RESEARCH PAPER

Harmonisation of nanoparticle concentration measurements using GRIMM and TSI scanning mobility particle sizers

Manish Joshi · B. K. Sapra · Arshad Khan · S. N. Tripathi · P. M. Shamjad · Tarun Gupta · Y. S. Mayya

Received: 9 July 2012/Accepted: 25 October 2012 © Springer Science+Business Media Dordrecht 2012

Abstract Regional studies focusing on the role of atmospheric nanoparticles in climate change have gained impetus in the last decade. Several multiinstitutional studies involving measurement of nanoparticles with several kinds of instruments are on the rise. It is important to harmonize these measurements as the instruments may work on different techniques or principles and are developed by different manufacturers. Scanning mobility particle sizers (SMPS) are often used to measure size distribution of nanoparticles in the airborne phase. Two such commercially available instruments namely, GRIMM and TSI-SMPS have been compared for ambient and laboratory generated conditions. A stand-alone condensation particle counter (CPC) of TSI make was used as a reference for particle concentration measurements. The consistency of the results in terms of mean size and geometric standard deviation was seen to be excellent for both the SMPSs, with GRIMM always showing slightly (approximately 10 %) lower mean size. The integrated number concentration from GRIMM-SMPS was seen to be closer to stand-alone reference CPC compared to TSI-SMPS, for an

S. N. Tripathi · P. M. Shamjad · T. Gupta Department of Civil Engineering, Indian Institute of Technology, Kanpur 208016, India ambient overnight comparison. However, a concentration-dependent response, i.e. the variations between the two instruments increasing with the concentration, was observed and possible reasons for this have been suggested. A separate experiment was performed for studying the modifying effect of diffusion dryer and sheath air dryer on the measured aerosol size spectra. A significant hygroscopic growth was noted when diffusion dryer was attached to one of the SMPS. The introduction of sheath air dryer in GRIMM-SMPS produced a significant shift towards lower mean size. These results have been compared and discussed with the recent inter-comparison results to strengthen and harmonize the measurement protocols.

Keywords Nanoparticles · Harmonisation · SMPS · TSI · GRIMM · Sheath air dryer

Introduction

The relative significance of using aerosol number concentration limits in place of traditional particulate matter (PM)-based limits has been unfolding steadily. Ultrafine/nanoparticles (with geometric diameters less than 100 nm) contribute negligibly to the integral mass concentrations used in the PM limits; however, the number of these particles has shown to have a direct bearing on the health effects (Peters et al. 1997).

M. Joshi · B. K. Sapra (⊠) · A. Khan · Y. S. Mayya Radiological Physics and Advisory Division, Bhabha Atomic Research Centre, Mumbai 400094, India e-mail: bsapra@barc.gov.in

On the other hand, $PM_{2.5}$ and PM_{10} (particles with aerodynamic diameters less than 2.5 and 10 µm, respectively) may not be proper indices for linking the effect of ultrafine aerosols with human health (Biswas and Wu 2005). The findings of Particle Measurement Programme (Giechaskiel et al. 2008a, b) have prompted the introduction of particle concentration measurements in Euro 5/6 legislation. Simultaneously, a lot of research effort has been evolved in the past few years targeting towards estimating the potential hazard of nanoparticles. The first step towards the hazard assessment, however, is the correct measurement of the property of interest and proper interpretation of the data produced.

There are several methods available to measure particle concentrations and size distributions of nanoparticles (e.g. condensation particle counter, electrical low-pressure impactor, scanning mobility particle sizer, fast mobility particle sizer, etc.). Of these, condensation particle counter (CPC) for nanoparticle concentration and scanning mobility particle sizer (SMPS) for size distribution are widely used for environmental and workplace measurements. The latter is a CPC coupled with differential mobility analyzer (DMA). The CPC samples the aerosols at a constant flow rate through a saturator, a condenser and an optical detection assembly. It gives the integral number concentration of particles larger than the stated minimum detection size. The counting efficiency and the effective flow rate are required to be known precisely for correct measurements. Also, the uncertainties in these parameters and knowledge of coincidence error and shifting of counting logic from single particle mode to photometric mode (at high concentrations) should be known, while employing a CPC. Recent years have seen the development of CPCs based on water instead of butanol, and these have been compared and evaluated (Hering et al. 2005; Biswas et al. 2005; Mordas et al. 2008).

The SMPS employs the principle of size classification based on particle mobility in an applied electric field. It utilizes a continuous scanning voltage to impart varying mobility to particles and a complex inversion scheme to deduce the particle sizes from the mobility spectrum. The accuracy of SMPS measured size distribution is governed by several parameters such as the DMA construction, sampling and sheath air flow rates, voltage accuracy, particle charge distribution, CPC counting efficiency, particle transport time and particle transmission efficiency (Watson et al. 2011). The SMPS is generally calibrated using spherical particles (Mulholland et al. 2006). In most cases, calibration is only with respect to size and not particle concentrations due to the absence of reference particle number concentrations; although a few attempts have been made for the latter (Koch et al. 2008).

There are several versions of CPCs and SMPSs available, primarily developed by TSI (Shoreview, MN, USA) and GRIMM (Grimm Aerosol Technik GmbH & Co. KG, Ainring, Germany). The intercomparability of these commercially available systems has been an important issue of investigation. This is specially so in the context of the data reported in the literature using different versions. Meaningful inferences from these data are only possible if the systems used to measure them are well-evaluated vis-à-vis each other. Evolving a protocol for SMPS operation is also an important step in this direction. This is all the more essential for multi-institutional collaborative programs (such as field campaigns etc.) wherein quantities of interest are measured using systems from different manufacturers. Leskinen et al. (2012) highlighted the importance of produced data about the suitability of the aerosol measurement instruments for real-time nanoparticle exposure estimation.

In the absence of an absolute standard, intercomparisons become imperative and only means of checking the accuracy and reasonableness of measurements. Some inter-comparison studies have been carried out on size-classifying particle concentration measurement systems. Ankilov et al. (2002) reported an agreement within a factor of 2 in a comprehensive comparison exercise involving sixteen different instruments. Asbach et al. (2009) compared four mobility sizers (TSI-SMPS, GRIMM-SMPS and Fast Mobility Particle Sizer) against laboratory generated sodium chloride and diesel soot particles. Helsper et al. (2008) compared the TSI-CPC results with the GRIMM and TSI-SMPS results. They reported 1.48 times higher concentrations with GRIMM (with short DMA) compared to a simultaneously running TSI-CPC. In a recent study by Watson et al. (2011), four SMPS instruments (TSI nano, TSI standard, GRIMM-SMPS and MSP wide range spectrometer) were compared for a month-long ambient exposure.

This work presents the detailed inter-comparison of GRIMM-SMPS (model no 5.403C) available at Bhabha Atomic Research Center (BARC) and the TSI-SMPS (classifier 3080 with CPC 3775) available at the Indian Institute of Technology, Kanpur (IITK). This will serve as a prelude and also strengthen the confidence on the aerosol measurements to be carried out as part of a collaborative project between the two laboratories. Also, inferences will be drawn about the capabilities of these instruments in measuring the nanoparticles. Experiments have been carried out under both controlled and ambient conditions. The instruments have been challenged to laboratory test particles (generated by atomisation of sodium chloride and ammonium sulphate solutions) and ambient particles, respectively.

A more intuitive and appropriate approach for a systematic evaluation of the performances would be to compare the responses of the accompanying CPCs before comparing the SMPSs. This will help in identifying the sub-system which is a likely source of the underlying variations, if any, observed in the SMPS measurements. Hence, as a first level of comparison, only the CPCs of both the SMPSs were compared to a stand-alone TSI-CPC (available with IITK, model no CPC 3776) which was taken as a reference. The results indicated the concentration-dependent relative differences between these units. Subsequently, the second level of comparison was between the two SMPSs. The results again showed an increase in the variations as the sampling conditions varied from ambient low aerosol concentrations to high concentration environment. This study discusses the reasons for the CPC differences at differing concentrations. The study also attempts the re-assessment of the SMPS differences observed for the past studies, but conducting experiments for similar device conditions with varying aerosol concentrations at the same place. The main aim of this study is to harmonize the differences observed for SMPS measurements by linking it with CPC differences and other factors such as the role of neutralisation efficiencies, inversion schemes, etc.

Another important issue presented as a part of this study is the effect of diffusion dryer and sheath air dryer (recommended in the recently developed protocols for using SMPSs) on measurements, particularly under humid conditions. The modification of results with the use of these accessories and its implications have been experimentally studied and discussed.

Experimental methods

Experiments were performed at Indian Institute of Technology (IIT) campus in Kanpur, India (26.5°N, 80.3°E, 142 m above mean sea level). For comparison with laboratory generated aerosols, a small cuboidal chamber of volume 40 L with an in-built fan to homogenize the aerosols was used. The chamber had four sampling ports which were judiciously used depending on the context and objective of the experiments performed. The experimental set-up and the SMPS versions are shown in Fig. 1a, b, respectively. The lower port of the chamber was connected to a commercial atomizer (TSI aerosol generator 3079) which was operated at the same air flow rate for all chamber experiments. The atomized aerosols were conditioned using silica bead diffusion dryer before entering into the chamber. One of the upper ports was used with a flow divider to which GRIMM-SMPS, TSI-SMPS (hereafter, referred to as G-SMPS and T-SMPS, respectively) and a TSI-CPC (referred to as T-CPC) were connected. One of the ports was connected to other devices used for other measurements (not part of this study). The features of the three CPCs and two SMPSs are listed in Table 1.

The flow rate at every sampling port was always verified prior to and usually during the experiments. All three instruments were operated at their default flow setting i.e. at aerosol sampling flow rate of 0.3 Lmin^{-1} and sheath air flow rate of 3 Lmin^{-1} . The aerosol exit provided at one port was through a HEPA filter. Electrically non-conducting flexible sampling tubes were used to minimize the losses due to aerosol charges. To avoid ambiguities, similar length (and orientation) of sampling tubes was used for all the instruments being compared, with the tube length after the flow divider being 0.5 m. Total tube length representing the sampling path was 1 m for each of the instruments. For this length and tube geometry, aerosol losses during tube transit were found to be insignificant. The scan time for distribution measurement was also matched for both the devices. The best available standard protocols (Wiedensohler et al. 2012) were followed for intercomparison exercises.

For the chamber experiments, sodium chloride (NaCl) and ammonium sulphate $((NH_4)_2SO_4)$ solutions were used for generating aerosols. For ambient aerosol experiments, sampling was performed on two



Fig. 1 a Experimental set-up used for chamber experiments b Photographs of GRIMM-SMPS (5.403) and TSI-SMPS (3775) used in the study

Table 1	Parameters	of the	SMPSs	used	in	the	study
---------	------------	--------	-------	------	----	-----	-------

Parameter	G-SMPS	T-SMPS	Stand-alone T-CPC
Model	5.403C	3696	_
DMA	Vienna type	TSI-3081	-
Aerosol sampling rate (L min ⁻¹)	0.3	0.3	-
Sheath air flow rate (L min^{-1})	3	3	_
Neutralizer	Am ²⁴¹ (alpha emitter)	Kr ⁸⁵ (beta emitter)	-
Diameter range (nm)	11.1-1083.3 nm	14-800 nm	-
Impactor	1,185 nm	1,282 nm	-
CPC type	Butanol based	3775: Butanol based	3776: Butanol based
CPC maximum concentration	$10^7 {\rm ~cm^{-3}}$	$10^{7} { m cm}^{-3}$	$10^{6} {\rm ~cm^{-3}}$
CPC lower limit	4.5 nm	4 nm	2.5 nm
Single particle counting threshold	$1.4 \times 10^4 {\rm ~cm^{-3}}$	$5 \times 10^4 \mathrm{~cm^{-3}}$	$3 \times 10^5 \text{ cm}^{-3}$

separate days, one in February 2011 (4–5 February) and other in July 2011 (19 July). The February sampling was performed overnight while July sampling was during the daytime. A third experiment was performed in controlled chamber conditions to determine the effect of diffusion dryer and sheath air dryer

on the SMPS measurements results. The reasons, benefits and possible effects of these dryers have been mentioned in the recommended measurement protocol for SMPS measurement (Wiedensohler et al. 2012). We analysed the effect of these devices on comparative SMPS measurements as an extension to our study. For all experiments, TSI data were analysed using Aerosol Instrument Manager (version 7) while GRIMM used SMPS version 1.35 build 1.

Results and discussions

The significance of carrying out experiments with both ambient and laboratory generated aerosols was to study the concentration-dependent response of the instruments. For example, Schlatter (2006) showed that the CPC of the SMPS itself accounts for the sizable differences in the aerosol concentrations reported for values more than $5,000 \text{ cm}^{-3}$. Below a threshold (see Table 1), single count mode with coincidence correction is applied in CPCs while above this concentration; photometric mode is used where calibration is performed with respect to total scattered light intensity. With increase in concentration, shifting of the counting logic to photometric mode can contribute to the differences between CPCs. However, prior to commenting on the concentration-related performance, calibration of the systems used in the study using standard particles was undertaken. The results of the experiments performed are discussed here.

Calibration tests using standard particles

In order to check the sizing accuracy of G-SMPS and T-SMPS, calibration tests were performed in the test chamber. Certified (Duke Standard) Polystyrene Latex (PSL) particles of two different sizes (299 and 499 nm) were used in these tests. Atomized PSL particles were injected into the test chamber after passage through the diffusion dryer. After establishing steady state concentration, average size distribution recorded by G-SMPS and T-SMPS were compared. Figure 2 presents the SMPS distributions for PSL stated sizes of 299 and 499 nm. As may be seen, the observed peaks for G-SMPS and T-SMPS were 2.68 and 4.01 %, respectively, away from the stated PSL size of 299 nm. Similarly, for the 499 nm PSL size, this difference was seen to be 4.41 and 1.20 %, respectively. Further, we nebulized blank de-ionized water (without adding PSL) and no significant numbers were seen at these stated sizes. Given the uncertainty in the PSL size $(\pm 2.5 \%)$ and other possible experimental uncertainties, the results were



Fig. 2 Size response of G-SMPS and T-SMPS for 299 and 499 nm PSL particles

well within the confidence to proceed further. The calibration of CPC's was not performed for number concentration but their performances for low concentration condition was tested. All CPC's matched well within acceptable limits as will be shown in ambient comparison results.

Comparisons using laboratory generated particles

Prior to comparing the SMPSs, the CPCs of both the SMPSs were compared with the stand-alone T-CPC in the test chamber, using particles generated from atomized sodium chloride solution (0.01 % v/v). Just prior to the injection of atomized aerosols, stand-alone T-CPC which recorded 21172(\pm 1290) cm⁻³ average particle concentration showed higher concentration by a factor of 1.089(\pm 0.096) and 1.049(\pm 0.100) compared to CPCs of T-SMPS and G-SMPS. On injection of the test aerosols (concentration measured by stand-alone T-CPC was 40752(\pm 6452) cm⁻³), this factor changed to 1.177(\pm 0.273) and 1.070(\pm 0.241) for CPCs of T-SMPS and G-SMPS, respectively (Fig. 3).



Fig. 3 Time series plot of the NaCl particle concentrations recorded by the three CPCs

This observation is in agreement with the work of Schlatter (2006) wherein a 5 % variation (factor of 1.05) was seen up to 1,000 particles cm^{-3} which increased to 10 % (factor of 1.1) for 10,000 particles cm^{-3} . A larger variation in the present study is seen owing to higher observed concentrations. The limits of single particle mode counting for these devices is shown in Table 1. Considering stand-alone CPC as reference for this case (since it uses single particle counting mode for both concentrations), the factor of difference increased for both CPCs i.e. of G-SMPS & T-SMPS when concentration was increased in the chamber. Since CPC of G-SMPS was measuring concentrations in the photometric mode for both cases (chamber ambient and particle injection), the factor increased slightly from 1.049 to 1.07. Relatively, this factor increased more in case of CPC of T-SMPS since it measured concentrations in single particle mode and transition mode for background and after injection, respectively. The concentration difference factor of the two CPCs (ratio of concentration measured by CPC of G-SMPS and of T-SMPS) increased from 1.038 to 1.095 for the above case. The transition to photometric mode at differing thresholds and the inherent calibration, instrumental and sampling variations contributed to these observed differences. It should also be noted that, both CPCs of TSI had a difference of 8.9 % even at lower chamber ambient case which still can be taken as acceptable. It has been shown in previous studies that small changes in instrument settings or flows inside the instruments can contribute to the measurement differences between different systems. For example, even a small change in thermistor settings can cause a difference of concentrations between CPCs (Lui and Deshler 2003). So, it is reasonable to accept the variations of different models (of different age) even if they are factory calibrated. However, it would be interesting to see the performances of these CPCs at still lower ambient concentrations.

The second step was the comparison of G-SMPS and T-SMPS in controlled chamber conditions using two different types of test particles generated from sodium chloride (0.01 % v/v) and ammonium sulphate (0.03 % v/v) solutions. After conditioning through the diffusion dryer, these were passed into the chamber. The steady state average size distribution for NaCl and (NH₄)₂SO₄ aerosols measured by the G-SMPS and T-SMPS are as depicted in Figs. 4 and 5. For NaCl particles, the geometric means recorded by the T-SMPS and the G-SMPS were 64 and 53 nm (G-SMPS 15.6 % lesser than T-SMPS), respectively. The geometric standard deviations obtained from the size distributions were similar at 1.88 and 1.87, respectively. The total number concentrations were compared in the common size ranges of the two SMPSs. It was found that the G-SMPS showed a higher concentration by a factor of about $1.881(\pm 0.078)$. For $(NH_4)_2SO_4$ particles, the geometric mean measured by G-SMPS was 10.3 % lesser than the T-SMPS and the total particle concentration was higher by a factor of $1.725(\pm 0.279)$. Asbach et al. (2009), in their study on laboratory comparisons with NaCl aerosols, obtained a factor of 1.42-1.7 with GRIMM showing higher number concentrations with almost similar inferences for mean size differences.



Fig. 4 Size distribution comparison for NaCl aerosols



Fig. 5 Size distribution comparison for (NH₄)₂SO₄ aerosols

An internal analysis of the size-wise variations in the particle concentrations was also carried out and the relative concentration factor (RCF) was estimated as:

$$\mathrm{RCF} = \{C_{\mathrm{G}} - C_{\mathrm{T}}\}/C_{\mathrm{T}}$$

where $C_{\rm G}$ and $C_{\rm T}$ are the particle concentrations measured by the G-SMPS and T-SMPS, respectively. RCF is introduced here to compare the results of this study in view of size-based differences discussed in the previous studies. As indicated in Table 2, larger RCFs of 4.33 and 1.70, respectively for NaCl and (NH₄)₂SO₄ particles, were observed in the lower size ranges (13–30 nm). These can be compared with the work of Asbach et al. (2009) wherein, factors of up to 2.6 were obtained for lower size ranges. The RCFs were lower for higher size ranges.

Size range (nm)	Relative concentration factor			
	NaCl	$(NH_4)_2SO_4$		
13–20	4.33	1.70		
20-30	2.13	1.16		
30–50	0.67	0.39		
50-70	1.00	0.85		
70–100	0.37	0.36		
100-150	0.79	0.98		
150-200	0.84	1.11		
200-300	0.26	0.55		
300-400	1.10	1.50		

The results for the concentration difference of the SMPSs re-assessed the previous studies carried out for laboratory-controlled high concentration conditions. The sources of uncertainty which might be causing these differences have been discussed elsewhere (Wiedensohler et al. 2012; Watson et al. 2011). The most significant might be CPC responses, DMA transfer functions, efficiency corrections, instability of the flows and the differences in neutralized charge distributions. Liu and Deshler (2003) have discussed the effect of aerosol flow changes and insufficient neutralisation on the difference between CPC and SMPS. Before examining these aspects, it is worthwhile to also check the differences of CPCs of these units at low ambient concentrations. The next step for our study thus was the comparisons in ambient conditions before attempting the discussion of the above results for the concentration differences.

Comparisons in ambient conditions

Although in some past studies, efforts were made to check the inter-variations for ambient measurements, we carried out experiments so that the similar condition devices could be tested for both high and low concentration conditions. This would help us to harmonize the measurements for different concentration conditions. These experiments in ambient environments were conducted during 4–5 February, 2011 and 19 July, 2011. First, all the three CPCs (T-CPC, CPC of G-SMPS and the CPC of T-SMPS) were compared to check the differences in the total number concentrations recorded by the two instruments. Figure 6 shows the results in the form of time series recorded on February 4, 2011 for a period of about 2.5 h in the ambient environment of IIT Kanpur site. As can be seen, in comparison to higher concentration conditions, as in chamber experiments, CPC variations were low. The CPC of T-SMPS and G-SMPS, respectively showed a factor of $1.013(\pm 0.014)$ and $1.047(\pm 0.022)$ times higher concentrations than the stand-alone T-CPC. The average aerosol concentration as measured by T-CPC during this period was $11,363(\pm 2555)$ cm⁻³. As the concentration was low (below the threshold of single counting mode), close matching of CPCs indicates that coincidence corrected single particle counting for all these CPCs is reasonable.

The CPCs were then coupled with their respective DMAs to form the SMPSs. The two SMPS (i.e. G-SMPS and T-SMPS) along with standalone T-CPC were connected to a flow divider, and similar protocols as followed during test chamber experiments were followed. However, for ambient comparisons, the tube exit at the other end of flow divider was directly exposed to ambient environment. Figure 7 shows the time series of overnight recording of all instruments used for ambient comparisons (February 4–5, 2011).

All comparisons yielded extremely confident results in terms of the trend of the data. It can be seen clearly that, both SMPS followed the ambient changes perfectly. Although, the correctness of the produced data from both the units cannot be checked in absence of an absolute standard, we attempted a preliminary comparison of SMPS integral number concentration with the standalone T-CPC concentration assuming it as a reference standard. As seen in Fig. 7, the G-SMPS concentrations were closer to T-CPC and remained higher constantly w.r.t. T-SMPS. The representative mean size estimated by G-SMPS shifted to lower size compared to T-SMPS. The geometric standard deviation for both instruments followed each other.

Figure 8a shows a representative size distribution simultaneously recorded by T-SMPS and G-SMPS. The geometric mean obtained for the G-SMPS was 122 nm (which was 10.2 % lesser than T-SMPS). However, the GSDs for both the size distributions were similar ($\cong 2.04$). Instead of comparing the total number concentration as provided by the instrument software, we compared the integrated concentrations only for the size range common to both the instruments. With this, results from G-SMPS were found to be a factor of $1.252(\pm 0.163)$ higher than T-SMPS. Figure 8b depicts the similar result obtained for the comparison on July 19, 2011 performed to check the repeatability of the February results. For this case, the aerosol concentration from G-SMPS was a factor of $1.161(\pm 0.321)$ higher while the mean was 10.2 % lesser than T-SMPS with almost similar GSD. These results are comparable to those of a recent work by Watson et al. (2011) comparing similar units at Fresno Supersite (ambient) wherein the G-SMPS number concentrations were higher than T-SMPS by a factor of 1.26 (for 10-30 nm) which gradually reduced for the higher sizes finally leading to a trend reversal (T-SMPS > G-SMPS). Figure 9 shows the hourly averaged distributions for three different times. All environmental changes e.g. bimodality were captured



Fig. 6 Time series of particle concentrations recorded by the three CPCs in ambient environment on February 4, 2011



Fig. 7 Time series for inter-comparison data for February 2011

by both the instruments. No convincing size segregated effect was observed. As observed for low concentration conditions, the G-SMPS number concentration results were approximately 20 % higher than T-SMPS. A small part of this difference can be linked to the CPC differences (≈ 5 %) and the remaining may be attributed to similar factors discussed at higher concentration measurements. The next section discusses the possible reasons for the observed differences. Harmonisation of particle concentration measurements

Based on the results of the measurements as discussed in the previous sections, an attempt to achieve harmonisation when measuring particle concentrations using systems from different manufacturers was made. As shown in Fig. 10a, the ratios of the concentrations recorded by CPCs of the two SMPSs to the T-CPC were plotted as a function of the concentration (measured by



Fig. 8 A typical size distribution comparison in ambient environment on **a** Feb 4–5, 2011 and **b** July 19, 2011

T-CPC). It was observed that, in concentration range of $10,000-40,000 \text{ cm}^{-3}$, concentration ratio for both CPC increased with concentration. However, CPC of G-SMPS (to T-CPC) ratio was seen to be saturating, while that of CPC of T-SMPS was observed to be increasing, in the above-stated concentration range. Similarly, Fig. 10b shows the ratio of the concentrations measured by G-SMPS and T-SMPS as a function of the aerosol concentration (average of G-SMPS). This ratio increased with increase in aerosol concentration.

The role of single particle counting mode and the transition effect (to photometric mode) has already been discussed in CPC measurement results. This study also showed that G-SMPS measured higher particle concentrations compared to T-SMPS (consistent with the similar studies performed world-over). For low concentrations, a fraction of this difference may arise due to CPC differences (as observed in our



Fig. 9 Comparison of hourly averaged size distributions for ambient comparison (4–5 February 2011)

work). While inversion scheme differences were ruled out as a possible reason, the other possible reasons may be the differences in CPC efficiency curves, diffusion losses and the other sampling variations (Wiedensohler 2012). As the SMPS difference for ambient measurements were not too large for our study, the small differences in device characteristics and measurement uncertainties during measurements can account for the observed response. Considering above arguments, it seems reasonable to accept the SMPS differences for the ambient measurements.

At higher concentrations, the CPC differences became large, but these may not contribute to the



Fig. 10 Concentration dependence of concentration ratios a for CPCs of SMPS relative to stand-alone T-CPC (aerosol concentration is of T-CPC) and b for G-SMPS and T-SMPS (aerosol concentration is average of G-SMPS and T-SMPS integrated aerosol concentration)

large SMPS differences. When the CPC is connected as a part of SMPS, the particles reaching the CPC would be size segregated and hence, at lower concentrations. Hence, the counting mode for this small concentration would be single counting and CPC responses matched fairly well for single counting mode. Then, a possible explanation for the observed SMPS differences is based on the neutralisation efficiency of these systems. In comparison to ambient case, the charges produced due to atomisation will be large. No additional neutralizer was used in our study except the neutralizers of these devices. An inefficient neutralisation would result in higher number concentration as well as lower mean size. Liu and Deshler (2003) demonstrated the effect of such neutralizing inefficiency to explain the larger differences of CPC and SMPS at lower sizes. Since this charging-related effect would be prominent for lower sizes, it also explains the larger RCF (for smaller sizes) observed in our study. The neutralisation efficiency can thus be tested for such experiments so as to understand and negate observed effects.

The results of these experiments are being used by the participating laboratories for their collaborative work. For ambient conditions, these laboratories are using a multiplication factor of 1.2 for converting the total number concentration measured by T-SMPS to mirror it with the G-SMPS. However, in the absence of standardized size-based interpretations, use of such a relative factor will not be valid for size distributions. Also, at high concentration conditions, more experiments (such as with hydrophilic particles, with lower average charge, etc.) are required to discuss and implement any such kind of conversion factor.

Effect of silica gel trap (sheath air dryer) in G-SMPS

An important part of this study was to test the effect of diffusion dryer and sheath air dryer on the measured aerosol size spectrum. Due to reasons of effect on bipolar charge equilibrium and to limit fluctuations of relative humidity (RH) inside the DMA, it is recommended to use diffusion dryer at sample inlet and sheath air dryer (with heat exchanger) in sheath air path (Wiedensohler et al. 2012). In continuation to exploring SMPS performance related to RH studies, we continued inter-comparison experiments with two different objectives.

The first objective was to measure the hygroscopic growth of atmospheric aerosols at high humidity conditions. This was required to analyse the effect of diffusion dryer on the size spectrum. In many practices, these dryers are used without any RH control so the sample RH reduces to a very low value. In such cases, the actual and the measured inferences can be very different. Towards this, G-SMPS and T-SMPS were used to measure hygroscopic growth of ambient aerosols (Shamjad et al. 2012). T-SMPS was used to measure the ambient size distribution while the G-SMPS was used to measure the dry distribution (diffusion dryer was attached to the inlet). The silicabased dryer reduced the RH at the exit of the dryer to as low as 5 %. This RH and the chamber humidity conditions were measured by Vaisala Humidcap (HMT 330, serial no. B4050039) with an accuracy of 1 % for RH <90 and 1.7 % above 90 %. As shown in Shamjad et al. 2012, the hygroscopic growth factor (ratio of modal diameter for wet and dry distributions) varied from 1.02 to 1.18 for RH variations between 59.3 and 76.5 %. The details of these observations have been discussed in Shamjad et al. (2012). As growth factors also depend on the chemical composition, it is inappropriate to relate RH to aerosol growth. But as can be seen, the measured size can be quite different from the actual size for such cases. This understanding becomes particularly important when such dryers are used without RH control and the measured parameters are used for other estimations and data interpretation.

The second objective was to analyse the effect of sheath air drying on the measured spectrum. Controlled studies with particles produced using an atomizer, were performed to analyse the effect of sampling from a humid environment. T-SMPS was connected to the chamber without any sheath air dryer (with no RH control and heat exchanger) while a silica beads dryer was connected in the sheath path of G-SMPS. The RH in the chamber was noted, and it was seen to be maintained between 20 and 30 %. In a separate exercise, the sheath air dryer (not connected in SMPS path) was seen to be reducing RH to less than 10 %. The RH conditions inside the DMA were not measured except the noted temperature response of DMA sensor which was seen to be fluctuating within low acceptable range. In two different experiments, one with NaCl (0.01 % v/v) and the other with $(NH_4)_2SO_4$ (0.03 % v/v) solutions, the effect of using a dryer in the sheath air path on the resulting size distribution was studied. For NaCl particles, the mean size observed with the G-SMPS was 32 nm (compared to 58 nm with T-SMPS) with the dryer in the sheath air path corresponding to a variation of 44.8 % with respect to the T-SMPS. In the absence of the dryer, the mean sizes were found to be 54 and 64 nm for the G-SMPS and T-SMPS, respectively, i.e. a change of 15.6 % relative to T-SMPS. These are depicted in Fig. 11.

Similar results were obtained with $(NH_4)_2SO_4$ particles as well (Fig. 12). The size variation in this case reduced from 24.4 % (with dryer) to 10.3 % (without the dryer) w.r.t. the mean size given by T-SMPS. These results can be taken as the reflection of the interaction of aerosol stream with the surrounding sheath flow. The RH of the sheath air can influence the aerosol drying, particularly for wet aerosols. In such cases, the aerosol size exiting neutralizer will change



Fig. 11 Size distribution comparison using 0.01 % NaCl particles **a** with and **b** without sheath air dryer

during the flight towards the DMA slit. As the flow rate of sheath air was ten times higher than the sample flow rate (3 against 0.3 Lmin^{-1}), dried sheath air reduced the mean size significantly.

This shift in the mean size on using such a dryer can be significant, especially if the particles are hygroscopic. Moreover, the use of the dryer is likely to alter the size distribution of the particles from that in the real environment from which they are sampled. In event of requirement of wet aerosol sampling, if sheath drying is used then its effect should be known to the end users. Hence, it is important that a correct protocol for measurements pertaining to the use of the sheath air dryer be evolved based on the application and end point of the measurements. In context of a significant change in the mean size due to insertion of dryer in sheath air path, a correction factor should be included in software for use in cases where these dryers are being supplied to the users in closed loop



Fig. 12 Size distribution comparison using $0.01 \% (NH_4)_2 SO_4$ particles **a** with and **b** without sheath air dryer

measurements (without RH control). The estimation of this important correction factor (particularly in view of the recent protocols) requires the specific studies which can be focused on the above aspects. Also as mentioned in Shamjad et al. (2012), similar RH conditions might lead to different growth factors due to changes in the chemical compositions hence a careful controlled composition dependent study can be advantageous to assist the protocol development.

Conclusions

The CPCs of the G-SMPS and T-SMPS were compared with each other and with a stand-alone CPC for ambient and laboratory generated conditions. For ambient conditions, the CPC results were within a factor of 1.05 while for high concentration comparisons, the CPC differences increased to a factor of 1.18. These CPC were coupled with their respective DMAs and G-SMPS and T-SMPS were compared following the similar protocols. For ambient conditions, **G-SMPS** particle concentration results were 1.16-1.25 times higher than T-SMPS results. An excellent consistency was observed while comparing the mean size and geometric standard deviation from both the instruments. G-SMPS mean size was always approximately 10 % lower than T-SMPS mean size while GSD was seen to be almost similar. For laboratory generated aerosols, the difference of G-SMPS and T-SMPS results increased to 1.7-1.9 with almost similar inferences as ambient case for mean and GSD. Although the above-mentioned factors may be valid for one particular set of instruments and settings, these can provide sufficient information for harmonizing the measurements during field campaigns. An attempt made for comparing ambient integral number concentrations obtained from SMPS results with a stand-alone CPC showed that GRIMM results were closer to the stand-alone CPC. A definite trend of increase in CPC differences and SMPS differences with increase in aerosol concentration was observed. The CPCs were found to be matching for low concentrations verifying the correctness of the coincidence corrected single counting measurements. For these concentrations, the possible reasons for SMPS differences have been stated. For high concenmeasurements, CPC differences tration were increased due to shifting to photometric mode at different thresholds. However, these differences would not contribute to the SMPS differences for these high concentration conditions. The neutralizing inefficiency can be a possible reason for consistently observed large differences for laboratory high concentration measurements. The size-wise inferences showed large differences for lower size ranges which got reduced for higher size ranges.

The use of diffusion dryer at the inlet of one SMPS was utilized to measure the hygroscopic growth of ambient aerosols. The introduction of sheath air dryer or similar device in the sheath air path introduces a significant shift (towards lower end) in the mean size of the distribution. This highlights the need for a proper guideline for the use of the sheath air dryer when making measurements with an SMPS. If the use of such a dryer is imperative, then a correction factor may be incorporated so as to predict the size distribution close to that in the environment which is being sampled. The quantification of such a shift

(and correction factor), however, requires detailed study performed over a range of humidity conditions and aerosol hygroscopicity.

In general, it is necessary to understand the importance of inter-comparison exercises for harmonisation of the measurements, especially when carrying out regional studies using different versions of SMPSs in multi-institutional programmes. Following a correct protocol can be advantageous if the user knows the effect of sub-systems used in the measurements. The variations between instruments for nanoparticle ranges should be taken care while drawing conclusions, since a variation by a factor of about 2-4 is seen in the number concentrations at low particle size ranges (<30 nm). The concentration-dependent responses have shown that the data obtained from one SMPS can be utilized to relate it to other SMPS performance (for the ambient comparisons). It will help both of the collaborating laboratories to conduct studies at their respective locations and to correlate the conclusions. Since nearly all recent protocols highlight the importance of using diffusion dryer and/or sheath air dryer for SMPS measurements, the implications of RH-based studies can be taken as a preamble for the other specific RH-related studies.

Acknowledgments This study was carried out with support from Board of Research in Nuclear Sciences, Department of Atomic Energy, India (under BRNS Project no. 2009/36/119-BRNS/3384 dated 18/03/2010). We acknowledge the help of Ms. Monika Srivastava in conducting the experiments.

References

- Ankilov A et al (2002) Intercomparison of number concentration measurements by various aerosol particle counters. Atmos Res 62:177–207
- Asbach C, Kaminski H, Fissan H, Monz C, Dahmann D, Mülhopt S, Paur HR, Kiesling HJ, Hermann F, Voetz M, Kuhlbusch TAJ (2009) Comparison of four mobility particle sizers with different time resolution for stationary exposure measurements. J Nanopart Res 11:1593–1609
- Biswas P, Wu CY (2005) Critical review: nanoparticles and the environment. J Air Waste Manag Assoc 55:708–746
- Biswas S, Fine PM, Geller MD, Hering SV, Sioutas C (2005) Performance evaluation of a recently developed waterbased condensation particle counter. Aerosol Sci Technol 39:419–427
- Giechaskiel B, Dilara P, Andersson J (2008a) Particle Measurement Programme (PMP) Light-Duty Inter-Laboratory

Exercise: repeatability and reproducibility of the particle number method. Aerosol Sci Technol 42:528–543

- Giechaskiel B, Dilara P, Sandbach E, Andersson J (2008b) Particle Measurement Programme (PMP) Light-Duty Inter-Laboratory Exercise: comparison of different particle number measurement systems. Meas Sci Technol 19:095401
- Helsper C, Horn HG, Schneider F, Wehner B, Wiedensohler A (2008) Intercomparison of five mobility particle size spectrometers for measuring atmospheric submicrometer aerosol particles. Gefahrst Reinhalt Luft 68:475–481
- Hering SV, Stolzenburg MR, Quant FR, Oberreit DR, Keady PB (2005) A laminar-flow, water-based condensation particle counter (WCPC). Aerosol Sci Technol 39:659–672
- Koch W, Pohlmann G, Schwarz K (2008) A reference number concentration generator for ultrafine aerosols based on Brownian coagulation. J Aerosol Sci 39:150–155
- Leskinen J, Joutsensaari J, Lyyränen J, Koivisto J, Ruusunen J, Järvelä M, Tuomi T, Hämeri K, Auvinen A, Jokiniemi J (2012) Comparison of nanoparticle measurement instruments for occupational health applications. J Nanopart Res 14:718
- Lui PSK, Deshler T (2003) Causes of concentration differences between a scanning mobility particle sizer and a condensation particle counter. Aerosol Sci Technol 37:916–923
- Mordas G, Manninen HE, Petäjä T, Aalto PP, Hämeri K, Kulmala M (2008) On operation of the ultra-fine water-based CPC TSI 3786 and comparison with other TSI models (TSI 3776, TSI 3772, TSI 3025, TSI 3010, TSI 3007). Aerosol Sci Technol 42:152–158
- Mulholland GW, Donnelly MK, Hagwood CR, Kukuck SR, Hackley VA, Pui DYH (2006) Measurement of 100 nm and 60 nm particle standards by differential mobility analysis. J Res NIST 111(4):257–312
- Peters A, Wichmann HE, Tuch T, Heinrich J, Heyder J (1997) Respiratory effects are associated with the number of ultrafine particles. Am J Respir Crit Care 155:1376–1383
- Schlatter J (2006) Comparison of Grimm and TSI condensation particle counters. 10 ETH-Conference on Combustion Generated Particles Zurich, 21–23 August. (http://www. metas.ch/metasweb/Fachbereiche/Partikel_und_Aerosole/ Annexes/Dokumente_Nanopartikel/ETH2006GrimmTSI. pdf)
- Shamjad PM, Tripathi SN, Aggarwal SG, Mishra SK, Joshi M, Khan A, Sapra BK, Ram K (2012) Comparison of experimental and modeled absorption enhancement by black carbon (BC) cored polydisperse aerosols under hygroscopic conditions. Environ Sci Technol 46(15):8082–8089
- Watson JG, Chow JC, Sodeman DA, Lowenthal DH, Chang MCO, Park K, Wang X (2011) Comparison of four scanning mobility particle sizers at the Fresno Supersite. Particuology 9(3):204–209
- Wiedensohler A et al (2012) Particle mobility size spectrometers: harmonization of technical standards and data structure to facilitate high quality long-term observations of atmospheric particle number size distributions. Atmos Meas Tech 5:657–685