We thank both reviewers for corrections and suggestions which improved the manuscript. Both reviewers shared the concern of the manuscript being a random collection of experimental results. Due to this concern we changed the manuscript structure so that there is a section for all CPCs, further comparison between 3777 and v-WCPC, and CPC specific experiments. The title was also edited to highlight the fact that the experiments were conducted during a workshop in Helsinki, when all CPC were brought to the same laboratory. Also, we language of the manuscript was improved.

Below are our point-to-point responses for all concerns of the reviewers, and below shown the modifications to the manuscript. Line numbers refer to the document with no track changes.

Reviewer 1

General Comments

The major outcome of this work is systematic comparisons between two newest CPCs for detecting sub-3 nm particles, which are TSI-3777 and ADI v-WCPC. The reported results are valuable to the potential users of these instruments. However, readers are expected to feel that B3010 are not compared a systematically with v-WCPC and 3777. For example, authors are showing that the detection efficiencies of v-WCPC and 3777 shifts to large sizes when TDDAB are used as the test particles. Reader would expect to see whether the butanol based instruments are also affected in a similar way or not. The same comments apply to the effect of moisture content on the detection efficiencies. Some readers may wonder whether the detection efficiencies of butanol instruments are different between unsheathed and sheathed. It is interesting to know the effect of flowrates on the detection efficiencies of B3010. However, since authors believe that the results are less impressive than their previous results obtained using 3772, it is probably not worth to presenting this results in this paper. I personally recommend to remove the results associated with B3010 in this paper, and gather and emphasize positive aspects of B3010 in another paper.

See general response above.

Specific Comments

Line 15-16. This statement communicates well but it sound too casual. I recommend to use more intellectual expressions since it is the first line of the abstract.

Line 15 Silence is golden. Removed the statement.

Line 24-26 Authors do not clearly state whether high dT setting detect ions generated by bipolar ion source or not throughout the paper. Please clarify somewhere in the text.

Added statement to line 136 “At the high dT settings both 3777 and v-WCPC are able to detect ions from a radioactive source.”

Line 73-74. I believe that one great benefit of using water as working fluid is that water vapor is generally not considered as a source of contamination whereas the organic vapor are often considered as contaminates.

Edited the sentence at line 75 as: “The disadvantage of all the previous CPCs is the slight toxicity of the working fluids butanol and DEG, and these organic liquids can introduce contaminant molecules to vapor phase.”

Line 90 “effect of electrical charge” sounds more proper.

Edited as suggested

Line 98-110 The statement in line 101-102 “possibly altering the detection efficiency: : :.” is not needed at this point since the purpose of this paragraph to describe the structure of the 3777, not to comment on its performance. Instead, authors may emphasize that saturator of the 3777 has a meandering path in a metal block instead of a porous wick used in butanol based ultrafine-CPCs. It is cumbersome to

remove DEG liquid absorbed in a porous wick since DEG is viscous and has a relatively low vapor pressure.
Thanks for the detail, edited as suggested to line 111.

Line 127 “Cheap second hand” sounds inappropriate. It give an impression that authors are looking down on older models. Is it true that simpler electronics of the older model made the modifications much easier? The style of the schematic for B3010 are very different from those of 3777 and v-WCPC. If the data for B3010 are going to be included in this paper the style of the schematic should be similar to 3777 and v-WCPC.
Replaced “cheap second hand” with “robust” at line 138. Figure 3 changed to a better fitting one. The point was to show that the saturator and condenser temperature decoupling can be done for the 3010, and it can be modified to detect particles of and smaller than 3 nm. In the 3772 the saturator and condenser temperature control is already decoupled.

Line 182-184 Uncertainty should include the particles size after neutralization since recombination between a charged particle and ions of opposite polarity may not transfer just electrical charge. The particle and ion may stick together to generate a larger particles as shown by Sipilä et al (2009).
While we agree with this comment, and added a statement about this uncertainty, Sipilä et al. 2009 only speculate about this problem in case of measuring detection efficiency of charger ions. Indeed to our knowledge such experiments have not been conducted where the recombination products are studied at molecular level, which is probably due to experimental difficulties in probing the neutral recombination products. Edited the statement at line 179-> as “This method yields uncertainties in the resulting d50 due to possibly size dependent neutralization efficiency, unknown neutralization mechanism (ion recombination leading to larger physical size, or charge transfer) and chemical composition of the neutralized particles, however, it is being the only method to measure d50 for neutral particles for sub-3 nm particles.”)

Line 184-185 “it is the only method to measure d50 for neutral particles: : :” This statement is not entirely true since Winkler (2008, Science) measured the activation efficiencies for electrically neutral and charged particles using their expansion chamber.
Added clarification after the statement “Winkler et al. (2008) used similar method to measure nucleation probabilities of electrically charged and neutral clusters, the difference being that they used bipolar neutralizer.”

Line 188: Title of the section 2.3 should be “Concentration Calibration and Atmospheric Sampling” to be consistent with the titles of 3.4 & 3.5.
Edited as suggested

Line 211 to 212 Resolution with respect to mobility diameter is about twice of the resolution with respect to the electrical mobility in free molecular regime. It seems more conventional to express uncertainty as the square root of a variance not as the full width half maximum.
Thanks. This is correct, it should have been ±FWHM/2 (2.5%) which is closer to σ. Now corrected so that normal distribution was fitted to the THABr positively charged monomer spectrum, and from that square root of variance ($\sqrt{(\sigma^2)}$) was taken as the uncertainty, resulting as uncertainty of ± 2%. Corrected at line 236 -> as “X-axis uncertainty can be taken from the Herrmann DMA resolution of approximately 20, which leads to relative uncertainty of ± 2%, which is the square root of variance of the normal distribution fitted to the tetraheptylammonium bromide positively charged monomer peak.”

Line 215-216 The statement “such as commonly used for mobility based : : :.” Does not seem necessary since the role of the bipolar ion source is already introduced in previous section
Removed as suggested

Line 243-254 The results shown in Figure 7 is very interesting although the measured values are being affected by several sources of uncertainties. It is recommended that authors discuss the sources of observed differences between positively and negatively charged particles after neutralization. One potential source is the difference in their chemical compositions as already stated by authors in line 235-236. Isn't it also possible that the neutralization efficiency depend not only on particle size but also on the polarity of the bipolar ions due to the difference in their mobility?

Added clarification to line 282 ->: "The difference in the d50s between the negatively and positively charged particles after neutralization are possibly mostly explained by their differences in the chemical composition. Positively charged particles contain more contaminant species than the negatively charged particles, which is still observed in the d50 when they both are neutralized: lower d50 for the neutralized negative particles than for the neutralized positive particles. For more details, refer to Kangasluoma et al. (2016b).".

The reviewer is correct in that we observed different neutralization efficiency for different polarities. However, it does not affect the obtained d50s since the data is normalized to 90% at the curve plateau region.

Line 260-261, and Line 338-342 The statements in these lines are rather extreme or too demanding. It is generally true that compositions of freshly nucleated nanoparticles are partially known from other measurement techniques or previous studies. It is still very useful to be able to measured particle size distributions and their uncertainties in sub 3 nm range after size-classification although their chemical compositions are not known completely. For example, if we are to investigate the effect of conditioning on the freshly nucleated particles it is not important to know the chemical composition of the DMA-classified particles since the material dependence of the detection efficiencies cancels out between before and after the conditioning.

Here we slightly disagree. First, there are not many experiments where the composition of the nucleating particles are exactly known, CLOUD experiment in Cern could be one. The only atmospheric experiment is by Sipilä et al. 2016, Nature. Second, even if the composition of the nucleating species is known, or partly known, it does not mean that the CPC detection efficiency curve is known for that experiment, since the CPC should be calibrated with the same aerosol. Almost always this is not possible, but it does not mean that it is not a large source of uncertainty for the d50. Indeed, we think that efforts should be focused on this problem to reduce the particle counting uncertainties.

Having for example a rough idea of the d50 with the accuracy of ± 0.5 nm can lead to uncertainties from basically -∞ to +∞ (form zero detected particles to all detected, the exact uncertainty depends on the sample size distribution) at the sizes close to the d50. This d50 uncertainty can lead to huge uncertainty in the measured particle concentration, if strictly looking at the measured particle concentration at a fixed mobility diameter.

We agree that the measurements should be done regardless of this uncertainty, but more effort should be put to understand the sources of uncertainty in the obtained concentrations (and parameters obtained from the concentrations, such as growth and nucleation rates).

Edited line 294-296 a little "To obtain accurate particle concentration measurements, these differences in the d50 imply that the CPCs should be calibrated with the same aerosol composition as with the real experiment is conducted."

Edited line 363-367 as: "Due to the variations in the d50 with composition for the vWCPC and 3777, a careful CPC calibration should be conducted with the same particle composition as of the sampled particles. If the composition of the sampled particles is completely unknown, the obtained particle concentrations at the size range of the d50 can have significant uncertainties."

Line 265 It is unclear the "error" stated by the authors refer to what measured variables.

Edited to line 309 as “Because water was observed to alter the d50 in the original laminar-flow DEG instruments, this question was examined for the 3777”

Line 274-276 I understand that authors would like to support the instruments developed by their colleagues, but this statement is somewhat irrelevant to the objective of this paper. In addition readers would not understand why replacing internal pump with MFC reduces the water content.
Removed as suggested. As it was written, MFCs are usually fed by dried compressed air while internal pumps just draw ambient air without drying.

Line 308-317, 3.5 Atmospheric sampling There seems to be equal number of bus departure time which does not show clear spikes. I believe that most reader would see from Figure 13 are the followings. The number concentration generally high during traffic hours, and both CPCs reacts instantaneously to the occasional spikes in the number concentration. Readers would be able see the concentration dependence more clearly if the data in Figure 14 are plotted on a log-log scale. One-to-one lines needs to be shown. Plotting data on log-log scale does not stop authors stating that there is an offset.
Changed fig14 to log-log scale. Edited to line 300-> as suggested “Clear spikes up to 200 000 cm^{-3} in the measured concentrations are observed throughout the morning. The number concentration generally high during traffic hours, and both CPCs reacts instantaneously to the occasional spikes in the number concentration. From the data of Figure 13, a correlation plot between the v-WCPC and 3777 is presented in Figure 14 for concentrations below 50 000 cm^{-3}.”

Line 336: not perfect => imperfect?

Corrected

Reviewer 2

General comments:
This manuscript describes some calibration and comparisons performed with 3 CPCs, chosen for their abilities to measure particle sizes below 3 nm. Good performance data on CPCs is critical for interpreting their measurements. As such, the manuscript would make a contribution in this area. I have two main concerns and a number of minor suggestions.

Main concern 1: Overall the manuscript is fairly easy to follow but there are times when I feel it could benefit greatly from a careful review for English grammar and typographic errors.

Main concern 2: As described specifically below, the paper often reads like a random collection of data from lab experiments and the reader is not told why these experiments were chosen, why some experiments were performed on one instrument and not another, etc. The authors should address this early in the manuscript to allow the reader to make better use of these observations.
See general response above for both main concerns.

Minor edits/questions/comments:
49: I believe that Brechtel began commercialization of their mixing-type CPC before 2011, so this statement should be modified to “the use of a mixing CPC for a booster” or some-such.
Edited as “DEG based mixing type CPC technology”

100: correct typo “pm”
Corrected

108 and 124: state activity of the radioactive source

Added to line 133, it is 185 MBq

127: “cheap second hand” seems rather up to interpretation : : : I could argue that even used CPCs are not “cheap” and it’s unclear how the fact that this CPC was “second hand” impacts its performance. Please consider rephrasing.
Removed as already suggested by the reviewer 1, replaced by “robust”. The fact that it is second hand does not affect the performance, but relates to that the CPC is widely used, and we show that it can be modified for small particle detection too.

137: details -> detail
Corrected

154: why was the line length made half that of the other CPCs “for the same reason”?
This was badly formulated, corrected to line 161 -> as “The tubing lengths downstream of the DMA were selected based on the inlet flow rates so that the particle penetration through the tubes can be considered equal.”

155: It is sometimes difficult to understand why the authors chose the parameter space for operating the instruments in the way they did. For example, why did the authors decide to measure just the 3777 at different dew points? Also why was the sample flow rate only changed on the B3010? Also why were both of the above two issues mentioned in the section devoted to aerosol generation? [Note: I now realize that an explanation for the dew point is provided in line 265. I suggest having such a sentence earlier in the paper so the reader better understands the experimental parameters.
This is assessed in comments to the general concerns of both reviewers

175: insert “source” after radioactive?
Corrected

184: remove “being” or replace with “currently”
Corrected

243, 261: Awkward and possibly grammatically incorrect sentences : : : please rephrase.
Edited to line 272 as “Figure 7 presents the d50 curves measured with the neutralized tungsten oxide particles for 3777 and v-WCPC.”, and line 294-> as “To obtain accurate particle concentration measurements, these differences in the d50 imply that the CPCs should be calibrated with the same aerosol composition as the real experiment is conducted.”

292: Similar to the criticism of line 155, why was concentration dependence calibration performed only for the v-WCPC? Could it not also be an important factor for the other CPCs?
Same answer as 155

342: show -> shown

Corrected

Characterization of three new condensation particle counters for sub-3 nm particle detection during Helsinki CPC workshop: ADI versatile water CPC, TSI 3777 nano enhancer and boosted TSI 3010

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Abstract

~~The scientific need to understand nanoparticle dynamics at sizes below 3 nm has pushed companies to develop commercial solutions to measure particles down to 1 nm.~~ In this study we characterized the performance of three new particle counters able to detect particles smaller than 3 nm during Helsinki CPC workshop in summer 2016: Aerosol Dynamics Inc versatile water condensation particle counter (v-WCPC, ADI, Berkeley, USA), TSI 3777 nano enhancer (TSI Inc., Shoreview, USA) and modified and boosted TSI 3010 type CPC from Clermont Ferrand University called as B3010. The performance of all CPCs was first measured with charged tungsten oxide test particles at temperature settings which resulted in supersaturation low enough to not detect any ions produced by a radioactive source. Due to similar measured detection efficiencies, additional comparison between ~~The~~ the 3777 and v-WCPC were ~~characterized~~ conducted using electrically neutral tungsten oxide test particles~~ with all charging states: negative, positive and neutral~~, and with positively charged tetradodecylammonium bromide. Furthermore, ~~The~~ the detection efficiencies of the 3777 and v-WCPC ~~particle counters~~ were measured with boosted ~~two different~~ temperature settings~~: low temperature difference settings so that the CPCs did not detect any ions from a radioactive source; and high temperature difference settings so that they~~yielding supersaturation ~~was~~ which was at the onset of homogeneous nucleation for the 3777, or confined within the range of liquid water for the ADI v-WCPC. Finally, CPC specific tests were conducted to probe the response of the 3777 to various inlet flow relative humidities, of the B3010 to various inlet flow rates, and of the v-WCPC to various particle concentrations. For the 3777 and v-WCPC ~~The~~ the measured 50% detection diameters (d50) were in the range of 1.3 – 2.4 nm for the tungsten oxide particles depending on the particle charging state and CPC temperature settings, and between 2.5 and 3.3 nm for the organic test~~-~~ aerosol, and 3.2 – 3.4 nm for tungsten oxide for the B3010~~aerosol for the 3777 and v-WCPC~~. ~~The d50s were measured for the B3010 with negatively charged tungsten oxide particles with four different inlet flow rates. The v-WCPC and 3777 were also compared side by side by measuring atmospheric aerosol, exhibiting an excellent agreement.~~

1 Introduction

The work of Stolzenburg and McMurry (1991) started a new chapter in aerosol research with their prototype laminar flow condensation particle counter (CPC) capable of detecting 3 nm aerosol particles via~~–~~ condensation of butanol vapor. Compared to the previous CPC designs, ~~The~~ the significant improvements in the instrument included minimized diffusion losses in the sampling line and a sheath flow in the condenser to focus the particle beam ~~in~~ to the maximum butanol supersaturation region in the middle of the condenser (Wilson et al., 1983). This instrument is the predecessor of the ultrafine CPC 3025A and 3776 (TSI Inc., Shoreview, USA), which currently are widely used in various fields of aerosol science to study particle dynamics at particle sizes larger than 3 nm (e.g. Weber et al., 1996; Aalto et al., 2001).

It was not possible to detect particles smaller than 3 nm with the CPC technology until 1997, when Seto et al. (1997) published their design on the particle size magnifier (PSM) used to study heterogeneous nucleation of dibutyl phthalate vapor onto small ions. Their advances were made possible by the development of a new differential mobility analyzer (DMA) combined to an electrospray source, allowing ~~the~~ the CPC testing ~~of the CPC~~ with well-characterized monomobile samples. Their CPC ~~itself~~ was based on the design of Okuyama et al. (1984), which is a mixing type CPC. It took until 2011 to commercialize the diethylene glycol (DEG) based mixing type CPC technology, when Vanhanen et al. (2011) published their version of the ~~diethylene glycol (~~DEG~~)~~ based PSM, today sold as the Airmodus A10 PSM (A11 nano condensation nuclei counter when combined to Airmodus A20 butanol CPC).

The first use of DEG as a CPC working fluid~~-~~ was reported by Iida et al. (2009), who studied sub-3 nm particle detection via heterogeneous nucleation with ~~various~~ many different working fluids theoretically and experimentally. They modified the TSI 3025A to operate with DEG and showed particle activation and growth ~~down to~~starting from 1 nm in mobility diameter. Because the grown DEG droplets ~~formed~~ are too small for direct optical detection, a traditional~~,~~ butanol based CPC ~~is~~ was used as the droplet~~a~~ detector. The idea of ~~using~~ modifying the commercial TSI instrument ~~with modifications~~ to operate with DEG has been followed by several other researchers (Jiang et al., 2011a; Jiang et al., 2011b; Kuang et al., 2012a; Kuang et al., 2012b; Wimmer et al., 2013). In 2016 TSI commercialized the~~a~~ DEG based laminar type ~~instrument~~ CPC based on the work of Iida et al. (2009). This instrument, the TSI 3777 nano enhancer (3777), is one of the three instruments characterized in this study.

Generally, laminar flow ultrafine CPCs use a sheathed condenser, which makes the CPC design more complex compared to non-sheathed CPCs. Yet recent efforts have shown comparably low~~er~~ detection limits with unsheathed laminar~~-~~ flow instruments. Particle detection with the butanol~~-~~based TSI 3010 has been shown down to 2.5 nm from the factory settings d50 (diameter at which 50% of sampled particles are detected) of 10 nm (Mertes et al., 1995; Russell et al., 1996; Wiedensohler et al., 1997). Kangasluoma et al. (2015a) showed 1 nm particle detection with the commercial unsheathed ~~condenser~~ laminar type CPCs TSI 3772 and Airmodus A20 by increasing the temperature difference between the saturator and condenser up to 40 °C. The second CPC characterized in this study is a boosted TSI 3010 (B3010), which is a modification of the commercial TSI 3010 developed at the Université Blaise Pascal. ~~in which~~In this instrument the temperature control of the saturator and condenser is decoupled to allow free selection of the temperatures, and critical orifice is replaced with a flow meter and a miniature rotary vane pump.

The disadvantage of all the previous CPCs is the slight toxicity of the working fluids butanol and DEG, and these organic liquids can introduce contaminant molecules to vapor phase. Hering et al. (2005) addressed this issue by developing a water based, laminar flow technology (Hering and Stolzenburg, 2005), which was commercialized as the TSI WCPC models 3785 (Hering et al., 2005) and 3786~~-~~ (Iida et al., 2008)~~(Iida et al, 2008)~~, and subsequently as the models 3783, 3787 and 3788. In the ~~Model~~ model 3786, and later in the ~~Model~~ model 3788 (Kupc et al., 2013), ~~small~~ 3 nm particle detection was enabled by introducing similar sheathed condenser as in the butanol based CPCs.

The ADI versatile WCPC (v-WCPC), which is the third CPC characterized in this study, advances the laminar-flow water-based CPC through a three stage design that reduces the water vapor ~~concentration~~ saturation and temperature in the growth tube after the peak supersaturation is achieved, and yet allows for continued particle growth (Hering et al., 2016). This three-stage approach facilitates higher temperature differences between the first two stages, and can produce higher peak supersaturation values than the ultrafine TSI 3786 or TSI 3788. The v-WCPC is an unsheathed instrument, operating at an aerosol flow rate of 0.3 litres per minute (lpm) and at more extreme temperatures than all of the current commercial TSI WCPCs. In contrast to the DEG-based instruments, which require a separate CPC as a detector due to the small size of the DEG droplets, the droplets formed in the growth tube of the v-WCPC are sufficiently large ~~to be detected directly~~for direct optical detection.

The aim of this study is to make intercomparison experiments for the three new particle counters. Each of the CPCs are operated with different working fluid utilizing different geometries, and first we find the d50 for tungsten oxide test particles for each CPC at temperature settings that they do not detect ions from a radioactive source. As the 3777 and v-WCPC exhibited very similar performance in terms of d50, we conduct further comparison to the two CPCs by testing their response at higher supersaturation than the factory settings, to electrically neutral particles, to organic test particles, and to urban ambient particles. Further, we conducted CPC specific experiments to probe the response of 3777 to varying sample flow relative humidity, of B3010 with various inlet flow rates and of v-WCPC to sampled particle concentration.~~characterize the performance of the v-WCPC and 3777 with two different types of test particles, to measure effect of charge to the detection efficiency and to compare the instrument responses in atmospheric sampling. The performance of the B3010 was characterized with tungsten oxide particles for different aerosol flow rates.~~

2 Experimental

2.1 Condensation Particle Counters

A flow diagram of the 3777 is presented in Figure 1. The design is largely similar to the TSI ultrafine 3776. The inlet flow rate is 2.5 lpm, of that 1.5 lpm being transport flow and 1 lpm split as the sheath flow (0.85 lpm) and aerosol flow (0.15 lpm). The sheath flow passes through a dessicant drier to remove most water vapor entering the condenser~~, possibly altering the detection efficiency of a DEG based CPC (Iida et al., 2009; Kangasluoma et al., 2013)~~. Downstream of the drier the sheath flow is saturated with DEG before entering the condenser around the aerosol flow, which is guided in the centre line of the condenser. The saturator has a meandering path in a metal block instead of a porous wick used in ultrafine butanol based CPCs. The 3777 does not have its own optics head, as the droplets formed by DEG condensation are too small for direct detection. Instead the detector is a TSI 3772 CPC, which further enlarges and then counts the droplets pre-grown by DEG in the condenser. The factory settings of the 3777 are: saturator 62 °C and condenser 12 °C (low temperature difference (dT) settings). At these settings the 3777 did not detect any ions produced by a 185 MBq radioactive ^{241}Am source. It was also operated at boosted settings so that the supersaturation was at the onset of homogeneous nucleation. With the boosted settings the saturator temperature was set to 70 °C and condenser to 7 °C (high dT settings).

Flow diagram of the ADI v-WCPC is presented in Figure 2. The v-WCPC does not require a separate CPC for droplet detection, nor does it use a sheath flow, making it a relatively simple CPC. The v-WCPC has two flows, a transport flow and an aerosol flow, both of which are controlled by critical orifices. For experiments conducted here the inlet flow rate of the v-WCPC was 2.2 lpm, of which 1.9 lpm is transport flow and 0.3 lpm aerosol flow. The aerosol flow passes upward through a three-stage growth tube consisting of a cool-walled conditioner, followed by a short, warm-walled initiator, and subsequently followed by a cool-walled moderator (Hering et al., 2014). A continuous wick spans all three growth tube sections. Liquid water is injected at a rate of 1 µL/min at the initiator, and excess drains toward the inlet and is removed with the transport flow. Peak supersaturation and particle activation occurs within the initiator, and growth continues in the moderator. The formed droplets are counted by an optics head mounted directly at the outlet of the growth tube. Further detail is presented by Hering et al. (2016). The v-WCPC was tested at two different temperature settings: conditioner at 8 °C and initiator at 90 °C (low dT settings), corresponding to supersaturation low enough to not detect any ions from ~~a~~ the 185 MBq radioactive ^{241}Am source, and boosted settings with conditioner at 1 °C and initiator at 95 °C (high dT settings), which is close to the extremes attainable without freezing or boiling. In both instances the moderator was operated at 22°C, and the optics head at 40°C. At the high dT settings both 3777 and v-WCPC are able to detect ions from the ^{241}Am source.

The B3010 is based on ~~a~~ the robust ~~cheap second hand~~ TSI 3010, from which everything except the saturator block, the condenser and the optical detector are removed. The original electronics have been ~~completely~~ replaced with custom made boards~~,~~ to handle the higher power consumption, and operate off 28 VDC, the primary power supply in aircrafts. The whole system is controlled by a credit card sized ARM computer, running a tailor-made embedded Linux operating system. It features a touchscreen, a TSI-like serial port protocol, and TTL pulse output. With these modifications the saturator heating and condenser cooling are decoupled. In addition, the critical orifice and external heavy pump are replaced by a laminar flowmeter and a miniature rotary vane pump. The user may set the temperature of the saturator, condenser and optics as well as the flow rate, independently from one another. The B3010 was operated at saturator temperature 55 °C, optics head 56 °C and condenser 11 °C. The B3010 will be described in more detail~~s~~ in a dedicated article, presently in preparation. Table 1 summarizes the instrument operation conditions.

2.2 ~~Aerosol generation~~Direct comparison of all CPCs

Two methods were used to generate the test aerosol: glowing wire generator (GWG) and electrospray source. In the GWG (Peineke et al., 2006), a thin, 0.4 mm in diameter, tungsten wire is heated resistively in a metal chamber. The wire is flushed with 5.0 N_2 flow and it has been shown that negatively charged tungsten oxide clusters are formed into the N_2 flow without additional charging (Kangasluoma et al., 2015b). Positively charged clusters contain some hydrocarbon molecules clustered with tungsten oxide, explaining why usually the measured d50 usually is larger for positively than negatively charged clusters (Kangasluoma et al., 2016b). 18 different sizes of particles between 1 and 4.5 nm were selected with the Herrmann type high resolution DMA (Kangasluoma et al., 2016a) (Figure 4), and guided to a test CPC and TSI aerosol electrometer (3068B). The tubing lengths downstream of the DMA were selected based on the inlet flow rates so that the particle penetration through the tubes can be assumed equal. The d50 for all three CPCs~~,~~ ~~at two different~~at low dT ~~temperature~~ settings ~~for the 3777 and v-WCPC and at one settings for the B3010,~~ was measured with tungsten oxide particles.

2.3 Comparison between the 3777 and the v-WCPC

The dT of the 3777 and the v-WCPC was increased to the onset of homogeneous droplet formation, and the d50 was measured similarly as described in 2.2 for tungsten oxide particles.

To measure the d50 for neutral particles, we followed the approach presented in our previous studies (Kangasluoma et al., 2015b; Kangasluoma et al., 2016b). The sample flow downstream of the DMA passes through a mixing chamber, to which a tube containing a ^{241}Am radioactive source is connected. 0.2 lpm of the sample flow is drawn through the tube, and ions from the radioactive source are drifted to the mixing chamber against the counter flow with an electric field. A fraction of the sample particles are neutralized by the opposite polarity ions drifted to the mixing chamber. An ion precipitator is placed downstream of the mixing chamber to allow sampling of only neutral particles with the CPC. The concentration detected with the CPC is normalized against the electrometer. The detection efficiency curve is further normalized with detection efficiency at the largest selected diameters where the role of charge on the detection efficiency is assumed to be negligible. This method yields uncertainties in the resulting d50 due to possibly size dependent neutralization efficiency, unknown neutralization mechanism (ion-ion recombination leading to larger physical size, or charge transfer) and chemical composition of the neutralized particles, however, it is currently the only method to measure d50 for neutral particles for sub-3 nm particles. Winkler et al. (2008) used similar method to measure nucleation probabilities of electrically charged and neutral clusters, the difference being that they used bipolar neutralizer. Neutral d50 was measured for both instruments with high and low dT by neutralizing both negatively and positively charged particles.

particles by size selecting 18 different sizes of particles between 1 and 4.5 nm with the Herrmann type high resolution DMA (Kangasluoma et al., 2016a) (Figure 4). The tubing lengths downstream of the DMA were selected to be equal for the vWCPC, 3777 and electrometer so that the particle penetration through the tubes can be considered equal. For the B3010 the line length was approximately half of the electrometer tubing for the same reason. The d50 of the 3777 was measured at four different sample flow dew points with negatively charged tungsten oxide particles. Water vapor was added to the sample flow with a humidified dilution flow downstream of the DMA. The d50 for the B3010 was measured also at four different aerosol flow rates, 0.5, 1.0, 1.4 and 1.6 lpm, by varying the rotary vane pump speed.

To test the response of the 3777 and the v-WCPC to organic test particles, tetradodecylammonium bromide (TDDABr) (Ude and Fernández de la Mora, 2005) particles were generated with an electrospray source. The electrospray source produces charged sample molecule containing droplets, which contain the sample molecules, by spraying liquid at high voltage out of a capillary needle against a grounded electrode. The charged droplets are close to the Rayleigh limit, and produce charged sample molecules and clusters to the gas flow by series of Coulomb explosions, and ion and solvent evaporation from the droplet. The highly charged droplets can be close to 2 nm in mobility diameter (Ude and Fernández de la Mora, 2005), for which we neutralized the flow exiting the electrospray with a radioactive ^{241}Am source to also be able to sample the singly charged clusters which are larger than 2 nm (Kangasluoma et al., 2016a). The electrosprayed sample in the experiments was tetradodecylammonium bromide (TDDABr) (Ude and Fernández de la Mora, 2005). d50 was measured for the 3777 and v-WCPC with for positively charged TDDABr with the low dT settings, and for the v-WCPC at the high dT settings. For the 3777 we could not measure the d50 at high dT settings due to the fact that the aerosol-to-sheath flow ratio is very sensitive to the CPC inlet pressure, and TDDABr was produced by drawing the flow out of the DMA, leading to a pressure drop of approximately 5 kPa at the CPC inlets. This pressure drop was enough to alter the aerosol-to-sheath flow ratio in the 3777 and cause homogeneous droplet formation at high dT settings.

Finally, the 3777 and v-WCPC were placed to sample atmospheric aerosol from Helsinki city area. The instruments were sampling from the same inlet for approximately 18 h to compare the measured concentrations from atmospheric aerosol. The v-WCPC data were dead-time corrected using the dead time correction factor derived from the concentration dependent response for 4.4 nm (see next chapter).

To measure the d50 for neutral particles, we followed the approach presented in our previous studies (Kangasluoma et al., 2015b; Kangasluoma et al., 2016b). The sample flow downstream of the DMA passes through a mixing chamber, to which a tube containing a ^{241}Am radioactive is connected. 0.2 lpm of the sample flow is drawn through the tube, and ions from the radioactive source are drifted to the mixing chamber against the counter flow with an electric field. A fraction of the sample particles are neutralized by the opposite polarity ions drifted to the mixing chamber. An ion precipitator is placed downstream of the mixing chamber to allow sampling of only neutral particles with the CPC. The concentration detected with the CPC is normalized against the electrometer. The detection efficiency curve is further normalized with detection efficiency of the largest selected diameters where the role of charge on the detection efficiency is assumed to be negligible. This method yields uncertainties in the resulting d50 due to possibly size dependent neutralization efficiency and chemical composition of the neutralized particles, however, it is being the only method to measure d50 for neutral particles for sub-3 nm particles. Winkler et al. (2008) Neutral d50 was measured for both instruments with high and low dT by neutralizing both negatively and positively charged particles.

2.3 4 CPC specific tests Ambient sampling setups

As previous literature has reported that water vapor in the sample flow can affect the detection efficiency a DEG based CPC (Iida et al., 2009; Kangasluoma et al., 2013), we measured the d50 of the 3777 at various sample flow dew points. Water vapor was added to the sample flow with a humidified dilution flow downstream of the DMA. ~~The tubing lengths downstream of the DMA were selected to be equal for the vWCPC, 3777 and electrometer so that the particle penetration through the tubes can be considered equal. For the B3010 the line length was approximately half of the electrometer tubing for the same reason.~~ The d50 of the 3777 was measured at four different sample flow dew points with negatively charged tungsten oxide particles.

Based on previous literature (Kangasluoma et al., 2015a), the detection efficiency of the laminar type butanol CPCs can be increased by increasing the inlet flow rate. We tested the performance of the B3010 at four different inlet flow rates. The d50 for the B3010 was measured at inlet flow rates, 0.5, 1.0, 1.4 and 1.6 lpm, by varying the rotary vane pump speed.

Water based CPCs are known to be sensitive for vapor depletion effects (Lewis and Hering, 2013). Therefore the response of the v-WCPC was measured against the TSI electrometer (model 3068B) ~~at~~ for different concentrations at sizes 1.4nm, 1.8nm, 2.4nm and 4.4 nm. The concentration at each size was controlled by adding a dilution flow of compressed and filtered air downstream of the DMA. Simultaneous data were collected for the 3777, however the dilution flow was again enough to change the aerosol-to-sheath flow ratio of the 3777 due to a small change in the inlet pressure, and therefore the 3777 data of this experiment are not presented. However, assuming that any possible undercounting at high concentration originates from particle coincidence in the optics, the concentration calibration of the 3777 should be practically the same as of the 3772 CPC when the dilution of 0.15/1 is taken into account.

~~Finally, the 3777 and v-WCPC were placed to sample atmospheric aerosol from Helsinki city area. The instruments were sampling from the same inlet for approximately 18 h to compare the measured concentrations from atmospheric aerosol. The v-WCPC data were dead-time corrected using the dead time correction factor derived from the concentration dependent response for 4.4 nm.~~

3 Results

3.1 ~~Detection efficiency~~Direct comparison of all CPCs

Figure 5 presents the d50 ~~measurements~~ curves for the B3010, 3777 and v-WCPC at low dT settings for positively and negatively charged tungsten oxide particles. The standard deviation in the detection efficiency data was in most cases < 5%, which ~~is why it is not plotted in the figures~~is why we do not plot detection efficiency error bars. X-axis uncertainty can be taken from the Herrmann DMA resolution of approximately 20, ~~which leads~~leading to relative uncertainty of ± ~~5~~2% ~~based on the selected mobility peak full width at half maximum of 5%~~, which is the square root of variance of the normal distribution fitted to the tetraheptylammonium bromide positively charged monomer peak. Therefore, uncertainties in the data arise mostly from other sources, such as possibly unequal sampling line penetration or possibly changing particle chemical composition as a function of size. At these settings none of the CPCs detect the ions generated by a bipolar ion source~~, such as is commonly used for mobility based particle size distribution measurements~~. We find that the v-WCPC exhibits slightly lower d50 than the 3777, while the d50 of the B3010 is clearly the highest. The d50 of 3.2 – 3.4 nm for the B3010, however, shows that the conventional TSI 3010 can be boosted to similar performance as the TSI ultrafine 3776, just with a shallower d50 curve due to larger particle diffusion losses, by decoupling the heating and cooling of the saturator and condenser. Respective d50 values for the B3010, v-WCPC and TSI-3777 are 3.4 nm, 1.7 nm and 1.8 nm for negatively charged tungsten oxide, and 3.2 nm, 1.9 nm and 2.0 nm for positively charged.

3.2 Comparison between the 3777 and the v-WCPC

At high dT settings the d50 curves are presented in Figure 6. For the 3777 the temperatures were selected as those that are just below the limit of homogeneous nucleation of the DEG working fluid. For the v-WCPC, the temperatures are simply the largest extremes attainable without freezing or boiling the water working fluid. Unlike the DEG instrument, the high dT operation of the v-WCPC is not near the homogeneous nucleation limit, as no evidence of homogeneous nucleation was observed even at reduced inlet pressures. At these higher dT settings, we find somewhat more efficient detection of smaller particles by the 3777 than the v-WCPC. The d50s are lowered to 1.4 nm and 1.3 nm for negatively charged, and to 1.5 nm and 1.4 nm for positively charged for the v-WCPC and 3777, respectively.

Table 2 summarizes the measured d50 for all experiments. The d50 for 3777 and v-WCPC at both settings is lower for negatively charged particles than for positively charged particles. This is observed throughout the past literature (Stolzenburg and McMurry, 1991; Winkler et al., 2008; Sipilä et al., 2009; Kuang et al., 2012b; Kangasluoma et al., 2014), and explained by hydrocarbon contaminants in the positively charged particles (Kangasluoma et al., 2016b). Based on previous literature (Kuang et al., 2012b; Kangasluoma et al., 2014) slightly lower d50 values can be expected for inorganic salt particles than the measured d50s for tungsten oxide particles in this study. TSI states in their instrument brochure a d50 of 1.4 nm for negatively charged NaCl particles at factory settings (low dT in this study), which is well in line with this study. Similarly, the d50 values reported here for the v-WCPC are close to those observed by Hering et al. (2016) who measured d50 of 1.6 nm and 1.9 nm for high dT and low dT operation, respectively, for particles from a heated NiCr wire.

Figure 7 presents the d50 curves ~~for~~ measured with the neutralized tungsten oxide particles for 3777 and v-WCPC. The data is normalized so that the mean detection efficiency ~~of~~ at 3 largest diameters is 90% based on the assumption that at those sizes the particle charge does not affect the detection efficiency anymore. Also is assumed, through the normalization that the neutralization efficiency does not change as a function of the particle size. Further uncertainties arise from the unknown processes that take place during neutralization. Due to these uncertainties, the curves are not as smooth as for the charged particles. However, an estimate for the neutral d50 will be obtained from these experiments, which are 1.6 nm and 1.5 nm for v-WCPC and 3777 at high dT, and 2.0 nm and 1.9 nm at low dT settings, respectively, for neutralized negatively charged tungsten oxide. For neutralized positively charged particles the respective values are 2.2 nm and 2.1 nm at high dT settings and 2.4 nm and 2.3 nm at low dT settings (Figure ~~9~~8). The difference in the d50s between the negatively and positively charged particles after neutralization are possibly mostly explained by their differences in the chemical composition. Positively charged particles contain more contaminant species than the negatively charged particles, which is still observed in the d50 when they both are neutralized. For more details, refer to Kangasluoma et al. (2016b). The neutral d50s are greater than for charged d50 values by approximately 0.1-0.5 nm at low dT settings, similar to the values ~~that~~ obtained in Kangasluoma et al. (2016b) for water-tungsten oxide and DEG-tungsten oxide system.

The d50 curves for positively charged TDDABr for the 3777 and v-WCPC are presented in Figure 9. For both instruments the d50 values are higher than for tungsten oxide particles, but this is most pronounced for the v-WCPC. At the low dT settings d50 values are 3.3 nm and 2.5 nm at for the v-WCPC and 3777 respectively, and 2.8 nm for the v-WCPC at high dT. At the high dT and the reduced inlet pressure for these TDDABr tests, the 3777 produced homogeneously nucleated particles, and hence its high dT d50 value could not be measured. To obtain accurate particle concentration measurements, ~~These~~ these differences in the d50 imply that the CPCs should be calibrated with the same aerosol composition as ~~with~~ the real experiment is conducted.

A fraction of the data measured from atmospheric aerosol is presented in Figure 10. The measurement location is above a bus stop, which several busses pass daily through. The bus stop times are marked to the figure. The background aerosol concentration during that morning was around 3 000 – 10 000 cm^{-3}. Clear spikes up to 200 000 cm^{-3} in the measured concentrations are observed throughout the morning. The number concentration is generally high during traffic hours, and both CPCs reacts instantaneously to the occasional spikes in the number concentration. From the data of

Figure 10, a correlation plot between the v-WCPC and 3777 is presented in Figure 11 for concentrations below 50 000 cm^{-3}. With R^2 of 0.99 the two CPCs show remarkably good agreement with slope of 1.02 and offset of 340 up to concentrations of 50 000 cm^{-3}.

3.2 ~~Effect of sample dew point for the 3777~~CPC specific tests

Because water ~~contamination~~ vapor ~~was~~ has been observed ~~as a source of error~~ to alter the d50 in the original laminar ~~-~~flow DEG instruments, this question was examined for the 3777. The response of the 3777 for negatively charged tungsten oxide particles as a function of sample flow dew point is presented in Figure 1~~2~~0. The observed variation with dew points ranging from completely dry gas to 20 °C in the d50 is only approximately 0.1 nm. The apparently increased plateau value for the highest dew point can be due to slightly higher inlet pressure, increasing the aerosol flow of the instrument. The variation in the d50 due to changing dew point is less than compared to for example 0.3 nm reported in Kangasluoma et al. (2013) for the Airmodus A09 PSM. This is due to the smaller amount of sample flow water vapor reaching the condenser in the 3777, since 85% of the condenser flow is dried, as compared to 0% of the condenser flow of the PSM of that time~~. At that time the PSM used internal pumps, today they are replaced by mass flow controllers which are usually fed by dry compressed air, resulting to dried condenser flow fraction from 4% to 34% depending on the instrument operation.~~.

~~3.3 Effect of flow rate on the B3010~~

Results from the inlet flow rate experiment for the B3010 is presented in Figure 1~~3~~1. The d50 curve at aerosol flow rates of ~~0.5~~, 1, 1.4 and 1.6 lpm are rather similar within the experimental uncertainties, while at flow rate of 0.5 the detection efficiency clearly deviates to lower values at particle diameters larger than 3 nm. This can be possibly due to larger final droplet diameters and subsequent gravitational losses at the low flow rate. Similar increase in the detection efficiency with higher flow rate as in Kangasluoma et al. (2015a) was not observed, which can be due to the differences in the saturator designs between the 3010 and 3772: 3010 has a single hole reservoir type saturator while 3772 has 8 hole multitube saturator which possibly saturates the sample flow better than the one hole saturator at higher flow rates.

~~3.4 Concentration calibration~~

As with all CPCs, the peak supersaturation, and hence the lowest detectable particle size ~~is~~ can be affected by the presence of other particles in the flow~~,~~ due to a combination of condensational heat release and vapor depletion. These effects for the original WCPCs were explored by Lewis and Hering (2013), and is evaluated here for the v-WCPC. Figure 1~~4~~2 shows the concentration dependent response at four particle sizes for the v-WCPC. The maximum concentration at each size was determined by the maximum concentration we were able to pass through the DMA. The data are corrected for dead time, as described by Hering et al. (2005), and as is standard for most of the commercial CPCs. This approach uses the instrument dead time multiplied by a dead time correction factor, which accounts for the increase in effective dead time due to overlapping tails in pulses below the threshold. For this data set the dead time correction factor was set to 1.23 to yield a linear response to concentration at 4.4 nm. Then this same dead time correction factor was applied to measurements at other sizes. The curves of the three smallest particle sizes have a negative slope due to the reduction in supersaturation at high concentrations caused by condensational heating (Lewis and Hering, 2013). However, the effect is relatively small, with the detection efficiency at 1.8 nm dropping from 36% at a concentration of 3000cm^{-3} to 33% at a concentration of 90000cm^{-3}.

~~3.5 Atmospheric sampling~~

~~A fraction of the data measured from atmospheric aerosol is presented in Figure 13. The measurement location is above a bus stop, which several busses pass daily through. The bus stop times are marked to the figure. The background aerosol concentration during that morning was around 3 000 – 10 000 cm^{-3}. Clear spikes up to 200 000 cm^{-3} in the measured concentrations are observed throughout the morning, of which timing match quite well the scheduled bus departure times. From the data of Figure 13, a correlation plot between the v-WCPC and 3777 is presented in Figure 14 for concentrations below 50 000 cm^{-3}. With R^2 of 0.99 the two CPCs show remarkably good agreement with slope of 1.02 and offset of 340 up to concentrations of 50 000 cm^{-3}.~~

4 Conclusions

Three new sub-3 nm CPCs, boosted 3010 type CPC, ADI versatile water CPC and the TSI 3777 nano enhancer were characterized for the d50 diameter. The boosted 3010 type CPC was shown to be able to detect tungsten oxide particles smaller than 3 nm. The v-WCPC and 3777 were characterized with similar test aerosols with two different settings: low dT settings set so that the CPCs did not detect any ions from a radioactive charger, and high dT settings set either so that the supersaturation was at the onset of homogeneous droplet formation (3777) or set to the largest value that avoids freezing or boiling (v-WCPC). The d50 diameters for tungsten oxide were found to range from 1.7 nm to 2.4 nm at low dT and from 1.4 nm to 2.2 nm at high dT for the v-WCPC. For the 3777 the d50 ranged from 1.8 nm to 2.3 nm at low dT and from 1.3 nm to 2.1 nm at high dT. Both CPCs were observed to detect charged tungsten oxide particles better than neutral ones. The organic salt particles (TDDABr) were detected less efficiently, with low dT d50 diameters of 3.3 nm for the v-WCPC, and 2.5 nm for the TSI-3777. When measuring the same atmospheric aerosol the two CPCs showed a very good agreement with regression slope of 1.02 and R^2 of 0.99.

From the results we can make the following conclusions: The TSI 3010 hardware can be tuned to accomplish 3 nm particle detection by increasing the dT but not by increasing the inlet flow rate, which is in line with Buzorius (2001). This is possibly due to ~~not~~ imperfect flow saturation in the reservoir type saturator as opposed to the multihole saturator of TSI 3772 and planar type saturator of Airmodus A20 (Kangasluoma et al., 2015a). Due to the variations in the d50 with test particle composition for the v-WCPC and 3777, ~~their use as a detector downstream of a DMA is suggested only if the particle composition is known and~~a careful CPC calibration ~~is made accordingly~~should be conducted with the same particle composition as of the sampled particles~~,~~. ~~or with sizes above the highest d50 (approximately 2.5 – 3 nm) i~~If the ~~particle~~ composition of the sampled particles is completely unknown, the obtained particle concentrations at the size range of the d50 can have significant uncertainties. The effect of particle charge on the d50 was shown to be up to approximately 0.5 nm, which has implications on to system characterizations where the fraction of charged particles can be expected to be high (Wang et al., 2017), or CPC calibration is conducted with charged particles and sampled particles are neutral, and high precision d50 is required.

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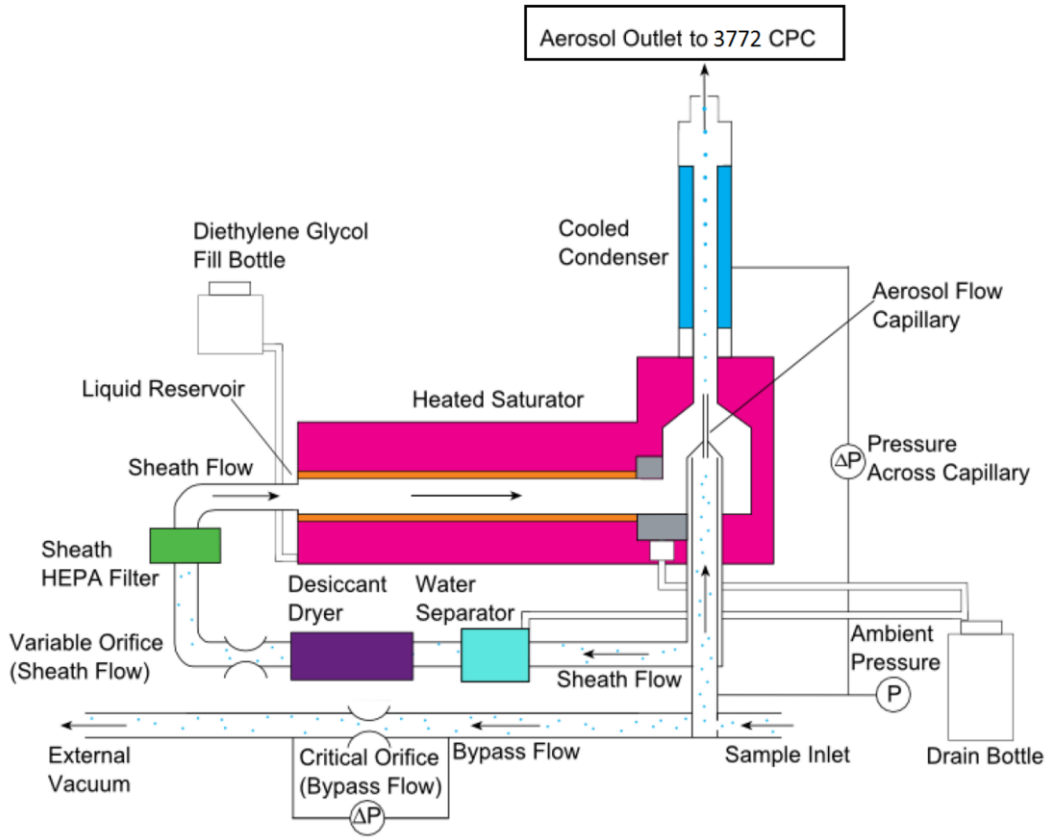

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590 Figure 1. TSI 3777 nano enhancer (courtesy of TSI Inc.)
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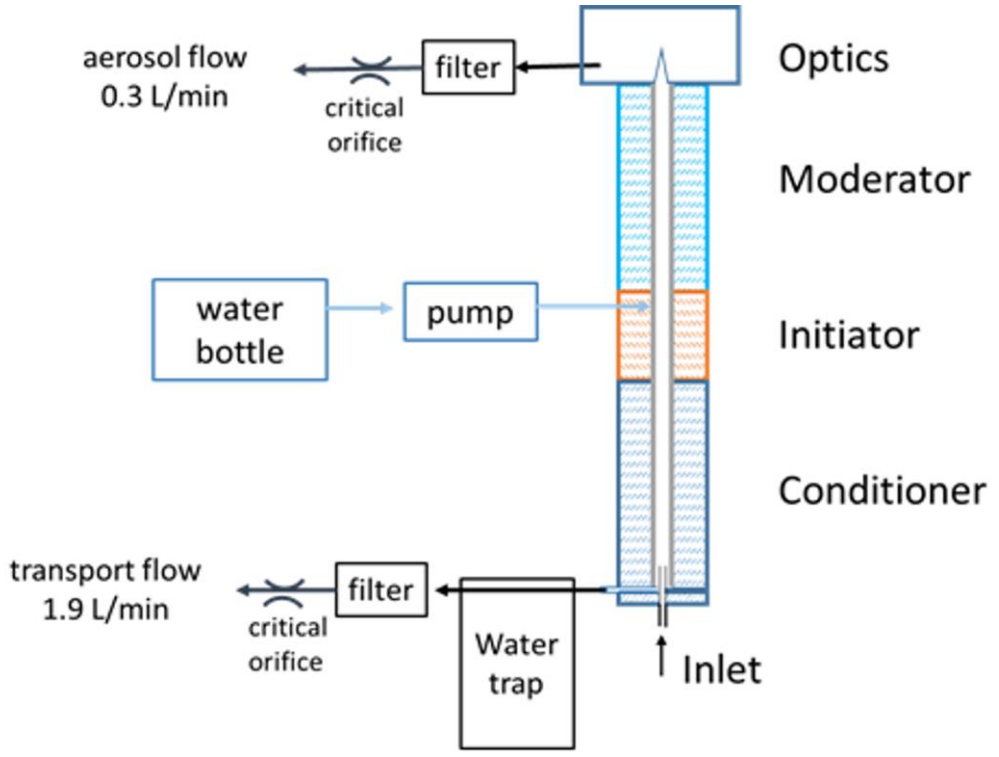

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593 Figure 2. ADI v-WCPC
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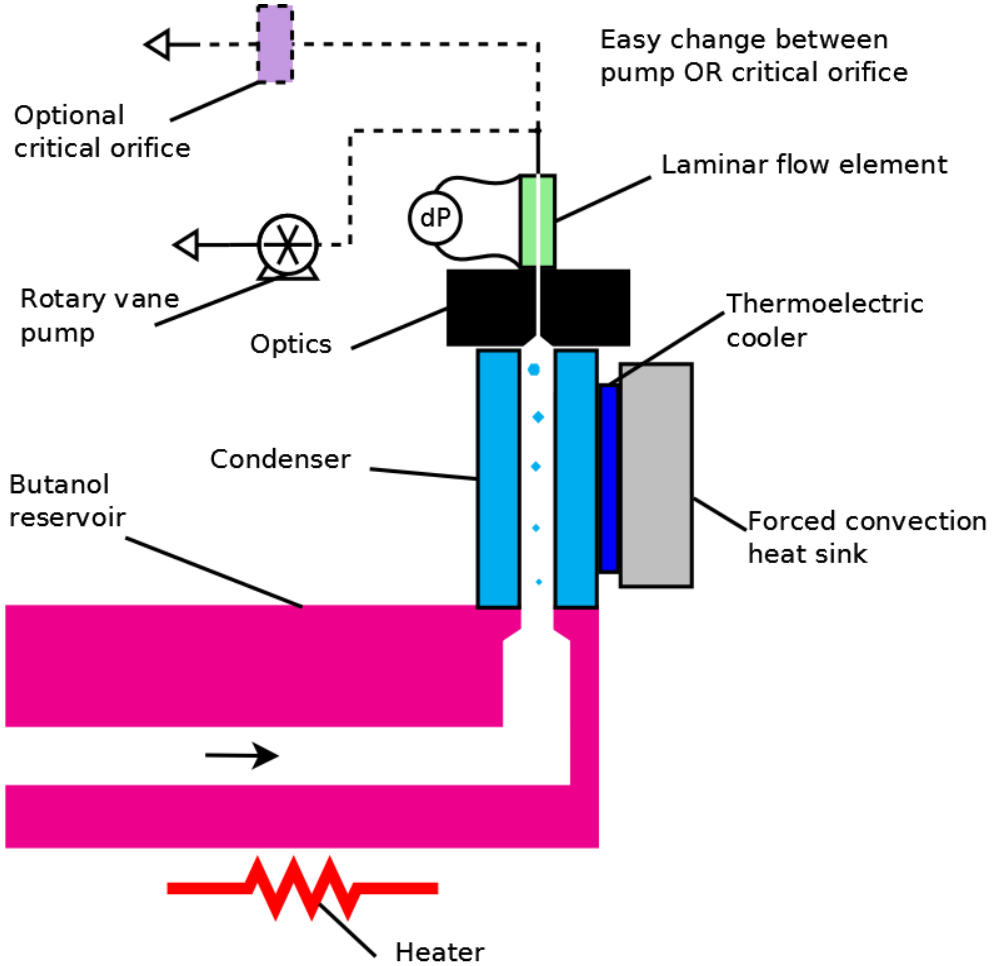

Figure 3. B3010.

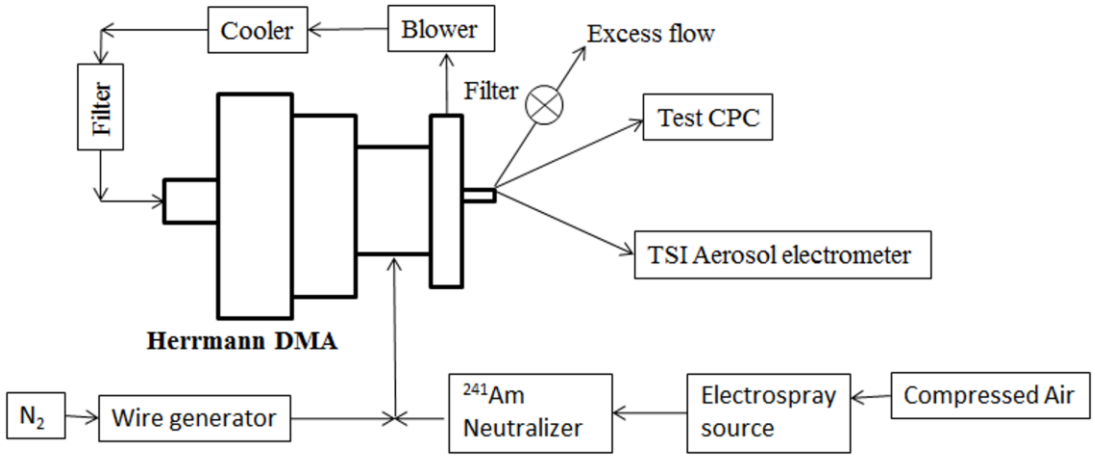

Figure 4. Experimental setup to measure d50 for charged particles

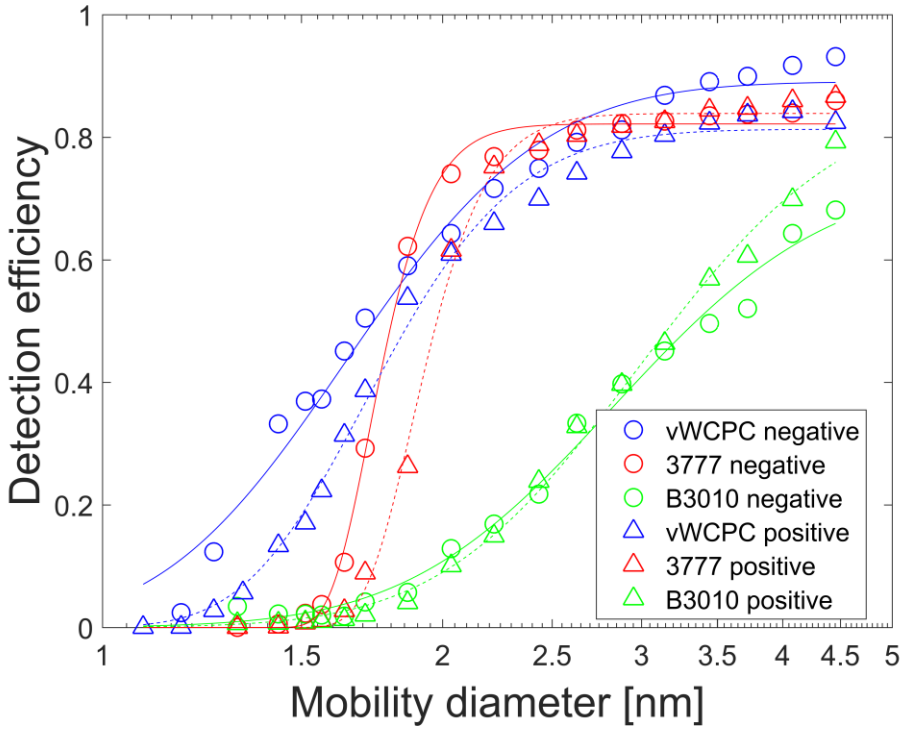

Figure 5. Detection efficiency of the CPCs as a function of size for negatively and positively charged tungsten oxide particles at low dT settings.

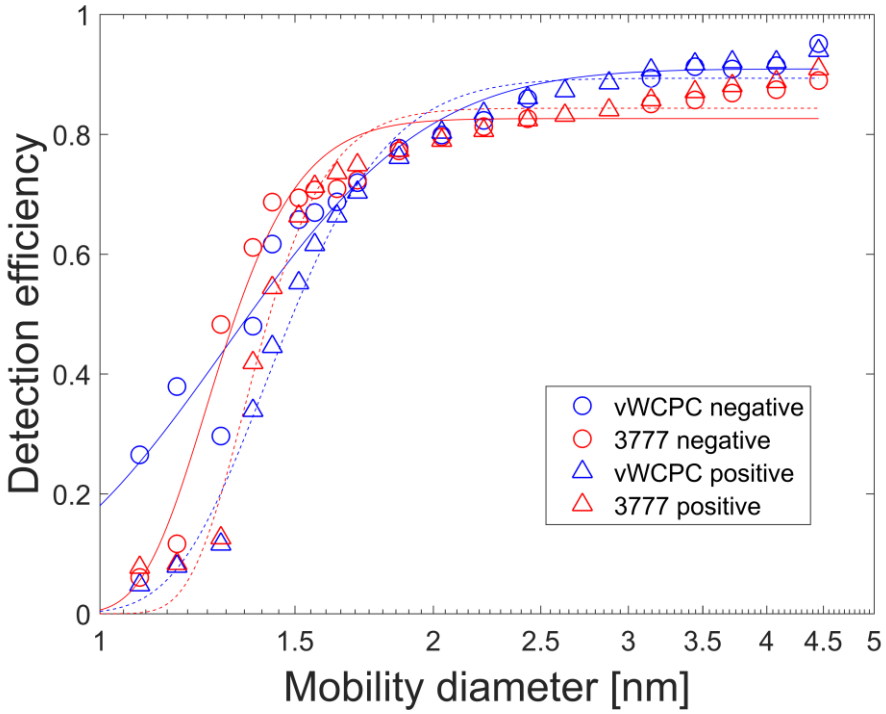

Figure 6. Detection efficiency of the CPCs as a function of size for positively and negatively charged tungsten oxide particles at high dT settings.

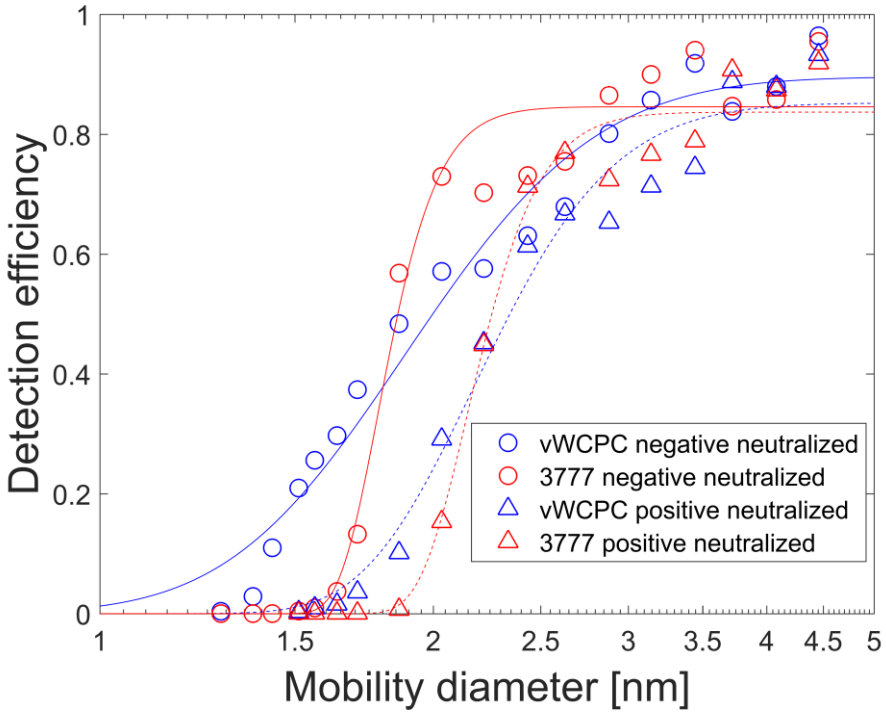

Figure 7. Detection efficiency of the CPCs as a function of size for negatively and positively charged tungsten oxide particles that are neutralized at low dT settings.

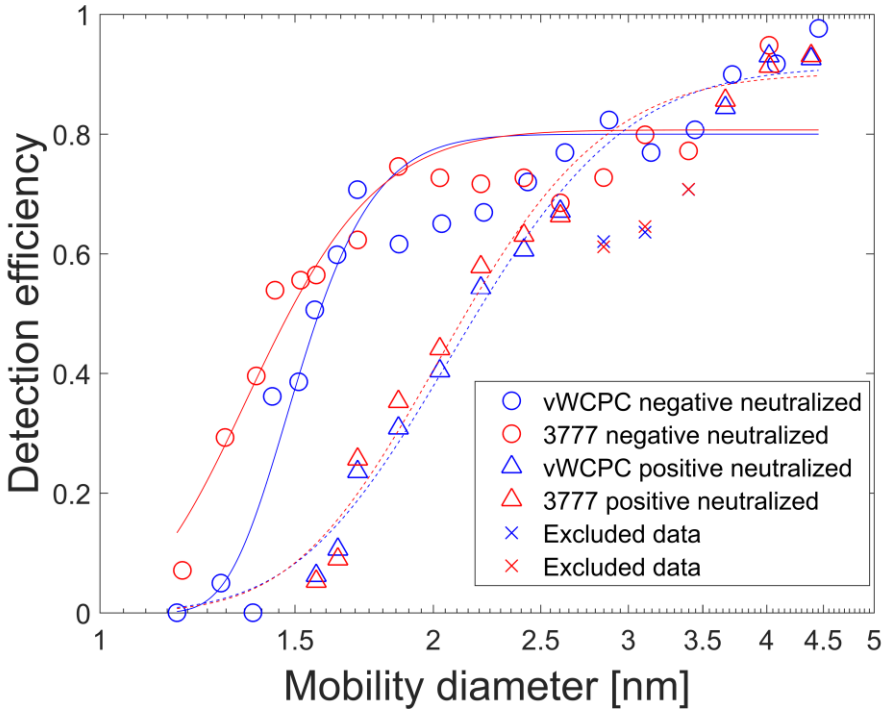

Figure 8. Detection efficiency of the CPCs as a function of size for negatively and positively charged tungsten oxide particles that are neutralized at high dT settings.

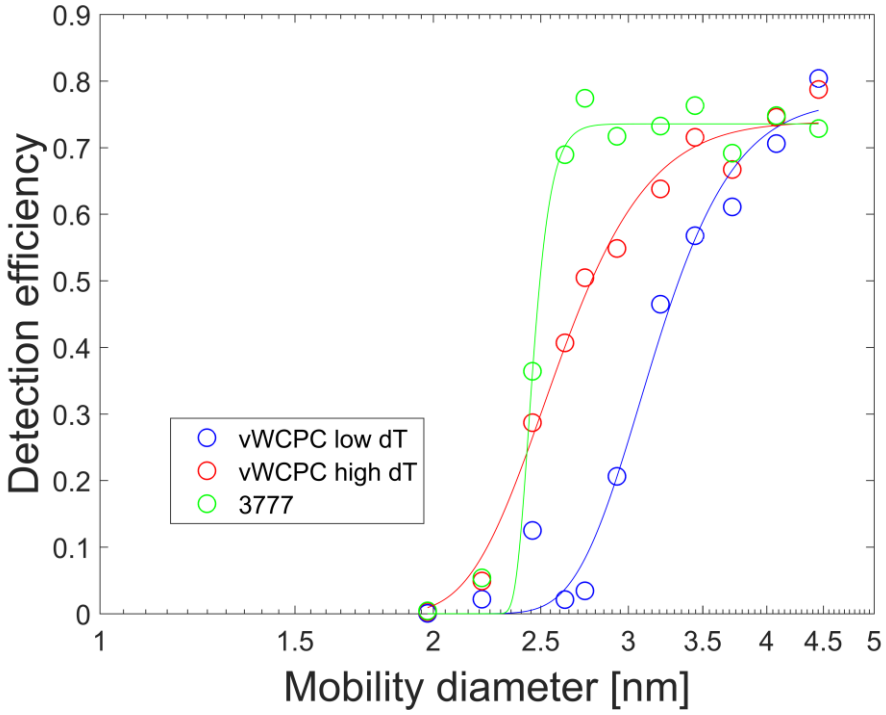

Figure 9. Detection efficiency of the CPCs as a function of size for positively charged TDDABr particles at low and high dT settings for v-WCPC and at low dT settings for the 3777.

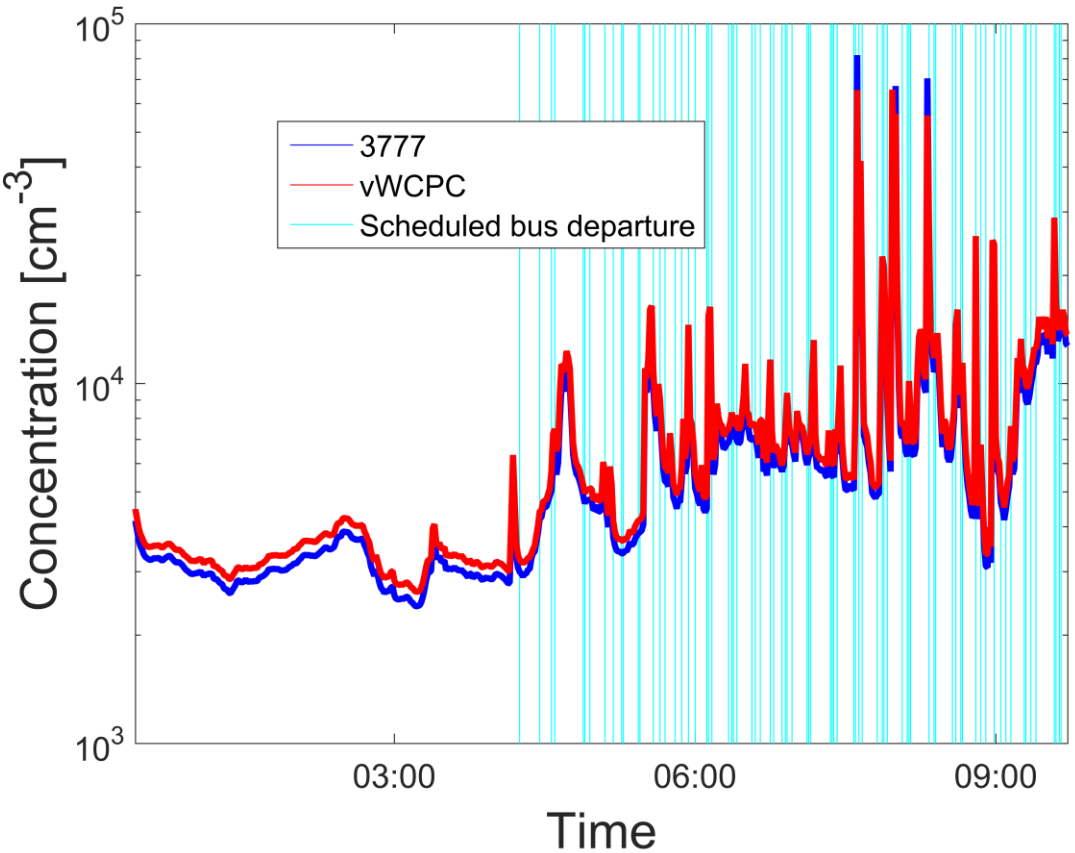

Figure 103. Concentration measured by the 3777 and v-WCPC from urban atmospheric air.

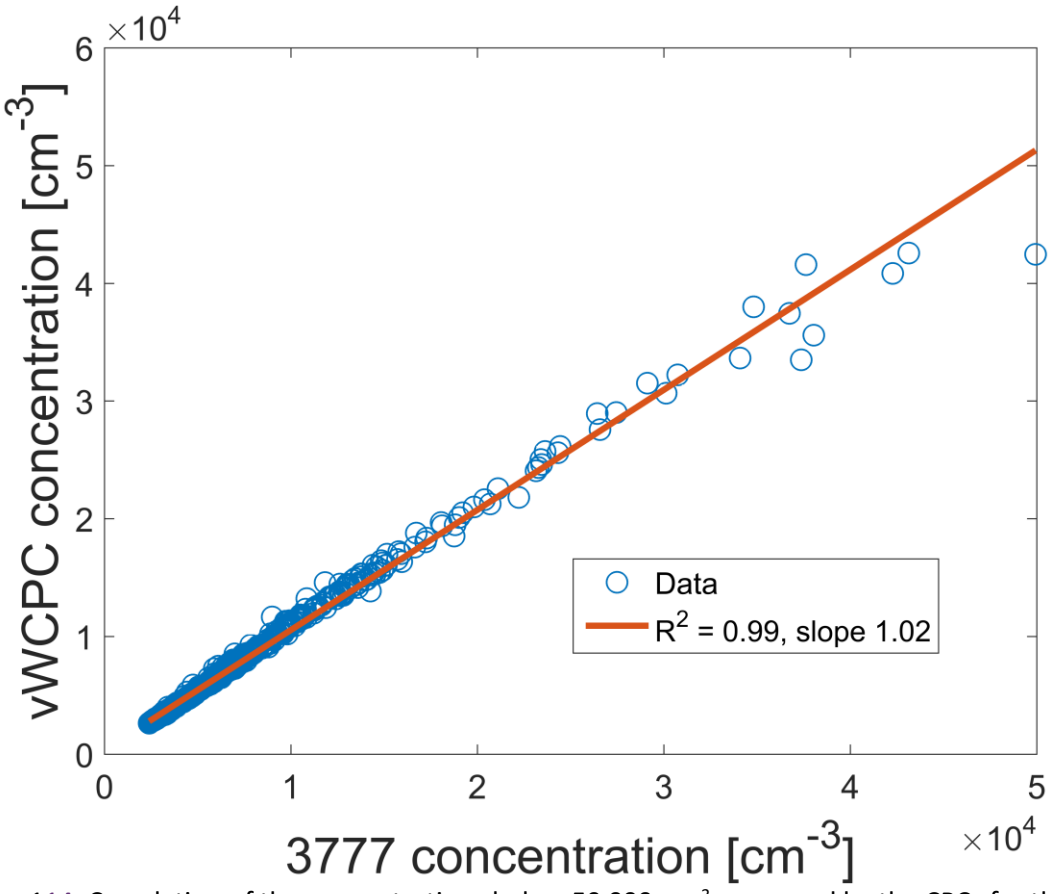

Figure 1~~3~~14. Correlation of the concentrations below 50 000 cm^{-3} measured by the CPCs for the same data as in Figure ~~13~~10.

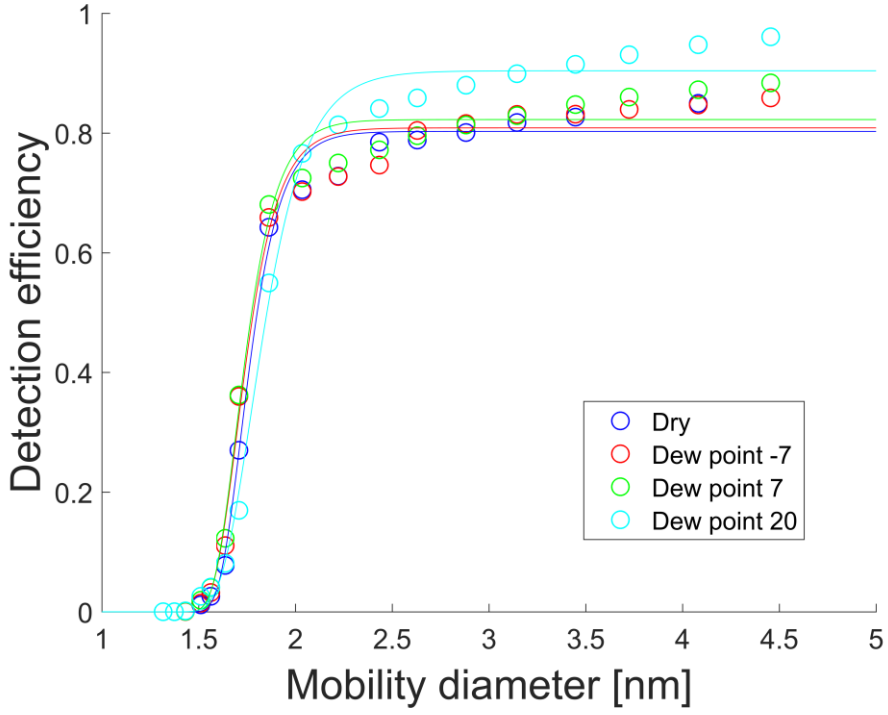

Figure 1~~2~~0. Detection efficiency of the 3777 as a function of the diameter and sample flow relative humidity.

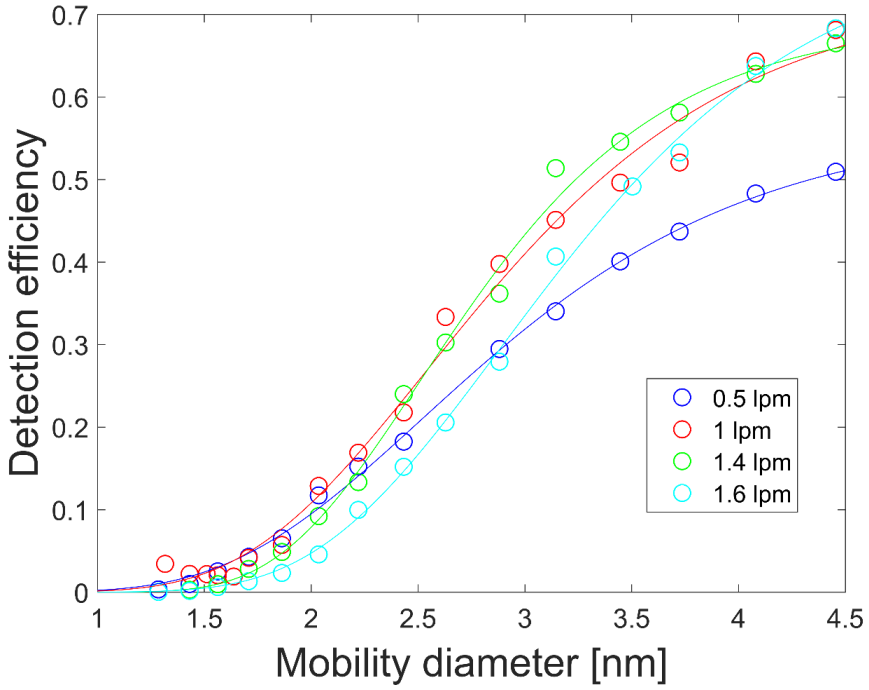

Figure 1~~3~~1. Detection efficiency of the B3010 as a function of the inlet flow rate.

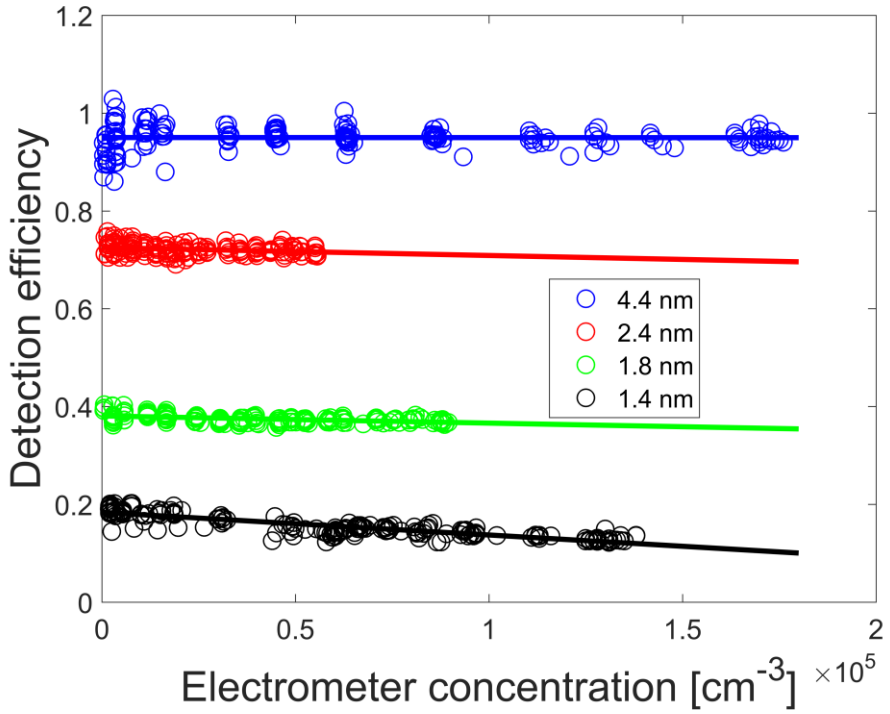

Figure 1~~4~~2. Ratio of the v-WCPC to the electrometer as function of the particle concentration.

Table 1. Instrument operation conditions

Instrument	Qinlet [lpm]	Qaerosol [lpm]	Settings	Ts [oC]	Tc [oC]	Tm [oC]	To [oC]
B3010	1	1	Low dT	55	10		56

v-WCPC	2.2	0.3	Low dT	8	90	22	40
v-WCPC	2.2	0.3	High dT	1	95	22	40
3777	2.5	0.15	Low dT	62	12		
3777	2.5	0.15	High dT	70	7		

Table 2. Indicated Cutpoints

Conditions	Aerosol	Charging state	ADI v-WCPC	TSI-3777	B3010
High dT	WOx	negative	1.4	1.3	NA
High dT	WOx	positive	1.5	1.4	NA
High dT	WOx	neutral from -	1.6	1.5	NA
High dT	WOx	neutral from +	2.2	2.1	NA
Low dT	WOx	negative	1.7	1.8	3.4
Low dT	WOx	positive	1.9	2	3.2
Low dT	WOx	neutral from -	2	1.9	NA
Low dT	WOx	neutral from +	2.4	2.3	NA
High dT	TDDAB	positive	2.8	NA	NA
Low dT	TDDAB	positive	3.3	2.5	NA