Performance study of various Condensation Particle Counters (CPCs): development of a methodology based on steady-state airborne DEHS particles and application to a series of handheld and stationary CPCs

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Abstract. Strategies for measuring occupational exposure to aerosols composed of nanoparticles and/or ultrafine particles highlight the use of techniques for determining airborne-particle number concentration as well as number size distribution. The objective of the present work was to set up a system for conducting laboratory verification campaigns of condensation particle counters (CPCs). Providing intercomparison data as well as calibrating and checking CPCs are among the key elements in ensuring reliable laboratory or field measurement campaigns. For this purpose, the reproducible aerosol source "Calibration Tool", initially developed by the Fraunhofer ITEM, was acquired by the Laboratory of Aerosol Metrology at INRS. As a first part of this study, a detailed characterization of the Calibration Tool developed at the laboratory is the subject of the parametric study presented here. The complete installation is named the "DCC" for "Device for Counter Check". Used in combination with a reference counter, the DCC can now be used for routine laboratory measurements. Unlike that used for primary calibration of a CPC, the proposed protocol allows a wide range of number concentrations and particle sizes to be investigated and reproduced. The second part of this work involves comparison of the number concentrations measured by several models of CPC in parallel at the exit of a flow splitter, with respect to a reference.

1. Introduction

Atmospheric, indoor and workplace air naturally contains particles below 1 µm in size [1, 2]. In workplace atmospheres, these submicron particles may originate from a variety of sources, including combustion processes, diesel exhaust, thermal spraying of metals, or energetic processes such as welding and grinding [3-7].

Nanomaterials offer applications in fields as wide-ranging as health, food and agriculture, energy, materials, and transport. However, their unique properties have raised questions about their potential related health effects. Due to the rising use of nanomaterials, the number of exposed workers in research laboratories and public or private industry is probably increasing at all stages of the lifecycle of these products – from synthesis, use and ageing [8], through to disposal [9, 10], waste treatment, and maintenance [11, 12] – as well as in accidental exposure situations [13, 14]. Assessing inhalation exposure to airborne nanoparticles therefore constitutes an important challenge [15], and providing robust data related to the performances of instruments devoted to the measurement of submicron particles is crucial prior to their wider use in occupational hygiene.

To complete conventional sampling approaches, which provide information on the average exposure of workers, different strategies for measuring occupational exposure to airborne nanoparticles, highlighting the use of time-resolved techniques, have been developed [16-20]. 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 [21]. When possible, a multi-metric approach is advised [22-24].

1.1. Context and outline of the study

This work focuses on the condensation particle counter (CPC), an instrument devoted to the measurement of submicron particle number concentrations. First developed over a century ago [25, 26], these instruments are based on the optical detection of particles artificially grown through the condensation of an adsorbed vapor on their surface. The devices record the number concentration of airborne particles per unit of air volume. Because of their field portability, CPCs are considered reliable devices for workplace air measurement.

In order to ensure adequate data interpretation, the performances of CPCs need to be well described. In most cases, calibrations performed by independent companies (except CPC producers and distributors) are limited to a concentration range of between approximately 100 cm^{-3} and 10 000 cm^{-3}. This range is narrow compared to the levels of aerosol number concentrations that can be measured in workplace atmospheres.

In parallel, occupational exposure limits (OEL) expressed in terms of number concentration of airborne nanoparticles have been proposed in Germany by the IFA [27] and in the United Kingdom by the BSI [28]. At present, limit values based on particle numbers already exist for clean rooms [29] as well as for diesel exhaust, for example in the framework of the Euro V label. Furthermore, number concentration is the most frequent characteristic used for airborne nanoparticle monitoring, task emission classification, and for evaluating the performance of protective equipment against nanoparticles.

Given these various issues, a methodology for checking CPCs is essential to ensure reliable laboratory or field measurement campaigns.

1.2. Objective

To date, there is no standard that allows the accuracy of a CPC to be verified [30]. *Calibration* of a CPC requires a combination of a differential mobility analyzer (DMA) and an aerosol electrometer [31], which are expensive devices.

This work aims were to develop, validate and test a methodology for *checking* CPCs at the INRS Laboratory of Aerosol Metrology. *In the first stage of this study*, the aerosol to be measured was characterized by different CPCs in terms of size distribution, total concentration, time stability, reproducibility, etc. *In the second stage*, the test protocol and data treatment procedure were developed and validated. Finally, *in the third stage of this work*, the complete protocol was carried out using several different types of CPCs (both handheld and stationary models). A freshly calibrated CPC was used simultaneously as a reference measurement in compliance with standard prEN 16897 [30].

2. Test aerosol characterization

2.1. Aerosol source: The Calibration Tool

Controlled concentrations of aerosols were generated using the Calibration Tool developed by Koch *et al.* [32, 33]. This generator produces DEHS droplets by evaporation/condensation processes, which are then fed into a continuously stirred tank reactor, as shown in Figure 1.

The feed aerosol is formed in a turbulent coaxial jet inside the reactor. A hot saturated stream of an organic vapor is fed through a nozzle and generates nuclei in the inner jet by homogeneous nucleation when the inner jet is mixed with the surrounding cold clean air flow. These particles grow further

through condensation and coagulation. The product aerosol in the tank reaches a stationary state that is spatially and temporally homogeneous (self-preserved distribution) after around one hour of operation. This results in a very stable and reproducible production of particles.

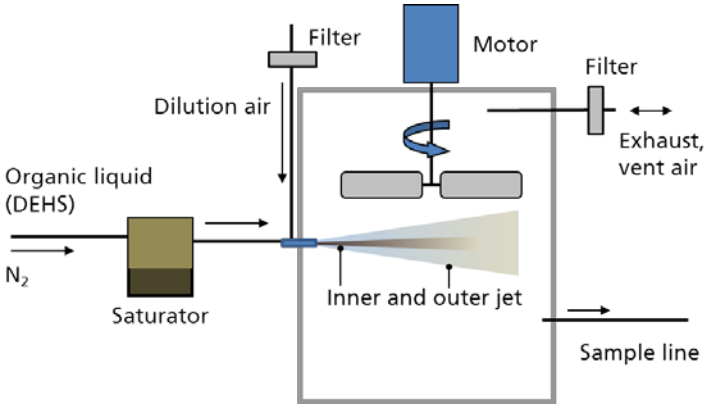

Figure 1. Schematic diagram of the Calibration Tool (courtesy of W. Koch).

As an example, Figure 2 presents the number size distribution of the aerosol produced, measured over 6 days after 5 hours of continuous operation. It can be concluded from Figure 2 that the mode of the distribution is around 60 nm, with less than 7 % variability observed over the 6 days. Furthermore, the total number concentration is around 2.10^7 cm^{-3}, associated with a variation coefficient of less than 3 %.

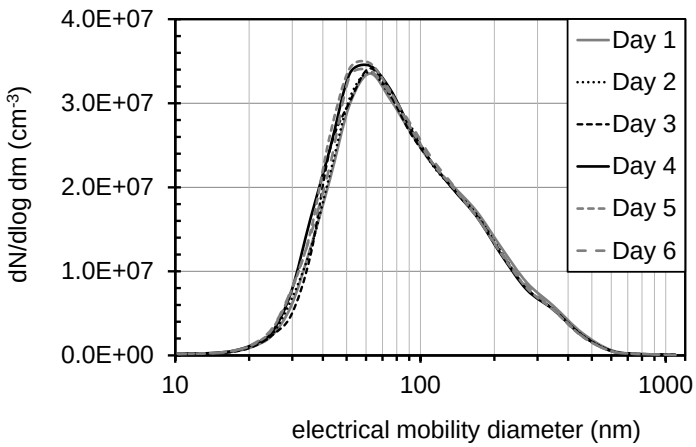

Figure 2. Number size distribution of the aerosols produced within the Calibration Tool over 6 days.

2.2. The Device for Counter Check (DCC)

The DCC consists of a generator (the Calibration Tool), a specific sampling and dilution line, and a reference CPC, as shown in Figure 3. In terms of the technical configuration, a manual valve was placed directly in the aerosol line, which is connected to a HEPA-filtered air inlet and a homogenization chamber. Thus, the aerosol concentration at the outlet can be easily controlled by turning the valve.

Because of the dilution and coalescence processes that occur between the sampling from the reactor and measurement at the CPC, the number size distribution as well as the total concentration of the

aerosols are different to those presented in Figure 2; the modal diameter of the size distribution of the aerosols ranges from 220 nm to 140 nm for total concentrations of 2.10^4 to 2.10^5 cm^{-3} (Figure 4).

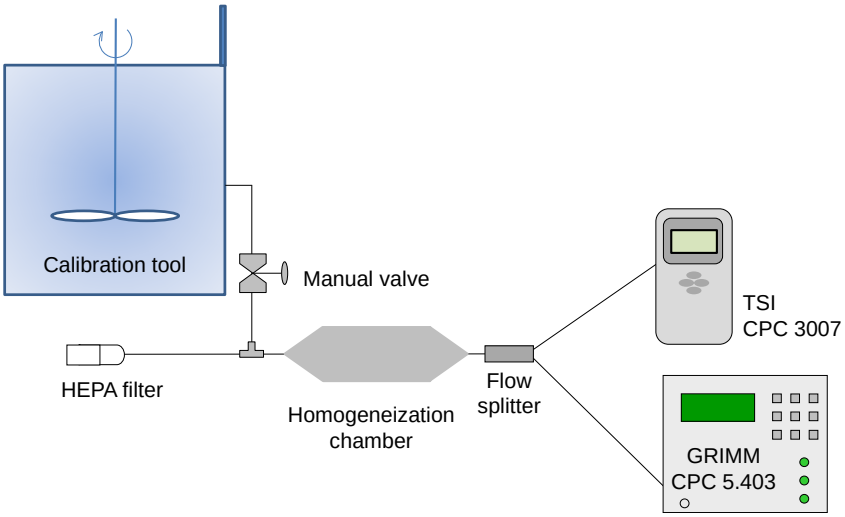

Figure 3. Schematic diagram of the Device for Counter Check (DCC).

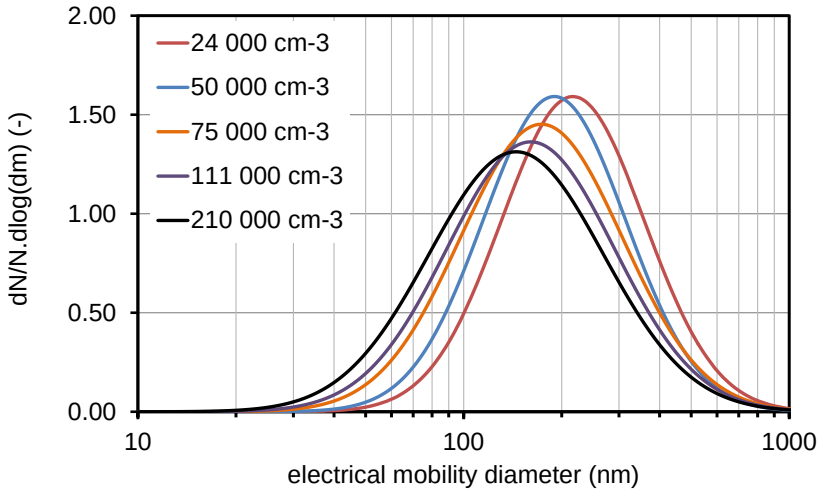

Figure 4. Number size distribution of the aerosols for different total number concentrations.

3. Testing methodology and data treatment

The following steps must be rigorously adhered to when a CPC checking campaign is conducted:

- Turn on the Calibration Tool and wait for one hour for the aerosol to stabilize.
- Turn on the CPC under study and the reference CPC.
- Adjust the dilution ratio using the manual valve so that it fits within the concentration range for all CPCs.
- Once the concentration is stable, perform a measurement for 10 minutes.
- Modify the dilution ratio to cover the widest concentration range (10^2 to 10^5 cm^{-3}).

The data treatment procedure involves the following steps:

- For each concentration level, calculate the average concentration $\bar{X}$ and the corresponding standard deviation σ for all CPCs (those being studied as well as the reference CPC):

$$\bar{X} = \frac{\sum_{i=1}^{n} x_i}{n}$$

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{X})^2}{n}}$$

where n is the number of points and x_i is the number concentration measured at time i.

- Disregard any data points presenting a coefficient of variation of more than 5%, i.e. when:

$$\frac{\sigma}{\bar{X}} > 5\ \%$$

- For each of the remaining data points, calculate the ratio R between the concentration measured by one of CPCs under study ($\bar{X}$) and the corresponding reference concentration ($\overline{X_{\mathrm{ref}}}$):

$$R = \frac{\bar{X}}{\overline{X_{\mathrm{ref}}}}$$

- Perform this calculation for all concentration levels tested, and present the data as boxplots. In these graphs, the box surrounding the median value corresponds to the 1st and 3rd quartiles, while the error bars represent the 95% confidence interval.

4. Implementation of the methodology on various CPCs and discussion

The reference CPC used in this study was a butanol-based stationary CPC, Grimm model 5.403, operated in high flow mode (1.5 L.min^{-1}). The instrument was calibrated prior to the measurements. The levels of concentration investigated ranged from 10^3 to 10^5 cm^{-3}, thus corresponding to the specified range of concentration for all of the CPCs tested.

4.1. Handheld CPCs

The experimental results for the different handheld CPCs are presented in Figure 5.

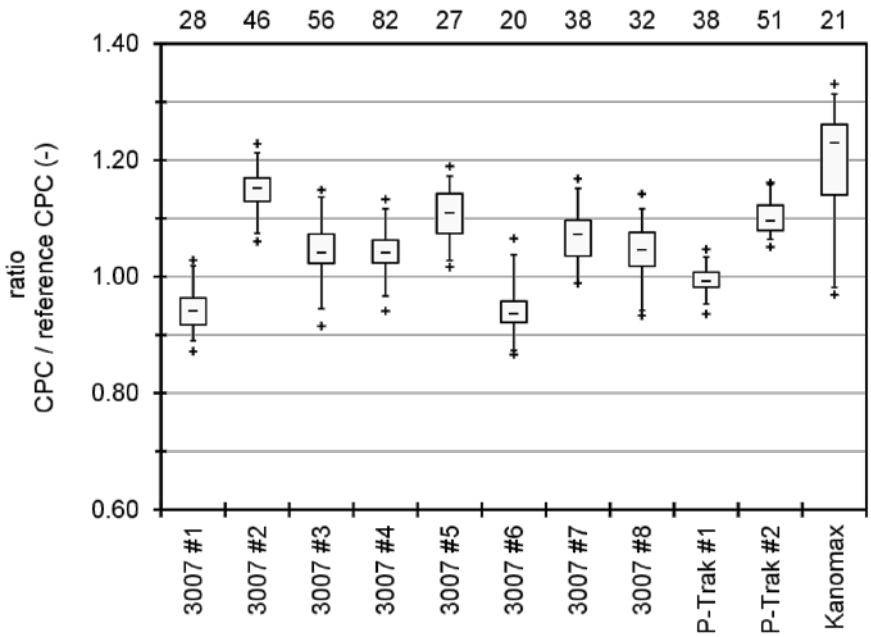

Figure 5. Boxplot of the responses of the different handheld CPCs studied.

As seen in Figure 5, all CPCs were found to lie within ± 25% deviation from the reference, except for the Kanomax CPC, which also presented the largest span, from 0.97 to 1.33. Furthermore, it can be observed from Figure 5 that different specimens of the same CPC model (TSI 3007) can differ significantly, e.g. the response of CPC 3007 #2 and 3007 #6 varies by up to 25%.

4.2. Stationary CPCs

The experimental results for stationary CPCs are presented in Figure 6.

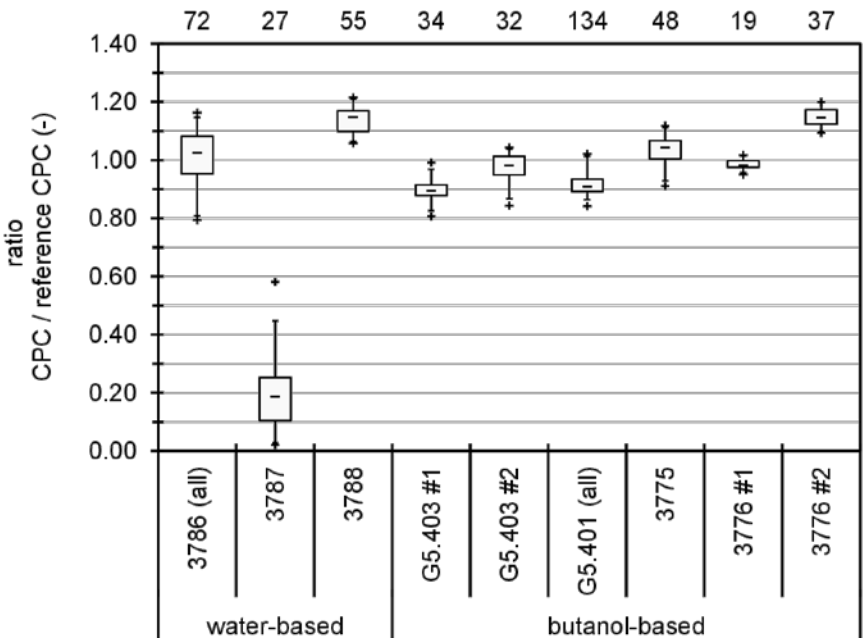

Figure 6. Boxplot of the responses of the different stationary CPCs studied.

Figure 6 shows that all of the CPCs studied were found to lie within ± 25 % of the reference, except model TSI 3787, which is known to be highly sensitive to particle hydrophobicity. Nevertheless, large spans, in particular the magnitude of the 95% confidence interval compared to the 50% confidence interval, are observed in the experimental data from CPC models TSI 3786 and Grimm 5.401.

4.3. Discussion

The compared behaviors of CPCs need to be considered when two specimens of the same model of CPC are used in workplace situations. Indeed, strategies for exposure assessment to airborne nanomaterials [16-20] advise the parallel use of a CPC near the source and another positioned far-field. Combined with results from intercomparison studies, the measured concentrations should be further interpreted by means of statistical analysis [34-38].

Although the median ratios lie within the tolerated uncertainty, significant differences between different models of CPC may lead to wrong conclusions if the devices are used in parallel. In the case of handheld CPC model TSI 3007, placing 3007 #2 near the source and 3007 #6 far-field may result in the conclusion that airborne particles are emitted by the process (as the concentration measured by CPC 3007 #2 near the source is higher than that measured far-field by 3007 #6) even in the absence of additional particles from the expected aerosol source.

The example of CPC model TSI 3786 is detailed in Figure 7, which presents the results of the concentrations measured by the CPC and the corresponding reference concentration, as well as the ratio (top, right axis) calculated for each situation.

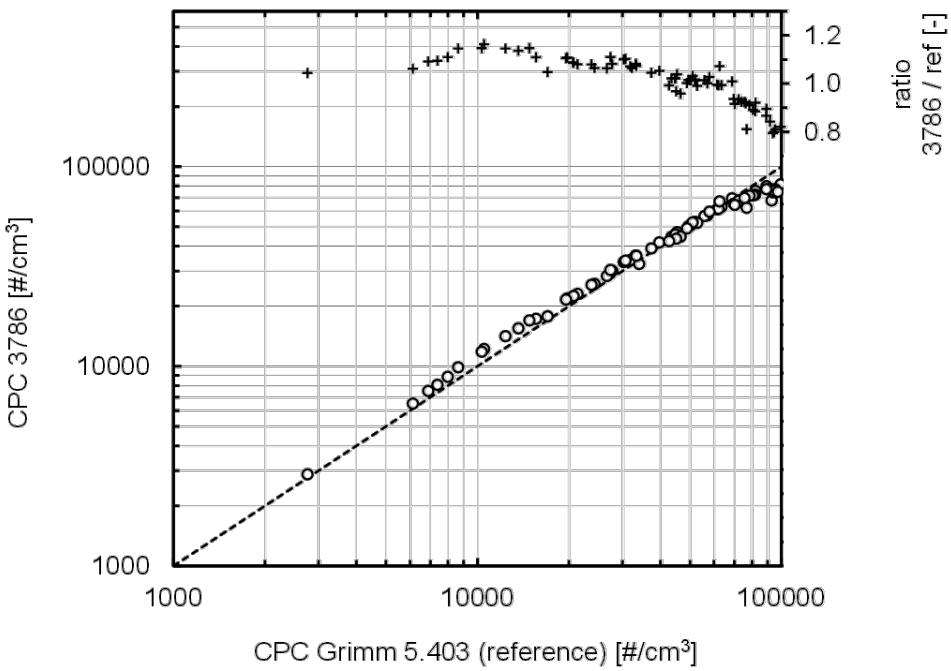

Figure 7. Response of CPC model 3786 (absolute concentration and concentration relative to the reference).

It is clear from Figure 7 that particle concentration has an effect on the response of CPC model TSI 3786. In particular, the ratio seems quite constant at around 1.1 for total number concentrations below approximately 35 000 cm^{-3}. However, at higher concentrations, the CPC under investigation starts to underestimate the number concentration of the aerosol.

This decrease in the number concentration reported by CPC model TSI 3786 might be related to unsaturated nuclei within the saturation chamber due to particle hydrophobicity. In contrast, CPC model TSI 3788 is not affected by particle hydrophobicity, as can be seen in Figure 6. This can be explained by differences in saturation / condensation temperatures, as well as in sheath air and aerosol flows within the instruments.

The case of CPC model Grimm 5.401 is described in Figure 8. This case is interesting because it clearly highlights a change in the concentration ratio from 1.0 for concentrations below 10^4 cm^{-3} to 0.9 for concentrations above 10^4 cm^{-3}. The 10^4 cm^{-3} limit corresponds to the switch from single count mode to photometric mode.

As a consequence, restricting TSI model 3786 response to number concentrations below 35 000 cm^{-3} and considering two different intervals ($< 10^4$ cm^{-3} and $> 10^4$ cm^{-3}) for the Grimm model 5.401 results in the boxplots presented in Figure 9. Compared to Figure 6, these results now show smaller confidence intervals, suggesting that the restricted intervals of concentration considered are compliant.

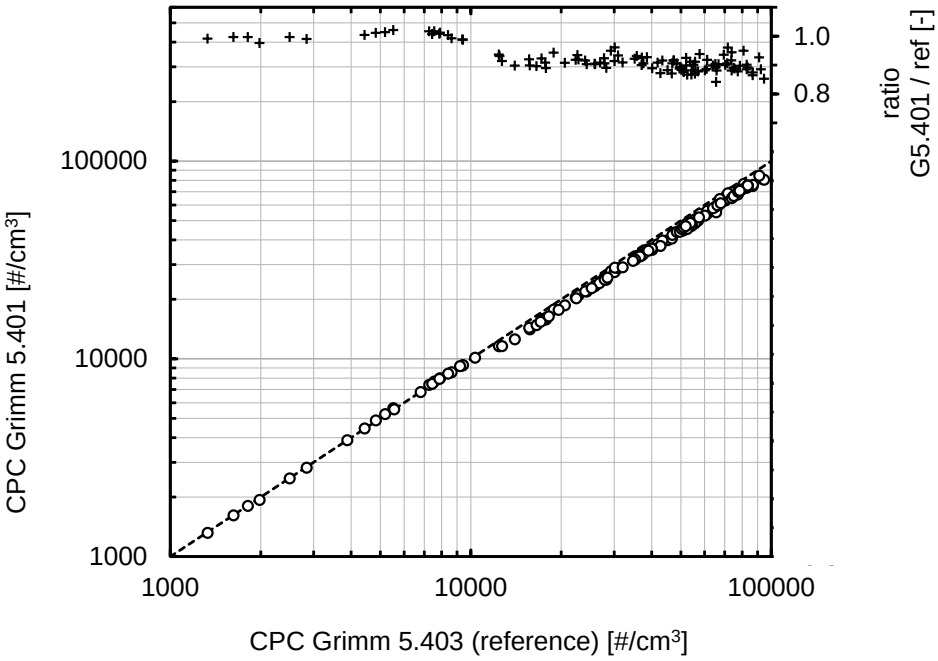

Figure 8. Response of CPC model 5.401 (absolute concentration and concentration ratio compared to the reference).

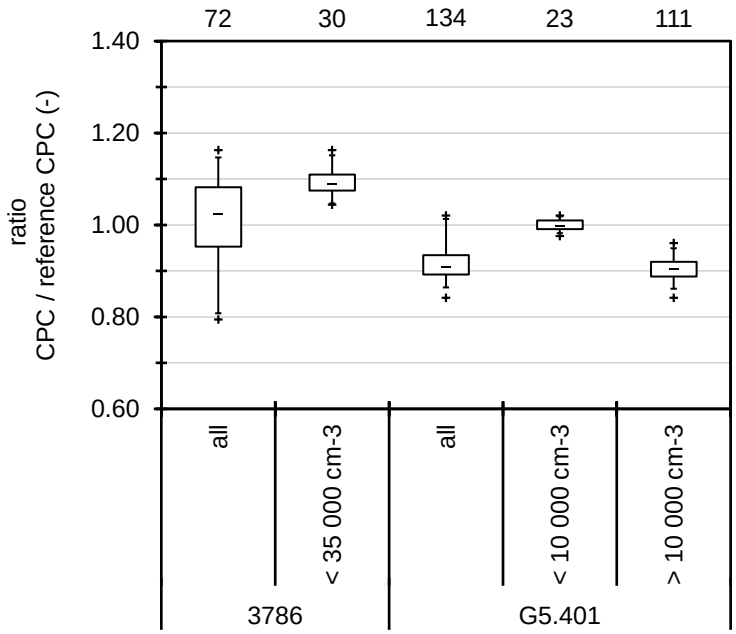

Figure 9. Detailed boxplot of the responses of CPCs 3786 and 5.401.

5. Conclusion

Strategies for assessing occupational exposure to airborne nanomaterials highlight the use of time-resolved techniques to determine, among others, number concentration and size distribution. The objective of this work focused on development of a methodology to check the accuracy of Condensation Particle Counters (CPCs) prior to laboratory or field measurement campaigns.

For this purpose, the Calibration Tool initially designed by ITEM Fraunhofer was acquired by the laboratory of Aerosol Metrology at INRS. Combined with an in-house dilution line and a reference CPC, the Device for Counter Check (DCC) can now be used under routine conditions according to a specific protocol.

This work must now be pursued for a wider range of CPCs in order to establish a map of their performance. Once checked, an inter-comparison campaign using various CPCs must be carried out on a wide variety of aerosols. This step will help to better define their scope of use and to investigate their performance when challenged by aerosols representative of those encountered in the air in workplaces.

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