A New Working Fluid for Condensation Particle Counters for Use in Sensitive Working Environments

Patrick Weber[1,4], Oliver F. Bischof[1, 2], Benedikt Fischer[5], Marcel Berg[1], Jannik Schmitt[1], Gerhard Steiner[3], Lothar Keck[3], Andreas Petzold[1,4] and Ulrich Bundke[1]

[1]Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research 8 – Troposphere (IEK-8), Jülich, Germany

[2]TSI GmbH, Particle Instruments, Aachen, Germany

[3]GRIMM Aerosol Technik Ainring GmbH & Co. KG, Dorfstraße 9, 83404 Ainring, Germany

[4]Institute of Atmospheric and Environmental Research, University of Wuppertal, 42119 Wuppertal, Germany

[5]Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research 5 – Photovoltaic (IEK-5)

Correspondence to: Patrick Weber (p.weber@fz-juelich.de) and Ulrich Bundke (u.bundke@fz-juelich.de)

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ABSTRACT. The working fluid of a condensation particle counter (CPC) is one of its essential characteristics. Butanol is commonly used as the working fluid in alcohol-based CPCs due to its proven performance in various applications and a wide range of working conditions over the past almost five decades. At the same time, butanol has several disadvantages including its strong, unpleasant odour, negative effects when inhaled over prolonged periods, and flammability, making it troublesome to use in all places with strict safety regulations. We are proposing to address these negative issues by replacing it with dimethyl-sulfoxide (DMSO), a substance that has not been used as the working fluid in a CPC up to now. DMSO is an odourless, non-flammable, non-toxic substance that is easily accessible and inexpensive. During thorough experiments, this new substitute working fluid has proven to be stable in its performance in CPC and storage. We could show that DMSO behaves equivalent to butanol when used to operate a CPC in terms of the instrument`s counting efficiency, D50 cut-off diameter and concentration linearity. In addition, we have demonstrated this for operating pressures ranging from ambient down to 200 hPa without the need for any safety precautions. Our new working fluid was tested on three CPC units representing two different models, almost always in side-by-side measurements. So far, we have achieved the best results with operating temperatures of 40 °C for the CPC's saturator and 5 °C for its condenser. To address a less desirable property of DMSO, it could be mixed with a slight amount of water to decrease its freezing point significantly. When mixed accordingly, the substance stays liquid even in work environments with temperatures ≤ -10 °C and without any impact on the CPC`s counting efficiency performance.

1 Introduction

Aerosol science has come more into focus in recent years. This was driven by the ongoing pandemic (Somsen et al., 2020) and rising awareness of the adverse effects of aerosol particles on aspects such as

climate change, air quality, and public health, and all their interrelations (Von Schneidemesser et al., 2015). Specifically, the monitoring of atmospheric aerosol (Mcmurry, 2000; Rose et al., 2021), including at extreme environmental conditions like measurements on airborne platforms (Petzold et al., 2013), exhaust aerosol from various sources (Giechaskiel et al., 2009; Petzold et al., 2011; Bischof et al., March 2020), indoor aerosol (Salimifard et al., 2020), and airborne viruses are current key applications of condensation particle counters.

A condensation particle counter (CPC) can measure the aerosol particle number concentration by increasing the size of nanometre-sized particles in a supersaturated environment to optically detectable droplets. In short, the measurement principle of a common CPC can be expressed in three process steps:

1) saturation, by which vapour is formed from a working fluid inside the flow path of the aerosol sample;

2) supersaturation of the vapour in presence of the sample flow, so that the aerosol particles subsequently act as condensation nuclei, get activated (non-equilibrium growth) and grow by several orders of magnitude to an optically detectable size; and

3) the detection of individual particles through scattered light that occurs when they pass through an optically focused, incident radiation source. In order to collect the scattered light, a photosensitive element e.g. a photomultiplier or a photo diode (Bischof, June 2022) is typically used.

This basic principle dates back to John Aitken, known for his early experiments in which he manually counted particles that had grown due to supersaturation of water vapour (Aitken, 1888). Today, three working fluids are most commonly used, namely n-butyl alcohol (or n-butanol), isopropyl alcohol (2-propanol or isopropanol;) and water. For all working fluids, the detection efficiency has been characterised over a specific range of operating pressures (Brock et al., 2000; Bundke et al., 2015; Gallar et al., 2006; Hermann et al., 2007) which demonstrated the applicability of each working fluid for low-pressure operation CPCs. It should be noted that both butanol and isopropanol have a strong, unpleasant odour and adverse effects when inhaled over prolonged periods and that their use is limited

by the fact that both are highly flammable liquids. In contrast, water has the advantage of avoiding the health and safety concerns of alcohol. The disadvantages of water are that it has a three times higher mass diffusion coefficient (Hering et al., 2005; Mei et al., 2021) which increases the consumption of the working fluid during operation and the possible growth of organisms during prolonged times of inactivity. Further with water as the operating fluid, the activation of particles can be hindered, e.g. by aerosol properties like water solubility and lipophilicity. In the past, there were several attempts to find an optimal working fluid. A theoretical approach for working fluids was demonstrated by Magnusson et al. (2003) including mostly alkanes, organic acids, aromatic compounds and alcohol substances, while sulphuric compounds were not included. Diethylene Glycol (DEG) was discovered by Iida et al. (2009) with great application for sub 3-nm particles, but droplets only grow to very small sizes, so a "booster" CPC is needed. Dibutylsebecat (DOS/DEHS) and more substances were tried by Kupper et al. (2020) with the advantage of not being classified as hazardous by the international Globally Harmonized System (GHS), but those were only applicable for high temperature (above 100°C) in the CPC saturator.

Our search for a new, non-toxic, non-flammable, odourless working fluid was motivated by the requirements of aviation authorities that severely restrict the use of instrumentation on passenger aircraft. The European research infrastructure "In-Service Aircraft for a Global Observing System" (IAGOS) (Petzold et al., 2015; www.iagos.org) has been created to monitor all essential climate variables of the atmosphere, including aerosol particles (Bojinski et al., 2014). The monitoring takes place through regular and global-scale measurements conducted on board a fleet of commercial passenger aircraft equipped with automated scientific instrumentation. The IAGOS aerosol package uses a butanol-based CPC as described in detail by Bundke et al. (2015) and provided two years of measurement onboard the IAGOS CARIBIC flying laboratory. It obtained special permission of the German airline Lufthansa and its use included the observation of the Raikoke volcanic ash plume. However, the fact that butanol is a flammable liquid strongly hinders the international certification of this instrument for use aboard passenger aircraft.

The new working fluid dimethyl-sulfoxide (DMSO; C_2H_6OS; CAS-Nr. 67-68-5; 99,9%) that we introduce in this study is hitherto unknown for use in a CPC. Yet it is actually known within the aerosol community, since it is an intermediate step of the well-documented chemical reaction beginning with DMS (dimethyl sulphide). The reaction´s final product is sulphate, which serves as cloud condensation nuclei (Fung et al., 2022). The principal benefit of DMSO for use on passenger aircraft is that DMSO does not require any safety regulations according to the GHS classification of chemicals. According to this internationally agreed-upon system, it does not have any physical or health hazard characteristics. Therefore, this working fluid does not present an obstacle during the certification process for aviation operation. In a global scale, the effect of using DMSO as the working fluid in a CPC is considered minimal for stations that measure DMSO and DMSO products, as the amount of DMSO released to the environment is far less than natural production.

This study is part of the ongoing development of the IAGOS instrumentation package, in response to these flight safety aspects. For the next generation of the IAGOS aerosol package, we will operate two butanol condensation particle counters (model 5411 Sky-CPC; Grimm Aerosol Technik, Ainring, Germany), which is a variant of the Grimm model 5410 CPC that uses aviation-grade components and materials, alongside an optical particle counter (OPC, model 1.129, Grimm). One CPC is dedicated to measure the total aerosol concentration and the other is equipped with a thermodenuder operated at 250 °C upstream to measure only the non-volatile fraction of aerosol particles.

1.1 Working Fluid characteristics

A working fluid's physical characteristics are important for condensation particle counter performance. One governing parameter is the maximum saturation ratio which can be achieved in a specific CPC design. Our first objective was to find a substance with similar physical-chemical properties to butanol or water, which are widely used as working fluids in condensation particle counters. The second motivation was to address any safety restrictions that make the working fluid suitable for

sensitive working environments such as hospitals, schools, public spaces, industrial manufacturing, but also commercial passenger aircraft. DMSO was eventually identified as a candidate substance based on the authors' experience with organic solvents. Besides the advantages of not having any physical or health hazard characteristics, DSMO is also soluble in water. Therefore, the relatively high freezing point of DMSO of 18°C can be adjusted to -100°C or even below simply by adding defined amounts of water (Havemeyer, 1966).

The supersaturation of the working fluid vapour determines the smallest possible particle size which will be activated to grow. For pure liquids this p/p_s ratio can be expressed through the Kelvin equation (1) (Hinds, 1999; Thomson, 1871):

$$\frac{p}{p_s} = \exp\left(\frac{4\sigma M}{\delta R T d_k}\right) \tag{1}$$

where the following parameters are used: the surface tension of the liquid σ, the solvents molecular weight M, the density δ, the general gas constant R, the absolute temperature T and the Kelvin diameter d_k. For DMSO, a surface tension of 0.043 N/m, a molecular weight of 0.078 kg/mole and the liquid density of 1100 kg/m^3 is used (CRC Handbook, Internet Version 2022).

The Kelvin diameter is the droplet diameter at saturation rate p/p_s at which the droplet is at equilibrium and neither starts to grow nor shrink to due condensations processes or evaporation.

When a soluble nucleus is considered, the particle growth can be initiated by a mere percentage needed for a pure liquid. A given mass of a salt reduces the given vapor pressure at the droplet surface. The relationship between the Kelvin ratio and the particle size with dissolved matter is given by Hinds (1999):

$$\frac{p}{p_s} = \left(1 + \frac{6imM}{M_s \delta \pi d_p{}^3}\right)^{-1} \exp\left(\frac{4\sigma M}{\delta R T d_p}\right) \tag{2}$$

where m is the mass of the dissolve material and M_s the molecular weight of the dissolved substance. The constant i is the number of molecules the salt will dissolved into and d_p is the droplet diameter This

ratio can then be solved for a particle size when the supersaturation ratio is known. To calculate the saturation vapour pressure, the empirical Antoine equations can be used (Antoine, 1888):

145     $$log_{10}p = a - \frac{b}{c+T} \qquad\qquad (3)$$

for which a, b and c are component-specific constants, p is the vapour pressure and T the temperature. Solving the Antoine equation for two temperatures and taking the ratio of the two results yields the supersaturation for this calculated temperature difference. For DMSO, the component-specific constants are a= 5.23; b= 2239.2; and c= -29.2 (Domalski and Hearing, 1996).

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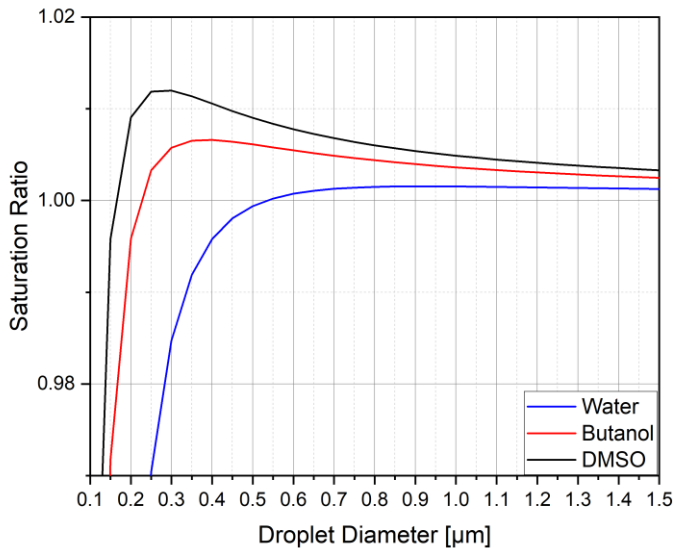
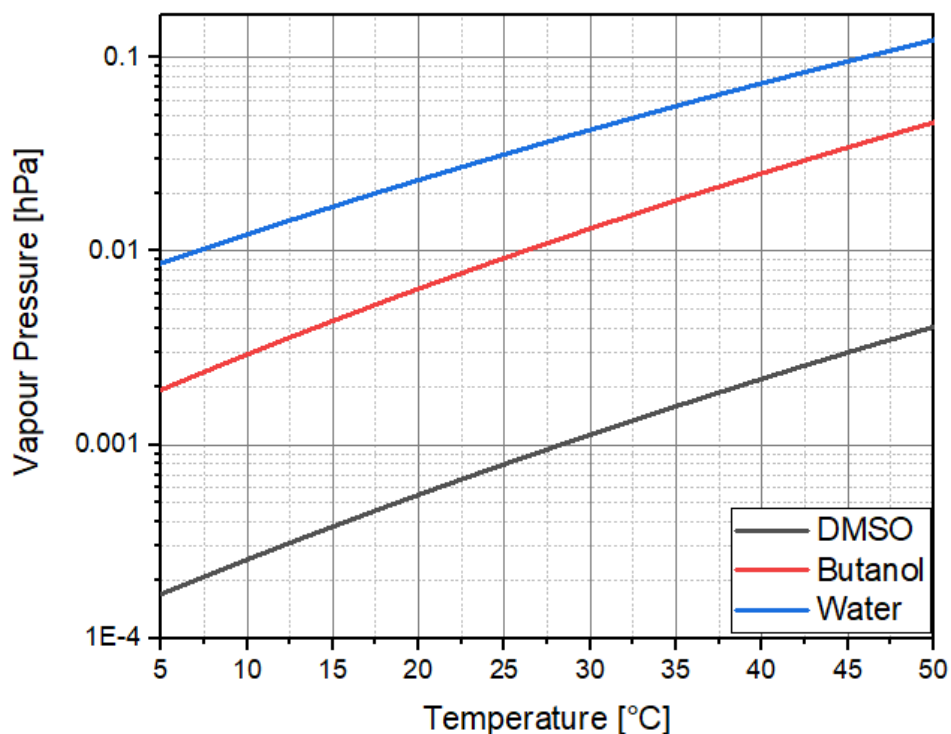


Figure 1. Saturation ratio of three working fluids as a function of the droplet diameter for a sodium chloride particle with an initial diameter of 13 nm (Hinds, 1999).

155   To understand the influence of the working fluid on the activation process inside a CPC, the process can be summarised as follows. The vapour pressure above the curved particle surface is described by the Kelvin Köhler equation (Thomson, 1871) as visualized in Figure 1 and calculated with Eq. (2). Here the saturation ratio is defined by the ratio of the actual vapour pressure to the vapour pressure above a flat surface at a given temperature. Particles smaller than the critical diameter grow or shrink in equilibrium

160 with the vapour in their vicinity. If the critical saturation ratio is exceeded in the particle vicinity the particle will grow past the critical diameter. If the saturation ratio is above 1 (i.e., supersaturation) then the particles will experience non-equilibrium growth. This process is known as particle activation. The critical supersaturation depends on the initial size of the aerosol particles and will be higher for smaller particles (Hinds, 1999). As shown in Figure 1, the saturation ratio necessary to activate a sodium chloride

165 particle of an initial size of d_p = 13 nm is at 1.012 for DMSO, 1.007 for butanol and 1.002 for water. The necessary supersaturation for activation increases with decreasing particle size. For example, for DMSO, particles with diameters 6 nm and 3 nm require saturation ratios of 1.037 and 1.078, respectively.

170 **Figure 2. The theoretical saturation vapour pressure of butanol, water and DMSO as calculated by the Antoine equations (Antoine, 1888; Gutmann and Simmons, 1950).**

As can be seen in Figure 2 and calculated with Eq. (3), the saturation vapour pressure of DMSO is far below that of butanol, but with a similar slope of 0.031, while the slope is 0.026 for water. This indicates the same supersaturations could be achieved with the same temperature difference between the

saturator and condenser of condensation particle counters, but with a much lower consumption of the working fluid. For DMSO, we achieved a supersaturation of about 10% (saturation ratio of 1.1) with a saturator temperature of 40 °C and a temperature drop to 5 °C in the condenser part of the CPC used. We are not certain if the signal is generated by droplets or solid crystals, because the freezing point of DMSO is below the condenser temperature.

2 Methods

In the experimental set-up shown in Figure 3, the sample-line pressure is regulated using the flow mass balance using mass flow controllers (MFC). The test aerosol is size classified by a differential mobility analyser (DMA, Model M-DMA 55-U, Grimm) while a Faraday cup electrometer (FCE, Model 5.705, Grimm) serves as a reference instrument for the particle concentration. There are two Sky CPC 5.411 instruments designated B-CPC and to indicate the use of butanol and DMSO as the respective operating fluid . In parallel, a TSI® CPC 3772-CEN (TSI Inc., Shoreview, MN, USA) that was also operated with DMSO was investigated as well. A more detailed description of the experimental setup is provided in prior studies (Bundke et al., 2015; Bischof, June 2022). To provide a steady and constant particle production from a NaCl-water solution, a continuous output atomiser (COA, model 3076, TSI Inc.) was used (Liu and Pui, 1975). After the nebulised aerosol flow passes through a diffusion dryer tube, it moves through an aerosol neutraliser equipped with a radioactive Am-241 source. Subsequently, a monodisperse aerosol flow is generated utilising a Vienna-type Differential Mobility Analyzer (DMA, model M-DMA 55-U, Grimm). This monodisperse aerosol is guided to the low-pressure zone by passing through a critical orifice. The aerosol flow is then diluted in a controlled manner within the mixing chamber. The mixing chamber is also used as a buffer volume to smoothen the pressure oscillation generated by the mass balance. The complete test setup is operated by a LabVIEW^{TM} (National Instruments Corp., Austin, TX, USA) program that was custom-made in our laboratory. Here several mass flow controllers function as controlling elements with a PID approach. Additionally, the relative humidity can be actively controlled by adding a stable humidified air flow into the mixing chamber. With the

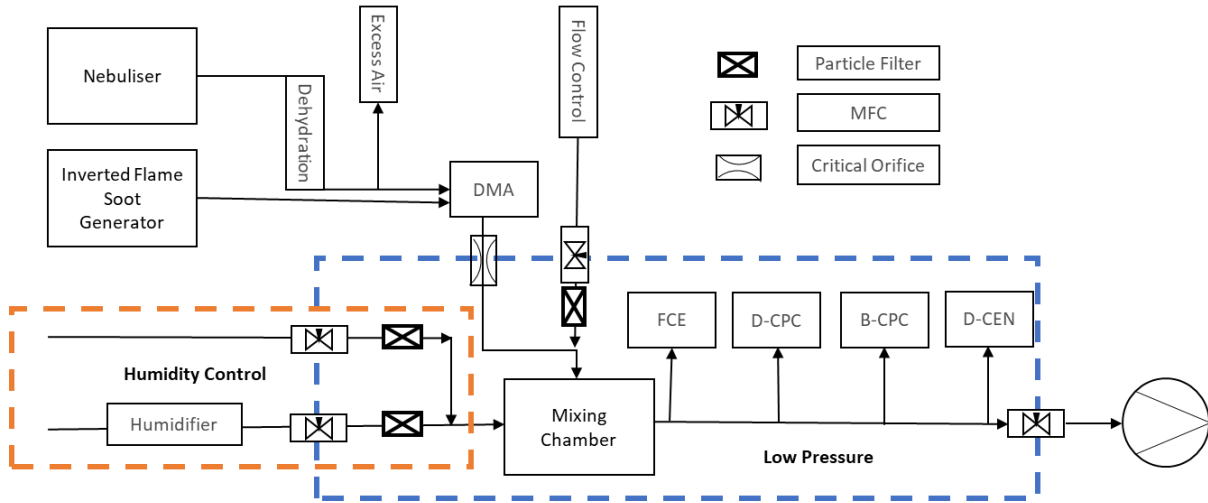
added humidified air flow, the relative humidity inside the mixing chamber is limited to approximately 30% RH. After passing the mixing chamber, the aerosol flow is provided to the measuring instruments along a common sampling line. An individual isokinetic, iso-axial sample inlet in the centre of the sample line guides the aerosol flow to each device.

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Figure 3. Flow schematic of the laboratory set up for the low-pressure characterisation with two aerosol sources.

During our experiments, the DMA was operated stepwise for 30-second periods to avoid time delays and undefined transition states of aerosol characteristics in the different instruments. Each voltage level corresponds to a different particle sizes starting at an upper limit of 140 nm and going down to 2.5 nm in diameter. To avoid transition effects and to achieve an equally distributed aerosol inside all measuring instruments, the first 15 seconds for each particle size setting of the DMA were excluded from the dataset used for the final analysis.

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An inverted flame soot generator (Argonaut Scientific Corp., Edmonton, AB, Canada) was used as a second aerosol source. For best performance, the soot generator was operated with an oxidation-air-to-propane ratio of 7.5 L/min air to 0.0625 L/min propane. Previous studies have determined that this flow ratio ensures stable aerosol production with low organic carbon soot (Bischof et al., March 2020; Kazemimanesh et al., 2018).

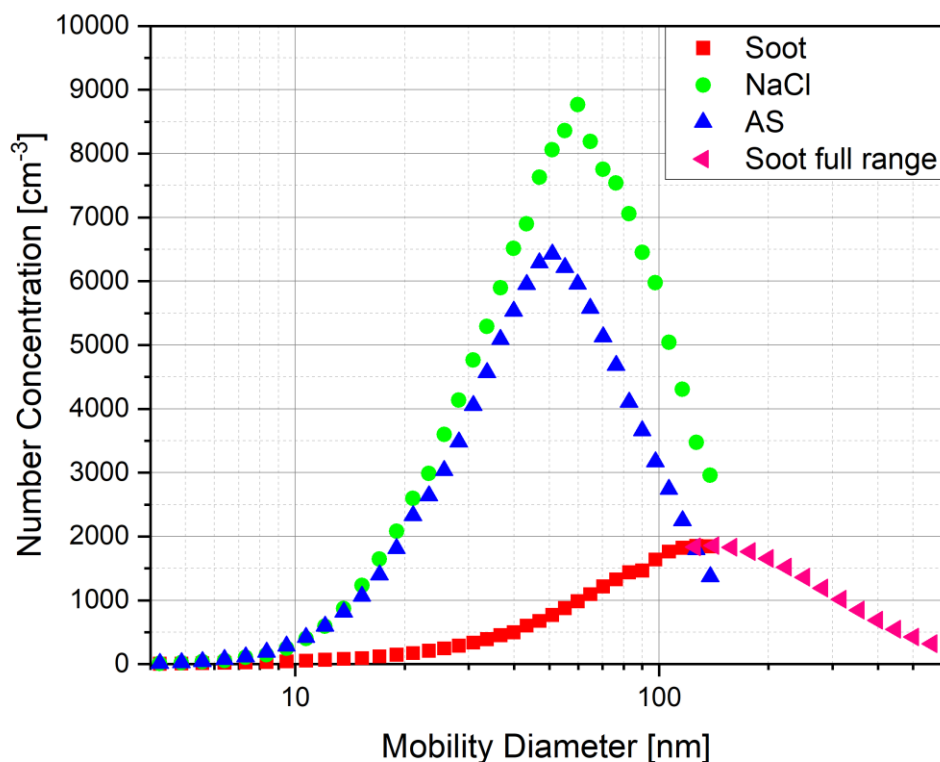



Figure 4. Particle size distributions of ammonium sulphate (AS), sodium chloride (NaCl) and fresh combustion soot as measured by the combination of DMA and electrometer.

As mentioned earlier, the atomiser was used to nebulise salt solutions. Sodium chloride (NaCl) and ammonium sulphate were both used for this purpose. Additionally, fresh combustion soot was measured. In Figure 4, the corresponding size distributions for these aerosol types are shown. The DMA settings were chosen, to provide the greatest possible size resolution at the smallest particle sizes near

the range of the expected cut-off diameters. This resulted in a maximum particle mobility size of 138 nm on the upper end for the salts and for the soot. Complete particle size distribution for the soot were taken from Weber et al. (2022).

2.3 Data analysis procedure

An important aspect of measuring nanometre-sized particles by the DMA technique is the misclassification of larger, multiply charged particles leaving the DMA with the same mobility as the singly charged particles. This effect leads to a notable difference in the counting rate between a condensation particle counter and an aerosol electrometer. To address this artefact, the correction procedure introduced by Bundke et al. and later on adapted by Bischof was used (Bundke et al., 2015; Bischof, June 2022).

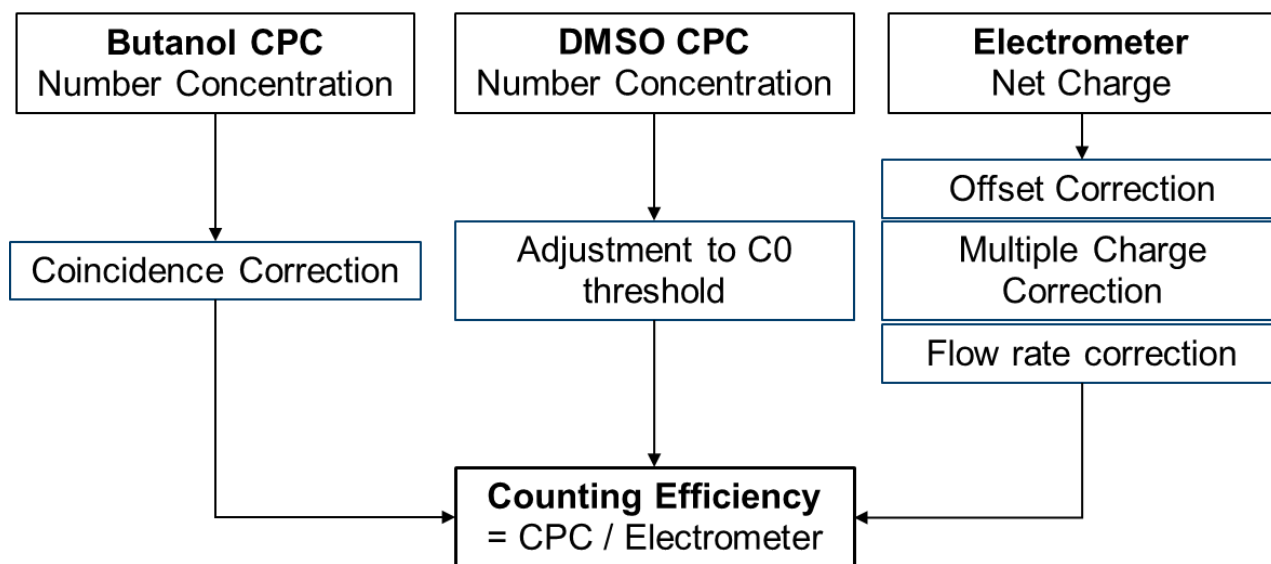



Figure 5. Flowchart of the data inversion procedure for particle concentration determination.

The multiple charge correction is calculated with a correction scheme that is based on measured size

245 distribution from the condensation particle counter and the electrometer in accordance to DMA theory

by Bundke et al. (2015)

The SKY CPC 5.411 reports an internal diagnosis of the particle growth which is displayed as the C1/C0 value. The C1/C0 reports the ratio of counts that have a higher and a lower detection threshold, which is used as CPC-internal check for sufficient particle growth (described in Fig 6.). A value below 1 indicates,

250 that the particles give a lower scattering signal due to a smaller particle size or due to overall light scattering behaviour. Only particles reaching and exceeding both signal threshold levels are counted. The C1/C0 correction is implemented simply by dividing the reported number concentration through the C1/C0 value. In Figure 6, signals of different droplet sizes are illustrated, along with detector thresholds C0 and C1. By dividing the reported number concentration by C1/C0, the CPC counts all

255 particles that reach the first detector threshold. DMSO droplets smaller than 2.5 µm will not be counted.

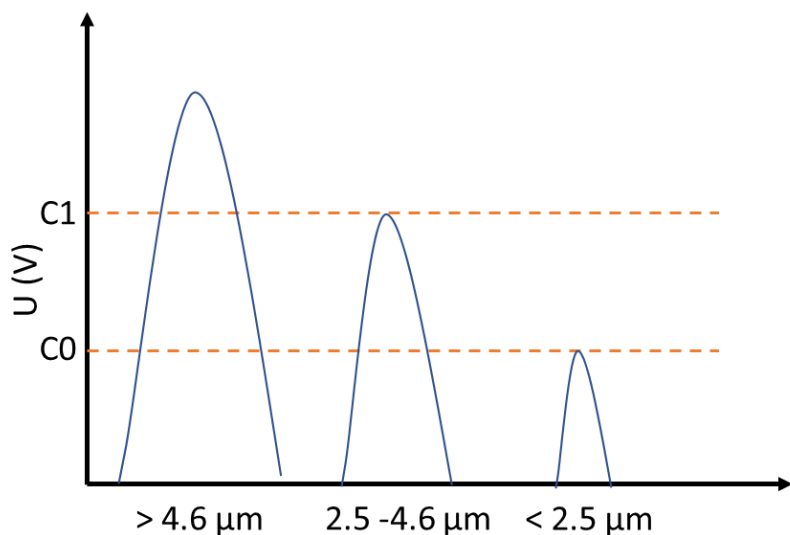



Figure 6. Illustration of the pulse height of DMSO-Droplets of different sizes with corresponding detector threshold levels.

The very need for this correction is due to the low vapour pressure of DMSO. If less material is available for condensation growth, the droplets cannot grow. The diameters of the DMSO droplets, which

260 correspond to the signal heights of C0 and C1, are 2.5 – 2.9 um and 4.0 – 4.6 um respectively to the different thresholds. The values were estimated from the signal heights of latex test particles, a model

for scattered light intensities as a function of particle diameter for the Grimm measuring cell, assuming spherical homogeneous particles, a wavelength of 660 nm, linear polarization, and refractive indexes of 1.59 + 0.0i for latex and 1.47 + 0.0i for DMSO.

265   To parameterise the efficiency curves, an exponential fit function introduced by Wiedensohler et al. (2018) was applied

$$\eta = A(1 - \exp \frac{(B-Dp)}{(C-B)} ln2) \ .$$

Here, η is the counting efficiency, D_p is the particle size, and A, B, C are fitting parameters calculated using a multi-parameter fit (Banse et al., 2001; Wiedensohler et al., 1997) where C corresponds to the

270   D_{50} cut-off diameter.

The fitted function was then used to robustly calculate the efficiency for the cut-off of D_{90}.

3 Results

275   During initial experiments we used DMSO from a bottle of our laboratory stock that was first opened two years prior to these experiments. We started by completely drying a Sky CPC 5411. Prior to filling it with DMSO, we performed a test run in the measurement setup and the dry CPC reported zero counts. The instrument wick was then wetted with DMSO by the refilling valve and worked as intended. The CPC internal fluid controls operated as they do with butanol. We operated this unit, which from now on

280   we refer to as the D-CPC, with the same parameters as the structurally identical B-CPC which was also included in the experimental set-up (Fig. 3). For the first run we applied a particle filter to the inlet to check for homogeneous nucleation. No particle counts were observed during zero particle air measurements, independent of instrument temperatures, humidity, or pressure levels. As we started aerosol measurements with pressure levels below 700 hPa, the C1/C0 value decreased to 0.9 and

285   dropped further down, as soon the pressure decreased. As a consequence, we increased the saturator temperature from 36°C to 40°C and decreased the condenser temperature from 10°C to 5°C. With this procedure, the C1/C0 value stayed at 1 down to a pressure level of 250 hPa and only decreased slightly

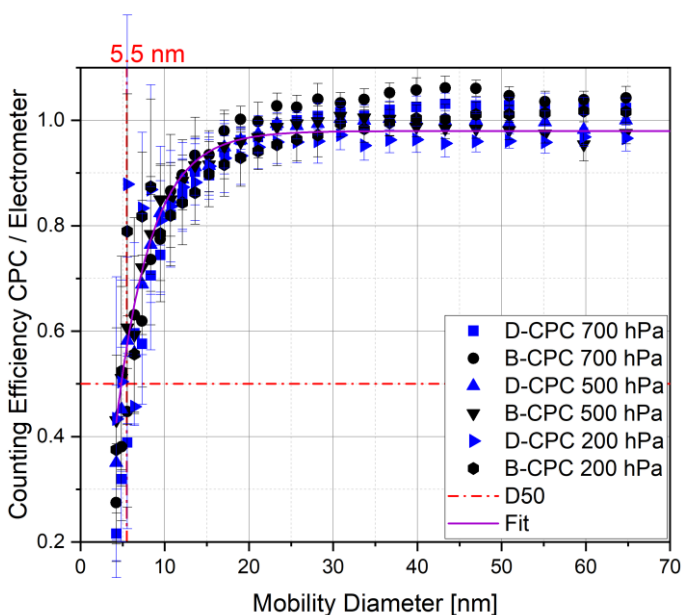
to 0.95 at 200 hPa. All values given as number concentration from the D-CPC are corrected by dividing

by the C1/C0 value to report all particles at the lower counting threshold as explained previously. The

290 initial results were obtained with ammonium sulphate particles. The D_{50} cut-off diameter is used as the

primary criterion, as it describes the particle size where only 50% of the particles are detected compared

to a reference method. Figure 7 shows that the D-CPC has an identical D_{50} cut-off diameter as the B-

CPC.

295 **Figure 7. Counting efficiency curves of the Sky CPC 5.411 operated with butanol (B-CPC) and DMSO (D-CPC) at different operation**
pressures using ammonium sulphate particles.

As second step, we tested DMSO in a CPC of a different kind. For the CPC 3772-CEN the main operating

principle is the same, but there are slight differences to the Sky-CPC. The Sky-CPC has a horizontal wick

and a continuous draining of condensed water/butanol mixture located downstream of the saturator

300 working fluid reservoir. The 3772-CEN has a vertical wick, where condensed water may flow through

before reaching the fluid reservoir. This different design will explain some differences we observed

during long-term experiments described later on. To start with, we dried the 3772-CEN for over two

days until no particle counts were reported. We then added the DMSO. We changed the temperature parameters to be equivalent to the D-CPC with 40°C at the saturator and 5°C at the condenser. Therefore, the 3772-CEN was not operated as intended by the European Committee for Standardization (CEN). in order to highlight this, we will refer to the 3772-CEN operated with DMSO as the D-CEN. As shown in Figure 8, counting efficiencies for all CPC´s do not significantly differ from each other, regardless of the instrument and applied pressure.

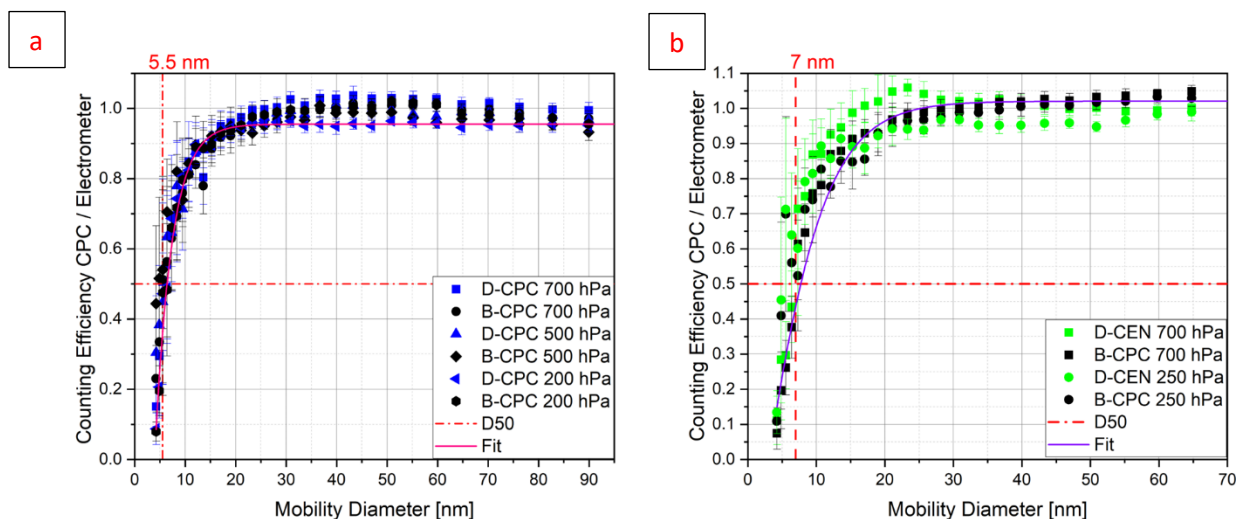
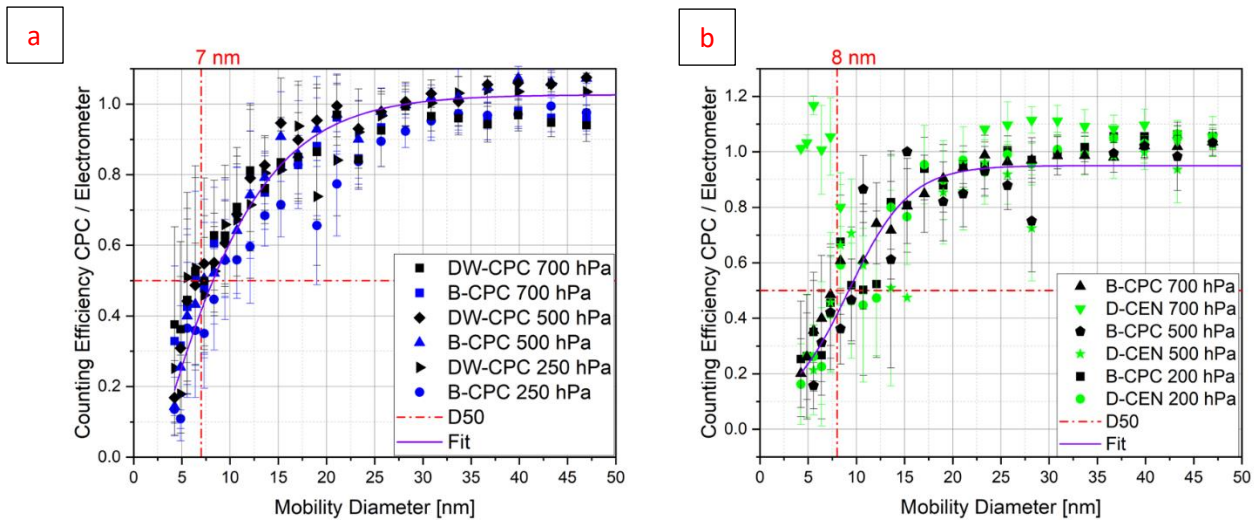



Figure 8. Counting efficiency curves for sodium chloride particles with respect to the electrometer reference instrument and corrected for multiple charge of the Sky CPC 5.411 (a) as well as the CPC 3772-CEN (b), both operated with butanol (B-CPC) and DMSO (D-CPC; D-CEN) at different operating pressures.

To test another particle type, we chose fresh combustion soot aerosol, as it is a non-soluble substance and is not hydrophilic. As in the previous experiments, the counting efficiencies for the different CPCs do not differ (Figure 9).

We repeated all experiments using a mixture of 10% volumetric water to 90% DMSO in the Sky CPC 5.411 (points labelled as DW-CPC in Figure 9). This mixture does not influence the measurement performances. We observed, that the C1/C0 value decreased to below 0.2 for about a minute as soon we reached pressure levels below 250 hPa, indicating that water is evaporating and influencing the

particle growth. After a span of one minute, the C1/C0 value rapidly increased to over 0.98. Using this mixture, the lower range of operating conditions is extended to -10°C.

325 **Figure 9. Counting efficiency curves with respect to the electrometer reference instrument and corrected for multiple charges at different operating pressures using fresh combustion soot particles for (a) Sky CPC 5.411 operated with butanol (B-CPC) and mixture of DMSO and water (DW-CPC) and (b) Sky CPC 5.411 operated with butanol (B-CPC) and the CPC 3772-CEN operated with DMSO (D-CEN).**

330 The counting efficiency of the D-CEN for soot particles at 700 hPa exhibits a sudden increase at around 5 nm as shown in Figure 9b. This phenomenon needs further investigation because it could not be explained.

We tested DMSO in our measurement set up at various conditions. For example, we increased the inline humidity (RH) to 30%, although we normally measure at RH below 5%. Even then, the counting

335 efficiencies as well as the overall behaviour did not change. The instrument cut-off diameters for D_{50} and D_{90} do not differ significantly from each other regardless of particle type, operating fluid or pressure level. In Table 1 the fitting parameters and the derived values for the D_{90} cut-off diameter are reported for the lowest pressure level studied (either 200 hPa or 250 hPa, depending on experiment). The

significant parameters for the high of the plateau (A; ±0.05) and the cut-off diameter D_{50} (Parameter C;

340 ±1.5) did not change significantly at different pressure levels (200 – 700 hPa) and humidity levels (0-30

% RH).

Table 1. Coefficients of the exponential function of the counting efficiency curves and the D90 cut-off diameter (at either 200 or 250 hPa) for different particle types for the Sky CPC 5.411 operated with Butanol (B-CPC) and DMSO (D-CPC); DMSO-Water mixture (DW-CPC) and CPC 3772-CEN operated with DMSO (D-CEN).

Particle Type	Instrument	A	B	C	D_{90}
				[nm]	[nm]
Sodium Chloride	B-CPC	0.99	3.9	6.7	13.6
Sodium Chloride	D-CPC	0.96	3.9	6.3	13.5
Sodium Chloride	D-CEN	1.02	1	6.7	18.6
Ammonium Sulphate	B-CPC	0.98	2.1	4.8	11.9
Ammonium Sulphate	D-CPC	1.02	2.8	6.5	14.2
Fresh Combustion Soot	B-CPC	0.95	3.4	6.8	17.8
Fresh Combustion Soot	DW-CPC	1.02	2.7	5.6	11.7
Fresh Combustion Soot	D-CEN	0.95	3.7	7.5	19.8

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After the characterization in the lab we conducted several measurements of outside air at the campus

of Forschungszentrum Jülich. The longest measurement lasted 5 consecutive days, both the D-CPC and

the B-CPC measured the same particle concentrations (Figure 10a). We observed that the 3772-CEN had

issues during the measurements caused by DMSO. Here the valves for draining and priming got blocked

350 by a swollen gasket. First of all, we needed to extract excess fluid from the device manually. Since the

overall ambient humidity ranged between 60 and 80%, it is certain that water condensed at the condenser and dropped into the wick of the 3772-CEN, weakening its activation efficiency. This is seen in Figure 10b, where the D-CEN trace is lower than the B-CPC trace starting around minute 45. Because DMSO appears to affect the drain and priming valve gaskets the instrument needed to be manually drained (minute 60 to minute 80 in Figure 10b). After that, the 3772-CEN returns to the same concentration levels as the B-CPC.

For the ambient aerosol measurement, we recorded the consumption rate: the Sky-CPC was filled with 5 ml of DMSO, whereas the second Sky-CPC was filled with 20 ml butanol. We run those measurements overnight. The B-CPC ran dry in the late morning as expected and was refilled, the D-CPC was still running and counting. For the first set of ambient measurements, the C1/C0 value of the D-CPC stayed at 1 and decreased slowly until it oscillated around 0.8 At a second approach, we added a Water/DMSO mixture and the C1/C0 value decreased towards 0.6 slowly going up again to 0.8. Anyhow, the D-CPC number concentration was corrected with simultaneously logged data of the C1/C0 value, which was ranging around 0.8 in Figure 10.

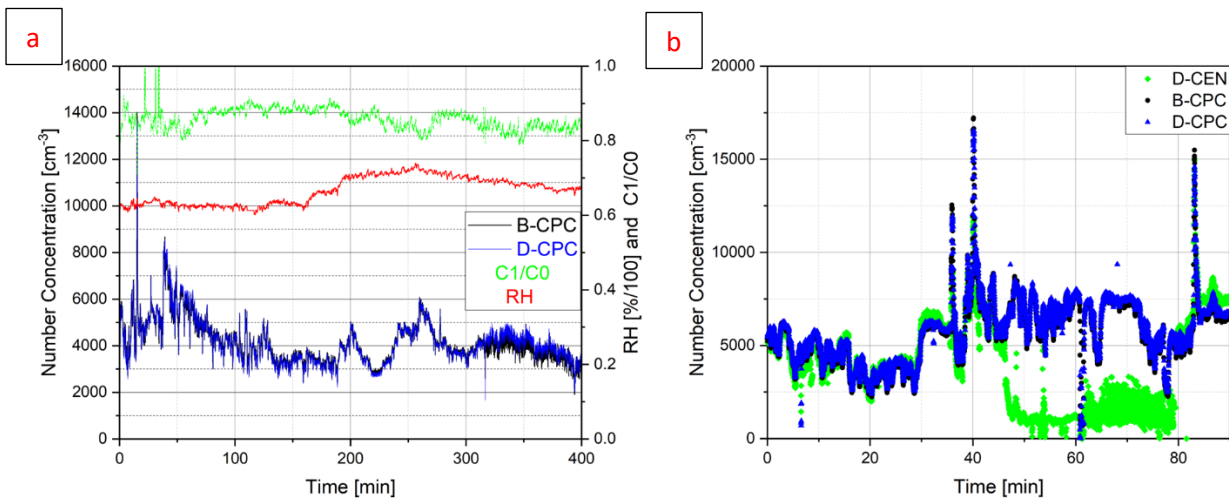



Figure 10. Ambient air as measured by the Sky CPC 5.411 operated with (a) Butanol (B-CPC) and DMSO (D-CPC) as well for the (b) CPC 3772-CEN operated with DMSO (D-CEN), that needed manual extraction of condensed water, which caused the number concentration to drop." change to "Figure 10. Ambient air with relative humidity and C1/C0 values displayed as measured by (a) the Sky CPC 5.411 operated with butanol (B-CPC) and DMSO (D-CPC) and (b) the B-CPC, D-CPC and CPC 3772-CEN operated with DMSO (D-CEN). D-CEN needed manual extraction of condensed water, which caused the number concentration to drop (see discussion in text).

Figure 11 demonstrates that the measurements made using DMSO as the working fluid are not distinguishable from the measurements performed with butanol. The overall linearity for the new working fluid is shown in Figure 11. The slope of the linear correlation is 1.01 ±0.02 (r²>0.99) for laboratory measurements as well as ambient air measurements. For atmospheric measurements we used the B-CPC as well-known reference.

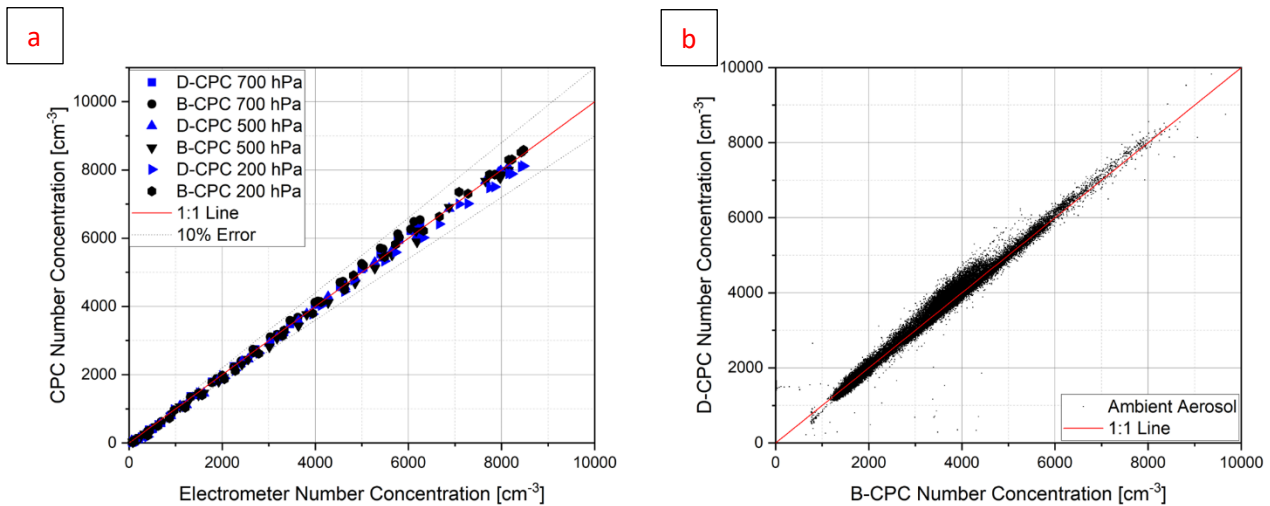
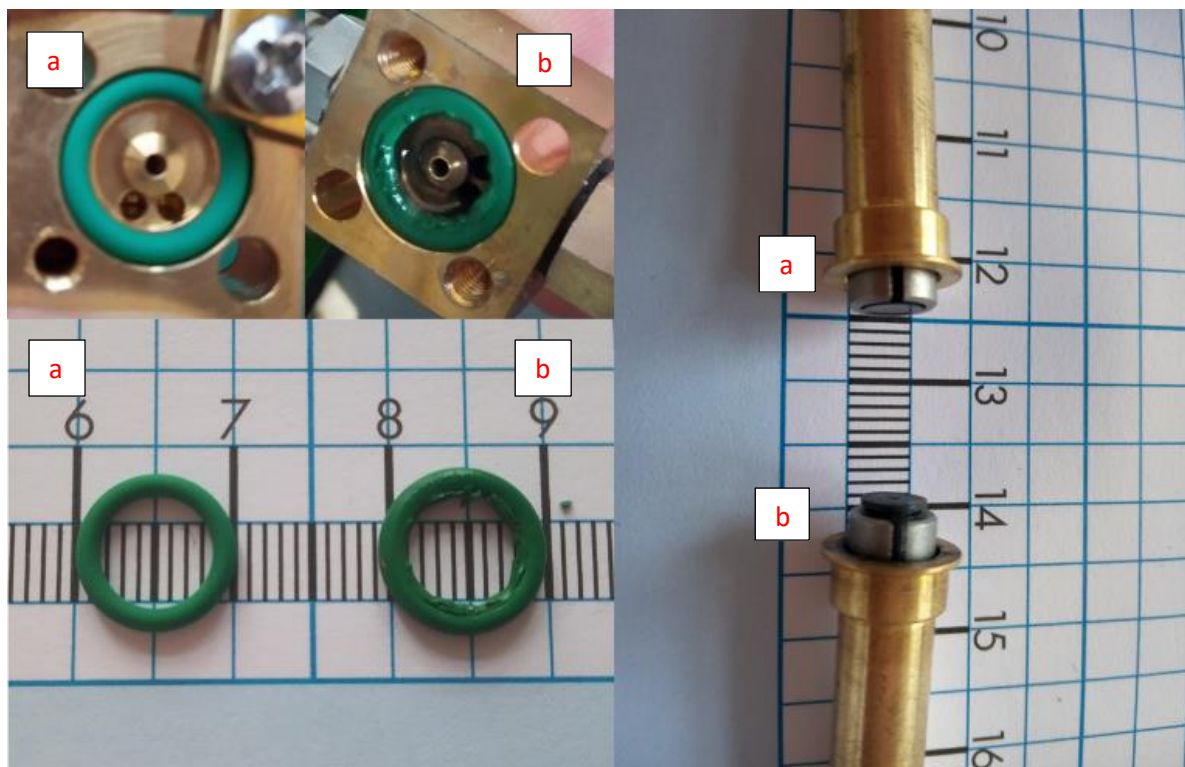



Figure 11. (a) Comparison of the concentration linearity of two Sky CPC 5.411 units to the electrometer reference at different pressure levels for ammonium sulphate and (b) comparison of correlation between B-CPC and D-CPC on ambient air.

380

4 Precautions

As already mentioned, the CPC 3772-CEN needed manual draining and refilling, and the Sky CPC 5.411 needed manual refilling as well. This is because rubber parts soak themselves with DMSO and swell, so they increase in size. With this behaviour, the o-rings expanded inside the valves for refilling and could no longer perform as intended, although it took several days to weeks before the valves stopped working. In order to address this issue, we exchanged those parts with silicon o-rings. We operated the instruments for at least three months with the new working fluid and apart from the valves, no essential parts were affected since the device kept working. We repeated the process using DMSO as the operating fluid in a third Sky CPC 5.411 - this unit performed the same as the D-CPC in the first

390 experiments, including agreeing well with the B-CPC and the swollen o-ring. As can be in Figure 12, the o-ring, as well as the stamp of the valve, increased by about 1 mm in size.

395 **Figure 12. Picture of the CPC o-ring (left, top and bottom), and the stem of the liquid supply valve (right). (a) indicates operating fluid was butanol and (b) indicates operating fluid was DMSO .**

With this increase in size, the sealing ring blocked the stamp and prevented the further flow of liquid to the wick. The continuous pump for draining in the Sky CPC 5.411 was still working as intended. Cross-sensitivities between DMSO and several reactive atmospheric substances were not tested. We

400 measured atmospheric aerosol for several weeks using instruments with DMSO as the operating fluid. We did not observe any significant shift in measured particle number concentrations between the reference B-CPC and the D-CPC. However, higher ozone or nitrogen oxides concentrations could trigger secondary organic aerosol activation within the instrument using DMSO.

In the CPC 3772-CEN, one of critical orifices in the supply line of the working fluid started leaking and had to be replaced. It is not clear that this issue can be attributed to the use of DSMO, as the instrument's maintenance state or operational errors could also have been factors.

DMSO can bring chemicals into the body by transporting dissolved chemicals through the skin. Bacteria can convert DMSO into dimethyl sulphide. Therefore, DMSO should not be disposed of into the sewer (Tucker, 2014).

Another precaution that should be mentioned here is that DMSO should not be heated to temperatures of over 150°C, since at that threshold it will lose its thermal stability. When exceeding 150 °C, DMSO slowly starts to degrade into its by-products, which may have different characteristics.

From an instrument manufacturer's point of view, DMSO seems to be an interesting alternative working fluid to the commonly used butanol. Furthermore, at first glance, the modifications required for the correct and safe operation of a Grimm 5411 Sky-CPC appear to be relatively straightforward. However, as demonstrated in the experiments shown here, there is a need to adapt the CPC design to the specific properties of DMSO, specifically material durability. Also, the detailed condensation process so far remains an open question that needs to be addressed in future studies in order to adapt and optimize the particle detection in upcoming CPC models.

Equally important, the benefits of using DMSO as a substitute working fluid by far exceed the effort needed to prepare a CPC for its use, from a user or an instrument manufacturer's perspective. In TSI's most recent generation of butanol-CPCs, there are only few places where DMSO comes in contact with materials that it could degrade or swell quickly. In practice this means that those o-rings and gaskets that are by default made of polycarbonate (PC), polyvinylidene fluoride (PVDF) like Kynar®, or polyvinyl chloride (PVC), will need to be exchanged by their silicone equivalents. While this is not technically difficult, the exact replacement should be assessed and approved separately for every CPC generation and model by the manufacturer. Also, all modifications will need to be tested over much longer periods of time than the brief test period in this work as components such as the instrument optics might get impacted only after several weeks or months of exposure to DMSO. Of course, this would change with

the introduction of a next-generation of alcohol-based CPCs that are designed for use with DMSO from the beginning.

5 Conclusions

In this work, we have introduced dimethyl sulfoxide (DMSO) as an appropriate new substance to replace butanol as the working fluid in alcohol-based condensation particle counters (CPC). DMSO is an odourless, non-flammable and non-toxic substance. We would like to emphasize that DMSO overcomes the notable health and safety concerns that arise when using butanol in sensitive working environments, and this fact alone makes it a desirable candidate for aircraft operation. Secondary benefits include the lower consumption when operating CPCs and its lower cost.

In our experiments we have demonstrated that the two different CPC models that we tested continued to operate as expected under several operational conditions. When changing the operation pressure from ambient level down to 200 hPa, which corresponds to the cruising level of passenger aircraft used within the IAGOS research infrastructure, the DMSO-operated CPC units displayed the same counting efficiencies as the butanol-operated CPCs. Even in very humid environments with a relative humidity of around 80%, the CPC operated with DMSO performed equivalent to a butanol CPC. It should be noted that at those high levels of humidity, the CPC 3772-CEN had to be drained frequently, while the Sky CPC 5.411 had to be corrected using its internally recorded C1/C0 value. Nevertheless, for all pressure levels and particle types investigated, the DMSO-operated CPC performed essentially identical to the equivalent butanol-operated CPC. Further investigations with different temperatures for saturator and condenser are planned.

The introduction of DMSO as the working fluid requires no significant modifications of a CPC's hardware apart from minor changes to its liquid supply valve and a replacement of any gasket that comes in contact with the working fluid. Our initial results also indicate that the lower detection limit of the CPC might even be smaller with the new working fluid as a higher supersaturation can be achieved. This is

due to the fact that DMSO has a far higher flaming point than butanol. This will be investigated further in cooperation with CPC manufacturers by using a custom-designed saturator block, heating and reservoir.

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465   *Contributions of co-authors.* PW and UB had the idea, PW performed all instrument maintenance, experiments and data analysis. PW and UB, OB performed the instrumental set-up. UB, PW and BF designed the LabVIEW environment of the experimental set up. MB and JS helped during instrument preparations. LK calculated the droplet size for the threshold detection. PW, OB, GS, UB and AP contributed to the manuscript and the interpretation of the results.

470

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Conflict of interest.

475   OFB is a full-time employee of TSI GmbH, a subsidiary of TSI Inc., which has a potential direct or indirect financial interest in the subject matter discussed in the manuscript.

GS and LK are full-time employees of Grimm Aerosol Technik Ainring GmbH & Co. KG, which has a potential direct or indirect financial interest in the subject matter discussed in the manuscript

The other authors declare that they have no conflict of interest.

480   *Pending Patent*

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