Intercomparison of a Personal CPC and Different Conventional CPCs

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ABSTRACT

We here report on a study that examines the performance of a water based personal condensation particle counter (CPC) PUFP C100 (Enmont, LLC) when sampling a variety of different test aerosols. Three additional CPCs were included in the study, namely, the general purpose water based CPC model 3787 (TSI) as well as the more than 20 year old CPC model 3022 (TSI) and ultrafine CPC model 3025A (TSI), both based on butanol. The responses of these CPCs were compared to a reference ultrafine CPC model 3776 (TSI). Test aerosols included hydrophilic NaCl, moderately hydrophobic carbon and highly hydrophobic DEHS aerosols of various sizes and concentrations. The CPC PUFP C100 measured according to its specifications with high precision and accuracy as long as the particles were not highly hydrophobic, but failed to adequately measure the concentrations of highly hydrophobic DEHS aerosols. Its detection efficiency for very small particles, e.g., 5.4 nm, was decreased, which was expected based on its particle size detection limit. The TSI water CPC model 3787 showed a similar behavior for all aerosols, except that this CPC was able to accurately measure the concentration of 5.4 nm NaCl particles. The concentrations measured with the two old and unserviced butanol CPCs were highly correlated with the concentrations delivered by the reference CPC. Nevertheless, the concentrations measured with both old CPCs were clearly below the reference concentrations.

Keywords: CPC; Personal monitor; Hydrophobic; Hydrophilic.

INTRODUCTION

Condensation particle counters (CPCs) are commonly used to measure the number concentration of airborne submicron particles with sizes down to a few nanometers. They are employed in a multitude of applications, including ambient air quality monitoring, workplace exposure measurements, laboratory testing of e.g., the filtration efficiency or as a particle counter downstream of a differential mobility analyzer (DMA) in a scanning mobility particle sizer (SMPS; Wang and Flagan, 1990). In a CPC, the incoming particles are exposed to a supersaturated vapor atmosphere. The vapor condenses onto the particles' surfaces to make them grow to optically detectable sizes. Different working fluids are used. Butanol is the most commonly used fluid (McMurry, 2000), because it can be easily evaporated and condenses onto particle surfaces almost independent of the particle composition. More recently, water based CPCs have also entered the market (Hering *et al.*, 2005), which have the great advantage over butanol based CPCs that they do not

release intense odors or hazardous gases. However, the counting efficiency of water based CPCs depends on the particle hydrophobicity (Keller *et al.*, 2013). Other, especially battery operated CPCs use isopropyl alcohol (IPA), because IPA requires less energy to be evaporated, but has the disadvantage that it can absorb water from the atmosphere. The CPC measurement principle dates back to the late 19th century (Aitken, 1892; McMurry, 2000), but has been refined over the decades. Modern instruments can be grouped into regular CPCs with lower size detection limits between 5 nm and 20 nm and ultrafine CPCs with detection limits between 2.5 and 5 nm (Stolzenburg and McMurry, 1991; Kesten *et al.*, 1991). Most recent CPCs are even able to detect particles down to 1 nm, by using diethylene glycol (Wimmer *et al.*, 2013) as working fluid and/or a size magnifier technique (Iida *et al.*, 2009; Vanhanen *et al.*, 2011; Kangasluoma *et al.*, 2016). The lower size detection limits are defined as the diameters d_{50}, where the CPC detection efficiency reaches 50%. Besides the d_{50}, the steepness of the detection curve is another quality criterion for a CPC.

In principle, CPCs can have two detection modes. All CPCs use the single particle count mode for lower concentrations. In this mode, the light scattering events of single droplets, formed upon condensation of the vapor onto the particle surfaces, are counted. When the concentration

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increases, the likelihood of the presence of more than a single droplet in the measurement volume increases. In that case, the multiple particles simultaneously scatter light, which cannot be differentiated, resulting in an undercounting of the particles, known as coincidence error. When this occurs, some CPCs switch to a photometric mode. In the photometric mode, the number of particles is determined from a measurement of the total intensity of the scattered light, based on the assumption that all droplets have the same size and refractive index.

Most available CPCs are rather bulky and mains operated and therefore only useable as static devices. Human exposure to airborne particles, however, should be measured in the breathing zone of an individual, requiring battery operated, personal measurement instruments. Although a few battery operated handheld CPCs like the TSI model 3007 or the Kanomax model 3800 have existed already for several years, none of them can be considered as a personal monitor. These handheld CPCs always have to be maintained in a horizontal orientation to avoid spillage of the working fluid (IPA) and hence require permanent attention. The only personal monitors able to determine the exposure to submicron particles in terms of their number concentrations have so far been the DiSCmini (testo AG, Titisee-Neustadt, Germany, Fierz *et al.*, 2011) and the NanoTracer (oxility BV, Eindhoven, the Netherlands, Marra *et al.*, 2010). Both instruments use an indirect measurement principle, based on unipolar diffusion charging and subsequent measurement of the particle induced current. These instruments require assumptions regarding the number size distribution of the aerosol, resulting in a lower accuracy of the instruments compared with CPCs (Asbach *et al.*, 2012; Kaminski *et al.*, 2013; Meier *et al.*, 2013). Only very recently, the first personal CPC has been introduced. The PUFP C100 (Enmont, New Richmond, OH, USA; Ryan *et al.*, 2015) is a battery operated water CPC that is small enough to be carried on a belt and sample from the breathing zone through flexible tubes.

The aim of the present study was to compare the response of the Enmont PUFP C100 and a new TSI water based CPC model 3787 with a reference butanol-based ultrafine particle counter (TSI model 3776) for well defined test aerosols. In addition two old butanol CPCs (TSI model 3022 and model 3025A) were included in the study. Both are more than twenty years old and were very successful instruments that are still commonly found in many laboratories around the globe. A few years ago, the manufacturer stopped servicing these instruments, so another aim here was to study whether these old and unserviced CPCs are still able to deliver

trustworthy results.

METHODS

Instruments Tested

Five different CPCs were tested as summarized in Table 1. One is a battery powered personal monitor, four of the CPCs are static and mains powered instruments. The Enmont personal ultrafine particle counter PUFP C100 is the smallest among the CPCs included in this study. With a size of 19 cm × 11 cm × 7 cm it is small enough to be carried on a belt and be used as a personal monitor. The PUFP C100 is a water based CPC that can be operated independent of its orientation and is therefore suitable for personal exposure measurements. The water reservoir and the battery lifetime allow for 6–8 hours of continuous measurements. The lower size limit is 4.5 nm and the maximum concentration 200,000 cm^{-3}. The PUFP C100 has an in-built GPS receiver that allows for tracking the position of the monitored person and linking the measured concentration to the measurement location. It should be noted that the PUFP C100 was a loan unit, supplied by the manufacturer. This unit had been shipped to various locations around the globe for several months without recalibration or servicing. The TSI model 3787 is the latest generation water based condensation particle counter with a lower size limit of 5 nm and a concentration limit of 250,000 cm^{-3}. The CPC 3787 has no photometric mode.

The TSI models 3022 and 3025A have both been discontinued by the manufacturer more than ten years ago. The model 3022 has a specified lower size limit of 7 nm and is the only instrument used here that also offers a photometric mode for the measurement of high concentrations between 10,000 cm^{-3} and 10^7 cm^{-3}. Concentrations below 10,000 cm^{-3} are measured in the single particle count mode. The CPC 3025A is an ultrafine condensation particle counter that can detect particles down to 3 nm (Kesten *et al.*, 1991) with concentrations up to 100,000 cm^{-3}. Unlike the other instruments, the CPC 3025A will not display the measurement result above its specified concentration limit. Instead a concentration of 9.99×10^4 cm^{-3} is reported back by the instrument.

The TSI model 3776 is an ultrafine condensation particle counter that uses butanol as working liquid. The lower size limit is 2.5 nm and the concentration limit 300,000 cm^{-3}. Above this concentration, the instrument still displays the measured concentration, which is, however, biased because of the coincidence error. The instrument has no photometric

Table 1. Overview of condensation particle counters used in the study.

Manufacturer	Model	Mobility	Working liquid	d_{50} (nm)	Max. concentration (cm^{-3})	Accuracy[1]
Enmont	PUFP C100	Personal	Water	4.5	2×10^5	± 10%
TSI	3787	Static	Water	5	2.5×10^5	± 10%
TSI	3022	Static	Butanol	7	1×10^4 (single)	± 10%
					1×10^7 (photom.)	± 20%
TSI	3025A	Static	Butanol	3	1×10^5	± 10%
TSI	3776	Static	Butanol	2.5	3×10^5	± 10%

[1] Accuracy for concentrations below max. concentration, as specified by manufacturer.

mode. As previous studies have shown (Mordas *et al.*, 2008; Kupc *et al.*, 2013), the UCPC 3776 is a very robust and precise instrument, with particle chemical composition having minor influence on the counting efficiency of the instrument. The calibration of the UCPC 3776 has been checked and verified prior to the measurements. Therefore, the concentrations reported by the CPC 3776 were used as a reference here. All UCPCs in the test are specified by the manufacturer to have an accuracy of ± 10%, except for the photometric mode of the CPC 3022 which is specified to be ± 20% accurate. Prior to commencement of the measurements, all CPCs were completely drained and dried and refilled with fresh working fluid.

Two different set ups were employed in the study. Test set up 1 was used to compare the CPCs with test aerosols with different compositions and different concentrations with polydisperse particle number size distributions within the size range of all CPCs. The reasoning to use this set up was to produce particles with different levels of hydrophobicity. Test set up 2 was used to produce polydisperse NaCl aerosols with size distributions which are at least in part outside the specified size ranges of the CPCs.

Test Set up 1

Test set up 1 is located in the Nano Test Center of the Institute for the Research on Hazardous Substances (IGF). Different aerosol generators can be connected to an approximately 20 m long wind tunnel with a diameter of 0.7 m. In the wind tunnel, the generated aerosol is homogenously mixed with a defined amount of clean dilution air. The wind tunnel feeds into a 23 m³ chamber, where the aerosol is spatially homogenously distributed, which has been demonstrated in the past (Asbach *et al.*, 2012). The particle number concentration inside the chamber can be adjusted by changing the dilution flow rate in the wind tunnel. In the present study, dilution flow rates between 750 m³ h⁻¹ and 3,000 m³ h⁻¹ were used. Prior to introduction into the wind tunnel all test aerosols were neutralized with a ⁸⁵Kr neutralizer (TSI model 3054A with an initial activity of 740 MBq). The size distributions of the test aerosols were monitored with a scanning mobility particle sizer (SMPS TSI model 3936 equipped with long DMA and CPC model 3772). The tested instruments were placed inside the chamber. Due to the spatial homogeneity of the aerosol all tested CPCs sampled identical aerosols. The flow rates of all CPCs were checked with a mass flow meter (TSI model 4140) prior to each experimental run. This set up has been intensively used for similar intercomparison measurements (Dahmann *et al.*, 2001; Asbach *et al.*, 2009, 2012; Kaminski *et al.*, 2013, Todea *et al.*, 2017). A detailed description of

the test facility can be found in Kaminski *et al.* (2013). In the present study, five different test aerosols were used as summarized in Table 2. The normalized number size distributions are shown in Fig. 1. Errors bars indicate the standard deviation during a measurement duration of at least 30 minutes. Two different NaCl test aerosols were produced by dispersing an aqueous NaCl solution with a home-built atomizer, followed by a home-built silica gel dryer and the neutralizer. NaCl was chosen as a particle material as it is known to be hygroscopic and should hence be well detectable with all, especially with water based CPCs. NaCl aerosols with modal diameters of approximately 35 nm and 92 nm were produced by dispersing aqueous NaCl solutions of 1 g L⁻¹ and 50 g L⁻¹, respectively.

Carbon aerosol was chosen as a representative for hydrophobic, soot-like particles and produced with a spark generator (Palas GFG digital 3000). The generator was set to a current of 14.4 mA, an argon and air flow rate of 5 L min⁻¹ each to produce an aerosol with a modal diameter of 82 nm.

Di-Ethyl-Hexyl-Sebacate (DEHS, $C_{26}H_{50}O_4$, obtained from Topas GmbH) aerosols were produced with an atomizer by dispersing either pure or with isopropyl alcohol (IPA) diluted DEHS. The material was chosen as a representative for highly hydrophobic droplets. Pure DEHS was used to produce a size distribution with a modal diameter of 233 nm, whereas a 1:25 DEHS:IPA solution was dispersed to produce a size distribution with 111 nm modal diameter. DEHS was chosen, because its strong hydrophobicity may hinder the condensation and hence the particle growth particularly in water based CPCs.

Test Set up 2

Test set up 2 was used to produce aerosols consisting of very small particles with size distributions that are at least in part below the nominal detection limits of the CPCs. The test aerosols were produced with a flame nanoparticle generator FG2 (MoTec Konzepte, Bochum, Germany; Monsé *et al.*, 2014). Inside the FG2, an aqueous sodium chloride solution is dispersed into a hydrogen-oxygen flame, where both the water and the sodium chloride evaporate. Upon cooling downstream of the flame, the NaCl vapor supersaturates and nucleates to form small particles. The freshly produced aerosol was fed directly into a filter test rig according to DIN-EN779:2012 with adjustable flow rate up to > 5,000 m³ h⁻¹. The almost instantaneous strong dilution in the test rig stopped the growth of the particles and minimized coagulation to keep the particles small. The modal diameter of the number size distributions of the NaCl test aerosols could be adjusted by the concentration of NaCl in the stock solution, the feed rate of the solution,

Table 2. Overview of test aerosols generated with the test set up 1.

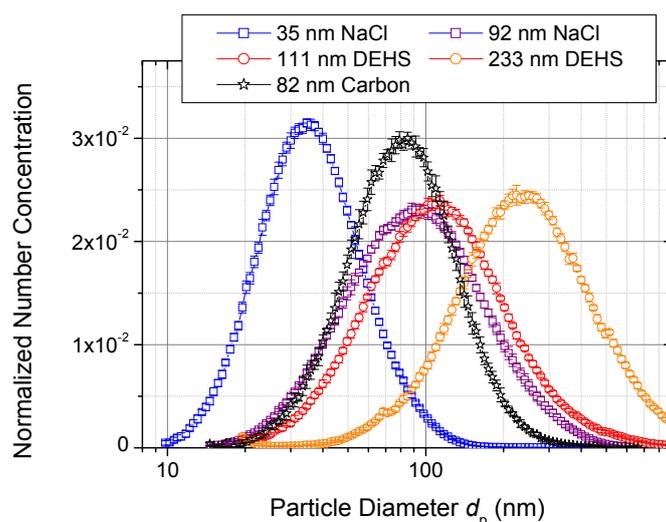| Material	Property	Modal diameter (nm)	Geometric standard deviation	Max. concentration (cm⁻³)
NaCl	hydrophilic	34.9 ± 0.81	1.584 ± 0.004	1.93×10^5
		92.1 ± 4.88	1.835 ± 0.018	3.05×10^5
Carbon	hydrophobic	81.6 ± 5.12	1.862 ± 0.006	5.81×10^4
DEHS	highly hydrophobic	110.6 ± 5.27	1.827 ± 0.004	3.98×10^5
		232.9 ± 17.98	1.628 ± 0.004	3.46×10^5

Fig. 1. Number size distributions of the five different test aerosols generated at IGF, due to (deliberately) changing number concentrations, each one normalized with respect to the total number concentration.

which was controlled by means of a syringe pump, and the dilution air flow rate in the EN779 test rig. Since the dilution flow rate affected both the number concentration and the particle size, a variation of the number concentration was not possible in test set up 2. Three different NaCl test aerosols were produced with this set up. The resulting number size distributions are summarized in Table 3 and shown in Fig. 2 along with the nominal lower detection limit (d_{50}) of the tested CPCs. The smallest particles were produced with a solution of 0.5 g L^{-1} NaCl in deionized (DI) water, a feed rate of 50 mL h^{-1} and a dilution flow rate of 1700 m^3 h^{-1}; a 10 g L^{-1} NaCl solution, 50 mL h^{-1} feed rate and 1700 m^3 h^{-1} dilution flow rate was used for the medium sized particles and a 10 g L^{-1} NaCl solution, 50 mL h^{-1} feed rate and 600 m^3 h^{-1} dilution flow for the largest particles.

The smallest particles had a modal diameter of 5.4 ± 0.1 nm with a geometric standard deviation (GSD) of 1.271 ± 0.051. As can be seen in Fig. 2, the size distribution was completely within the covered range of the reference ultrafine CPC (TSI model 3776), whereas the other CPCs only covered different fractions of the size distribution. The medium sized particles had a modal diameter of 13.6 ± 0.3 nm and a GSD of 1.401 ± 0.012 and were hence also completely covered by the nominal size ranges of the CPC model 3025A and PUFP C100, whereas a small fraction was outside the nominal range of the water based CPC model 3787 and a larger fraction was outside the range of the CPC model 3022. The size distribution of the largest particles produced with test set up 2 had a modal diameter of 25.2 ± 0.1 nm and a GSD of 1.400 ± 0.011. The latter size distribution was completely covered by all CPCs. The aerosols were sampled from the

test rig, using a stainless steel tube with an inner diameter of 6 mm. The concentrations inside the EN779 test rigs were very high ($\geq 10^7$ cm^{-3}) and hence above the detection limits of the CPCs. The test aerosols were therefore diluted with a rotating disk thermodiluter (TSI model 379021) to concentrations below 100,000 cm^{-3}, which could be handled by all CPCs (see Table 1). The flow rates of all CPCs were frequently checked with a mass flow meter (TSI model 4140).

RESULTS AND DISCUSSION

Test Set up 1

Scatter plots showing the correlation between the different CPCs in comparison with the reference UCPC 3776 for all test aerosols generated with test set up 1 are shown in Fig. 3. The white background in the graphs indicates the specified concentration ranges of the two CPCs, whereas the grey areas indicate the number concentrations beyond the instruments' specifications. The straight black line represents the 1:1 ratio and the dashed lines ± 10% deviation from the 1:1 ratio. All correlation data are listed in Table 4. The column "all data" in Table 4 refers to all concentration data shown in Fig. 3, whereas all concentrations beyond the range of the CPCs specifications as well as data during obvious instrument failures were removed from the dataset in the "cleaned data" column.

The correlation of concentrations measured with the PUFP C100 and the reference UCPC model 3776 is shown in the top row of Fig. 3. It can be seen that the agreement between PUFP C100 and UCPC 3776 was good and within the manufacturer specification for sodium chloride particles (left).

Table 3. Overview of test aerosols generated with the test set up 2.

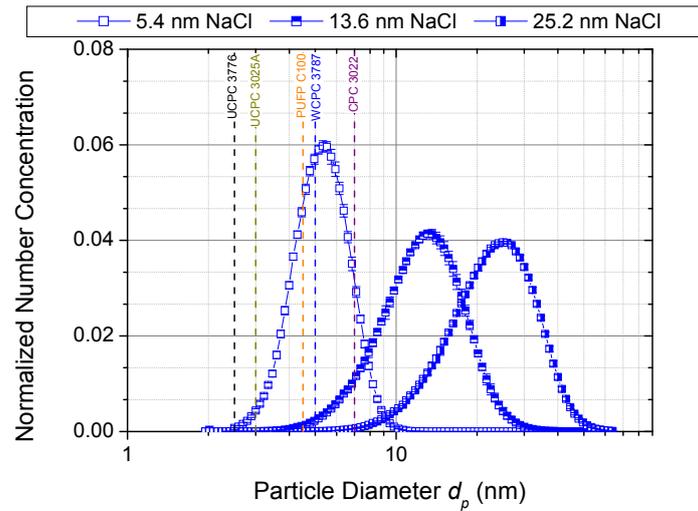| Material	Property	Modal diameter (nm)	Geometric standard deviation	Number concentration[1] (cm^{-3})
NaCl	hydrophilic	5.4 ± 0.1	1.271 ± 0.051	$77{,}580 \pm 6{,}650$
		13.6 ± 0.3	1.401 ± 0.012	$87{,}000 \pm 6{,}310$
		25.2 ± 0.1	1.400 ± 0.011	$89{,}180 \pm 2{,}020$

Fig. 2. Size distributions of the test aerosols used to test the lower size limit of the CPCs; vertical dashed lines indicated the nominal lower detection limits (d_{50}) of the different CPCs.
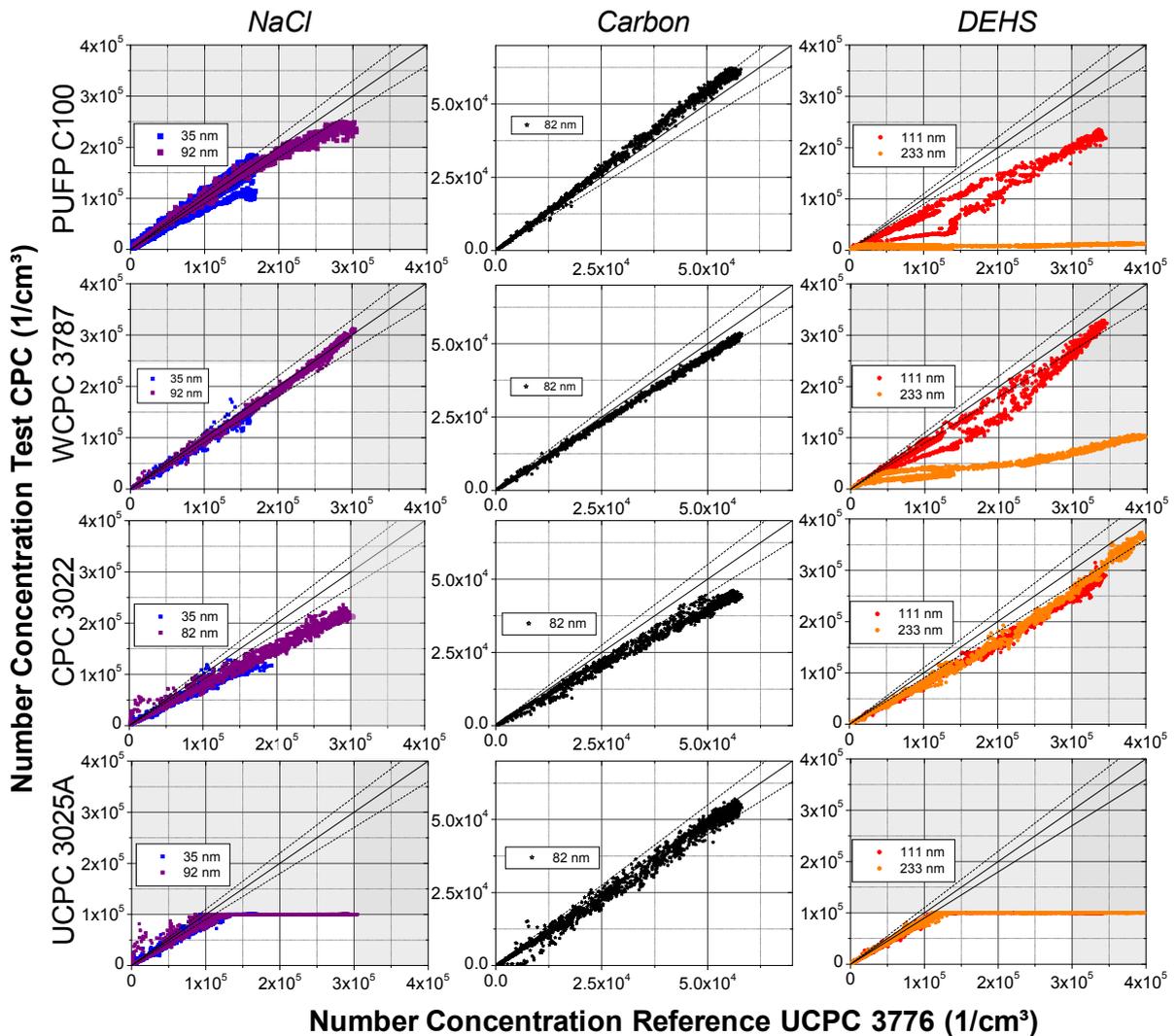

Fig. 3. Scatter plots of 1 s concentrations data measured with Enmont PUFP C100, TSI Water CPC 3787, TSI CPC 3022 and TSI CPC 3025A in comparison to TSI UCPC 3776 for three different aerosol substances, i.e., NaCl, carbon and DEHS; grey shaded areas indicate concentration ranges beyond the instruments' specifications.

Table 4. Correlation data for all CPCs in comparison to TSI CPC 3776.

CPC	Test Aerosol	All data	Cleaned data
PUFP C100	35 nm NaCl	y = 0.9765x – 482.68 R^2 = 0.9687	y = 0.9806x – 1631.6 R^2 = 0.9907
	92 nm NaCl	y = 0.8273x + 11983 R^2 = 0.9879	y = 0.9574x + 4527.7 R^2 = 0.9916
	82 nm Carbon	y = 1.0842x – 53.043 R^2 = 0.9966	y = 1.0842x – 53.043 R^2 = 0.9966
	111 nm DEHS	y = 0.6379x – 13883 R^2 = 0.8726	y = 0.3304x + 11479 R^2 = 0.5530
	233 nm DEHS	y = 0.0143x + 3840.9 R^2 = 0.1701	y = –0.0107x + 5569.2 R^2 = 0.9963
TSI 3787	35 nm NaCl	y = 0.9388x – 342.16 R^2 = 0.9981	y = 0.9388x – 342.16 R^2 = 0.9981
	92 nm NaCl	y = 1.0182x – 4926.3 R^2 = 0.9981	y = 0.9653x – 1479.8 R^2 = 0.9978
	82 nm Carbon	y = 0.9156x + 153.26 R^2 = 0.9992	y = 0.9156x + 153.26 R^2 = 0.9992
	111 nm DEHS	y = 0.9049x – 18077 R^2 = 0.9362	y = 0.6247x + 5825.4 R^2 = 0.8697
	233 nm DEHS	y = 0.2149x + 3407.5 R^2 = 0.9065	y = 0.1745x + 6625.5 R^2 = 0.829
TSI 3022	35 nm NaCl	y = 0.6834x + 1871.5 R^2 = 0.9939	y = 0.6834x + 1871.5 R^2 = 0.9939
	92 nm NaCl	y = 0.8407x – 3417.2 R^2 = 0.9970	y = 0.7378x + 2600.6 R^2 = 0.9955
	82 nm Carbon	y = 0.7379x – 756.09 R^2 = 0.9952	y = 0.7379x – 756.09 R^2 = 0.9952
	111 nm DEHS	y = 0.8407x – 3417.2 R^2 = 0.9970	y = 0.8106x – 787.8 R^2 = 0.9971
	233 nm DEHS	y = 0.8672x – 4834.4 R^2 = 0.9931	y = 0.8199x – 960.75 R^2 = 0.9969
TSI 3025A	35 nm NaCl	--	y = 0.829x + 501.88 R^2 = 0.9848
	92 nm NaCl	--	y = 0.8553x + 1147.3 R^2 = 0.9321
	82 nm Carbon	--	y = 0.961x – 514.02 R^2 = 0.9942
	111 nm DEHS	--	y = 0.8592x – 87.467 R^2 = 0.9954
	233 nm DEHS	--	y = 0.8569x + 165.14 R^2 = 0.9963

The slope of the regression fit for the cleaned data is 0.98 and 0.96 for 35 nm and 92 nm NaCl particles, respectively. The graph clearly shows that the agreement is best for particle concentrations below 150,000 cm^{-3}, whereas the effect of coincidence can be seen for higher concentrations. Up to the specified concentration limit of 200,000 cm^{-3}, the agreement is still within the range of ± 10%, however, larger deviations expectedly occur for higher concentrations. During the measurements with 92 nm NaCl aerosol, the water reservoir ran dry and had to be refilled. It was observed that the first measurements after refilling the water reservoir returned significantly too low concentrations as can also be seen in Fig. 3 (lowest blue branch in top left figure). According to the manufacturer, after running dry, the instrument requires some time to readjust the temperatures

of the condenser and saturator which can result in underreporting of the number concentration. These data were removed in the "cleaned data" column in Table 4. The number concentration of the moderately hydrophobic carbon aerosol (center) was slightly overestimated, however still within the ± 10% accuracy margin (slope 1.08, see Table 4). The number concentrations measured with pure DEHS aerosols (right, orange circles) were all much too low (see Fig. 3). The instrument reported an almost constant concentration of about 5,000 cm^{-3}, despite particle number concentrations of up to 400,000 cm^{-3}. This is likely caused by inefficient condensation of water vapor onto the DEHS droplets, thus producing too small water/DEHS droplets to be accurately counted. The concentration reported by the PUFP C100 likely stems from background particles in the

measurement chamber and/or particles from the upper end of the DEHS particle size distribution which even without condensation growth scatter sufficient light to be detected. When the DEHS was diluted 1:25 with IPA, the PUFP C100 results (red circles in top right graph) showed a better agreement with those from the UCPC 3776, however the discrepancy of the results was still significantly larger than the specified ± 10%. The scatter plot for the 111 nm DEHS particles shows two branches. The lower branch represents the first measurements with the diluted DEHS, whereas the upper branch represents the later measurements. The changing detection efficiency of the water based PUFP C100 CPC is assumed to be caused by an increasing amount of impurities in the DEHS-IPA solution, which enhance the water condensation on the test particles due to residues of polar groups caused by incomplete evaporation of IPA. Similar observations were made in different studies that investigated the effect of particles' chemical composition on the response of water based CPCs. Keller *et al.* (2013) found that a TSI water based ultrafine CPC (model 3788) had a drastically reduced counting efficiency for highly hydrophobic brown soot particles from combustion of a propane-rich fuel mixture, whereas the agreement with a reference CPC was much better in case of less hydrophobic black soot. Kupc *et al.* (2013) reported for the TSI CPC 3788 a shift of the d_{50} to 17.2 nm for very pure emery oil (EO) particles, while Hering *et al.* (2005) reported a d_{50} near 30 nm for pure dioctyl sebacate (DOS) particles in the case of the TSI CPC 3785.

The comparison of the water based TSI CPC model 3787 with the TSI ultrafine CPC model 3776 in the second row from the top in Fig. 3 shows that the concentrations measured with these two CPCs agreed very well for both NaCl aerosols as well as for the carbon aerosol. The agreement was well within the specified ±10% accuracy range, which is underlined by the slopes of the regression fits which are between 0.92 and 0.97 (see "cleaned data" column in Table 4). The agreement was still within the specified accuracy range, even when the number concentrations exceeded the concentration range of the water CPC 3787. Interestingly, the slope of the correlation increased when the concentration reached the limit. While the slope was slightly < 1 for concentrations below the concentration limit of the CPC 3787 (250,000 cm^{-3}), it increased to values > 1 for higher concentrations (thus also the higher slope in the "all data" column in Table 2 than in the "cleaned data" column). This may either be caused by an overcompensation of the coincidence error in the water CPC 3787 or by an earlier onset of the coincidence error in the ultrafine CPC 3776 than specified by the manufacturer. As in the case of the water based CPC PUFP C100 the agreement was much worse for DEHS particles. The number concentration of the pure DEHS particles (orange circles) was drastically underreported by the water CPC irrespective of the number concentration. The slope of the cleaned data was only 0.17 (see Table 4) and the y-intercept was very high. Consequently, also the TSI water CPC 3787 was not able to accurately measure the number concentration of highly hydrophobic pure DEHS droplets. The agreement of the two CPCs was better for the smaller DEHS particles generated by

aerosolizing a solution of DEHS diluted with IPA (red circles). Like in the case of the measurements with the water CPC PUFP C100, two branches can be observed in the data for the diluted DEHS. The lower branch represents the beginning of the measurement with diluted DEHS. During this time the slope of the correlation is only approximately 0.65, but after some time the agreement got better and was eventually within the specified ±10% range.

The data in Fig. 3 clearly show that both water based CPCs tested here were able to detect hydrophilic and moderately hydrophobic particles within the specified ± 10% accuracy range as long as the particle number concentrations were within the specified concentration limits. Highly hydrophobic DEHS particles, however, could not be adequately detected by either water based CPC, because of insufficient condensation of water vapor. When the DEHS contained impurities from isopropyl alcohol, the agreement was much better. While this should have no implications on ambient, indoor or workplace measurements, where such highly pure hydrophobic substances are rarely found, care should be taken in laboratory settings, where DEHS is a commonly used test aerosol, e.g., in filter tests.

The correlation graph for the TSI CPC 3022 is shown in the third row from the top in Fig. 3. A very high correlation between the concentration data from this and the reference UCPC 3776 was found for all test aerosols with correlation coefficients R^2 between 0.993 and 0.997 (see Table 4). This old CPC is hence still able to measure with high precision. However, all concentrations were clearly below those measured with the reference CPC with slopes of the correlation fits between 0.68 and 0.83, showing that the accuracy of the measurements is rather poor. In general the discrepancy was lower for DEHS particles than for NaCl and carbon particles. Data for the correlation between the UCPC model 3025A and the reference UCPC model 3776 are shown in the bottom row of Fig. 3. For concentrations above its specified limit of 100,000 cm^{-3}, the UCPC 3025A reports back a constant value of 99,900 cm^{-3}, which causes the horizontally aligned data points in the graph. A correlation analysis for all data would thus not be meaningful and hence no corresponding data is provided in Table 4 for "all data". All concentrations within the instrument's range were underreported by the UCPC 3025A with slopes of the regression curves between 0.83 for 35 nm NaCl and 0.96 for 82 nm carbon. The correlation coefficients were similar to those obtained with the CPC 3022. Hence, also this old UCPC was able to measure with high precision, but reduced accuracy over the entire specified concentration range. By the application of a correction factor, or its implementation in the data collection software as a calibration factor, these old and unserviced CPCs can hence still deliver meaningful results. However, due to the aging of the laser, a frequent check of the CPCs' performance will be required.

Test Set up 2

Three NaCl test aerosols with narrow size distributions and modal diameters of 5.4 nm, 13.6 nm and 25.2 nm were produced (see Table 3 and Fig. 2). As described above, this test set up does not allow for a variation of the number

concentration without changing the particle size distributions, so no scatter plots can be presented. Instead the ratios of the number concentrations measured with the different CPCs and the reference UCPC model 3776 were calculated and are shown in Fig. 4. The bars represent the average ratios and error bars the single standard deviations. The UCPC 3776 was also chosen here as the reference instrument, because it has the lowest particle size detection limit of 2.5 nm (see Table 1) and was nominally able to detect the entire size distributions (see Fig. 2).

The CPC PUFP C100 shows a clear size dependence of the ratio, with the ratio increasing with increasing particle size. The ratios are 0.46 ± 0.02, 0.70 ± 0.07 and 1.1 ± 0.03 for the 5.4 nm, 13.6 nm and 25.2 nm aerosol, respectively. The instrument has a nominal d_{50} of 4.5 nm. Therefore approximately 50% underreporting of an aerosol with a modal diameter of 5.4 nm can be explained. However, the ratio of 0.7 for the 13.6 nm particles indicates that the detection efficiency curve is not very steep. Consequently, care should be taken, when the instrument is used for personal exposure measurements in the presence of nucleation generated particles, which under certain circumstances can occur in ambient, indoor or workplace settings. However, it should be noted that the unit tested here was a loan unit from the manufacturer that prior to the tests conducted here had been shipped around the globe to various users for several months without servicing or calibration.

The water CPC 3787 showed an unexpected behavior, because the ratio of concentrations measured with the water CPC 3787 and the reference UCPC 3776 decreased with increasing particle size from 1.09 ± 0.06 for the size distribution with modal diameter of 5.4 nm to 0.95 ± 0.03 for the 13.6 nm particle and 0.91 ± 0.01 for the 25.2 nm particles. The average ratio of 0.91 for the 25.2 nm NaCl aerosol is very close to the ratio of 0.94 of the two instruments with the 35 nm NaCl aerosol in test set up 1 (see slope for this aerosol and CPC in Table 4). The increased ratio with decreasing particle size could be due to a combination of two factors: the difference in the aerosol flows of the two CPCs and a possible shift of the d_{50} to lower sizes in the case of the CPC 3787 for NaCl particles. The CPC 3787 has a larger aerosol flow rate (0.3 L min^{-1}) than the UCPC 3776 (0.05 L min^{-1}), thus an increased counting statistics and decreased diffusion loses. A shift to lower cut sizes for NaCl particles was observed in the case of other water based CPCs (Hering *et al.*, 2005; Kupc *et al.*, 2013) for which, as for the CPC 3787, the minimum detectable particle size was determined and specified based on measurements with sucrose. It should, however, be noted that the agreement between the two CPC was in any case within the specified accuracy range of ± 10%.

As in the case of the water CPC PUFP C100, the CPC 3022 shows a clear size dependence of the ratio, with the ratio increasing with increasing particle size. The ratios were 0.33 ± 0.20, 0.55 ± 0.13 and 0.71 ± 0.02 for the 5.4 nm, 13.6 nm and 25.2 nm aerosols, respectively. This CPC has a nominal d_{50} of 7 nm, but Quant *et al.* (2012) reported about a rather shallow detection curve, which for NaCl aerosol at a temperature of 20°C reaches 100% counting efficiency only

at about 40 nm. The increasing ratio with increasing particle size was hence to be expected.

The ratio of the concentrations measured with the UCPC 3025 and the UCPC 3776 was almost constant for all three test aerosols, namely 0.87 ± 0.02, 0.85 ± 0.02 and 0.83 ± 0.02, respectively, for the 5.4 nm, 13.6 nm and 25.2 nm aerosols. These values are very comparable with those obtained with the larger particles using test set up 1 (see Table 4). Quant *et al.* (1992) showed that the UCPC 3025 has a much steeper efficiency curve than the CPC 3022. The measurements presented here show that even after a very long period without servicing, the UCPC 3025 still had a very steep efficiency curve and the nominal detection limit of 3 nm is likely still valid.

SUMMARY AND CONCLUSIONS

The response of a water based personal condensation particle counter (Enmont PUFP C100) to different lab generated aerosols has been investigated. One butanol based ultrafine CPC (TSI model 3776) was used as reference. Three other CPCs were included in the study: a water based CPC (TSI model 3787), a butanol based CPC (TSI model 3022) and a butanol based ultrafine CPC (TSI model 3025A). The latter two are rather old instruments that are no longer serviced by the manufacturer. The intention was to compare the response of the CPCs to particles of different sizes, concentrations and materials. The test particle size distributions were polydisperse with modal diameters ranging from approximately 5 nm to 230 nm with concentrations between nearly zero and 400,000 cm^{-3}. Particle materials included hydrophilic NaCl, moderately hydrophobic carbon and highly hydrophobic DEHS. DEHS was used both pure as well as 1:25 diluted with isopropyl alcohol to reduce the size of the DEHS particles upon evaporation of the IPA.

The investigations revealed that the water based CPC PUFP C100 was able to accurately measure the number concentrations of hydrophilic NaCl and moderately hydrophobic carbon particles, as long as the number concentrations were within the specified concentration range of the CPC. In this case, the agreement with the reference CPC was within ± 10%. For very small NaCl particles, the PUFP C100 measured too low concentrations. For particles with a modal diameter of 5.4 nm, the detection efficiency was approximately 46%. Hence, the d_{50} of the specimen tested must have been slightly larger than the specified d_{50} of 4.5 nm. For a modal diameter of 13.6 nm, the efficiency was approximately 70% and for a modal diameter of 25.2 nm, the response of the PUFP C100 agreed with the reference CPC within ± 10%. For the DEHS aerosol, the agreement with the reference CPC was poor, the personal CPC PUFP C100 being blind to those particles. The CPC was obviously not able to sufficiently grow the highly hydrophobic DEHS particles by water condensation. When the DEHS was diluted with isopropyl alcohol, the agreement got better, likely due to the presence of remaining functional groups on the surface of the DEHS droplets. After some time and probably due to an increasing content of "impurities" in the test aerosol, the concentrations measured with the

personal CPC also increased and were approximately 34% lower than the ones reported by the reference CPC.

A similar behavior to the one of the personal PUFP C100 CPC, was observed also for the water based CPC 3787. For hydrophilic NaCl and moderately hydrophobic carbon particles the agreement with the reference CPC was within ± 10% for concentrations within the specified range of the instrument. For concentrations above the limit of the water CPC 3787, the instrument showed slightly higher concentrations than the reference UCPC 3776, whereas for lower concentrations the data from the water CPC 3787 were slightly below those reported by the reference CPC. This is a surprising result, because when reaching the coincidence limit, one would expect the instrument to report back increasingly too low concentrations. However, the concentrations were still well within the ± 10% margin, even for concentrations exceeding 300,000 cm^{-3}. The water CPC 3787 agreed with the reference CPC within ± 10% for all small NaCl particle sizes, i.e., also for particles with a modal diameter of 5.4 nm. This indicates that the d_{50} of the water CPC 3787 for NaCl particles may be smaller than the specified d_{50} of 5 nm. For the DEHS aerosol, the agreement with the reference CPC was poor, with the response increasing with increasing particle concentration. For the DEHS diluted with IPA aerosols the TSI water CPC agreed within ±10% with the reference CPC after some time.

The fact that the investigated water based CPCs are not able to accurately measure pure highly hydrophobic particles should have no implication on measurements in most ambient, indoor or workplace settings, where these particles are rarely encountered. Even in the case of oil aerosols, e.g. released from lubricants or coolants, these usually contain impurities which are sufficient to initiate water condensation on the surface. However, care should be taken when a CPC is employed in laboratory measurements of e.g., the filtration efficiency, where DEHS is a very common test aerosol substance.

Despite their old age (> 20 years) and long period without service (> 10 years) the concentrations measured with both the CPC 3022 and the UCPC 3025A showed a very high correlation with the reference CPC for all test aerosols. However, in both cases the delivered concentrations were clearly below the ones measured with the reference CPC, hence both CPCs measure with high precision, but reduced accuracy. The accuracy could be improved by applying a correction factor. For the small test particles produced in test set up 2, the CPC 3022 showed an increasing detection efficiency with increasing particle size, which was expected based on the nominal d_{50} of 7 nm and the reported rather shallow detection efficiency curve (Quant *et al.*, 1992). The comparability of the UCPC 3025A with the reference CPC was the same for the larger test particles in test set up 1 and the smaller particles in test set up 2. It can thus be concluded that this CPC specimen is still able to precisely measure particles down to its nominal d_{50} of 3 nm.

In conclusion, we have shown that both water CPCs measure according to their specifications, as long as the particles are not too hydrophobic. The tested specimen of the personal CPC PUFP C100 seemed to have a slightly larger

d_{50} than specified, but otherwise proved to be a reliable instrument, particularly taking into account that it had been shipped around the globe for several months without servicing. Both old CPCs were still able to measure number concentrations with high precision, however, with decreased accuracy.

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