In this file, the review comments are in black and our responses in green. Text in the paper is in *blue.* Removed text is ~~*crossed out.*~~ Added text in the paper is written in ***bold.***

Preface: Author-initiated Correction

In our original simulation calculation, we discovered an error in the code regarding the droplet growth, which did not account for different activation positions outside of the centerline of the condenser. The corrected starting position at which particle growth is triggered is now implemented, leading to a more uniform droplet size along the radial axis (growth analysis in figure 3b), where beforehand a reduction in droplet size was observed. A sketch of this is provided below with a Figure S2b from the supplemental information:

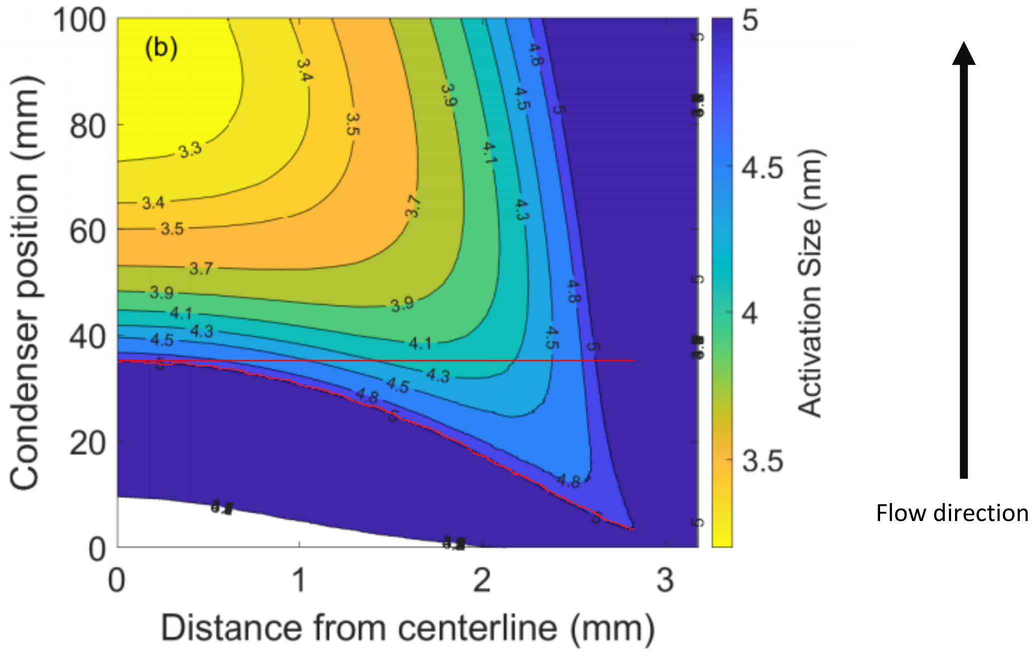


Figure S2b, altered: Equilibrium Kelvin diameter of the condenser. Particles are activated once they reach the position of their respective Kelvin equilibrium diameter. The upper red line indicates the position, from which the particle growth was initiated incorrectly in the first version for a 5 nm particle. The lower red line follows the equilibrium diameter and shows the corrected version.

While the contribution of the most outer positions is reduced due to its low flow speed, the more uniform sizes agrees better with the small standard deviation (1.12) obtained by the droplet growth measurements. A comparison of both versions (before and after the correction) is shown below.

The enhanced growth due to higher supersaturation at the center is partially offset by the reduced residence time, which is caused by the parabolic flow profile. Particles closer to the wall have an increased residence time within the condenser and therefore more time to grow. Both effects ~~*partially*~~ *mitigate each other,* ~~*however seed particles closer to the centerline are expected to grow into larger droplets.*~~ ***leading to a consistent droplet size with only a minor reduction on the most outer region of the condenser****. The calculated droplet sizes vary by* ~~*20 to 35*~~ ***up to 10*** *%, depending on the temperature setting and initial seed particle diameter*

The measured droplet sizes showed no significant size differences for particle seed diameters between 10 nm and 100 nm and averaged 1.94 µm, the average geometric standard deviation was 1.12. Therefore, the simulation overestimated the droplet size by about 6 %.

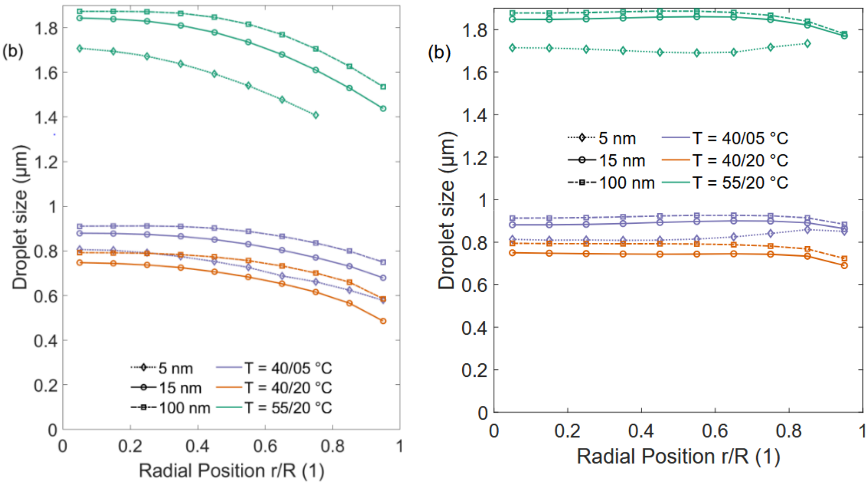


Figure 3b, before (left) and after (right). While the maximum droplet size remains unchanged, the influence of the radial position on the final droplet size is reduced.

Condensation Diffusion Charging – Particle Number Measurement of High Concentrations Down to 2.5 nm

Helmut Krasa, Victoria Miranda Fruhmann, Sebastian Schurl, Martin Kupper, and Alexander Bergmann

Review response AR-2025-20 to Reviewer 1:

In this manuscript an interesting new approach for particle counting is presented. Two techniques, condensation particle counting and electrical measurement based on diffusion charging are combined. Particles are first grown to micrometer sizes by condensation and are then charged in a corona charger and measured in a Faraday cup electrometer. This could result in a lower detection limit for size and concentration compared to DC-Devices and to higher measurable concentrations compared to CPC's. The paper is in most parts clearly written and easy to read.

We want to thank the referee for the valuable feedback and the comments on our submitted paper. We have addressed the comments raised by the author below.

Here are some remarks, which tom my opinion would be helpful for the reader:

It would be nice to have a real quantitative comparison between the new device and in particular CPC's, including the photometric mode offered by several CPC's. Now many statements are more qualitative, the photometric mode is not mentioned. What are the quantitative advantages?

While publications regarding CPC performance in the photometric mode is limited, a 2023 study by Giechaskiel et al (https://doi.org/10.19206/CE-161190) has shown, that the photometric mode suffers from a high dependency of the particles size on the measured PN concentration. A short discussion about the photometric mode of CPCs is now included in at the end of the first paragraph in section 6.1 (396 ff).

The raw signal of the CDC decreases by about 50 % at a concentration of 10^6 cm^{-3}. The observed reduction in raw counts at high concentrations is similar to the behavior of CPCs, which experience pulse overlap at high PN concentrations and apply internal coincidence correction to account for this reduction (Takegawa et al., 2017). ***For concentrations above the single count mode range, some CPCs use a photometric mode and integrate the total scattered light intensity to measure the PN concentration. However, these measured concentrations strongly depend on the initial seed particle diameter and can vary by a factor of up to three for initial sizes between 10 and 100 nm at a concentration of 10^6 cm^{-3} (Giechaskiel et al., 2023).***

Lines 55ff: A slightly more detailed description of the Saturator/Condenser would be helpful.

Additional information about the saturator and condenser are now stated.

The condensation stage combines a heated saturation section with a cooled condenser and was dimensioned based on simulation results, as discussed in Sect. 5.1. The saturator is 200 *mm in length and was made from **two solid 100x70x70 mm (LxWxH)** aluminum **blocks**. It features drilled channels for the wick and two **50 W** heating cartridges.*

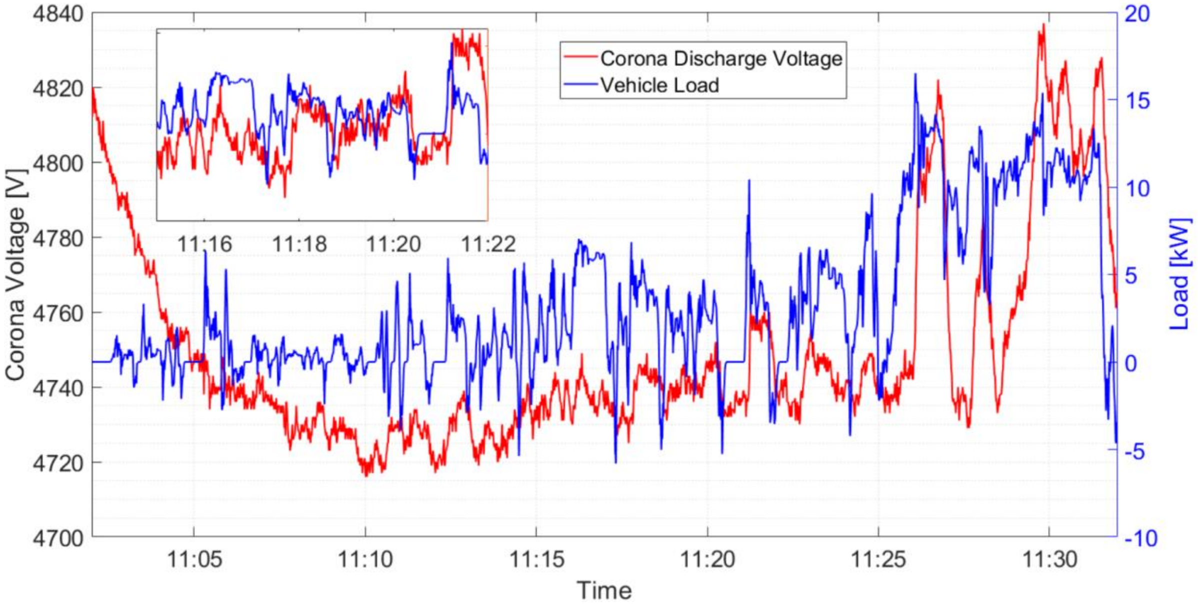
*The wick was custom made from a 3D-printed honeycomb mesh with a 6.35 mm (0.25 inch) flow channel inside **and has an outer diameter of 16 mm.** A silicate cord was wrapped around and soaked in a working fluid (WF), which was either 2-(2-Hydroxyethoxy)ethanol (also diethylene glycol, DEG) or Propan-1,2,3-triol (glycerol). Selection criteria and properties of the WF, are discussed in Sect. 4. An active working fluid management system was not required due to the low WF consumption rate. The condenser section is **made out of an 100x70x40 mm aluminum block** ~~100 mm long~~ **and is** cooled by a **Thorlabs TECH 4** Peltier element. **The 100 mm long flow channel has the same inner diameter as the condenser at 6.35 mm**. Temperature control was realized with a PT-100 element and a PID controller for both the saturator and condenser.*

*The 30 mm long thermal insulator between the saturator and condenser **and connections for the in- and outlet were** ~~was~~ resin 3D-printed. Temperatures of 55 °C or 40 °C for the saturator and 20 °C for the condenser were selected to achieve the desired supersaturation conditions **at a flow rate of 0.54 l/min.***

Information, how the diffusion charger is influenced by the working fluid should be given (may significantly influence ion mobility)

Unfortunately, no information regarding the change in ion mobility is known to the authors. The vapor pressure of DEG is very low at the end of the saturator (2 pa, see Figure S1b in the appendix) compared to the vapor pressure of water (~ 1500 Pa at 25°C at 50 % RH).

The influence of the gas composition on the discharge was further analyzed. The Figure below shows the influence of the vehicle load on the corona discharge process. At higher loads the CVS dilution is reduced and the CO, CO_2 and humidity levels increase, which also leads to an increase in the required corona voltage.



The statement was revised accordingly.

The resulting data are shown in Fig. 7. The CDC PN signal was reduced by a constant factor over the whole test cycle compared to the laboratory calibration. The reduction was ~~observed to be~~ correlated ***with*** *~~to~~ an increase in the required corona voltage for a set corona current****, suggesting the corona discharge process is affected by the gas composition*** *~~.This suggests that the WF vapor probably affects the corona discharge process~~ (Schaffer,2021).* ***The effect was most pronounced at higher engine loads, where increased levels of humidity and CO_2 - gases with much higher vapor pressures than DEG – could further influence the ion mobility.*** *While an increased temperature of the corona module reduced the corona voltage, this also led to re-evaporation of the droplets before charging*

Equation (2): as written here is for strictly monodisperse aerosol and the exponent (here 1.1) depends on the charger design, this should at least me mentioned or the integral form could be shown.

The integral form was implemented and the text changed accordingly:

~~However, the~~ ***The*** *charge acquired by a particle via diffusion charging is not constant but depends significantly on particle size****:*** *~~,roughly scaling with the particle diameter r (Jung and Kittelson, 2005; Fierz et al., 2011):~~*

$$\cancel{Q_{tot} \sim \cdot d_p^{1.1}} \quad Q_{\mathrm{tot}} = \int_{d_{min}}^{d_{max}} \bar{q}(d_p) \cdot N(d_p)\, d(d_p)$$

Q_{tot} is the total charge carried by the particles, ~~and~~ N the number concentration of the aerosol to be measured~~. The particle morphology can also influence the acquired charge of the particle \citep{Biskos2005UnipolarRegime}.~~ ***and $\bar{q}(d_p)$ the average charge per particle. The size dependency of the average charge is roughly proportional to the particle diameter ($\bar{q}(d_p) \sim d_p^{1.1}$), and is dependent on the exact charger design (Jung and Kittelson, 2005; Fierz et al., 2011) and particle morphology (Biskos et al., 2005).***

Equation (3): As the detector is operated in the mode where the induced current is measured, there is no stationary current while the precipitator is on or off (the stationary current is zero in both cases, this should be described better.

As per suggestion of reviewer two, parts of this chapter (description of the heterogeneous nucleation theory and detection of electrical currents) were moved to the supplemental information. This includes the description of equation three, where now a more detailed explanation is given. The text now before the equation reads:

This approach was chosen over pulsing of the corona for its operational stability within our instrument configuration. ***Since the detector is operated in the mode where the induced current is measured, the stationary current is zero when the precipitator is continuously ON or OFF.*** *The sensor signal is therefore proportional to the* ***change in the induced current*** *when the precipitator state is modulated:*

Line 161: an explanation why DEG can condense on sub 3 nm particles without homogeneous nucleation would be interesting

An explanation to why WFs like DEG, with a lower vapor pressure and high surface tension, can grow smaller particles, was appended. Furthermore, as suggested from reviewer 3, reasoning why DEG droplets grow to larger sizes compared to commercial instruments like the PSM, was given. Pargraph 2 and 3 in section 4.1 (129ff) now read:

Hao et al. analyzed 46 different WFs and optimized the saturator temperature to achieve the lowest possible d_{50} value without triggering homogeneous nucleation. Analysis showed the material parameters directly influence the ability to condense on sub-3-nm particles without causing homogeneous nucleation. A high surface tension increases the free energy barrier for particle conversion, while a lower vapor pressure reduces the vapor collision rate. Both effects increase the required saturation ratio for homogeneous nucleation to become significant (Iida et al., 2009). Therefore, DEG has the ability to condense on sub-3-nm particles without causing homogeneous nucleation (Kuang et al., 2011).

Due to its lower vapor pressure, however,** DEG droplets grow to smaller sizes compared to butanol due to its lower vapor pressure. **Mixing-type devices, like the Airmodus Particle Size Magnifier, grow droplets to approximately 100 nm and thus require a separate CPC for counting (Vanhanen et al., 2011). The laminar-flow approach used in this work, results in larger diameters. Simulations of laminar-flow DEG systems have yielded final droplet sizes of approximately 1 µm (Iida et al., 2009) to 1.5 µm (Hao et al., 2021), with the exact size being dependent on specific operating parameters and instrument dimensions.

~~Conversely, DEG has the ability to condense on sub-3-nm particles without causing homogeneous nucleation (Kuang et al., 2011). DEG droplets grow to smaller sizes compared to butanol due to its lower vapor pressure. The particle size magnifier by Airmodus, for example, grows particles into droplets with a size of approximately 100 nm (Vanhanen et al., 2011). Therefore, condensational DEG growth stages are not used in CPCs directly but as particle magnifiers and coupled with a butanol-based CPC as counting unit.~~

~~Hao et al. analyzed 46 different WFs and optimized the saturator temperature to achieve the lowest possible d_{50} value without triggering homogeneous nucleation. They found that WFs with lower saturation vapor pressures can activate smaller particles while avoiding homogeneous nucleation. Simulations for laminar-flow-based magnifiers further showed that, even for WFs with lower saturation vapor pressures, droplets can still grow to several µm for laminar-flow based systems.~~

Chapter 4.1, 4.2 and 4.3: effects are discussed qualitatively, but not the specific impact on the device.

Section 4.2 mainly concerns concentration-dependent effects, which were evaluated in section 6.5. The following statement was added at the end of section 4.2 (172ff).

As the DC signal is sensitive to particle size, smaller droplets, which form at elevated PN concentrations, lead to a reduction of the measured signal amplitude. This results in a non-linear response, where the signal no longer increases proportionally with the PN concentration. This non-linear behaviour was characterized in section 6.5.

Section 4.3 concludes with the influence of WF properties in general and the linearity effects to justify the use of DEG. An additional link to connect the choice of WF to the simulation -

which was the next of the step of the instrument design. Along with suggestion 3 from Reviewer two, the text now reads:

Two WFs, DEG and glycerol, were evaluated for their suitability of condensational particle magnification out of a wide range of potential candidates. *DEG is commonly used in booster stages for particle size magnifiers,* ***and proven in commercial instruments*** *and was therefore evaluated as one of two WFs within this work.* ***The thermodynamic properties of DEG, including vapor pressure, surface tension and diffusion coefficient, were used as inputs for the fluid dynamics simulation. As these parameters directly influence particle activation and droplet growth rates, the choice of WF therefore defined the viable range of temperature settings and boundaries for the optimization of the condensation stage geometry.***

Glycerol was also considered due to its significantly lower vapor pressure, approximately 30 times less than DEG, which was the lowest among the WFs evaluated by Hao et al (2021)..

5.1: Did I correctly understand that in a first step a COMSOL simulation treats the flow ant heat transfer, determining the space resolved supersaturation. Then the particle growth is calculated in Matlab? If I am right, how is the change in supersaturation by the condensation process considered?

Yes, the supersaturation profile is transferred from COMSOL to MATLAB, were growth is initialized. Concentration-dependent as discussed in section 4.3, were are modeled within this work. A simple approach, consisting of a global vapor sink and heat source was modeled, however results did not reflect experimental data shown in Figure 6. As the authors failed to mention this in the text, this is now stated in the second paragraph of 5.1.

The COMSOL model consists of a 2D-axially-symmetric model and couples the laminar flow, heat transfer in fluids, and stabilized convection-diffusion modules. The required temperature-dependent material parameters were taken from Yaw (2003) and are spatially resolved within the geometry. The 2D fields of the gas flow, temperature and WF vapor pressure of the condenser stage are then passed to MATLAB. ***To account for concentration-based effects as described in Section 4.2, a simple approach using a concentration-dependent vapor sink for vapor depletion and a corresponding heat source for condensational heating was modelled. However, this approach was excluded from the final analysis as its predictions were inconsistent with experimental observations.***

Experiment: Some experiments are done in pure N2, some in air, some with influence of the WF. This will result in different charging efficiencies, which are not mentioned or did I misunderstand something?

Wording regarding the influence of the working fluid was chosen inaccurately and was reworded accordingly as stated above. All charging tests (beside the reference measurement at 50 nm) were performed with the working fluid present. Within the laboratory setup, no significant difference between pure N_2 or pressurized air regarding the charging efficiency was observed. N_2 was used for consistency reasons, as the particle activation of DEG is known to be influenced by the relative humidity (Ilda et al 2009, 10.1080/02786820802488194) and to suppress the formation of silver oxides when generating silver particles (Hammer et al 2022, https://doi.org/10.1016/j.jaerosci.2022.105978). The use of N_2 was not explicitly stated in the text and is now added:

*A ceramic boat containing Ag for monodisperse tests and NaCl for polydisperse tests was placed inside an alumina tube in a Carbolite MTF 12/38/250 tube furnace****, which was operated with N_2 as carrier gas.***

Condensation Diffusion Charging – Particle Number Measurement of High Concentrations Down to 2.5 nm

Helmut Krasa, Victoria Miranda Fruhmann, Sebastian Schurl, Martin Kupper, and Alexander Bergmann

Review response AR-2025-20 to Reviewer 2:

In this file, the review comments are in black and our responses in green. Text in the paper is in *blue.* Removed text is ~~*crossed out.*~~ Added text in the paper is written in ***bold.***

Summary of review

The authors present a novel approach for measuring particle number concentrations of aerosols with a lower particle-cut-off diameter of 2.5 nm at concentrations exceeding 10^6 cm^{-3} using a condensation diffusion charging approach. The work is sound, well-presented and draws appropriate conclusions. The work would be a valuable addition to the literature. I would suggest that the article is accepted for publication provided that the comments below are address appropriately.

We want to thank the reviewer for the highly valuable comments to our manuscript. We have now addressed them, and you can find the point-by-point reply to all major comments below.

Technical comments for the authors

1. Figure 1: The caption should be improve to clearly indicated where the diffusion charger is located and, explain what DCEM is, and explain the meaning of the symbols used

The authors have expanded the Figure description to better explain the working principle. As the abbreviation FCEM is used here initially, it is introduced here. The figure caption now reads:

(IMPLEMENTED)

Figure 1. Schematic ~~drawing~~ of the CDC. ***The carrier gas is saturated after entering the device and then cooled in the condenser to induce supersaturation and subsequent particle growth. The enlarged particles then enter the detector section, where they are charged by ions from an external high-voltage corona which are drawn into the flow path with a small voltage. The charged particles are then periodically precipitated and finally counted by a Faraday cup electrometer (FCEM).***

2. Section 3: This theoretical background section is very long and should be made shorter by either / both: (a) summarising just the main point and including references to other sources where the information can be found; (b) moving most of the text to the supplementary information.

The theoretical section was trimmed down as suggested. The text about the hetereogenous nucleation theory was moved and slightly expanded in the SI. Furthermore, the electrical detection was also moved into the SI.:

The end of section 3.1 now reads:

A theoretical framework describing ***heterogenous nucleation and*** *time-dependent droplet growth, including the governing equations and assumptions, is provided in the supplemental information*

Lines 112ff now reads:

Particles ~~are~~ ***can be*** *collected on a filter, and the resulting deposited current ~~is~~ measured.* ***Alternatively, a filter-less method, that measures induced currents upon a change in charge state in the Faraday cup can be used. A more detailed description of the induced current detection method used in this work can be found in the supplementary material.***

3. Section 4.3: The authors state that a 2021 paper by Hoa et al, discusses 46 possible working fluids. This section should also describe why only two of those working fluids (DEG and glycerol) were considered for in this work.

DEG was used due to tis wide prevalence in particle magnifiers, while glycerol was used due to its exceptionally low vapor pressure. The text now states, why out of the 46 mentioned WFs, DEG and glycerol were used. Further changes as suggested by Reviewer one were also implemented. The text now reads:

Two WFs, DEG and glycerol, were evaluated for their suitability in condensational particle growth out of a wide range of potential candidates. *DEG is commonly used in booster stages for particle size magnifiers,* ***and proven in commercial instruments*** *and was therefore evaluated as one of two WFs within this work.* ***The thermodynamic properties of DEG, including vapor pressure, surface tension and diffusion coefficient, were used as inputs for the fluid dynamics simulation. As these parameters directly influence particle activation and droplet growth rates, the choice of WF therefore defined the viable range of temperature settings and boundaries for the optimization of the condensation stage geometry.***

Glycerol was also considered due to its significantly lower vapor pressure, approximately 30 times less than DEG, which was the lowest among the WFs evaluated by Hao et al (2021).

4. Lines 267-273: Please include a discussion as to whether it would be beneficial to use a larger delta_T which would result in an even smaller d_{50}?

Using a larger ΔT to achieve an even smaller d_{50} presents a trade-off. While the resulting higher supersaturation enables the activation and subsequent measurement of smaller particles, it also pushes the system closer to the threshold for homogeneous nucleation, where droplets form spontaneously without seed particles and create false counts. Before this limit is reached, a higher saturator temperature yields larger droplets that amplify the measurement signal but can introduce further non-linearities at high concentrations. Furthermore, increasingly smaller particles are more prone to diffusional losses within the system, which would require specific particle loss mitigation methods, such as the use of a sheath-flow design.

The following statement (now line 255ff) was added:

Increasing the ΔT further would allow the activation of particles down to 2 nm and below. However, due to the absence of a sheathed-flow design, diffusional losses in this size range become significant. Furthermore, the increased required supersaturation approaches that of homogenous nucleation, where clusters start to nucleate, leading to false counts in the detector.

5. Section 6.1: The calibration of the CPC and electrometer are not explained. Please include a summary of how the instruments were calibrated.

The plateau efficiency of CPC and electrometer used were compared to a calibrated TSI 3752 CPC before the measurements. A statement was included at the end of the first paragraph in 6.1.

For particles with a mobility diameter of 23 nm and below, we used a Palas Charme EM (Palas, Germany), and for particles of 23 nm and above, we used a TSI 3775 CPC (TSI Inc., USA). ***The plateau efficiency of both instruments was calibrated against a 3752 CPC (TSI Inc., USA) with a valid calibration certificate prior to the measurements. This allows for the limitations of both instruments to be accounted for:*** *~~This allows to account for the limitations of both instruments:~~*

6. Lines 318: Please comment on whether the performance of the instrument would be different for different types of polydisperse particles other than NaCl (most importantly real world soot).

Two influences need to be considered:

1) The material dependency on the activation of the particles in the condenser. This is only relevant in the transition region < 10 nm, and therefore mainly concerns particles within the transition regime, therefore below 5 nm (Wimmer et al 2013, doi:10.5194/amt-6-1793-2013). To the authors are not aware of a suitable generation of soot particles in this size range (2 – 10 nm).

2) The influence of the particle composition and shape on the detection efficiency of the DC (Hammer et al 2024, doi.org/10.5194/ar-2-261-2024). However, as the particles transform into spherical DEG-droplets, these effects are not relevant in this case.

Both effects are now discussed in the paper:

The particle shape and composition can influence the counting performance of DC-based instruments (Hammer et al., 2024). However, in this case, the particle surface is almost entirely composed of DEG, and the droplets become spherical after condensation. Therefore, once a particle is activated, its original composition is not expected to affect its counting behavior in the DC. Therefore, the particle composition primarily influences the activation efficiency, particularly for particles 10 nm and smaller. As no sufficient method for generating soot in this size range in the laboratory exists, silver particles were used to evaluate the counting efficiency in the transition regime of the CDC.

7. Line 334: Including a table of the measured droplet sizes at each particle seed diameter would be useful, perhaps in the Supplementary Information.

A table of all measured droplet sizes has been added in the supplemental information.

The average geometric standard deviation was 1.12. Therefore, the simulation overestimated the droplet size by about 6 %. ***The experimental data is listed in the supplemental information in Table 6.***

8. Figure 5: The authors should include error bars on each of the data points in order to allow the reader to assess any significance in differences between the plotted points and lines. Please also make the two shapes used for data points much more distinct and different colours.

The standard deviation of three consecutive measurements has now been plotted. The line styles have been changed to allow for better distinction between the different simulation models and the marker size was increased. We do think that a similar color for both experimental results is suitable as only the reference counter was changed.

9. Line 388: The type of polydisperse aerosol used should be re-stated at this point in the text

The second line in section 6.5 now reads:

The linear response of the CDC instrument was evaluated with polydisperse ***NaCl*** *aerosol.*

10. Figure 6: The authors should include error bars on each of the data points in order to allow the reader to assess any significance in the trend shown.

The standard deviation of three consecutive measurements has now been plotted. The increased uncertainty at lower concentrations is discussed within the next point.

11. Figure 6: Please comment on the scatter of the data below 10^4 cm^{-3}, as this is larger than would be expected for a CPC.

Firstly, the as the CDC directly measures the droplet size, slight changes induce a change in measured signal amplitude. This can be caused by slight variations in both the temperature of the saturator or flow rate. Furthermore, wick contamination is also known to influence the CPC performance (Giechaskiel et al 2009, doi: 10.1016/j.jaerosci.2011.01.002) and could therefore reduce the droplet growth. This effect however, would not only be present at reduced concentrations but also elevated levels in is therefore probably not the main cause.

Secondly, fluctuations in the measured DC concentrations caused increased uncertainty, which is also reflected by the larger scatter in the data, which is now visible after the addition of the error bars in the graph. The concentration in the reference instrument was very stable and this effect was not observed the linearity measurements, at which lower concentrations were measured. The authors suspect that this effect could be induced by slight, periodical changes in the pressure due to the rotational disk diluter (which was not used for the activation/CE measurements, for which the uncertainties are lower). As the signal amplitude from the particle concentration is lower at reduced PN concentrations, this effect increasingly concerns the lower PN concentration range. This effect is now described in section 6.5:

The resulting data are shown in Fig. 6. The measured PN concentrations for the three size distributions are within 25 %. It can be observed that the measured concentration begins to decrease from approximately 10^4 cm^{-3}. The raw signal of the CDC decreases by about at a concentration of 10^6 cm^{-3}. ***The larger spread observed at lower concentration levels can be attributed to fluctuations in the CDC concentration signal. This effect was not observed in the linearity measurements, which were conducted similar concentration levels. Sampling issues caused by the operation of the rotating disk diluter, could have influenced the counting performance of the CDC at reduced PN concentrations.***

12. Figure 7(c): The gradient of the line looks to < 0.9. Please explain why this gradient is not nearer to 1, as appears to be the case for Figure S5(c)

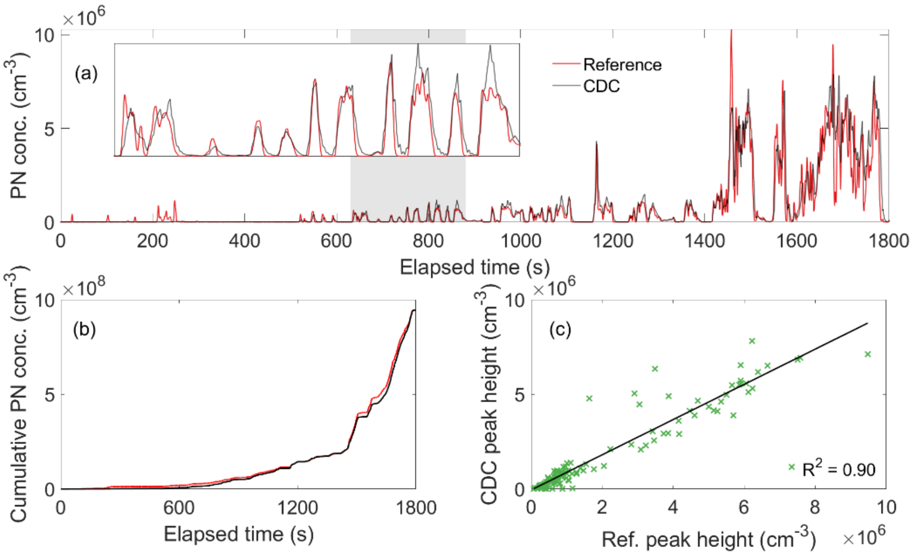
Figure 7 and S5 have been changed accordingly as per the next suggestion, however the phenomena remains the same in both cases.

The gradient of the slope was 0.92 and is now 0.94 and is determined by the ratio of each of highest value within the peak. As the CDC was correlated to match the cumulative PN concentration, the CPC has a slightly higher time resolution compared to the device under test after averaging the 10 Hz data to 2s, leading to higher, but marginally narrower emission peaks. 2 seconds averaging was chosen, as this is the theoretical time resolution of the CDC, as the precipitator switches on/off every 2s. A three second averaging of the CPC data would result in a gradient of 0.98, but then be below the theoretical response time of the DC.

The CDC shows a very good correlation with an R^2 of ***0.90*** *~~0.94.~~ The slope of the correlation was k=* ***0.94*** *~~0.92~~ and therefore underestimated the peak height by about ~~8~~* ***6*** *% compared to the cumulative PN concentration****. The slightly higher, but narrower peak shape for the concentration measured with CPC indicates*** *~~suggesting~~ that the response time of the CDC is slightly below that of the reference counter after time-averaging~~.~~* ***An averaging of 3 s for the CPC would result in a slope of k=0.98, indicating that the real response time of the CDC is closer to 3s.***

13. Figure S5 is very important as it is fundamental to demonstrate the claim that the device is suitable for operating at concentrations over 10^6 cm^{-3}, so should be brought into the main paper as Figure 8 (or combined with Figure 7).

Figure S5 and Figure 7 were exchanged and the wording changed accordingly. Additionally an inlet in the top figure was added to see more detailed comparison over a limited time series. Both Figures have been originally placed this way, as the second measurement does compare total PN vs solid PN only, as the catalytic stripper of the dilution system could not be removed. The Figure is shown below:



Section 6.6 now reads:

… The CDC system was placed parallel to the ~~CPC downstream of the~~ sampling system, ***which diluted the aerosol concentration by a factor of 1:196. As the volatile particle remover within the sampling system could not be removed, and the CDC measured without additional pre-treatment, two different metrics - solid PN vs total PN - were evaluated. To stay within the concentration limits of the CDC, the sampled aerosol was diluted by a factor of 1:10.***

~~Due to the narrow measured concentration range, no further concentration-dependent calibration, as shown in Fig. 6, was required.~~ ***To account for concentration-dependent effects of the CDC, a concentration dependent fit function obtained from the data in Figure 6 was used.***

~~At high PN concentrations at the end of the cycle, the CDC system slightly under-counts compared with the reference counter, which is caused by non-linear counting behavior as described above.~~ ***At high PN concentrations towards the end of the driving cycle, the CDC system slightly over-counts compared to the reference counter after implementation of the concentration-dependent fit function.***

The CDC shows a very good correlation with an R^2 *of* ***0.90*** *~~0.94.~~ The slope of the correlation was k=* ***0.94*** *~~0.92~~ and therefore underestimated the peak height by about ~~8~~* ***6*** *% compared to the cumulative PN concentration*. ***The slightly higher, but narrower peak shape for the concentration measured with CPC indicates*** *~~suggesting~~ that the response time of the CDC is slightly below that of the reference counter after time-averaging~~.~~* ***An averaging of 3 s for the CPC resulted in a slope of k= 0.98, indicating that the real response time of the CDC is closer to 3s.***

The last paragraph in section 6.6 was rewritten to match now the description for the plot in the SI:

~~To evaluate the CDC at elevated concentration levels, the instrument was placed in the CVS with an additional 1:10 dilution and the dilution system bypassed for measurement with the~~

~~*CDC. As the volatile particle remover within the sampling system could not be removed, and the CDC measured without additional pre-treatment, two different metrics - solid PN vs total PN - were evaluated. The resulting are shown in Fig. S5 and show show good correlation with an R2 of 0.90 and close tracking of the cumulative PN concentration after calibration. Further details are found in the supplemental information.*~~

For a direct comparison of the solid particle number concentration, a second measurement was performed. In this setup, the CDC was placed after the sampling system, parallel to the reference CPC, which resulted in a reduced concentration range for the measurement. The resulting data, shown in Fig. S5, demonstrate a strong peak correlation with an R² of 0.94.

Minor comments for the authors

1. Line 21-23: The discussion should be updated to describe the new European air quality directive (2024/2881).
2. Line 29: Include a reference to international standard ISO 27891 after ‘CPC calibrations’
3. Line 30: Suggest changing ‘doubly’ to ‘multiply’
4. Line 41: missing word: change to ‘however, they come’
5. Line 71: Should the unit be mm, not mm^2?+
6. Figure 2: The line styles are very similar so would be very difficult to distinguish for readers with colour-blindness. Please consider making the dashes and dotted lines much more distinct.

The European air quality guidline and the ISO standard have been implemented as suggested. The other changes have been implemented as suggested.

The dashed line was substituted to allow for better differentiation (unfortunately the number of line styles is limited with MATLAB which was chosen for plot creation). The linewidth was increased and the range of the plot slightly reduced and the line types changed. Colors are colorblind friendly (https://colorbrewer2.org/#type=qualitative&scheme=Dark2&n=3).

Figure 4: same comment for figure 2. In addition, the symbol shapes are very small and therefore difficult to distinguish. Please increase symbol size.

Similar to above, the line styles were adapted, line thickness was increased and symbols were enlarged. Figure S3 was also adapted accordingly.

Comment for the editor

1. Page 18: Is the data availability statement acceptable?

   The data availability was changed accordingly:
   The data is publicly available under the following DOI: 10.3217/tmhk6-rrd07.

Condensation Diffusion Charging – Particle Number Measurement of High Concentrations Down to 2.5 nm

Helmut Krasa, Victoria Miranda Fruhmann, Sebastian Schurl, Martin Kupper, and Alexander Bergmann

Review response AR-2025-20 to Reviewer 3:

We want to thank the referee for their very valuable feedback and the comments on our submitted paper. We have addressed the comments raised by the author below.

The work presents more or less, a CPC without an optical head. It's growth system where the optical head is substituted by a detector baser on an electrical charger and an aerosol electrometer. The authors pretend that the instrument can then measure high concentrations of particles (up to 106p/cm) without dilution. Of course this instrument cannot be used for low and very low concentration. It should appear in the text. Indeed the maximum concentration measured by the CPCs sensitive to 3 nm, are limited 105p/cm3.

The lower Concentration Limit is given in the last paragraph of section 6.5 and quantified via the 3σ-limit of the detection.

At 1 s measurement time, the 3σ-limit of detection was determined to be 40.8 cm^{-3}, which is about a factor 25 lower compared to conventional DC instruments, such as the Naneos Partector 2 at 10^{3} cm^{-3} (naneos particle solutions gmbh, 2024).

To clearly distinguish the difference in the lower detection limit of the CDC and a CPC, which has basically no lower concentration limit, an additional sentence was added inn the conclusion at line 455f

The CDC is capable of measuring concentrations above 10^{6} cm^{-3} at a flow rate of 0.54 L min^{-1}, exceeding the total particle count rate of a CPC operating in single-count mode at comparable flow rates by approximately an order of magnitude ***at the cost of an introduced lower detection limit due to the noise of the electrical detection method, making it unsuitable for very low concentration measurements. The 3σ-limit of detection was evaluated to below 50 of cm^{-3}, however the use of the rotating disk diluter led to an increased uncertainty during the linearity measurements in the lower concentration range.***

The increased spread in the PN measurement during the linearity tests is now discussed in section 6.5 as suggested per reviewer 2.

The larger spread observed at lower concentration levels can be attributed to fluctuations in the CDC concentration signal. This effect was not observed in the linearity measurements, which were conducted similar concentration levels. Sampling issues caused by the operation of the rotating disk diluter, could have influenced the counting performance of the CDC at reduced PN concentrations.

These CPCs (called ultrafine CPCs) don't use the photometric mode method (104-107p/cm3). They use only the counting mode. The reason is the risk of agglomeration because of the high diffusion of the sub 10 nm particles. High concentrations will 'probably' induce agglomeration which mill induce a shift in the diameters and a decay in the number concentration.

The ultrafine CPCs can activate and detect particles down to 2,5 nm because use a sheathed condenser where the particles are confined in the center of the condenser. Indeed the maximum sursaturation profile is locate in the center of the condenser. On the other-hand the sheath decrease the diffusion of the particles to the walls of the condenser where they will be lost. This method has been introduced by Stolzenburg and Mc Murry in 1991. The TSI ultrafine CPC is based on this design.

The inner diameter of the condenser is missed. The temperature of the saturator is between 55°C and 40°C depending on the working fluid I guess?

The diameter in the condenser remains unchanged, however this was not stated previously. Additional details have been added. The section now reads:

The condenser section is ***made out of an 100x70x40 mm aluminum block*** ~~*100 mm long*~~ ***and is*** *cooled by a* ***Thorlabs TECH 4*** *Peltier element.* ***The 100 mm long flow channel has the same inner diameter of 6.35 mm****. Temperature control was realized with a PT-100 element and a PID controller for both the saturator and condenser.*

The working fluid influences the required temperature differences for particle activation, as material parameters such as diffusion coefficient, surface tension vapor pressure change. For example, with a temperature setting of 40/20 °C, the simulated d_{50} diameter within this experimental setup according to the Kelvin theory are the following:

DEG	7.77 nm
Butanol	7.19 nm
Glycerol	7.24 nm

The flowrate in the saturator and the condenser is not well defined although its value is very important in terms of saturation of the air (or N2) at the outlet of the saturator. It's critical in the condenser too since the profile of the sursaturation is function of the flowrate (residence tie in the condenser). The reader can find that the flowrate in the AEM is 0,54 lpm

The flow rate remains unchanged at 0.54 lpm, however this was not stated within the text previously. The instrument description was expanded as per suggestion by another reviewer and now reads:

Temperatures of 55 °C or 40 °C for the saturator and 20 °C for the condenser were selected to achieve the desired supersaturation conditions ***at a flow rate of 0.54 l/min.***

Schmidt-Ott and Burtscher (2006) is it a paper? A patent? It's hard to find this work. The authors could cite many other works including other works of Andreas Schmidt Ott and Heinz Burtcher.

Yes, this is work is indeed a patent, however it is only available in German language and therefore not accessible to all non-German speakers. The text (which was moved to the supplemental information as per suggestion of Reviewer 2) now was slightly altered and further additional information was given. The text now reads:

~~Schmidt-Ott and Burtscher (2006) incorporated an electrostatic precipitator between the charger and the EM~~. ***Fierz et al. (2008) incorporated a diffusion stage precipitator between the charger and an electrometer. By measuring the current at two stages, they could estimate the average particle size and thereby determine the PN concentration. Schriefl et al. (2020) employed a different technique, using a precipitator to progressively remove larger particles to offset their greater charging efficiency.*** *The mobility scales…*

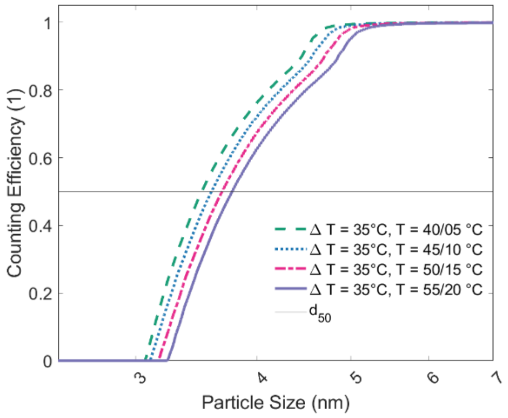
… Across a limited range, the measured average charge per particle becomes almost independent of the particle size, allowing for measurement of the PN concentration ~~(Schriefl et al., 2020)~~.

In the Figure 2 the working fluid is missing. Is it diethylene glycol or butanol? In the same figure, 40/05 couple of temperatures gives a better results 55/20°C. 50/15 and 45/10 would have been interesting couples to simulate to confirm the explanation and the behavior given by the authors.

The WF was specified in the figure description. It now reads:

Simulated activation efficiency of the growth stage ***with DEG as working fluid*** *at three different temperature settings according to the Kelvin equation.*

The suggested temperature settings of 50/15 and 45/10 were simulated as suggested by the reviewer. As all 4 CE curves with the same 35 °C temperature difference are very close to each other, they are not distinguishable in the initial plot. Therefore, an additional plot, containing all 4 CE curves and a limited size (x-Axis) range was put in the supplemental information.



The authors have used a TSI CPC model 3775 with a detection limit of 4 nm. I would suggest to limit the paper to 3 nm rather than 2,5 nm although the simulated results in the figure 3 for example are limited to 5 nm.

Although the particle counting below 3 nm was evaluated, the number of data points is very limited, and the measured d_{50} diameter is at 3 nm. Therefore, we do agree that 3 nm is more appropriate than 2.5 nm. The title was changed accordingly:

Condensation Diffusion Charging - Particle Number Measurement of High Concentrations Down to ~~2.5~~ ***3*** *nm*

Experiments characterizing the activation efficiency below 23 nm were performed with an electrometer as reference instrument as described in the start of section 6.1 and drawn in figure 4, to avoid using the 4 nm CPC in the size range, where the CE is significantly below 1.

(For particles with a mobility diameter of 23 nm and below, we used a Palas Charme EM (Palas, Germany), and for particles of 23 nm and above, we used a TSI 3775 CPC (TSI Inc., USA))

The CPC to be used on the chassis dynamo test was a 2.5 nm CPC:

The CPC previously used in the sampling system (nominal cut-off: 10 nm) was replaced with a 3756 CPC (TSI Inc., USA), with a nominal d50 value of 2.5 nm,…)

Figure 5 concerns more the linearity above the whole size range, than the particle activation itself which was modeled in Figure 4. The droplet growth was simulated above 5 nm, as otherwise very few radial diameters (only the inner ones with higher supersaturation ratios) actually lead to activation and the given information would be therefore more limited.

I have a deep question about the paper and the results. It’s well know that DEG as a working fluid in the ultrafine CPC design of TSI, cannot grow particles to more than 100 nm (0.1 µm). That is the reason why they use a a CPC as a booster to count the droplets. The present design seems to detect and grow particles of 2,5 nm up to 1.8 µm without booster nor a sheathed condenser. The authors must give the reason or the secret of their method in the paper. The inner diameter of the condenser is not given nor the profile of the supersaturation at different temperatures must be given too..

The authors are aware of the small droplet size between such as the particle size magnifier, which reported a size of about 100 nm (Vanhanen et al., 2011). The PSM is not a laminar-flow type counter, but mixes the hot, saturated DEG vapor, with the cooled, gas containing the aerosol, and the growth section is cooled down to 3 °C after mixing (Vanhanen et al., 2011). The differences in temperature in combination with an overall different approach (mixing-type for the PSM versus laminar flow-type for the device in this paper) are most likely the reason for differences in obtained droplet sizes. The droplet sizes are also in accordance with simulations performed for laminar flow-based DEG counters in previous papers, such as by Hao et al (2021, https://doi.org/10.1016/j.jaerosci.2021.105841) at about 1.5 µm and Ilda et al (2011, 10.1080/02786820802488194) at about 1 µm.

This is now specified in the text, along with additions suggested by reviewer 1, starting from paragraph 2 in 4.1 (128ff):

Hao et al. analyzed 46 different WFs and optimized the saturator temperature to achieve the lowest possible d_{50} value without triggering homogeneous nucleation. Analysis showed

the material parameters directly influence the ability to condense on sub-3-nm particles without causing homogeneous nucleation. A high surface tension increases the free energy barrier for particle conversion, while a lower vapor pressure reduces the vapor collision rate. Both effects increase the required saturation ratio for homogeneous nucleation to become significant (Iida et al., 2009). Therefore, DEG has the ability to condense on sub-3-nm particles without causing homogeneous nucleation (Kuang et al., 2011).

Due to its lower vapor pressure, however, *DEG droplets grow to smaller sizes compared to butanol.* ***Mixing-type devices, like the Airmodus Particle Size Magnifier, grow droplets to approximately 100 nm and thus require a separate CPC for counting (Vanhanen et al., 2011). The laminar-flow approach used in this work, results in larger diameters. Simulations of laminar-flow DEG systems have yielded final droplet sizes of approximately 1 µm (Iida et al., 2009) to 1.5 µm (Hao et al., 2021), with the exact size being dependent on specific operating parameters and instrument dimensions.***

~~Conversely, DEG has the ability to condense on sub-3-nm particles without causing homogeneous nucleation (Kuang et al., 2011). DEG droplets grow to smaller sizes compared to butanol due to its lower vapor pressure. The particle size magnifier by Airmodus, for example, grows particles into droplets with a size of approximately 100 nm (Vanhanen et al., 2011). Therefore, condensational DEG growth stages are not used in CPCs directly but as particle magnifiers and coupled with a butanol-based CPC as counting unit.~~

~~Hao et al. analyzed 46 different WFs and optimized the saturator temperature to achieve the lowest possible d_{50} value without triggering homogeneous nucleation. They found that WFs with lower saturation vapor pressures can activate smaller particles while avoiding homogeneous nucleation. Simulations for laminar-flow-based magnifiers further showed that, even for WFs with lower saturation vapor pressures, droplets can still grow to several µm for laminar-flow based systems.~~

The second question I have is about the final diameter of the droplets of sub 10 nm seed particles. It's well known in the pass that butanol droplets are size dependent in the sub 10 nm. People has used that in the method called Pulse Height Analyser (PHA) to size particles in the sub 10 nm. Is that not the case with di ethylene glycol?

Very small particles close to the cut-off diameter have a slightly reduced time in the condenser to grow, as smaller particles activate slightly later within the condenser. The droplets have less time to grow overall, before the are then being measured (either electrically or optically).

We suspect this effect is also present for DEG, as the thermodynamic aspects – the supersaturation and the resulting activation position within the condenser as well as the flow profile - are similar to the PHA using butanol. Similarly, this should therefore also concern particles in the transition region, which is in this case particles < 5 nm. Simulations of the droplet size showed a reduction of about 10 % for 5 nm aerosol (and 2-3 % for 15 nm) compared to 100 nm aerosol for both the 55/20 °C and 40/05 °C setting.

When analyzing the droplet sizes with the APS, we had to introduce additional tubing and mix in additional, unsaturated air, to accommodate the measurement with the APS. Within this setup only particles > 10 nm were evaluated, where no changes in droplet size were observed.

While very interesting, unfortunately, the authors had no access to a DEG-based system which would allow for pulse height analysis.