Intercomparison in the laboratory of various Condensation Particle Counters challenged by nanoaerosols in the range 6 – 460 nm

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Abstract. This study aims to compare the number concentration of airborne nanoparticles reported by 13 different Condensation Particle Counters (CPC) with regards to a reference CPC, for a set of aerosols of interest. Among the models investigated, 5 are handheld CPC, while the 8 others are stationary CPC. The latter include butanol-based CPC as well as water-based CPC. Polydisperse test aerosols with modal diameters between 6 and 460 nm were produced in the CAIMAN experimental facility. Non-hydrophobic aerosols consisted of metal-based particles (Ti, C, Al, Cu, Ag), as well as nebulized suspensions (SiO₂). Hydrophobic particles consisted of DEHS as well as alkanes (n-C₁₃ to n-C₂₀). Overall, about 400 different conditions were investigated to represent a wide range of aerosols potentially encountered in workplaces. The range of number concentrations provided by the reference CPC was 500 – 400 000 cm⁻³. To highlight the possible effect of particle counting efficiency on the total concentration reported by the different CPCs, 40% of the test aerosols presented a modal diameter below 40 nm. The influence of particle material for water-based CPCs was investigated through the generation of about 100 hydrophobic test aerosols. CPC response was found to be sensitive to the mode of the aerosols measured, depending on the counting efficiency curve of the CPC investigated. An effect of particle hydrophobicity on the response of some water-based CPC models was demonstrated, while one water-based CPC did not show any material dependence.

1. Introduction

Conventional exposure assessment provides information on the average exposure of workers. This approach can be completed by the use of time-resolved techniques, according to different strategies for measuring occupational exposure to airborne nanoparticles [1-6]. In addition to their chemical composition, airborne particles can be characterized by their number concentration as well as their size distribution. These characteristics are among the parameters of interest when aerosol toxicology is sought [7, 8]. When possible, a multi-metric approach is advised [9-11].

Number concentration is commonly used for airborne nanoparticle monitoring, task emission classification, or protective equipment performance evaluation against nanoparticles. The use of Condensation Particle Counters (CPCs) or their implementation as part of a strategy to assess exposure to airborne nanomaterials have been recently described in European standards (prEN 16897 [12] and
prEN 17058 [13], respectively) and guidelines from OECD [14], as well as in indoor air quality monitoring [15].

Developed over a century ago [16, 17], CPCs are based on the optical detection of particles artificially grown through the condensation of an adsorbed vapor on their surface. Because some models of CPC have been developed for being used in the field, they have been widely used (~ 60% of the cases) in workplace measurement campaigns according to a recent review [18].

Consequently, providing data on how instruments behave regarding a set of aerosols is of interest when the potential for occupational exposure is being evaluated. This study aim is to compare the number concentration of airborne particles reported by different models of CPCs with regards to a reference, freshly calibrated, CPC.

2. Materials and Methods

2.1. Test aerosols
Polydisperse test aerosols were produced in the CAIMAN experimental facility [19] produced either by electro-erosion (PALAS GFG 1000) or by nebulization (PALAS AGK 2000, home-built Laskin-type generator [20]). Overall, more than 400 different conditions were investigated to represent a wide range of aerosols potentially encountered in workplaces. Examples of number size distributions of the test aerosols are provided in Figure 1. The range of number concentrations provided by the reference CPC was $5 \times 10^2$ – $4 \times 10^5$ cm$^{-3}$, the modal diameters ranged between 6 and 460 nm.

![Figure 1. Test aerosols produced in the laboratory for the study of CPC performance](image-url)
To highlight the possible effect of particle counting efficiency on the total concentration reported by the different CPCs, 40% of the test aerosols presented a modal diameter below 40 nm. The latter were mainly produced by spark discharge between either Cu or Ag electrodes, as well as Al electrodes with low spark frequency and high dilution air flow. In addition, aerosols stemming from nebulized alkanes (n-C13 to n-C16), suspensions (SiO2) and salts (NaCl, CsCl) also led to modal diameters below 40 nm. On the contrary, aerosols with modal diameters larger than 40 nm consisted of metal-based particles (Ti, C, Al without dilution air and high spark frequency), and nebulized DEHS.

As to the influence of particle hydrophobicity for water-based CPCs, the generation of ~ 100 hydrophobic test aerosols (25%) was carried out. Hydrophobic particles consisted of DEHS as well as alkanes (n-C13 to n-C20). For each substance, a range of test aerosols was obtained by varying the nebulization device (two generators), the inlet pressure (from 0.5 to 3 bar), as well as the dilution airflow.

2.2. CPCs under study
An overview with the main technical characteristics of all CPCs is given in Table 1. In addition the CPC groups are briefly described in the following.

Table 1. Technical specifications of the different CPCs under study (manufacturers’ specifications)

| Working fluid | Model                  | Lower size (d50) [nm] | Sample flow [L min⁻¹] | Total inlet flow [L min⁻¹] | Maximum concentration [10³ cm⁻³] |
|---------------|------------------------|-----------------------|------------------------|---------------------------|---------------------------------|
| Handheld      | isopropanol            | 3007 (TSI)            | 10                     | 0.1                       | 0.7                             | 100                             |
|               |                        | 8525 (P-Trak) (TSI)   | 20                     | 0.1                       | 0.7                             | 500                             |
|               | n-butanol              | 3772-CEN (TSI)        | 7                      | 1.0                       | 1.0                             | 50                              |
|               |                        | 3776 (TSI) (TSI)      | 2.5                    | 0.05                      | 1.5                             | 300                             |
|               |                        | 3750 (TSI)            | 7                      | 1.0                       | 1.0                             | 100                             |
|               |                        | 3756 (TSI)            | 2.5                    | 0.05                      | 1.5                             | 300                             |
|               |                        | 3786 (TSI)            | 2.5                    | 0.3                       | 1.5                             | 250                             |
|               |                        | 3787 (TSI)            | 5                      | 0.6                       | 1.5                             | 400                             |
|               |                        | 3788 (TSI)            | 2.5                    | 0.3                       | 1.5                             | 10 000                          |
| Stationary    | n-butanol              | 5.403 (Grimm)         | 4.5                    | 1.5                       | 1.5                             | 10 000                          |
| Reference     |                        |                       |                        |                           |                                 |                                 |

2.2.1. Reference CPC. The CPC selected as the reference CPC is a stationary, butanol-based CPC, Grimm, model 5.403, operated in high flow mode (Qaero = 1.5 L.min⁻¹). This CPC has a counting efficiency of 50% for a particle diameter of d50 = 4.5 nm according to Heim et al. [21], operates in single-count mode for concentrations lower than 2.10⁴ cm⁻³ and in photometric mode above this limit. As mentioned above, this reference CPC was freshly calibrated before the experiment campaign.

2.2.2. Handheld CPCs. The 3007 (3 specimens) and the P-Trak (2 specimens) are small handheld devices that can be powered also on battery. They use isopropanol as working fluid which needs to be added regularly by charging the wicks. While the P-Trak has a higher d50 (20 nm) and higher maximum concentration, the CPC 3007 starts at 10 nm (d50) and has better defined internal features. Both the 3007 and the P-Trak operate in single count mode on the whole concentration range.

2.2.3. Stationary, butanol-based CPCs. The four butanol-based CPCs can be grouped into old (377x) and new (375x) CPC generation. The one CPC type is the most robust and common full-flow CPC (3772-CEN and 3750) with external vacuum pump. Both having a lower d50 of 7 nm. The other CPC type is the ultrafine butanol CPC (3776 and 3756), which uses a special design to activate also very small particles starting with d50 = 2.5 nm. All butanol-based CPCs in this work operate in the single counting mode with life-time correction, models with a photometric mode were not included.
2.2.4. Stationary, water-based CPCs. These WCPCs are the first and second generation of TSI water-based CPCs, where the older model 3786 has a different wick and water management technique compared to the 3787/-88 generation. In terms of their specifications, model 3788 is the follow-up of the 3786. Further details and characteristics on the 3788 are described in [22]. The 3786 and 3788 are designed to measure ultrafine particles from 2.5 nm (\(d_{50}\)), which means especially for the 3788 a high water supersaturation is provided to activate the growth of particles to detectable size inside the WCPC. The three models of water-based CPCs investigated in this work operate in single count mode on the whole concentration range according to the manufacturer’s specifications.

2.3. Experimental protocol
The experiments consisted in the simultaneous measurement of the number concentration by the CPCs under study and the reference CPC. In parallel, a SMPS (composed of a DMA Vienna Type, a \(^{241}\)Am neutralizer and CPC Grimm model 5.403) was used to determine the number size distribution of the test aerosols.

As stated in Bau et al. [23], the number concentrations were averaged over periods of time of 10 min and further processed as follows. Data points presenting a coefficient of variation of more than 5\%, i.e. when:

\[
\frac{\sigma}{\bar{X}} > 5\% 
\]

were disregarded. For each of the remaining data points, the ratio \(R\) between the concentration measured by one of CPCs under study (\(\bar{X}\)) and the corresponding reference concentration (\(\bar{X}_{\text{ref}}\)) was calculated according to:

\[
R = \frac{\bar{X}}{\bar{X}_{\text{ref}}} 
\]

Such calculation was performed for all the test aerosols involves, leading to a set of data for each CPC under study. The latter data were displayed as boxplots.

The range of number concentration investigated for each instrument is indicated in Table 2.

| Working fluid | Model       | Minimum concentration [\(10^3\) cm\(^{-3}\)] | Maximum concentration [\(10^3\) cm\(^{-3}\)] | \(n\) |
|---------------|-------------|---------------------------------------------|---------------------------------------------|------|
| Handheld      | isopropanol | 3007 #1: 0.46                             | 150                                         | 133  |
|               |             | 3007 #2: 5.91                             | 154                                         | 24   |
|               |             | 3007 #3: 0.44                             | 147                                         | 55   |
|               |             | P-Trak #1: 0.42                           | 169                                         | 137  |
|               |             | P-Trak #2: 0.58                           | 252                                         | 44   |
|               | n-butanol   | 3772-CEN: 8.57                            | 48.8                                        | 47   |
|               |             | 3776: 2.89                                | 315                                         | 44   |
|               |             | 3750: 2.88                                | 97.6                                        | 88   |
| Stationary    | water       | 3756: 3.09                                | 216                                         | 115  |
|               |             | 3786: 0.21                                | 161                                         | 138  |
|               |             | 3787 #1: 0.34                             | 262                                         | 150  |
|               |             | 3787 #2: 0.22                             | 190                                         | 40   |
|               |             | 3788: 2.74                                | 210                                         | 115  |
| Reference     | n-butanol   | 5.403: 0.55                               | 425                                         | 459  |
3. Results and discussion

3.1. Performance of handheld CPCs

Figure 2 presents the experimental results obtained for the category of handheld CPCs.

Generally speaking, number concentrations stemming from handheld CPCs are within an acceptable bias range of ± 20% in most cases.

As soon as the fraction of particles below 40 nm becomes large (grey boxes in Figure 2), handheld CPCs tend to underestimate the number concentration. This can be attributed to the difference in their counting efficiencies compared to the reference CPC. For this reason, grey boxes corresponding to CPC TSI 3007 are slightly higher than those obtained for P-Trak, since their cutoff diameters are 10 and 20 nm, respectively, according to Table 1.

On the other hand, for test aerosols with a modal diameter greater than 40 nm (yellow boxes in Figure 2), all handheld CPCs investigated here provide reliable number concentration, with median ratios ranging from 0.85 (3007 #3) to 1.06 (3007 #2).

3.2. Performance of stationary, butanol-based CPCs

Figure 3 presents the experimental results obtained for the category of butanol-based stationary CPCs. To our knowledge, these are the first experimental intercomparison data involving the new-generation CPCs 3750 and 3756.

Overall, when all data are considered (white boxes in Figure 3), it is worth noting that the butanol-based CPCs investigated in this work present concentration ratios close to unity, i.e. the number concentration measured by these instruments is equivalent to the one measured by the reference CPC (ratios within 0.9 – 1.1, corresponding to relative discrepancies within ± 10%). In addition, the boxes shown in Figure 3 are rather narrow, which indicates a high measurement repeatability compared to the reference.

As stated in section 3.1, it can also be noticed from Figure 3 an effect of CPC cutoff diameter on the response of the different devices. Again, this can be explained by the counting efficiency curves of the instruments. To date, the effect of the modal diameter on the response of CPC model 3750 remains unexplained. According to Table 1, this CPC should behave similarly to model 3772-CEN.
3.3. Performance of stationary, water-based CPCs

Figure 4 presents the experimental results obtained for the category of water-based stationary CPCs. In this Figure, contrary to Figures 2 and 3, the hydrophobic nature of particles constituting the test aerosols is used to investigate the behaviour of the different CPCs.

From a general point of view, Figure 4 shows wide boxplots for both 3786 and 3787 models (white boxplots), therefore involving a large variability in the number concentration reported by these instruments. On the contrary, the CPC model 3788 presents a very narrow global boxplot.

Figure 4. Experimental results for stationary, water-based CPCs
More specifically, Figure 4 highlights a significant effect of particle hydrophobicity on the response of CPC TSI models 3786 and 3787. This was already shown for model 3786 in our previous study on hydrophobic particles (DEHS) only [23], where it was demonstrated that concentration significantly decreased as soon as the reference concentration was above $\sim 35 \times 10^3$ cm$^{-3}$. This is probably due to a decrease in the efficiency of particle activation and growth inside the CPC when the water vapor saturation within the instrument is not sufficient. This can happen when the concentration of particles is too high or the size of particles is too small. On the contrary, the response of CPC 3786 is found to be equivalent to the reference CPC for non-hydrophobic particles (pink box), with a narrow 50%-confidence interval of 0.92-1.02 and a larger 95%-confidence interval ranging from 0.89 to 1.28.

In the same study [23], we previously established that model 3787 was highly sensitive to particle hydrophobicity. This has been again clearly observed on the two specimen tested in this study. Contrariwise, CPC 3787 are found to be in agreement with the reference CPC for non-hydrophobic particles (pink boxes), with median ratios of 0.91 (3787 #1) and 0.89 (3787 #2).

Concerning model 3788, experimental results underscore similar behavior whatever particle nature, since the three boxes are identical in Figure 4. This water-based CPC has a well-designed internal flow and a very high supersaturation to activate particles. It is therefore not sensitive to the material. This model of WCPC is found to be highly repeatable (narrow boxes), with 95%-confidence interval ranging from 0.93 to 1.13.

The results show clearly that a general conclusion on water-based CPCs and material dependence/underperforming with hydrophobic particle material cannot be drawn. It depends rather on the model and its design if it shows a sensitivity or not.

4. Conclusion

This study aimed at experimentally investigating the behavior of different CPCs. This work is based on the simultaneous measurement of the number concentration of test aerosols by means of a selected reference CPC (Grimm 5.403) and the CPCs under study. The test aerosols were all polydisperse aerosols with modal diameters between 6 and 460 nm, they consisted of metal-based particles (Ti, C, Al, Cu, Ag), nebulized suspensions (SiO$_2$), as well as hydrophobic particles (DEHS, n-C$_{13}$ to n-C$_{20}$). Altogether, about 400 different conditions were investigated, covering a range of particle concentrations from $5 \times 10^2$ to $4 \times 10^5$ cm$^{-3}$.

In total 9 different models of TSI CPC were investigated: handheld CPCs (3007, P-Trak), stationary, butanol-based CPCs (3772-CEN, 3776, 3750, 3756) and stationary, water-based CPCs (3786, 3787, 3788). Where possible, two or more specimens were studied to improve the robustness of the data produced. All data were displayed as boxplots to aggregate them into a single, easy-to-read, result.

The response of the CPCs was found to be sensitive to the mode of the aerosols measured, depending on the counting efficiency curve of the CPC investigated. Thereby, counter with the higher cutoff diameters, such as the P-Trak, underestimate the number concentration of test aerosols with the lowest modal diameters, when compared to the reference CPC, whose cutoff diameter is expected to be 4.5 nm. Reciprocally, for these low-mode aerosols, CPCs with the cutoff diameters lower than the one of the reference CPC indicate a concentration larger than the reference. Thus, as soon as all particles of the test aerosols are larger than the cutoff diameter of the CPCs investigated, and therefore efficiently counted, a ratio closer to unity was measured.

In addition, a significant effect of particle hydrophobicity on the response of some water-based CPCs (3786, 3787) was demonstrated; the Nano-Water CPC model 3788 was not affected. This effect is particularly important for the two specimens of CPC 3787 tested here, with all ratios below 0.6, and even as low as 0.03. Hydrophobic particles can be found in workplace atmospheres, such as in the purpose of measuring oil mists.

This work highlights the need for conducting such intercomparisons prior to field campaigns, especially when strategies involving parallel measurements are carried out. Indeed, such studies help
better define the scope of use of each instrument, and provide elements that enable explain the possible discrepancies between them when used in parallel.

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