrometer

Faraday cup electrometers (FCEs) are the simplest form of an electrical aerosol measurement instrument and mainly consist of two parts: an electrometer and a Faraday cup (Yang et al. 2018). In Fig. 3.6 a schematic of an FCE is shown.

The Faraday cup shield is made of conductive metal with a filter that collects charges inside (Intra et al. 2015). The conducting enclosure surrounding the filter is called Faraday cage and it allows the particles to pass through while isolating the electric field by inducing a charge equal to that carried by the particle (Kulkarni et al. 2011). This generates an electric current which is measured with the electrometer (Yang et al. 2018). According to Pihlava et al. 2016 the measured electric current is the sum of two components: the signal from the charged aerosol particles and the offset signal which is caused by disturbances in the electrometer itself. The offset is sensitive to measurement conditions (Pihlava et al. 2016), so for the best performance the electrometer should not be exposed to electric fields or humidity (Kulkarni et al. 2011). Moreover, the offset causes a lower detection limit in the measurement of number concentrations (Yang et al. 2018).

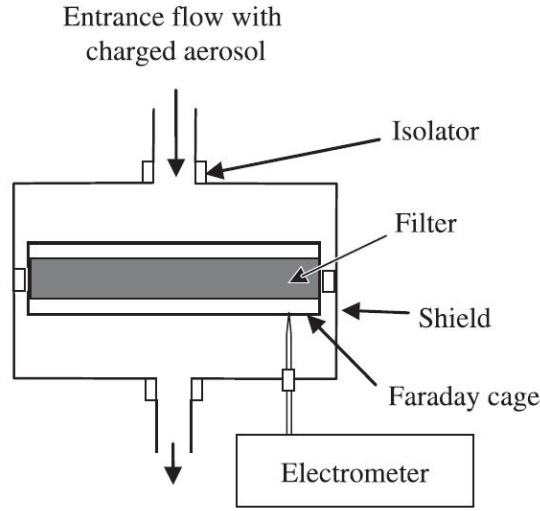


Figure 3.6: Schematic of a Faraday cup electrometer (FCE) (Kulkarni et al. 2011).

The electric current is connected to the particle number concentration with the following relation (TSI Incorporated 2018):

$$N = \frac{I}{e \cdot i \cdot Q_{FCE}}. \quad (3.1)$$

Here, N denotes the particle number concentration, I the electrical current, e the elementary charge, i the number of charges per particle, and Q_{FCE} the flow rate through the FCE (TSI Incorporated 2018). For this work the flow through the FCE is regulated with an Alicat mass flow controller and was set to either 0.6 L min^{-1} or 1 L min^{-1} to match the flow rate of the CPC in the setup. Furthermore, i is assumed to be 1 as explained in Section 3.1.2.

3.2 Experimental setup

For the experiments, two different setups are used. One is used for the characterization of the furnace size distribution and the other one is used for the characterization of the CPCs at different pressure levels.

3.2.1 Setup for the furnace size distribution characterization

For the characterization of the furnace size distribution the setup in Fig. 3.7 was used. Its main stages are:

- **Flow Generation:** Compressed air enters the system and then passes through two air volumes in order to compensate pressure fluctuations. At the end of this stage the flow is regulated to ambient pressure, i.e., 1 bar, with a pressure meter.
- **Particle Generation:** The flow is split up in two streams: One flow passes through the furnace and thus contains aerosol particles and the other is used as a dilution flow. Both flows can be adjusted with a valve and are dried, filtered and monitored with mass flow meters (TSI 4140 Mass-Flowmeter).
- **Dilution Mixing:** The two flows are mixed again in order to regulate the particle concentration. This stage also contains an outlet in order to exhaust excess air which is filtered for safety reasons.
- **Measurement:** The flow is split up again in two parts via a flow splitter: One part of the divided flow is led through the CPC and the other part flows through the neutralizer, the DMA and the FCE. While the CPC has a fixed flow rate, the flow in the part with the DMA and the FCE is controlled by a mass flow controller (MFC). Both flows are connected to the pump, which draws the air and directs it to the exhaust.

In this setup, the CPC measures the total particle concentration, while the combination of DMA and FCE measures the number size distribution by scanning stepwise over the entire DMA range.

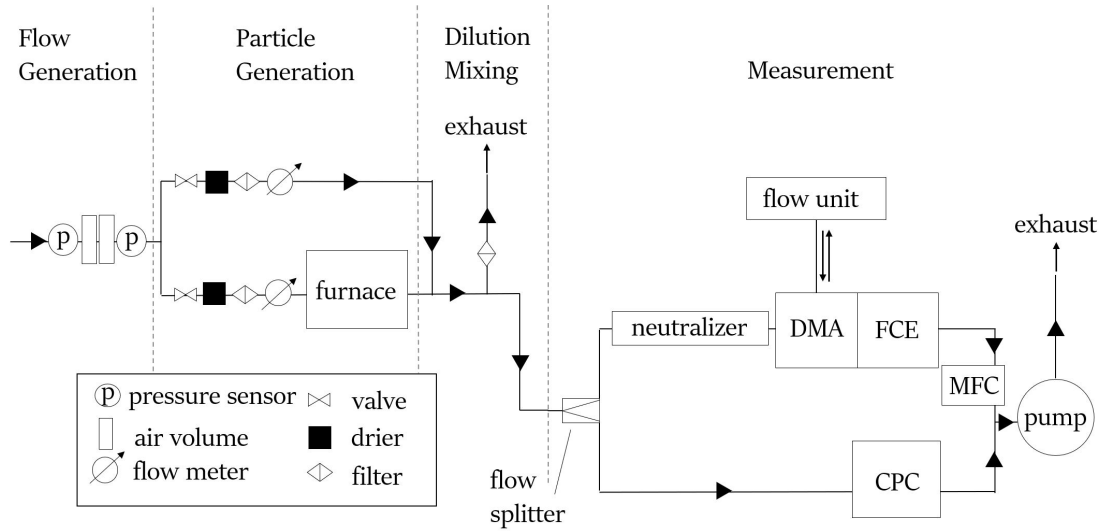


Figure 3.7: Setup for the furnace characterization.

3.2.2 Setup for measurements at different pressure levels

Initially, the setup for the measurements at different pressure levels was inspired by Spät 2020, but in order to keep the resolution of the DMA constant, it was adapted to the setup of Takegawa et al. 2011. With these changes, the biggest difference to the setup of Spät 2020 is the way in which low pressure conditions are generated. Spät 2020 used a pressure reducing valve, whereas, in this work, following Takegawa et al. 2011, the low pressure was generated with a limiting orifice (detailed explanation follows below). Additionally, in this work only one CPC is in the setup at a time, while in the setup in Spät 2020 both TSI CPCs were measured simultaneously. The setup for the experiments of this work is shown in Fig. 3.8.

The flow and particle generation as well as the dilution mixing are the same as in the previously described setup (Section 3.2.1) and thus will not be covered again. In the measurement stage the flow now passes through the neutralizer and the DMA, filtering certain particle sizes. For the measurements at low pressure levels also a limiting orifice is added. The resulting flow is split into the pump flow and the measurement flow via a turbulent mixing chamber. The measurement flow is split via a flow splitter which then feeds into the CPC and the FCE. The flow of the FCE is adjusted with the mass flow controller so that it is equal to that of the CPC. The pump flow can be regulated with a valve and is used to draw air out of the system. It is directly connected to the pump, which is already indicated by its name. The purpose of the pump flow depends on whether the measurements

are performed at ambient pressure or at low pressure levels.

- **Low pressure measurements:** Behind the DMA, a limiting orifice is built into the setup as an additional element. At the right pressure ratio it works like a critical orifice with a flow of 2 L min^{-1} . However, even in the case that the orifice does not work critical the flow is approximately 1.8 L min^{-1} , so it is close to the critical case. The orifice limits the amount of air in the system and is selected so that it provides enough air to fulfill the default flow requirements of the CPC and the FCE when the valve in the pump flow is closed. With this setting large pressure drops during installation of the orifice can be avoided and thus the CPC is not flooded. The purpose of the pump flow is to draw more air out of the system than the critical orifice allows in. This creates low pressure conditions, which can be monitored with the pressure sensor in the MFC and adjusted with the valve in the pump flow.
- **Ambient pressure measurements:** For the measurements at ambient pressure the purpose of the pump flow is now different. It serves to keep the flow through the DMA at a level of 2 L min^{-1} . This is the same level as enforced by the limiting orifice in the low pressure measurements and with that the DMA resolution is kept constant throughout all measurements.

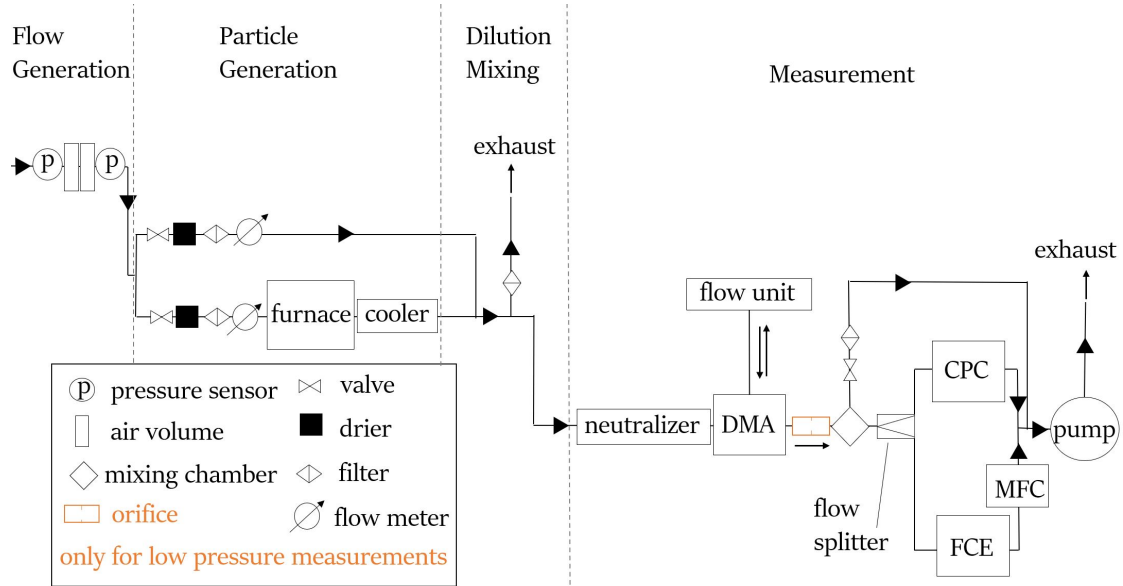


Figure 3.8: Setup for the measurements at different pressure levels. The orifice is only integrated for measurements at low pressure levels.

Note, that for the low pressure measurements the butanol bottles have to be disconnected from the CPCs to avoid flooding. After the measurements the bottles are reconnected. Table 3.4 shows the used flow rates for the measurements. Q_{furnace} and Q_{dilution} were varied in the specified range to obtain a suitable particle concentration. Under low pressure conditions Q_{DMA} is at 2 L min^{-1} due to the limiting orifice and was also kept at this flow rate at ambient pressure to always have the same DMA resolution. The sheath flow rate was chosen to be high enough to get a good DMA resolution. Both CPCs have a fixed flow rate and the flow rate of the FCE was always matched with the CPC in the setup. To make sure that the critical orifices in the two CPC models work critical and therefore their flow is constant an additional pressure sensor is installed after the MFC. More detailed information can be found in Appendix A.

Table 3.4: *Flow rates for ambient and low pressure measurements.*

	Flow [L min^{-1}]
Q_{furnace}	1.0-2.5
Q_{dilution}	0.5-8.0
Q_{DMA}	2.0
Q_{sh}	25.0
$Q_{\text{CPC,TSI}}$	1.0
$Q_{\text{CPC,Grimm}}$	0.6
Q_{FCE}	0.6/1.0 for Grimm and TSI, respectively

3.3 Data evaluation

3.3.1 Size distribution measurements

The particle size distribution (see Fig. 4.1) of the furnace was measured at different temperature- and flow settings. For each of the settings the DMA scans over a size range from approximately 2 nm to 30 nm and the FCE measures the concentration for each applied voltage. As described in Section 3.1.2 the particles are small enough so that they can be seen as single charged and thus only the first term of the sum in Eq. (2.35) will be considered. After rearranging Eq. (2.35) the formula to calculate the number size distribution is

$$\frac{dN}{d\ln D_p} = R(V) \cdot \frac{Q_{sh}}{Q_a^2} \cdot \frac{1}{\alpha(D, 1) \cdot \psi(D)}. \quad (3.2)$$

The calculated number size distribution is then plotted against the diameter.

3.3.2 Measurements at different pressure levels

For the measurements at ambient pressure and different low pressure levels two steps have to be taken: First, the number concentration of the particles has to be measured and afterwards, the counting efficiency has to be calculated. These two processes are described below.

Particle number concentration

For measuring the particle number concentration the actual concentration has to be in the range from 1000 cm^{-3} to $20\,000 \text{ cm}^{-3}$. The lower bound is necessary to be above the background from the FCE and the upper bound to avoid coincidence in the CPC. A particle diameter is selected by applying the right voltage to the DMA and the measurement and data evaluation runs as follows:

- **Concentration measurement:** The particle concentration for the set voltage is measured simultaneously with the CPC and the FCE for 2 min. Afterwards, the mean over that time period is calculated.
- **Background measurement:** The voltage is set to zero for one minute and the concentration is measured with both instruments. While the CPC can not measure any particles, the FCE still records its background signal. Again the mean over the measured time period is calculated.
- **FCE correction:** For each concentration measurement the background of the FCE is approximated by taking the mean of the preceding and the subsequent background measurement. This approximated background is then subtracted from the concentration measurement to get the correct particle number concentration. The number concentration of the FCE is calculated with Eq. (3.1), with $i = 1$.

The Grimm CPC converts the measured counts directly into the number concentration, therefore it is not necessary to perform further calculations. In contrast, for the TSI CPC, the raw counts must be converted to the number concentration, which is done using the following formula:

$$N = N_c \cdot \frac{10}{Q_{TSI}}. \quad (3.3)$$

Here N_c is the number of counts per second and Q_{TSI} the flow of the CPC which is 1 L min^{-1} . The factor 10 accounts for the fact that the TSI CPC makes 10 measurements per second.

Counting efficiency and CEN criteria

The performance of the CPCs is measured in terms of the counting efficiency which is the ratio of the concentration measured by the CPC to the concentration measured by the FCE:

$$\eta(D_p, p) = \frac{N_{CPC}(D_p, p)}{N_{FCE}(D_p, p)}, \quad (3.4)$$

which is equivalent to Eq. (2.9). Note that Eq. (3.4) describes the experimental approach to measuring the counting efficiency. The previously described counting efficiency equation (Eq. (2.10)) describes the components that it is composed of, but they can only be evaluated theoretically. The counting efficiency depends on the particle diameter D_p and the pressure level p . The calculated values are then plotted against the particle diameter to get a so-called cutoff curve. The fit function

$$Eff = E_\infty \cdot \left[1 - \exp \left(- \frac{D_p - D_0}{D_{50} - D_0} \cdot \ln(2) \right) \right] \quad (3.5)$$

from Tuch et al. 2016 will be used to evaluate certain parameters of the cutoff curve. The individual parameters describe the following (Tuch et al. 2016):

- E_∞ : The counting efficiency in the plateau region.
- D_{50} : The 50% counting efficiency, also called cutoff diameter.
- D_0 : The 0% counting efficiency, also called the onset, the point where the CPC first measures particles.

Note, that for CEN compliance, the following requirements must be met (CEN/TS 2016):

- D_{50} : The cutoff diameter has to be $7 \text{ nm} \pm 0.7 \text{ nm}$.
- D_{90} : The 90% counting efficiency has to be $< 14 \text{ nm}$.
- Linearity: At $(40 \pm 10) \text{ nm}$ the linearity has to be $1 \pm 5\%$.

D_{50} and D_{90} can be determined by calculating the counting efficiency and plotting the cutoff curve. The D_{50} can be directly determined through the plot or it can be calculated with the fit function. For the linearity additional measurements are taken and described in Section 3.3.3.

3.3.3 Linearity measurements

To check the linearity a diameter in the plateau region is taken. According to CEN, the diameter must be $(40 \pm 10)\text{nm}$. For the measurements 30 nm is chosen, since the particles are only singly charged here. The measurement and data evaluation is performed as follows:

1. The voltage of the DMA is set to select 30 nm particles at a certain dilution.
2. Both the CPC and the FCE measure the particle number concentration for two minutes and afterwards the mean of the measured time period is taken.
3. The background of the FCE is corrected as in Section 3.3.2.

This procedure is repeated for several dilution settings with a 1 min background measurement in between. Since the selected diameter is in the plateau region, both instruments should measure the same concentration. The measured concentration of the CPC is plotted against the measured concentration of the FCE and the points are expected to be on the identity line. This measurement is done for ambient pressure and all low pressure levels.

3.3.4 Error estimation

For all calculated values an error was estimated based on the systematic uncertainties of the instruments and a Gaussian error propagation. The instrument uncertainties are either specified in the instrument manual (e.g. the uncertainties of the CPCs) or the last displayed stable digit is taken. Table 3.5 shows the uncertainty values.

Table 3.5: *Systematic uncertainties of the used instruments. MFC stands for mass flow controller.*

Instrument	Quantity	Uncertainty
CPC Grimm	N	5%
CPC TSI	N	5%
FCE	I	1 fA
MFC	Q_{FCE}	0.01 L min^{-1}
MFC	p	1 hPa

With the Gaussian error propagation the uncertainties of the number concentration measurements and therefore for the counting efficiencies are calculated. Additionally, the selected diameter from the DMA has an uncertainty. This uncertainty

β , also called limiting resolution, can be calculated according to Eq. (2.31). With $Q_{sh} = Q_{ex} = 25 \text{ L min}^{-1}$ and $Q_a = Q_s = 2 \text{ L min}^{-1}$ the limiting resolution β is 0.08. To get the uncertainty this value has to be multiplied with the particle diameter.

4 Results and discussion

First, the results of the measured size distributions of the furnace are presented. Then, numerous cutoff measurements are discussed. The measurements are taken with either a Grimm 5410 CEN CPC, or with a TSI 3772-CEN CPC. The focus here is first on the measurements at ambient pressure, i.e. 1000 hPa, and on the measurements at different low pressure levels, i.e. 750-150 hPa. Here, special attention is paid to the parameters described in the CEN standard, namely the D_{50} and the D_{90} and it is checked up to which low pressure level the different devices still measure in conformity with the standard. The results of the two different CPC models will also be compared to see which of the two provides a better performance. After that the focus is put on the reproducibility of the measurement results and then a model comparison is performed. The latter is done for the Grimm CPC with four instruments, labelled ACTRIS1-ACTRIS4 and for the TSI CPC with two instruments, labelled TSI CPC1 and TSI CPC2. This examines whether different devices from the same manufacturer and the same model measure consistently. Lastly, measurements are made on linearity, which also serve to control a CEN parameter. All errors and error bars shown have been calculated with the values from Section 3.3.4 and with Gaussian error propagation.

4.1 Furnace size distribution

Size distributions can be used to determine which particle sizes are present and at what concentration. They are influenced by the temperature and flow rate. Fig. 4.1 shows the temperature dependence. Note that Fig. 4.1 a and b are measured with different flow rates. A lognormal fit which has the parameters μ and σ is also shown in the plot. μ describes the expectation value and σ the standard deviation. The calculated fit parameters are listed in Table 4.1. Fig. 4.1 shows that the size distribution shifts with higher temperatures towards larger diameters and higher concentrations. Fig. 4.2 illustrates the influence of the flow rate. The size distribution shifts towards smaller particles and lower concentrations when the dilution flow is turned higher at constant furnace temperature and furnace flow. What is striking about all measured size distributions is that the measured particle sizes are mostly below 40 nm. This has the effect that we do not have to consider any doubly charged particles.

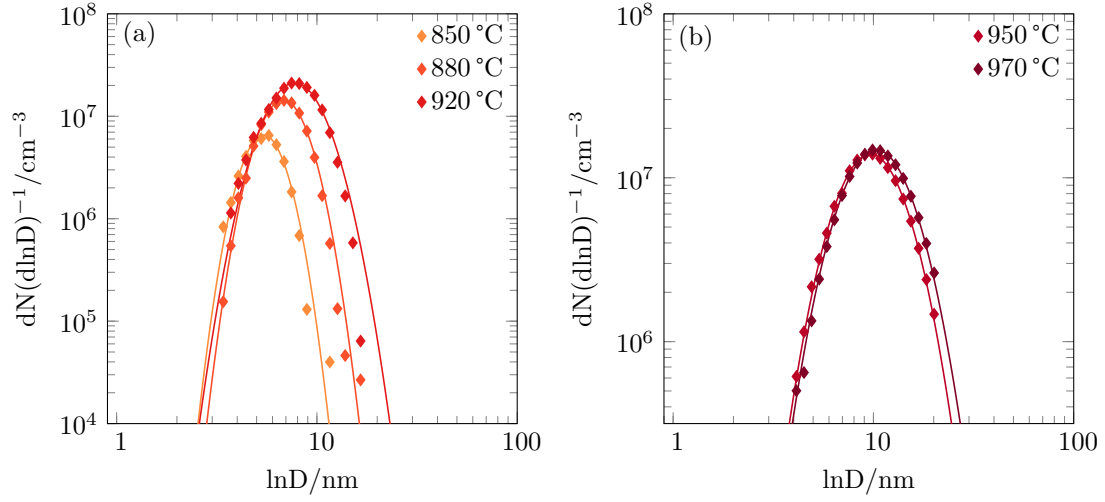


Figure 4.1: Size distributions at different furnace temperatures and constant flow conditions with lognormal fits. (a) shows different distributions with $Q_{\text{furnace}} = 1.80 \text{ L min}^{-1}$ and $Q_{\text{dilution}} = 1.74 \text{ L min}^{-1}$, whereas (b) shows distributions with $Q_{\text{furnace}} = Q_{\text{dilution}} = 1.50 \text{ L min}^{-1}$.

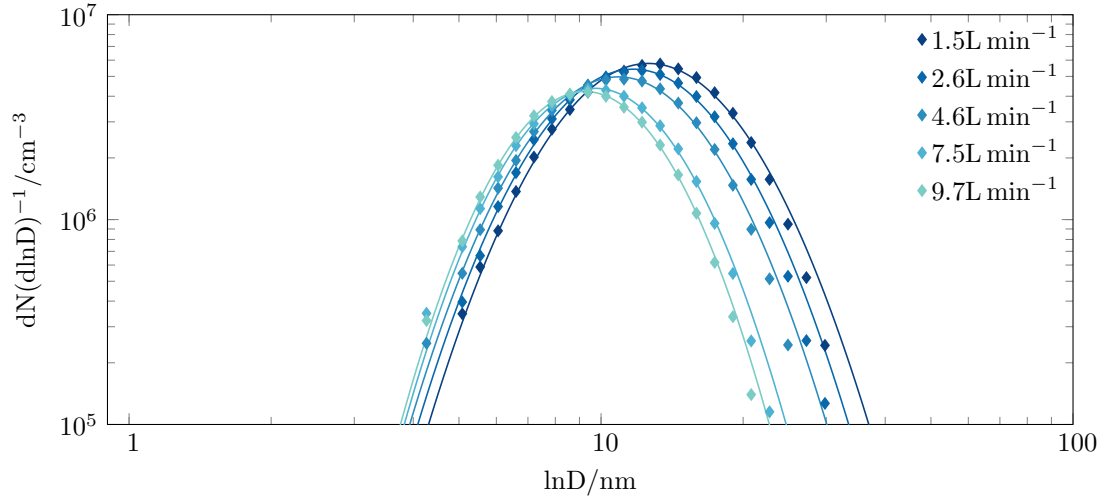


Figure 4.2: Size distributions at a constant furnace temperature $T_{\text{furnace}} = 950 \text{ }^\circ\text{C}$ and flow $Q_{\text{furnace}} = 1.64 \text{ L min}^{-1}$, but with different dilution flows Q_{dilution} .

Table 4.1: *Fit parameters of the lognormal fits for all size distributions.*

Figure	Distribution	μ	σ
4.1a	850 °C	1.73	0.21
4.1a	880 °C	1.97	0.23
4.1a	920 °C	2.13	0.28
4.1b	950 °C	2.38	0.34
4.1b	970 °C	2.46	0.35
4.2	1.5 L min ⁻¹	2.68	0.38
4.2	2.6 L min ⁻¹	2.59	0.37
4.2	4.6 L min ⁻¹	2.52	0.36
4.2	7.5 L min ⁻¹	2.39	0.34
4.2	9.7 L min ⁻¹	2.33	0.33

4.2 Ambient pressure measurements

According to the manufacturers, both CPC models are CEN compliant. The exact specification can be found in Section 3.3.2. The measurements at ambient pressure, i.e. at 1000 hPa, are intended to verify this. In this section and the next (Section 4.3) only the measurement results of one CPC per model are shown. A more detailed explanation for this can be found in Section 4.4 and Section 4.5.

The results of the measurements at ambient pressure are shown in Fig. 4.3a for the Grimm CPC and in Fig. 4.3b for the TSI CPC. There, the most important CEN parameters, namely the cutoff diameter D_{50} , the 90% counting efficiency D_{90} and the ideal plateau height (i.e. 1), are marked with gray lines. The determined values for each CPC model can be found in Table 4.2. The values in the table are either calculated with the fit function or are directly evaluated from the plot. As shown in Table 4.2, the results of our measurements are in agreement with the parameters specified in the CEN standard. Therefore it can be said that both devices are CEN compliant at ambient pressure.

Table 4.2: Important parameters at ambient pressure to check if the devices are CEN compliant. D_{50} and E_{∞} are determined via the fit function and D_{90} is evaluated from the plot.

CPC	p [hPa]	D_{50} [nm]	D_{90} [nm]	E_{∞}
Grimm	1000	6.6 ± 0.5 nm	11.8 ± 0.9 nm	1.02 ± 0.20
TSI	1000	6.4 ± 0.5 nm	11.8 ± 0.9 nm	0.98 ± 0.12

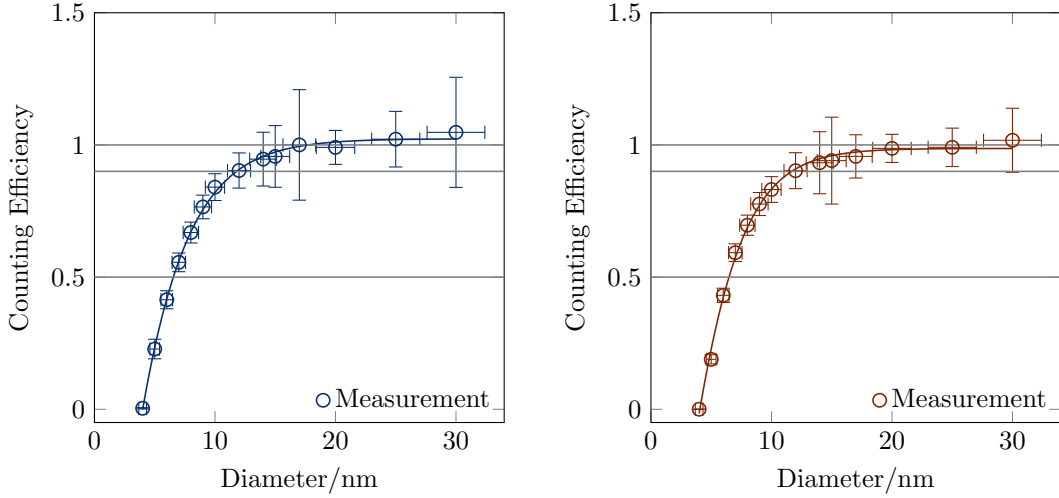


Figure 4.3: Counting efficiency for the (a) Grimm 5410 CEN CPC and (b) TSI 3772-CEN CPC at a pressure of 1000 hPa. Additionally marked are the 50%, the 90%, and the 100% (ideal plateau height) counting efficiency.

4.3 Low pressure measurements

The previous section has shown that the CEN specifications are met at ambient pressure. Now the aim is to find out how the two CPC models perform at different low pressure levels. To that end we will determine a lower bound on the pressure level up to which all CEN criteria can be met and also we will analyze which of the two models performs better under low pressure conditions.

4.3.1 Results Grimm 5410 CEN

The Grimm CPC is measured at four different low pressure levels, namely 750 hPa, 500 hPa, 250 hPa, and 150 hPa. Fig. 4.4a shows a detailed plot of the first measured low pressure stage, 750 hPa. Here error bars are included and, similar to Section 4.3, the CEN parameters are marked with lines. The detailed results of

the other low pressure levels can be found in Appendix C. Fig. 4.4b shows the results of all measured pressure levels. For visibility reasons, the error bars are excluded in this plot.

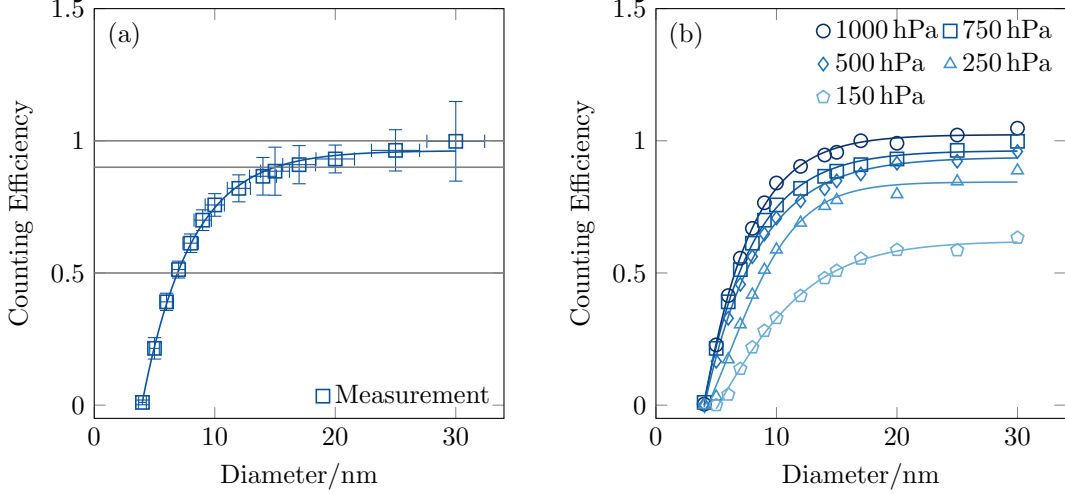


Figure 4.4: (a) shows the counting efficiency for the Grimm CPC at a pressure of 750 hPa. Additionally marked are the 50%, the 90%, and the 100% counting efficiency. (b) shows the counting efficiencies of all measured pressure stages for the Grimm CPC.

One can see a clear trend for the pressure dependence: The lower the pressure, the further the cutoff diameter shifts to higher diameters and the further the plateau shifts to lower counting efficiencies. Also the onset D_0 shifts slightly to the right for lower pressure levels. A distinct drop in the performance of this CPC model can be seen at 150 hPa. To illustrate the shifts better, the most important parameters to characterize the performance can be found in Table 4.3. The first three parameters, D_{50} , D_{90} and E_{∞} , are important for checking the CEN conformity. The last parameter D_0 can be determined with the fit function and gives the smallest particle size that can be detected with the CPC. In this table it is also marked whether the values fulfill the CEN requirements. The values are either calculated from the fit curve, or evaluated directly from the plot. This shows that the Grimm CPC meets all CEN criteria both at ambient pressure and at the first low pressure level, i.e. 750 hPa. All other low pressure stages can no longer fulfill one or more of the required CEN parameters.

Table 4.3: *Important parameters for the characterization of the Grimm 5410 CEN CPC and for checking the CEN compatibility. D_{50} , D_0 and the E_∞ (plateau height) are determined via the fit function and D_{90} is evaluated from the plot. Values marked with † are outside the CEN standard, but the CEN conform value is still within the measurement uncertainty around this value. All values marked with $*$ are outside the standard even with the measurement uncertainty taken into account.*

p [hPa]	D_{50} [nm]	D_{90} [nm]	E_∞	D_0 [nm]
1000	6.6 ± 0.5	11.8 ± 0.9	1.02 ± 0.20	4.1 ± 0.3
750	6.7 ± 0.5	$15.2 \pm 1.2^\dagger$	0.95 ± 0.15	4.0 ± 0.3
500	$7.6 \pm 0.6^\dagger$	$19.3 \pm 1.5^*$	$0.93 \pm 0.16^\dagger$	4.1 ± 0.3
250	$9.4 \pm 0.8^*$	-*	$0.87 \pm 0.19^\dagger$	4.5 ± 0.3
150	-*	-*	$0.52 \pm 0.18^*$	5.0 ± 0.5

Note that parameters that cannot be determined clearly are marked with a - in the table. This can happen for the D_{90} , if the plateau E_∞ is exactly at or below 0.9 (e.g. see 250 hPa in Fig. 4.4b), or at lower pressure stages for the D_{50} , if the curve has its plateau at or below 0.5, or the plateau has not yet been reached. This also accounts for Table 4.4 in Section 4.3.2.

4.3.2 Results TSI 3772-CEN

As mentioned earlier, both TSI 3772-CEN CPCs have already been characterized under low pressure conditions in the master’s thesis of Spät 2020. The focus of (Spät 2020) was on the pressure dependence of the detection efficiency and not on the cutoff curves. With that, Spät 2020 already concluded that the existing results can not be used to determine the cutoff diameter (the cutoff diameter is only evaluated at ambient pressure, but not at low pressure levels). This would be necessary to determine CEN compliance and, therefore, those two devices were measured again for this work. The results of these new measurements are described below.

The TSI CPC is also measured at four different low pressure levels, namely 750 hPa, 500 hPa, 375 hPa, and 250 hPa. The reason why different pressure levels were chosen for this model than for the Grimm CPC is explained in Section 4.3.3. As before with the Grimm, Fig. 4.5a first shows the detailed results for the first low pressure level, i.e. 750 hPa, and Fig. 4.5b shows the results of all measurements. The detailed results for the remaining low pressure levels can be found in Appendix C.

The TSI CPC shows the same behavior with decreasing pressure as the Grimm CPC did before. The lower the pressure, the further the cutoff curve shifts to higher diameters and the further the plateau shifts to lower counting efficiencies. For this CPC model, the shift of the onset to higher diameters can be seen more clearly. At 250 hPa a distinct drop in the performance of this CPC model can be seen.

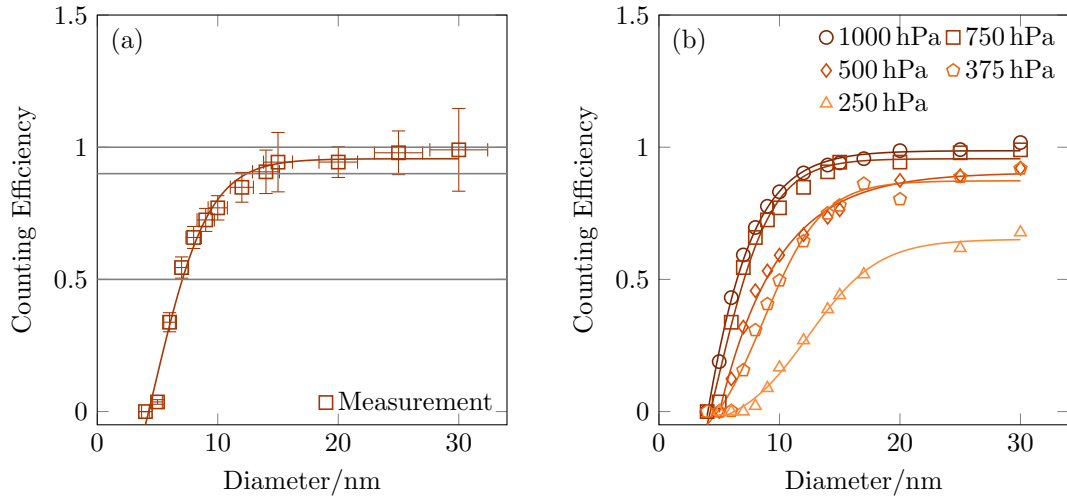


Figure 4.5: (a) shows the counting efficiency for the TSI CPC at a pressure of 750 hPa. Additionally marked are the 50%, the 90%, and the 100% counting efficiency. (b) shows the counting efficiencies of all measured pressure stages for the TSI CPC.

The important parameters are listed in Table 4.4. It is marked if the CEN requirements are fulfilled. The CPC model from TSI satisfies the CEN standard at 1000 hPa and at 750 hPa. For all other low pressure stages one or more requirements are not fulfilled.

Table 4.4: Important parameters for the characterization of the TSI 3772-CEN CPC and for checking the CEN compatibility. D_{50} , D_0 and the E_∞ (plateau height) are determined via the fit function and D_{90} is evaluated from the plot. Values marked with † are outside the CEN standard, but the CEN conform value is still within the measurement uncertainty around this value. All values marked with $*$ are outside the standard even with the measurement uncertainty taken into account.

p [hPa]	D_{50} [nm]	D_{90} [nm]	E_∞	D_0 [nm]
1000	6.4 ± 0.5	11.8 ± 0.9	0.98 ± 0.12	4.3 ± 0.3
750	6.8 ± 0.5	12.5 ± 1.0	0.96 ± 0.16	4.8 ± 0.4
500	$9.2 \pm 0.6^*$	$-^*$	$0.90 \pm 0.18^\dagger$	5.0 ± 0.4
375	$10.3 \pm 0.8^*$	$-^*$	$0.91 \pm 0.10^\dagger$	6.5 ± 0.5
250	$(16.3 \pm 1.3)^*$	$-^*$	$0.61 \pm 0.18^*$	7.5 ± 0.6

Although cutoff measurements were not a focus of Spät 2020, a trend towards a shift to larger diameters for decreasing pressure was found, but not quantified. The cutoff measurements performed in this work showed the same trend and also quantified the shift of the cutoff diameter at different pressure stages. Similarly, the results of our measurements for the counting efficiency are in good agreement with the results found in Spät 2020, in the sense that a drop in the counting efficiency was observed as the pressure decreased.

4.3.3 Comparison Grimm 5410 CEN and TSI 3772-CEN

Both CPCs meet the CEN criteria for the same pressure levels, i.e. 1000 hPa and 750 hPa. To see which model performs better under low pressure conditions, individual pressure levels are compared. Fig. 4.6a shows the comparison at ambient pressure and Fig. 4.6b at 500 hPa. It can be seen that the curves at ambient pressure almost overlap and that there is almost no difference in the performance of the Grimm CPC and the TSI CPC. At 500 hPa the Grimm CPC performs a bit better than the TSI CPC, but the difference is still within the measurement uncertainty.

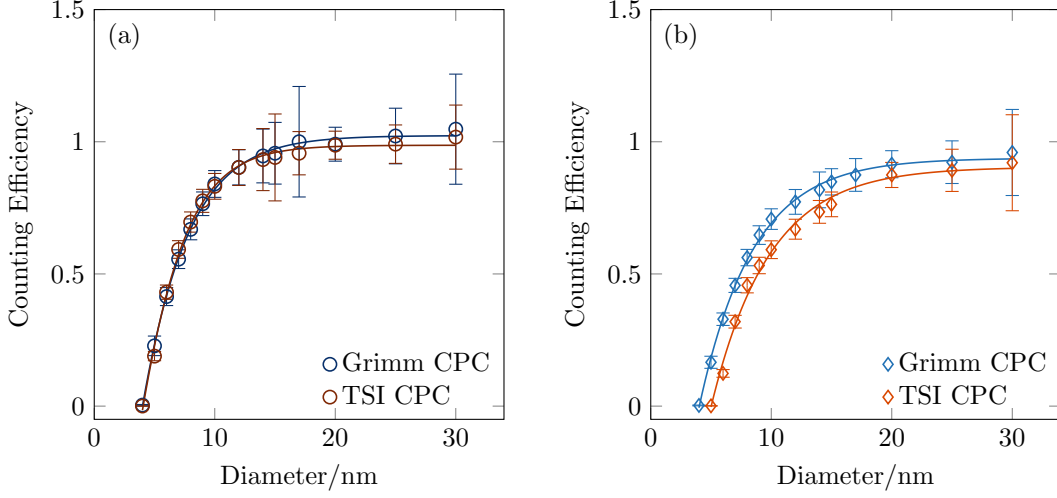


Figure 4.6: Comparison of the two CEN-CPCs at a pressure stage of (a) 1000 hPa and (b) 500 hPa.

The first major difference in performance is seen at 250 hPa, depicted in Fig. 4.7a. Here, the TSI CPC shows a much stronger shift of the cutoff diameter to higher diameters and a stronger shift of the plateau to lower counting efficiencies than the Grimm CPC. This strong difference in the performance of the two CPC models is also the reason for the choice of different low pressure levels. As the TSI CPC already displayed a sharp drop in the performance at 250 hPa, no additional pressure stage was measured, but instead an intermediate pressure stage at 375 hPa was added. In contrast, the Grimm CPC still shows a very good counting efficiency at 250 hPa. Therefore, it was decided to measure an additional low pressure level here, namely 150 hPa. This points out that the Grimm CPC performs better than the TSI CPC at pressure levels below 500 hPa.

In Fig. 4.7a to illustrate the difference in performance, additionally to the 250 hPa curves of both CPC models the 150 hPa curve of the Grimm CPC is plotted. It can be seen that the 150 hPa curve of the Grimm CPC and the 250 hPa curve of the TSI CPC are very similar, although they were measured at different pressure stages. The onset of the TSI CPC is clearly at a higher diameter than that of the Grimm. Their final plateaus (from about 18 nm on) have very similar values. In Fig. 4.7b, all curves can be seen. It is again clearly visible that the 150 hPa curve of the Grimm CPC and the 250 hPa curve of the TSI CPC have a clear drop in performance and are very similar to each other. This underlines that the Grimm CPC performs better at lower pressures than the TSI CPC. In addition, it can be seen that the 500 hPa curve of the TSI CPC is initially very similar to the 250 hPa curve of the Grimm CPC and only approaches the 500 hPa curve of the Grimm

CPC at higher diameters in the plateau.

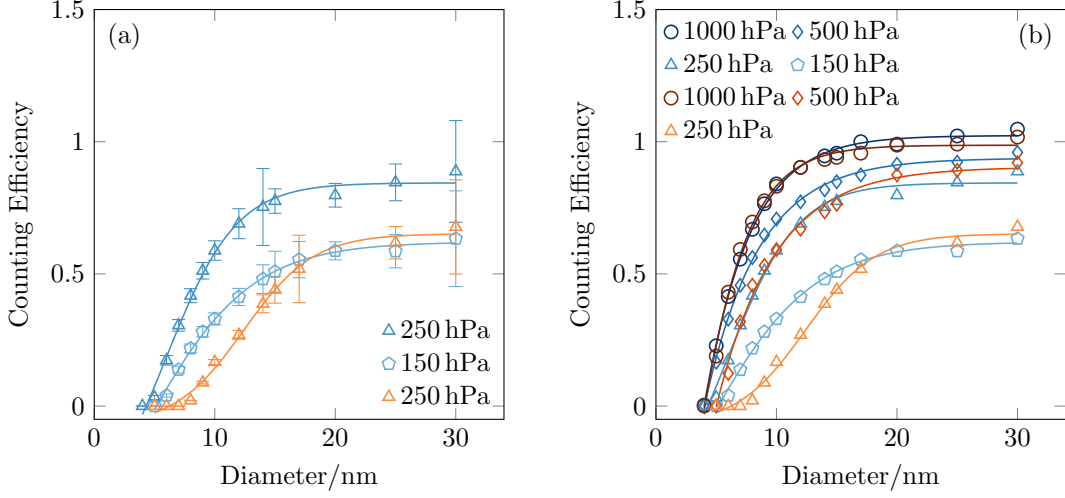


Figure 4.7: Comparison of the two CEN-CPCs: (a) 250 hPa of both CPCs versus 150 hPa of the Grimm CPC and (b) at different pressure stages. The bluish curves are measured with the Grimm CPC and the reddish ones with the TSI CPC.

4.4 Reproducibility

Since it is important to reproduce the results of an experiment, the same cutoff measurement was performed on different days for all instruments used, i.e. four Grimm 5410 CEN (labelled ACTRIS1 to ACTRIS4) and two TSI 3772-CEN CPCs (labelled TSI CPC1 and TSI CPC2). The measurements are then compared to see if they give the same results.

Performing the same measurement means that the same setup and temperature settings in the CPC are used for all measurements of that device. Parameters that were different on different measurement days are: The ambient pressure and temperature, the flow through the furnace, the dilution flow, and the furnace temperature. The first two are different due to natural fluctuations and the last three have to be adjusted on each day separately and therefore differ. The used setup is the one described in Section 3.2.2. The fit function and its parameters is described in Section 3.3.2.

Fig. 4.8 shows the reproducibility measurements for the Grimm CPC ACTRIS1 and the TSI CPC1. As the measurements of the other used instruments show basically the same results they are not shown separately here, but can be found in Appendix D. For low diameters the curves are nearly identical. For higher diameters (especially in the plateau region) small deviations can be seen, but they

are well within the measurement uncertainty. The results of the measurements show therefore that the setup is stable and that measurements on different days lead to the same results. For this reason, the day on which the measurement was performed is not mentioned separately.

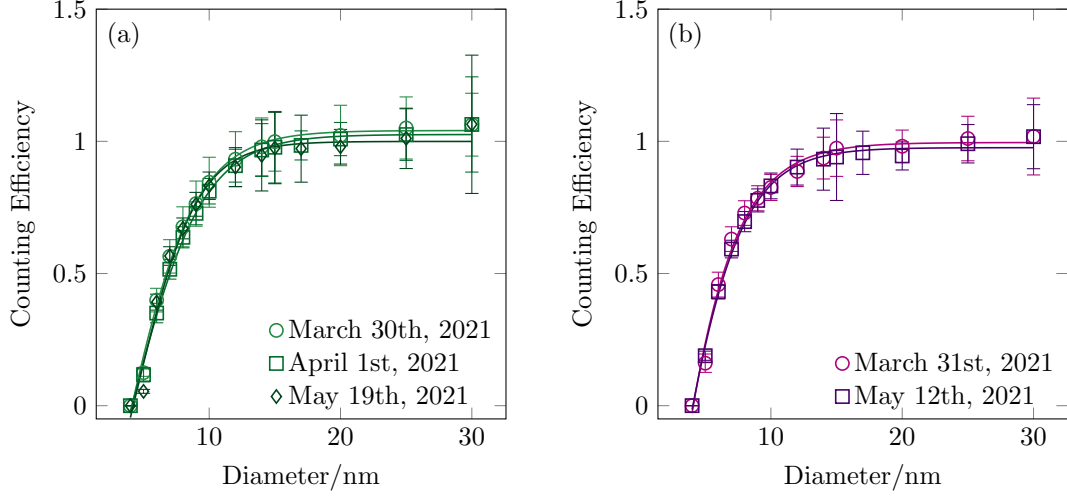


Figure 4.8: Counting efficiency measurements on different days at a pressure of 1000 hPa with the (a) Grimm CPC ACTRIS1 and (b) TSI CPC1.

4.5 Comparison of different CPCs of the same model

As the measurements are performed with four different Grimm 5410 CEN and two different TSI 3772-CEN CPCs it is interesting to see if all the instruments of the same model provide the same results and therefore measure consistently. The measurements are done for all pressure stages. Note that for the Grimm CPCs two different setups were used. The devices ACTRIS1, ACTRIS2 and ACTRIS4 are measured with the setup in Section 3.2.2, whereas the ACTRIS3 is measured with the setup in Appendix B. The results from the measurements with the ACTRIS3 are included in the comparison. Both devices from TSI CPC are measured with the setup shown in Section 3.2.2.

4.5.1 Results Grimm 5410 CEN

In Fig. 4.9 the measurement results at ambient pressure and at the 150 hPa low pressure stage are shown.

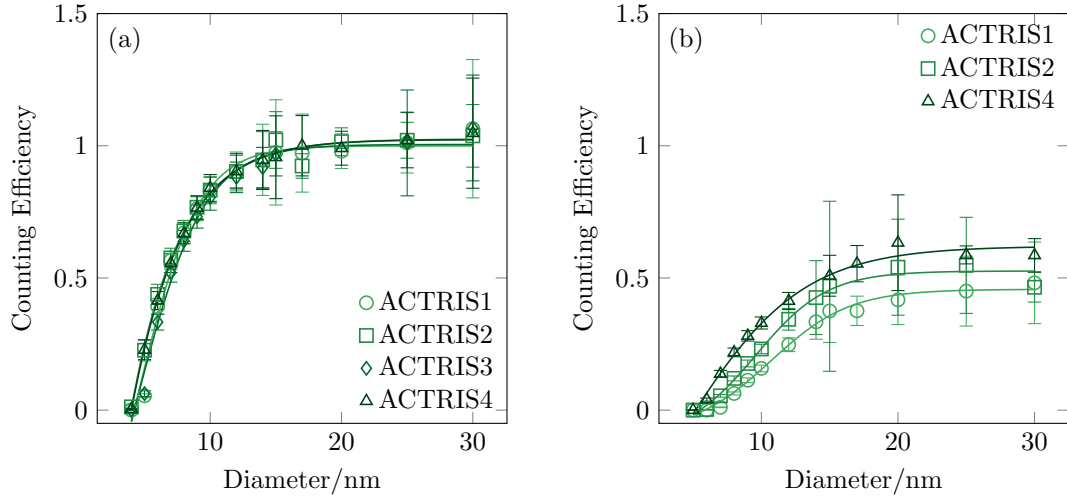


Figure 4.9: Comparison of the different Grimm 5410 CEN models at a pressure of (a) 1000 hPa and (b) 150 hPa.

Looking at the measurement results at ambient pressure in Fig. 4.9a it can be noticed that every of the used devices produces a similar cutoff curve. The small deviations are all within the range of the measurement uncertainty. Therefore, not only the different models give the same result, but also the two different setups produce comparable good results. Since the other measured pressure levels show the same results, they are not shown here and can be found in Appendix E. Only the lowest measured pressure level, 150 hPa, shows a greater deviation of the measurements of the different devices, see Fig. 4.9b. Note that there is no measurement at this pressure stage with the ACTRIS3, because the device was accidentally flooded and due to time reasons the measurement could not be made again. At 150 hPa the cutoff diameter can not be determined for any of the curves, because they do not, or only just reach, the 50% counting efficiency. Unlike at higher pressure stages the plateau height of the counting efficiency of the different CPCs now differs by up to 0.18. In comparison the plateau height at 1000 hPa differ only about 0.02. To better illustrate the differences, the fit parameters of the cutoff curves are listed in Table E.1.

Table 4.5: *Fit parameters of all the shown cutoff curves. The values are determined from the fit function.*

p [hPa]	CPC	D_{50} [nm]	E_{∞}	D_0 [nm]
1000	ACTRIS1	6.8 ± 0.5	1.00 ± 0.20	4.8 ± 0.4
1000	ACTRIS2	6.5 ± 0.5	1.02 ± 0.12	4.1 ± 0.3
1000	ACTRIS3	7.1 ± 0.6	1.02 ± 0.20	4.7 ± 0.4
1000	ACTRIS4	6.6 ± 0.5	1.02 ± 0.21	4.1 ± 0.3
150	ACTRIS1	-	0.45 ± 0.15	6.1 ± 0.5
150	ACTRIS2	-	0.52 ± 0.06	5.5 ± 0.4
150	ACTRIS4	-	0.63 ± 0.06	5.1 ± 0.4

4.5.2 Results TSI 3772-CEN

For the two TSI CPCs, the behavior is similar to the instruments from Grimm. At ambient pressure and at the first two low pressure levels, the two devices deliver the same results, within the limits of the measurement uncertainty. The results for the pressure stages which are not in the figures below can be found in Appendix E.

A deviation of the measured results can be observed at the lowest two pressure levels, 375 hPa and 250 hPa, which can be seen in Fig. 4.11a-b. For 375 hPa the plateau height differs by about 0.05 and the cutoff diameter by 1.6 nm. For the 250 hPa curve it is 0.09 and 3.2 nm, respectively. In contrast, for 1000 hPa the plateau height is nearly identical and the cutoff diameter only differs about 0.3 nm. This shows that the two lowest pressure stages show bigger deviations, but the deviation for 375 hPa is not as big as for 250 hPa. All the determined fit parameters are listed in Table 4.6.

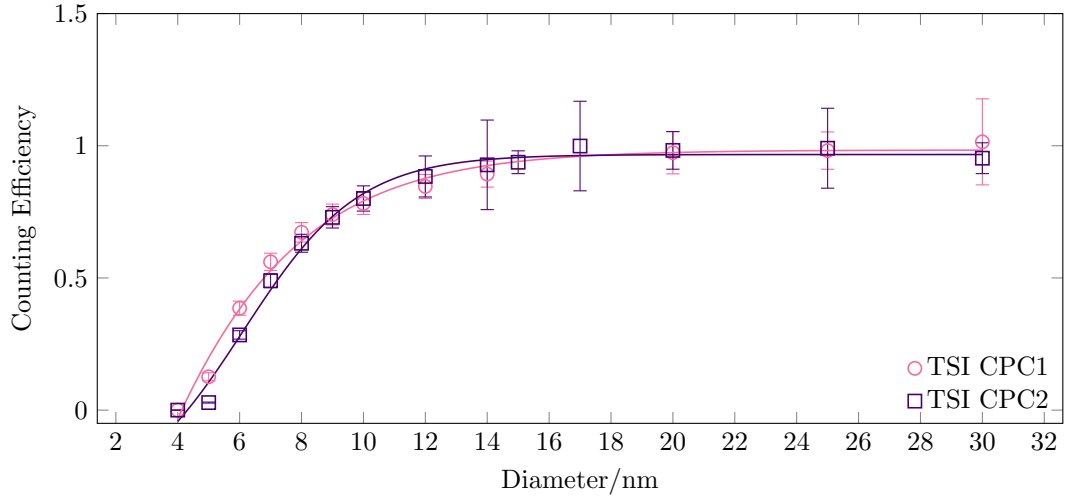


Figure 4.10: Comparison of the different TSI 3772-CEN models at a pressure of 1000 hPa.

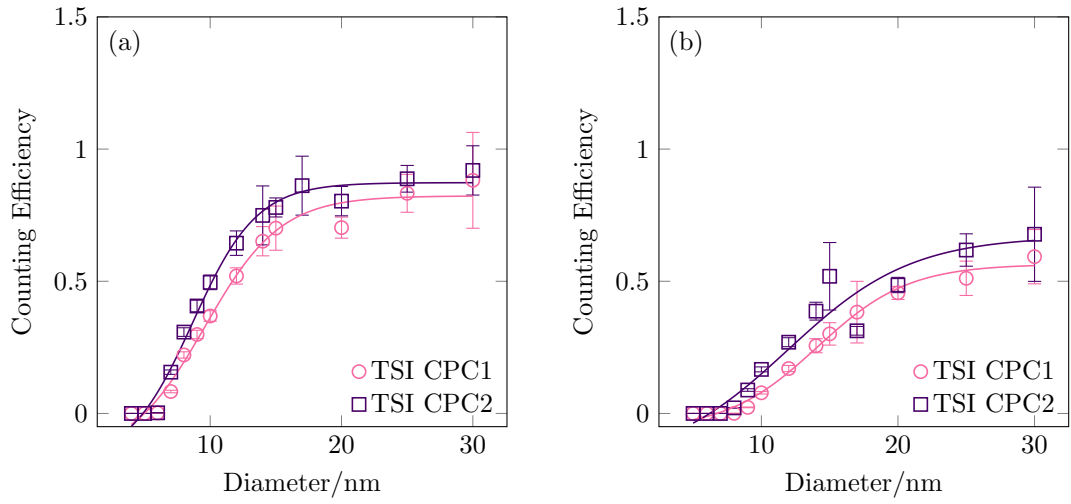


Figure 4.11: Comparison of the different TSI 3772-CEN models at a pressure of (a) 375 hPa and (b) 250 hPa.

Table 4.6: *Fit parameters of all the shown cutoff curves. The values are determined from the fit function.*

p [hPa]	CPC	D_{50} [nm]	E_{∞}	D_0 [nm]
1000	CPC1	6.7 ± 0.5	0.98 ± 0.16	4.5 ± 0.4
1000	CPC2	7.0 ± 0.6	0.98 ± 0.06	4.9 ± 0.4
375	CPC1	11.6 ± 0.9	0.82 ± 0.18	5.3 ± 0.4
375	CPC2	10.0 ± 0.8	0.87 ± 0.09	5.6 ± 0.5
250	CPC1	21.4 ± 1.7	0.56 ± 0.10	7.3 ± 0.6
250	CPC2	18.2 ± 1.4	0.65 ± 0.18	6.3 ± 0.5

Discussion and further approach

Both CPC models show a deviation for the lowest pressure stage. The presumption for this discrepancy is that the instruments, although they are the same model, are slightly different internally (e.g., slightly different flow rates) and this only becomes significant at really low pressures. To verify that the same instrument gives the same results at such low pressure stages, see Fig. 4.12. Here one can see that the TSI CPC1 gives the same result for two identical measurements at 250 hPa on different days, within the measurement uncertainty.

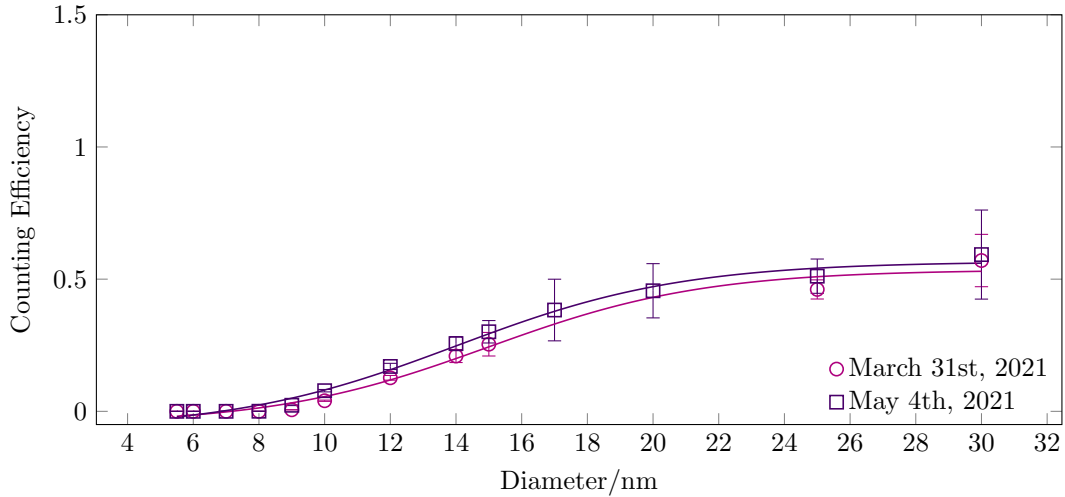


Figure 4.12: *Counting efficiency measurements on different days at a pressure of 250 hPa with the TSI CPC1.*

Leaving aside the lowest pressure stage for each CPC, it can be said that all four Grimm 5410-CEN CPCs and the two TSI CPCs deliver the same results. This

is the reason why in Section 4.2 and Section 4.3 the CPCs are only labelled with Grimm CPC and TSI CPC and are not distinguished more specifically. Since the lowest pressure level does not provide the same results, the curve that provides the best result, i.e. counting efficiency, is taken here for both models. For the Grimm, this is the curve of the ACTRIS4 and for the TSI CPC the curve of the CPC2.

4.6 Linearity measurements

Another measurement performed is the linearity measurement. According to CEN/TS 2016, the linearity should be 1 ± 0.05 at $(40 \pm 10)\text{nm}$. This means that the CPC and the reference instrument, the FCE, should measure the same particle concentration for diameters in the plateau region. Therefore, the measurement points should be on the identity line. The procedure of the measurement has already been described in Section 3.3.3.

4.6.1 Results Grimm 5410 CEN

Fig. 4.13 shows the measurement results for ambient pressure. To show the error margin in the following figures, an error band is shown around the identity line which represents exactly the 5% error margin in which the measurement points should be. A linear fit is calculated and is forced, according to CEN/TS 2016, through the origin. Therefore, it has the form $y = kx$, where k denotes the slope of the fit. It can be seen that for a pressure of 1000 hPa all the measured points are within the 5% error range and therefore fulfills the CEN requirement.

Fig. 4.14a-d shows the results for the measured low pressure stages. There it can be seen that the lower the pressure, the further the measured points deviate from the identity line. Moreover, within a pressure stage the higher the particle concentration the greater the deviation from the identity line. The deviation always occurs in the same direction, so that the FCE measures more particles than the CPC. Looking at the results in terms of CEN conformity, only the 750 hPa pressure level is still within the allowed deviation and thus meet the CEN requirements. For 500 hPa the fit result is at about 93% and for 250 hPa only about 82%. This means, that the measured points are not within the 5% error range and therefore do not fulfill the CEN standard. Despite the deviation from the identity line we always have a linear behaviour down to 250 hPa. At 150 hPa the Grimm CPC shows a non linear behaviour, which can be clearly seen by comparison with the linear fit.

The determined values of k can be found in Table 4.7. In addition, the determined plateau height of the cutoff curves is displayed, and it can be seen that the values agree well at almost all pressure levels. This is interesting, because the two values

are determined with different measurement procedures. At 150 hPa the value of the slope is put in brackets, because at this pressure stage the measured points are not linear.

Table 4.7: Calculated slope of the linear fit and the plateau height E_∞ from the cutoff curves, Table 4.3.

p [hPa]	k	E_∞
1000	$1.03 \pm 3.55 \cdot 10^{-3}$	1.02 ± 0.20
750	$0.98 \pm 2.09 \cdot 10^{-3}$	0.95 ± 0.15
500	$0.93 \pm 2.03 \cdot 10^{-3}$	0.93 ± 0.16
250	$0.82 \pm 4.54 \cdot 10^{-3}$	0.87 ± 0.19
150	$(0.37 \pm 1.63 \cdot 10^{-3})$	0.52 ± 0.18

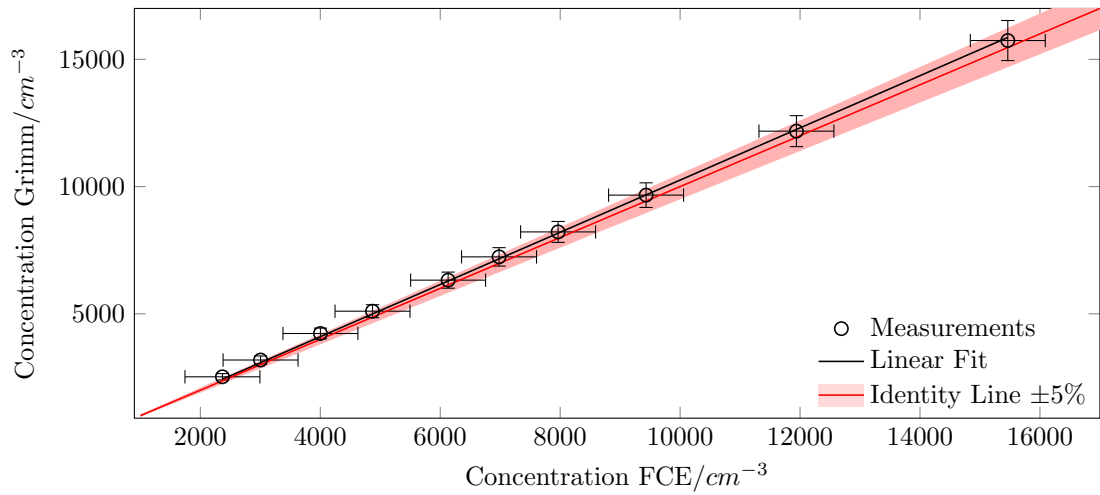


Figure 4.13: Measurements of the concentration of 30 nm particles at different dilutions at a pressure of 1000 hPa. Additionally a linear fit and the identity line with an error margin of 5% are shown.

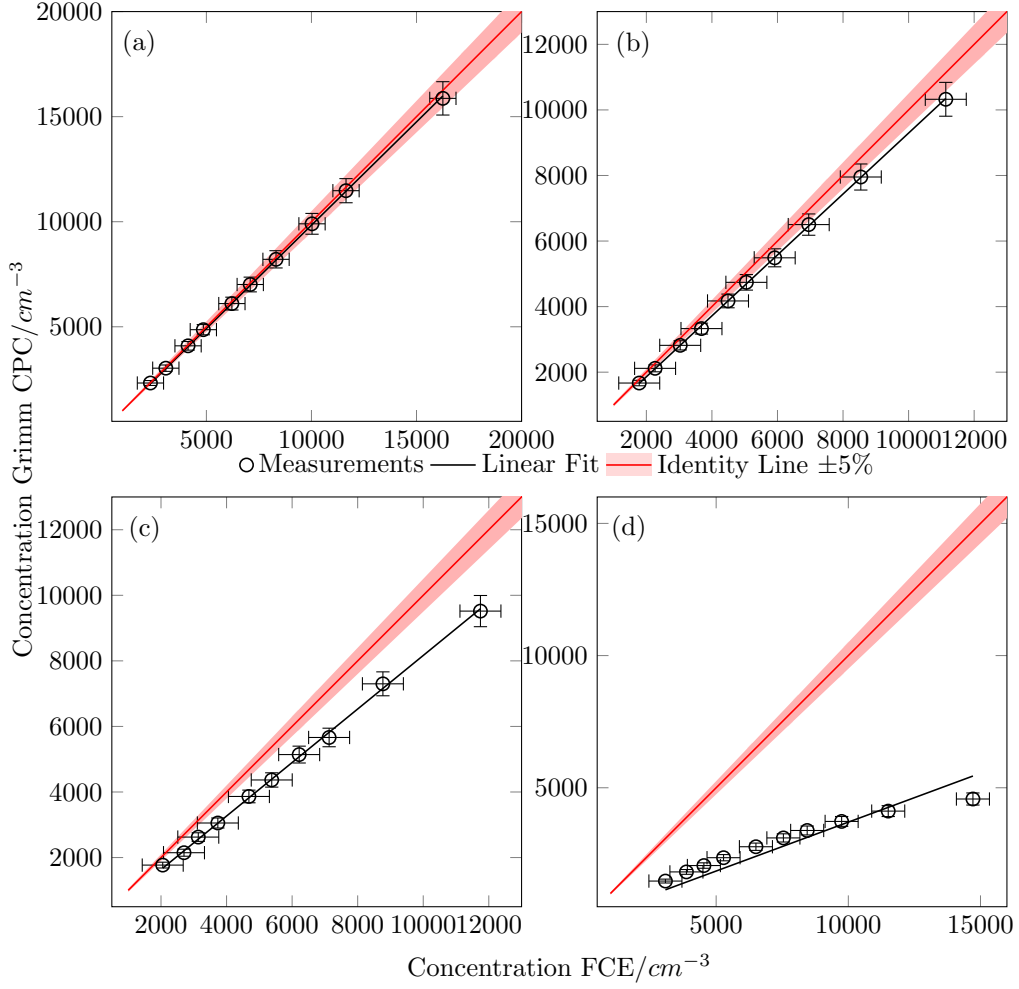


Figure 4.14: Measurements of the concentration of 30 nm particles at different dilutions at a pressure of (a) 750 hPa, (b) 500 hPa, (c) 250 hPa, and (d) 150 hPa. Additionally a linear fit and the identity line with an error margin of 5% are shown.

4.6.2 Results TSI 3772-CEN

The same linearity measurements were performed with the TSI CPC. Fig. 4.15 shows the measurement results at ambient pressure and Fig. 4.16a-d at all measured low pressure levels. The 5% error band of the identity line and the linear fit are also in the plots. Again at 1000 hPa the measured points match well with the identity line and are all within the allowed 5% error range and thus fulfill the CEN requirements.

The results in low pressure conditions show the same behavior as before with the

Grimm CPC. The lower the pressure, the greater the deviation from the identity line. For 750 hPa the measured points are within 5% of the identity line and is therefore CEN compliant. At 500 hPa the fit result is about 93% and at 375 hPa and 250 hPa it is 83% and 55%, respectively. So for all pressure stages below 750 hPa the CEN requirements can not be met. At all measured pressure stages a linear behaviour can be seen. In Table 4.8 the slope of the linear fits and the corresponding plateau heights from the cutoff curves can be found. Again they match well, except for the lowest pressure stage.

Table 4.8: Calculated slope of the linear fit and the plateau height E_∞ from the cutoff curves, Table 4.4.

p [hPa]	k	E_∞
1000	$0.99 \pm 5.01 \cdot 10^{-3}$	0.98 ± 0.12
750	$0.97 \pm 3.04 \cdot 10^{-3}$	0.96 ± 0.16
500	$0.93 \pm 3.44 \cdot 10^{-3}$	0.90 ± 0.18
375	$0.83 \pm 7.32 \cdot 10^{-3}$	0.91 ± 0.10
250	$0.55 \pm 7.91 \cdot 10^{-3}$	0.61 ± 0.18

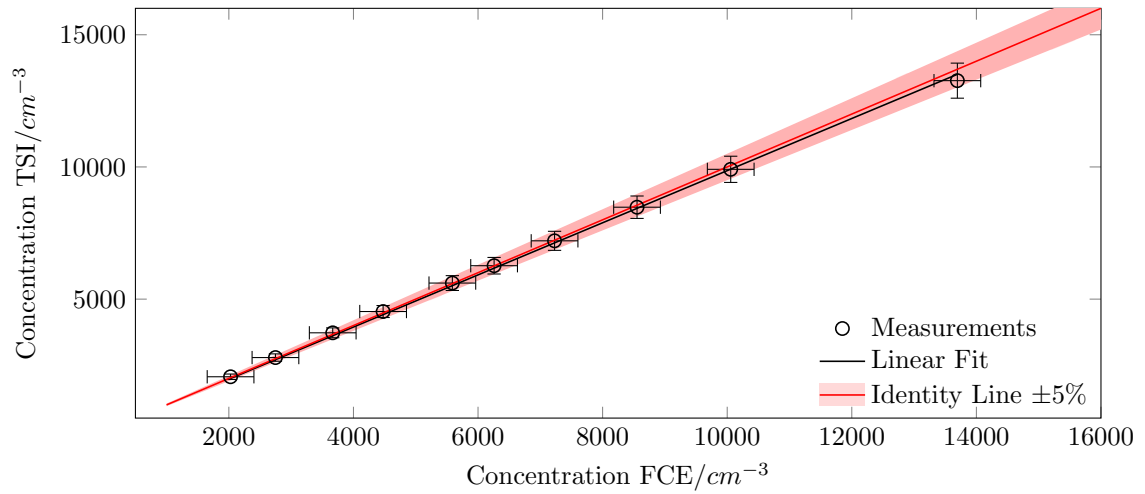


Figure 4.15: Measurements of the concentration of 30 nm particles at different dilutions at a pressure of 1000 hPa. Additionally a linear fit and the identity line with an error margin of 5% are shown.

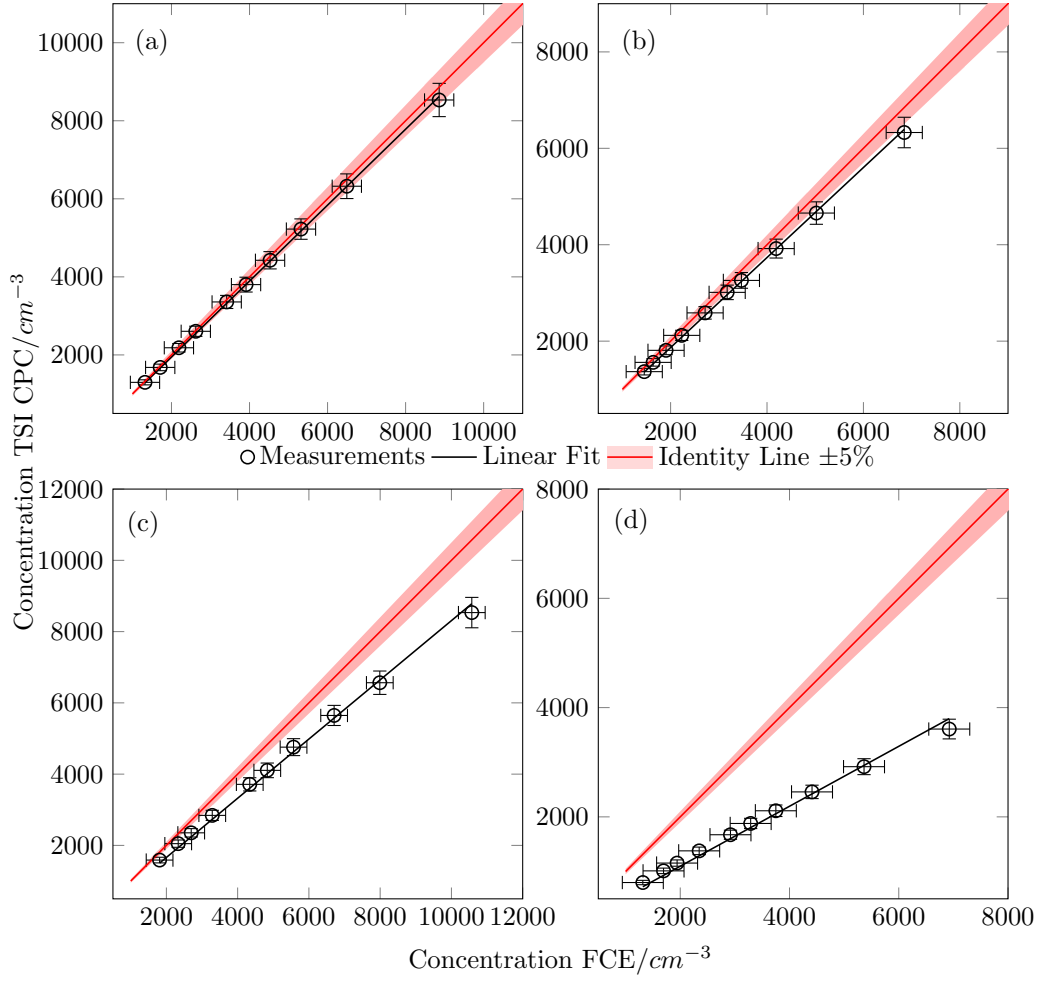


Figure 4.16: Measurements of the concentration of 30 nm particles at different dilutions at a pressure of (a) 750 hPa, (b) 500 hPa, (c) 375 hPa, and (d) 250 hPa. Additionally a linear fit and the identity line with an error margin of 5% are shown.

When comparing the results for the linearity measurements it can be noticed that both CPC models are CEN compliant at 1000 hPa and 750 hPa. All pressure stages below are outside the allowed 5% error range. For 500 hPa both CPCs have a fit result of about 93%, but while at 250 hPa the Grimm CPC has still a slope of 82% the TSI CPC has only a slope of 55%. These results show that the counting efficiency of the Grimm CPC is better than that of the TSI CPC below 500 hPa. Thus, the results of the low pressure measurements and the linearity measurements are in agreement.

5 Conclusion

The aim of this work was to determine the performance, i.e. counting efficiency, of two different CEN-certified CPCs as a function of particle size and at ambient pressure and different low pressure levels. The instruments used were four different Grimm 5410 CEN and two TSI 3772-CEN CPCs. The measurements were taken at ambient pressure, i.e. 1000 hPa, and at different low pressure levels, ranging from 750 hPa to 150 hPa. The results of the cutoff curves from the different models were compared. In addition, the CEN parameters were taken into account in all measured pressure levels in order to find out up to which low pressure level the devices measure in conformity with the standard. As part of the CEN standard linearity measurements, at all pressure levels, were performed. The important CEN parameters which are defined in CEN/TS 2016 are the following: the cut-off diameter D_{50} , the 90% counting efficiency D_{90} and the linearity at (40 ± 10) nm.

According to the CEN standard silver particles were generated to characterize the instruments. The resulting size distribution of the furnace was examined, as well as a reproducibility test was performed. The latter was achieved by identical measurements on different days. To test whether the different instruments of the same CPC model measure consistently, they were also compared. The results showed, that the measurement results were reproducible and that the different instruments of the same CPC model also measure consistently.

For the Grimm CPC the results at ambient pressure provide a cutoff diameter of 6.6 ± 0.5 nm, a D_{90} of 11.8 ± 0.9 nm, and a plateau height of 1.02 ± 0.20 . For the TSI CPC the results are 6.4 ± 0.5 nm, 11.8 ± 0.9 nm and 0.98 ± 0.12 , respectively. To be CEN compliant D_{50} has to be 7 ± 0.7 nm, D_{90} has to be smaller than 14 nm, and the linearity at (40 ± 10) nm has to be $1 \pm 5\%$. This means that the two models not only meet the manufacturer's specifications (Grimm 2020b, TSI Incorporated 2016), but are also CEN compliant.

For the measurements under low pressure conditions, the same trend in the behavior of the counting efficiency was observed for both CPC models. With decreasing pressure, the cutoff diameter shifted to larger diameters, and decreasing plateau heights and thus a decreasing maximum counting efficiency. These results are in agreement with other measurements of CPCs under low pressure conditions. Despite different CPC models, Takegawa et al. 2011 and Zhang et al. 1990 have observed the same trend in low pressure measurements. Also the work of Spät 2020, where the TSI 3772-CEN CPC is characterized, showed the same trend for decreasing pressure.

Although the CPC models of both manufacturers basically show the same behav-

ior at decreasing pressure, there are differences in their performance. While the Grimm CPC has a cutoff diameter of 9.4 ± 0.8 nm and a plateau height of 0.87 ± 0.19 at 250 hPa, the TSI CPC has 16.3 ± 1.3 nm and 0.61 ± 0.18 , respectively. This makes it possible to measure an even lower pressure level, namely 150 hPa, for the Grimm CPC. For this pressure level the maximum counting efficiency drops to 50% which is a clear drop in the performance of this instrument. However, the device from TSI records a similar drop already at 250 hPa, which is why this is the lowest pressure level measured with this model. A comparison of the individual pressure levels also shows that both models deliver comparable results up to a pressure of 500 hPa. Here, the cutoff diameter of the Grimm CPC is 7.6 ± 0.6 nm and that of the TSI CPC is 9.2 ± 0.6 nm. The plateau for both models is approximately 0.90. Comparing the models of the two manufacturers, one can say that up to a pressure level of 500 hPa, both deliver equally good results. Below 500 hPa, however, the model from Grimm performs much better than the model from TSI. The reason for the difference in performance was not investigated in more detail, as this is not the focus of this work. However, one assumption for the difference lies in the internal structure of the two models. While in the Grimm CPC the complete flow flows through the condenser (0.6 L min^{-1}), the TSI CPC has a multitube condenser which means that the flow is split up into eight parts, which leads to a much smaller flow through each condenser (0.125 L min^{-1}). Possible reasons for the difference in performance were studied by Dorian Spät with contributions by Paulus S. Bauer with numerical simulations of the temperature and vapor pressure profile of both CPCs. The results of these simulations will be published alongside the measurement results of the present work in (Bauer et al. 2022, in prep.).

Looking at the results of the low pressure measurements in terms of CEN requirements, one can say that both devices still meet all conditions at 750 hPa. Here the Grimm CPC has a cutoff diameter of 6.7 ± 0.5 nm, a D_{90} of 15.2 ± 1.2 nm and a plateau height of 0.95 ± 0.15 . The TSI CPC has 6.8 ± 0.5 nm, 12.5 ± 1.0 nm, and 0.96 ± 0.16 , respectively. For both the Grimm CPC and the TSI CPC, one or more CEN conditions can no longer be met at all pressure levels below 750 hPa.

In addition, the CEN standard (CEN/TS 2016) requires the concentration measured with the CPC to behave linearly, i.e., the measured concentrations for particle diameters in the plateau region must be within a margin of 5% of the concentrations measured with the reference instrument. For this purpose, the measured concentration of the CPC for particles with a size of 30 nm was compared with the measured concentration of the reference instrument, at different dilutions. This measurement was carried out for all pressure stages to verify the CEN conformity

of each level. Again, both CPC models show the same trend: The lower the pressure, the further the measured points deviate from the identity line. The deviation always has the form that the reference instrument measures more particles than the CPC. Most notably, only when measuring the Grimm CPC at a pressure of 150 hPa, the measurements show a non linear behaviour. At all other pressure levels and at all measurements of the TSI CPC, the measurements are linear despite the deviation from the identity line. If the focus is on CEN conformity, it must be determined whether the deviation from the identity line is less than 5%. For both models, this is only the case at 1000 hPa and 750 hPa. At all other pressure stages, the deviations are already too large.

Overall, the results show that the two CPC models are CEN compliant at 1000 hPa and 750 hPa and show a different drop-off in performance below 500 hPa. An interesting topic for further research would be to analyze why the different CPC models show a different behavior at low pressures. A first step in that direction was already taken by Bauer et al. 2022, in prep. Research in this direction could subsequently lead to the development of new CPC models that deliver an even better performance under low pressure conditions. Additionally, with the gained measurement results and further research an attempt could be made to correct the pressure dependent effects. It could also be a motivation to create a new standard, where the pressure dependent behaviour is considered.

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Appendix A Critical orifice control

The flows of both CPC models are adjusted by means of a critical orifice. In order for the flow to have the correct value and to be stable and constant, there must be a critical pressure ratio, which is

$$\frac{p_{\text{outlet}}}{p_{\text{inlet}}} < 0.5$$

for air (TSI Incorporated 2016). In the measurement setup used, the inlet pressure is measured with the mass flow controller (MFC) and the outlet pressure with an additional pressure sensor behind the MFC. A simplified representation of the setup can be seen in Fig. A.1. The pressure meter after the MFC measured a pressure of 50 hPa at all measurements. The inlet pressure varies between 150 and 750 hPa. The calculated ratios can be found in Table A.1 and it can be seen that all ratios are below 0.5 and therefore the flow of the CPCs are stable and constant and have the value which is specified in their manual (Grimm 2020b, TSI Incorporated 2016).

Table A.1: *Calculated critical pressure ratios for all measured low pressure levels.*

p_{inlet} [hPa]	ratio
750	0.06
500	0.10
375	0.13
250	0.20
150	0.33

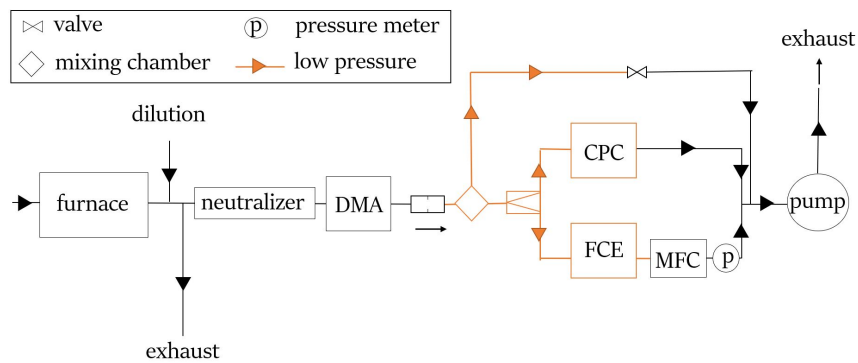


Figure A.1: *Setup for the measurements with an additional pressure meter to measure the outlet pressure. The parts which are in low pressure are orange.*

Appendix B Setup for measurements with the ACTRIS3

The Grimm ACTRIS3 CPC is the only of the six used instruments which is measured with a slightly different setup than the rest. Initially the setup was inspired by the work of Spät 2020 and it was used for the measurements of ARCTRIS3. In order to keep the DMA resolution constant the setup from Takegawa et al. 2011 was adopted after the first measurements. However, the measurements with the ACTRIS3 were already finished at that time the setup was adapted and due to the reason that the instrument was accidentally flooded, it was not measured again in the new setup. But as it can be seen in Section 4.5 the change in the setup did not affect the counting efficiency as all instruments from Grimm deliver the same results despite the different setup.

Fig. B.1 shows the measurement setup which is inspired by Spät 2020 which was used for the measurements of ARCTRIS3. The instruments before the DMA are identical to the other used setup for the pressure measurements. However, after the DMA the two setups differ: The low pressure is generated with a valve, directly behind the DMA. Afterwards, the flow passes through a turbulent mixing chamber and is then divided between CPC and FCE with a flow splitter, which means that in contrast to the other setup there is no additional pump flow in this one. In this setup, the measured particle concentrations are quite low for low pressure stages, which is why the critical orifice of the DMA flow unit was exchanged in order to lower the sheath flow and thus be able to measure higher concentrations.

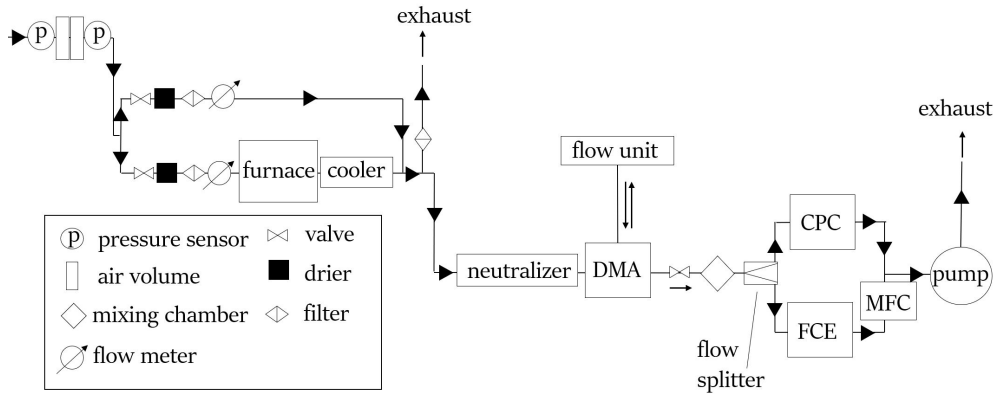


Figure B.1: Setup for the measurements with the ACTRIS3 CPC.

Appendix C Detailed results for low pressure measurements

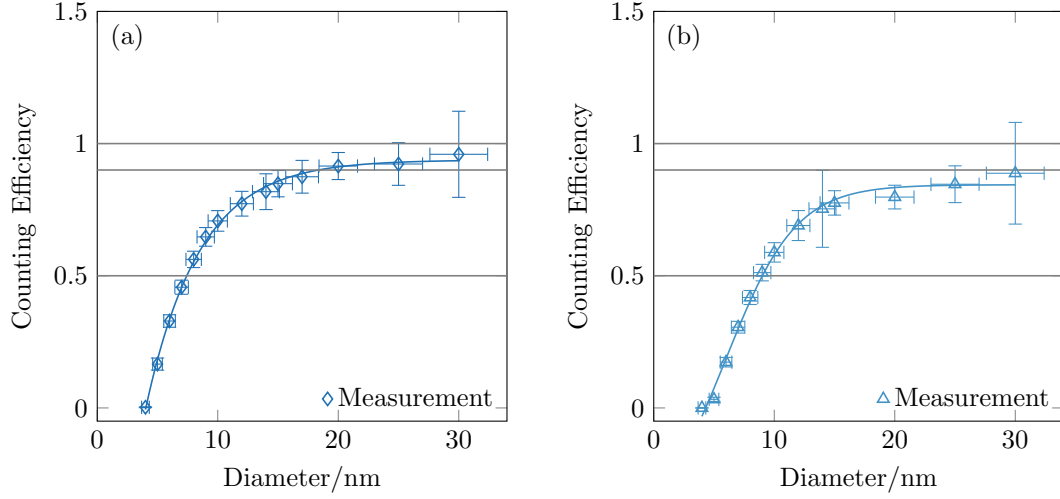


Figure C.1: Counting efficiencies for the Grimm CPC at a pressure of (a) 500 hPa and (b) 250 hPa. Additionally marked are the 50%, the 90%, and the 100% (plateau) counting efficiency.

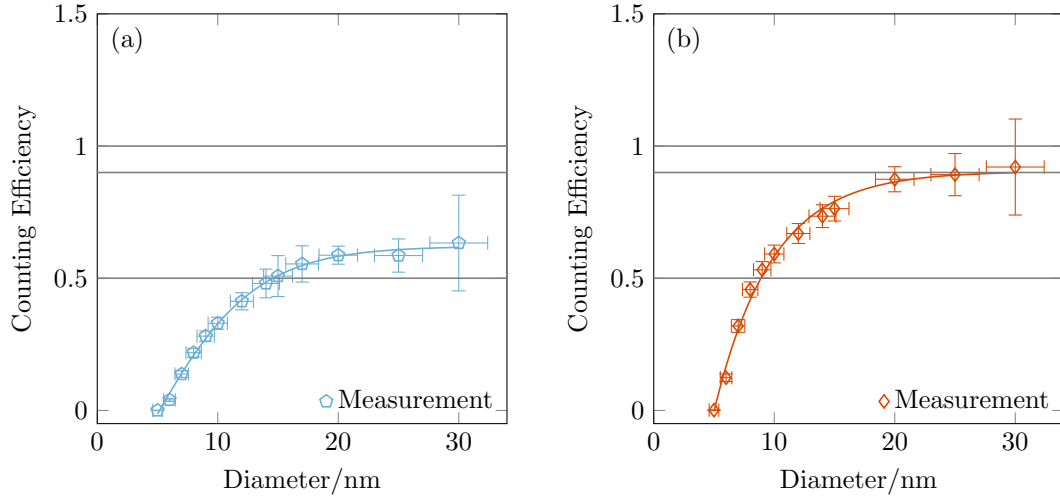


Figure C.2: Counting efficiencies for (a) the Grimm CPC at a pressure of 150 hPa and (b) the TSI CPC at a pressure of 500 hPa. Additionally marked are the 50%, the 90%, and the 100% (plateau) counting efficiency.

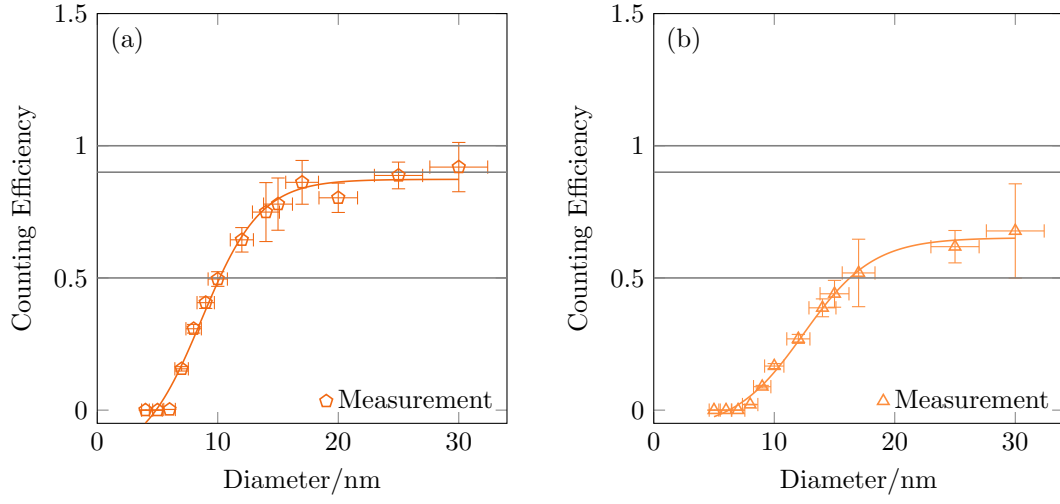


Figure C.3: Counting efficiencies for the TSI CPC at a pressure of (a) 375 hPa and (b) 250 hPa. Additionally marked are the 50%, the 90%, and the 100% (plateau) counting efficiency.

Appendix D Plots for reproducibility measurements

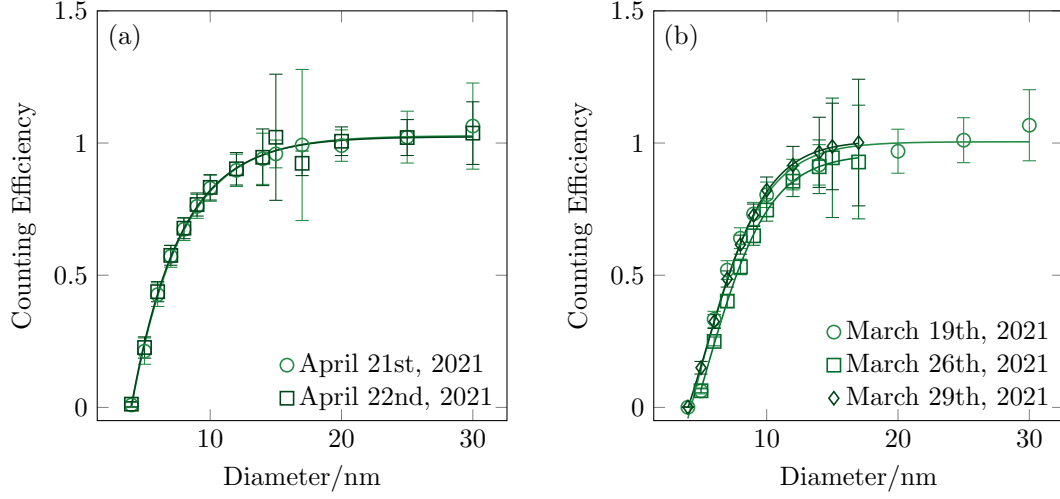


Figure D.1: Counting efficiency measurements on different days at a pressure of 1000 hPa with the (a) Grimm CPC ACTRIS2 and (b) Grimm CPC ACTRIS3.

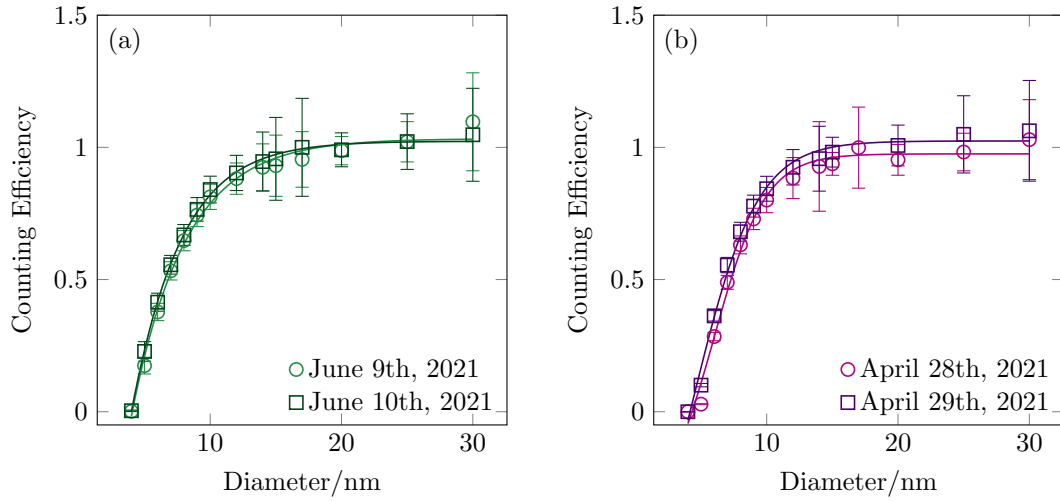


Figure D.2: Counting efficiency measurements on different days at a pressure of 1000 hPa with the (a) Grimm ACTRIS4 and (b) TSI CPC2.

Appendix E Model comparison measurements

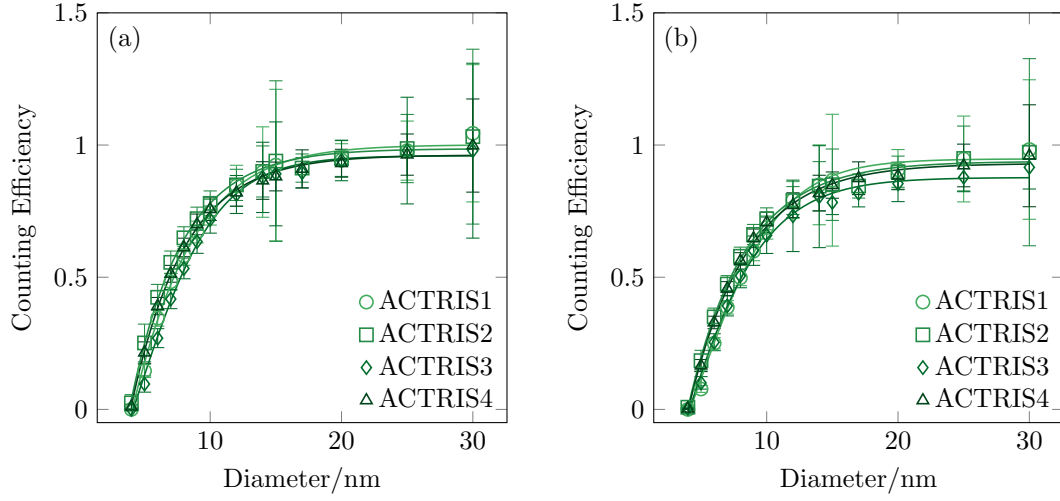


Figure E.1: Comparison of the different Grimm 5410 CEN models at a pressure of (a) 750 hPa and (b) 500 hPa.

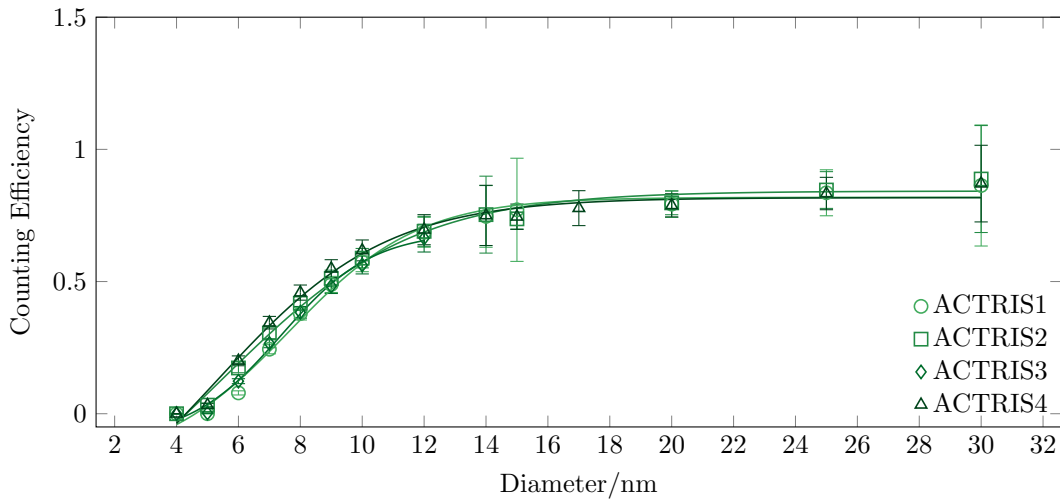


Figure E.2: Comparison of the different Grimm 5410 CEN models at a pressure of 250 hPa.

Table E.1: *Fit parameters of all the shown cutoff curves for the Grimm CPCs. The values are determined from the fit functions.*

p [hPa]	CPC	D_{50} [nm]	E_{∞}	D_0 [nm]
750	ACTRIS1	7.2 ± 0.6	1.00 ± 0.21	4.3 ± 0.3
750	ACTRIS2	6.6 ± 0.5	0.98 ± 0.25	3.9 ± 0.3
750	ACTRIS3	7.5 ± 0.6	0.98 ± 0.30	4.6 ± 0.4
750	ACTRIS4	6.8 ± 0.5	0.96 ± 0.18	3.9 ± 0.3
500	ACTRIS1	7.8 ± 0.6	0.96 ± 0.21	4.7 ± 0.4
500	ACTRIS2	7.0 ± 0.6	0.94 ± 0.26	4.0 ± 0.3
500	ACTRIS3	7.4 ± 0.6	0.88 ± 0.08	4.5 ± 0.4
500	ACTRIS4	7.1 ± 0.6	0.93 ± 0.19	4.1 ± 0.3
250	ACTRIS1	9.1 ± 0.7	0.84 ± 0.22	5.6 ± 0.5
250	ACTRIS2	9.0 ± 0.7	0.86 ± 0.20	4.9 ± 0.4
250	ACTRIS3	9.1 ± 0.7	-	5.5 ± 0.4
250	ACTRIS4	8.6 ± 0.7	0.82 ± 0.14	4.9 ± 0.4

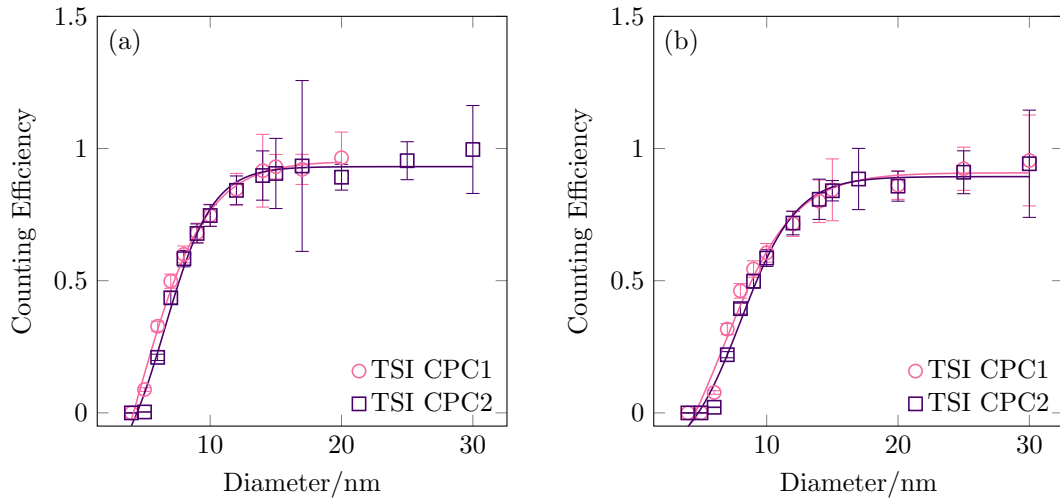


Figure E.3: *Comparison of the different TSI 3772-CEN models at a pressure of (a) 750 hPa and (b) 500 hPa.*

Table E.2: *Fit parameters of all the shown cutoff curves for the TSI CPCs. The values are determined from the fit functions.*

p [hPa]	CPC	D_{50} [nm]	E_{∞}	D_0 [nm]
750	CPC1	7.2 ± 0.6	1.97 ± 0.17	4.5 ± 0.4
750	CPC2	7.6 ± 0.6	-	5.0 ± 0.4
500	CPC1	8.9 ± 0.7	0.92 ± 0.17	5.2 ± 0.4
500	CPC2	9.2 ± 0.7	0.90 ± 0.20	5.7 ± 0.5