USE OF ALTERNATE CPCs WITH THE 1nm SCANNING MOBILITY PARTICLE SIZER™ (SMPS™) SYSTEM

APPLICATION NOTE SMPS-009 (US)

Contents

Objective

TSI has recently introduced the Model 3938E77 1nm Scanning Mobility Particle Sizer™ (SMPS™) System. The Model 3938E77 is the only fully integrated SMPS system on the market capable of measuring particles down to 1 nm. Many researchers may be interested in extending the lower size limit of their measurement capabilities, but may wonder if a Condensation Particle Counter (CPC) they already own can be substituted for the Model 3772 that is included in the 1nm SMPS system design. For this reason, TSI has investigated the function of the 1nm SMPS system using other current models of TSI CPCs.

Overview of the 1nm SMPS System

Figure 1 depicts a standard 1nm SMPS system. The standard system consists of a Model 3082 Dual-Polarity Classifier, a Model 3086 1nm Differential Mobility Analyzer (DMA), a Model 3777 Nano Enhancer, a Model 3772 Condensation Particle Counter (CPC), and a neutralizer, e.g., Model 3088 or Model 3077.

The 3938 SMPS Spectrometer is a modular system and the new components, introduced to push the lower size limit down to 1 nm are the Model 3777 Nano Enhancer and the Model 3086 1nm DMA.

Figure 1: The 3938E77 SMPS system, or 1nm SMPS system. The picture shows the standard configuration with the butanol-based Model 3772 CPC

As with other DMAs, the purpose of the Model 3086 is to size-classify the particles prior to the particles being counted by a Condensation Particle Counter (CPC), or other detector.

The Model 3777 Nano Enhancer is an additional first stage growth unit, in which diethylene glycol (DEG) is used to activate particles from 1 nm. Previous research (Iida *et al*, 2009) has shown that DEG is a suitable working fluid for such a growth stage, but only grows the sample particles to be larger than 30 nm. Particles of this size are not reliably detectable with conventional laser optics, but are easily detectable with conventional CPCs which will detect 100% of sampled particles in this size range. Therefore, in the 1nm SMPS system, the DEG droplets grown in the Model 3777 Nano Enhancer are then further enlarged by butanol condensation and counted via light scattering in the Model 3772 CPC.

The Model 3772 CPC is currently the only CPC supported for use in the 1nm SMPS system. The Model 3772 was chosen for use in this system due to its “full flow” design. This means that as the aerosol flow enters the CPC, 100% of the aerosols that enter the CPC enter the optical chamber, where the particles are counted. In nearly all of TSI’s other CPC models, a fraction of the incoming sample flow is diverted, scrubbed of particles, and recombined with the aerosol flow prior to the optical chamber. This “flow split” design is advantageous in many applications that contain high particle concentrations: an accurate reading can be obtained without overwhelming the optical counting system. In the case of sub-2 nm particles; however, concentrations may be small under some circumstances, and the original particle concentration should be preserved as much as possible. Thus, the 1nm SMPS system was designed around the use of the Model 3772 CPC.

Figure 2: A 1nm SMPS system using a Model 3788 water-based CPC in place of the standard Model 3772 butanol-based CPC. The white filter and needle valve depicted in front of the Model 3788 allow makeup air into the Model 3788 when it is operated at 1.5 L/min. This allows the Model 3777 to operate at its designed inlet flow rate (details are explained below).

As mentioned above, however, some users may be interested in a 1nm SMPS system, but desire to use a CPC they already own. A user may also wonder if measurements can be conducted down to 1 nm using a water-based CPC. The experiments described here were undertaken to provide answers to those questions.

Experimental Methods

Of TSI's current CPC models, the Model 3775 and Model 3788 were chosen for compatibility testing with the 1nm SMPS system. These models were chosen in order to represent:

- both working fluids (butanol and water)
- diversity in smallest detectable particle size

Researchers currently engaged in work requiring the measurement of sub-3 nm particles are frequently using the Model 3788 or Model 3776 CPCs. A separate forthcoming application note will show results comparing the use of a Model 3938N76 SMPS system (which uses a Model 3776 CPC and a Model 3085 Nano-DMA) with the Model 3938E77 SMPS system (the standard 1nm system).

The Model 3775 and Model 3788 have D_{50} cutpoints (minimum detectable particle sizes) of 4 and 2.5 nm, respectively. Because the Model 3777 grows DEG droplets to be larger than 30 nm, it can be reasonably assumed that the 1 nm CPC system counting efficiency curve is not affected by such small changes in cut point or similar choice of working fluid. Therefore, TSI did not re-characterize the full counting efficiency curve of the combined 1nm CPC systems with each counting CPC.

To verify their successful use with the Model 3777 Nano Enhancer then, the "non-standard" 1nm SMPS system was challenged with a particle size distribution containing a significant amount of particles below the detection limits of the counting CPCs. In order to produce such a size distribution, granulated sodium chloride was vaporized in a 430°C tube furnace (Scheibel & Porstendorfer, 1983). Figure 3 shows the experimental schematic.

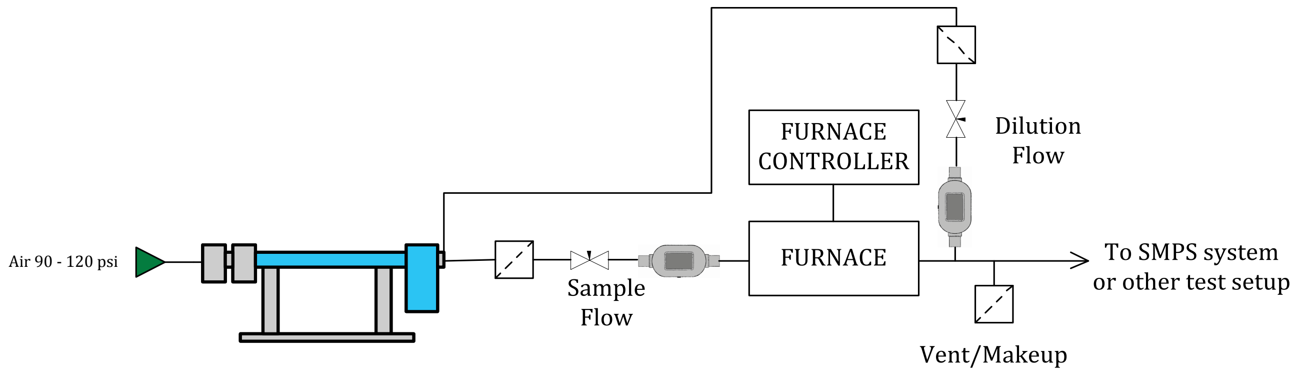

Figure 3: Schematic of experimental setup.

Aerosol generation: the furnace flow of 1.3 L/min was quenched with 3 L/min of room-temperature air to cool and dilute the particles prior to measurement.

Particle detection: the following configurations were used:

A) Model 3777 Nano Enhancer with Model 3772 CPC—this is the standard configuration and used as reference in the following analysis.

B) Model 3777 Nano Enhancer with Model 3775 butanol CPC operated in high flow mode

Note: While the Model 3772 operates at an inlet flow rate of 1 L/min, the Model 3775 and Model 3788 CPCs do not have 1 L/min as an available flow mode. In order to allow the rest of the 1nm system to operate at its design flow rate (which assumes a 1 L/min CPC flow), a flow equalizer was used between the Model 3777 and the CPC under test. Both the Model 3775 and Model 3788 CPC were operated in high flow mode (1.5 L/min) for these experiments. The flow equalizer's valve was set so that the makeup air entering the filter was 0.5 L/min.

C) Model 3777 Nano Enhancer with model 3788 water CPC operated in high flow mode.

Testing of the SMPS configurations B and C was done in an alternating fashion with the standard configuration A. This alternating test schedule permitted the standard 1nm SMPS system to regularly check on the stability of the NaCl particle size distribution.

Results

Stability of Aerosol Generation

A tube furnace is regarded as a reliable method of generating sub-10 nm particles (Scheibel & Porstendorfer 1983). Still, at sub-2 nm particle diameters, slight variability in the size distributions generated over time is expected. Figure 4 shows the individual scans by the Model 3938E77 SMPS system taken before and immediately after each of the tested alternate CPCs. These size distributions appear overall to be very comparable to one another, but they do contain some differences.

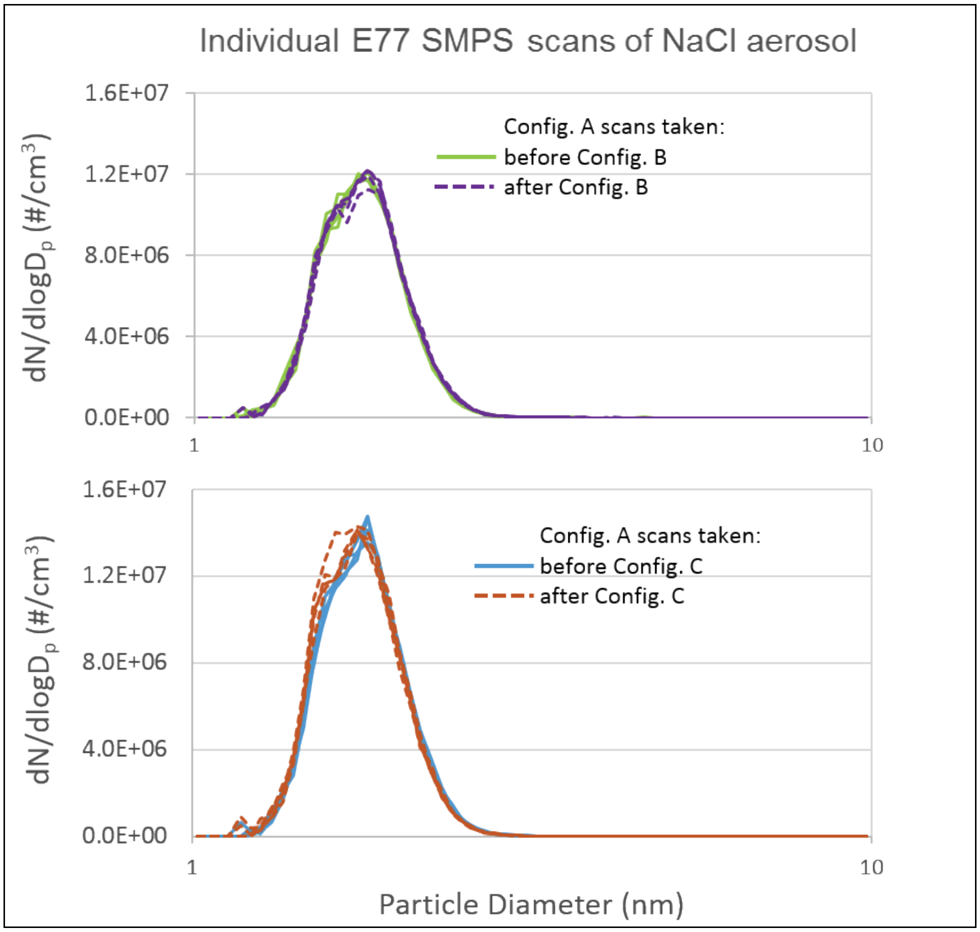

Figure 4: Model 3938E77 SMPS scans of the aerosol size distribution emitted from the tube furnace before and after measurements were taken using alternative configurations B (Model 3775 butanol-based CPC) and C (Model 3788 water-based ultrafine CPC).

While it is likely that no aerosol generator statistically produces identical size distributions over time, working at these sub-2 nm sizes likely guarantees at least some degree of fluctuation in the particle size distribution. The size distributions in Figure 4 have geometric standard deviation values ranging from 1.144 to 1.15—these low values indicate a fairly high degree of monodispersity. When this degree of monodispersity is coupled with the very small particle size, it translates to 95% of the particles being within 1 nm of each other in size. Considered from this perspective, these data suggest that the furnace generator method is satisfactorily stable.

Configuration B: Model 3777 Nano Enhancer with Model 3775 butanol CPC

Figure 4 shows size distributions of the furnace-generated NaCl particles as measured by the 1nm SMPS system when using a Model 3775 CPC, and when using a Model 3772 CPC both before and after the Model 3775 measurements. Each distribution is the average of at least four consecutive measurements.

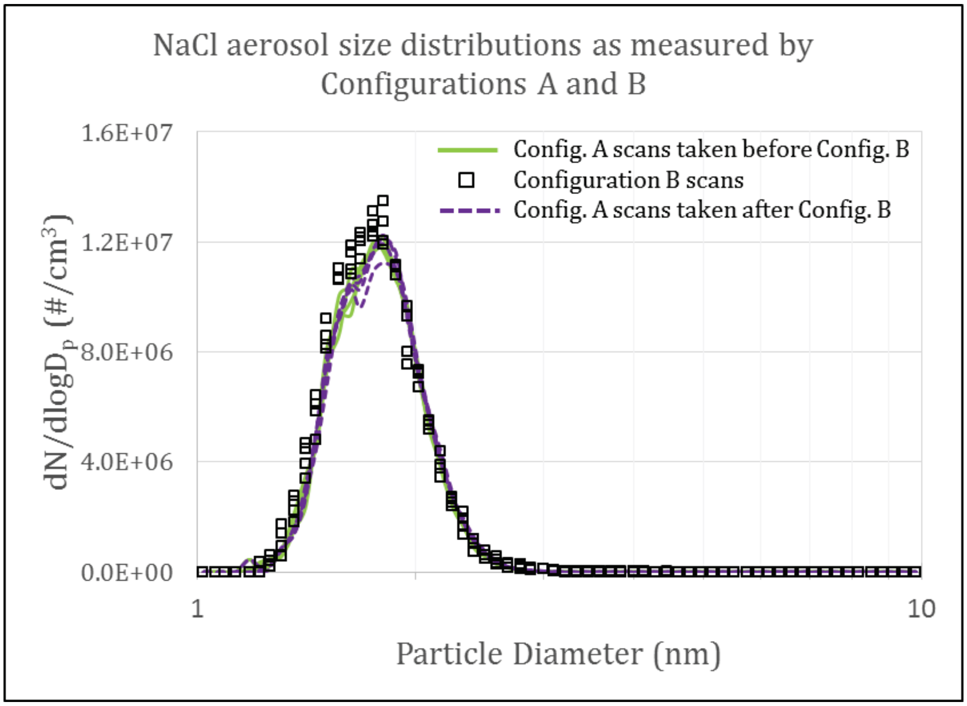

Figure 5: Particle size distributions as measured by a standard 1nm SMPS system, and by a 1nm system employing a Model 3775 CPC instead of a Model 3772 CPC.

Size distributions shown in Figure 5 suggest that results obtained using Configuration B (Model 3775 CPC) align very well with the data gathered by the standard configuration (A). The greatest differences seem to be in the region between 1.5 and 2 nm; outside of this range, the data agree remarkably well. Overall, the average integrated number concentrations from these three tests (Configuration A before and after, and Configuration B) agree with each other within 8%. This is within the commonly accepted threshold of ±10% for agreement between two CPCs. Additionally, a recently published large instrument intercomparison (Kaminski *et al.* 2013) showed that standard SMPS systems measuring the same NaCl aerosol in parallel may differ in measured number concentration by as much as 10% (notably, a competitor's SMPS systems differed from each other by as much as 40%). As such, Configuration B can be considered to be an acceptable substitute for Configuration A.

Configuration C: Model 3777 Nano Enhancer with Model 3788 Water-based CPC

Figure 6 shows size distributions of the NaCl aerosol as measured by the 1nm system when using the Model 3788 CPC as the detector as well as the standard configuration's measurements before and afterwards. As with the Model 3775, the data sets agree very well with one another, with the largest discrepancy again occurring between 1.5–2 nm. In the case of the Model 3788, however, it does appear that over the duration of the data collection (approximately 30 minutes), the size distribution of the generated aerosol did fluctuate somewhat, as evidenced by the slight differences between the two Configuration A data sets (green and blue). This fluctuation in the aerosol size distribution may at least partially explain the apparent discrepancy between the Configuration A and C data.

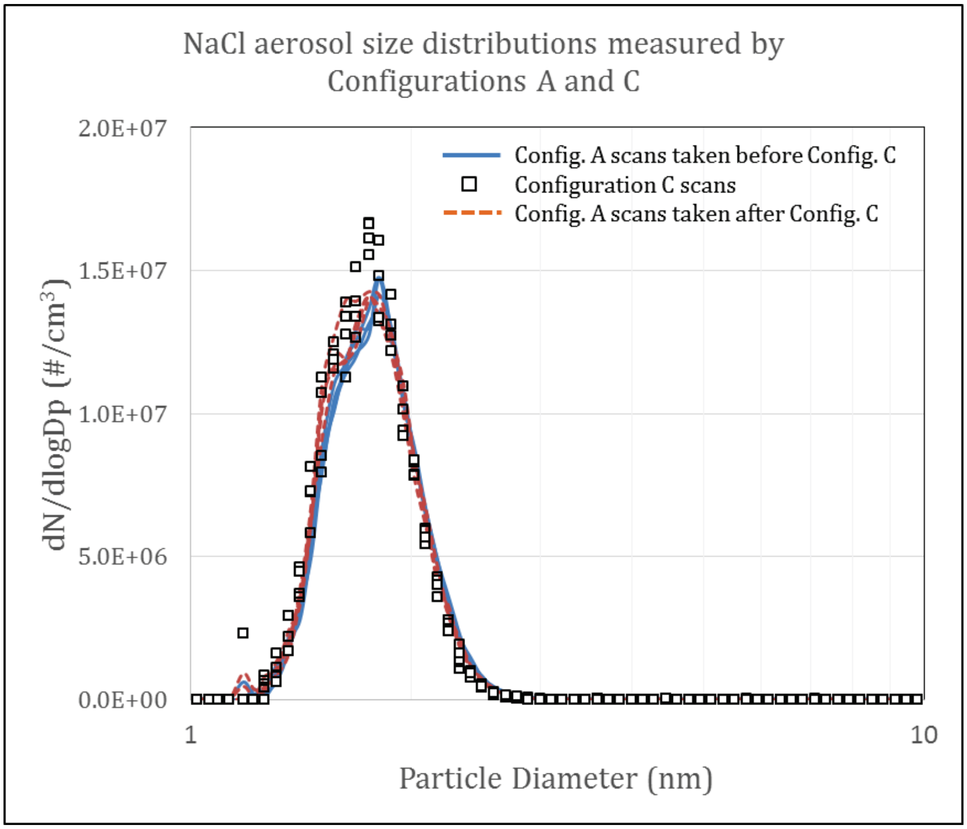

Figure 6: Particle size distributions as measured by a standard 1nm SMPS system, and by a 1nm system employing a Model 3788 CPC instead of a Model 3772 CPC.

Despite the apparent fluctuation in the generator's output, the average integrated number concentration among the three datasets (two datasets from Configuration A and one from Configuration C) agree within 6%. As was the case with Configuration B, this is well within the commonly accepted standard of CPC agreement within ±10%, and within the SMPS agreement margin published by Kaminski *et al*. As such, you can also consider Configuration C—which uses a water-based CPC—as an acceptable alternative to the standard Configuration A.

Application Considerations

The data above demonstrate the success of these alternate combinations. Depending upon your particular application, however, the following points may be worthy of your consideration:

- As of January 2017, TSI does not officially support the use of alternate CPCs within the 1nm system. Only experienced users should therefore use alternate CPCs with the 1nm SMPS system. Post-processing of data obtained with a non-standard system, such as corrections for internal dilution in the Model 3777 and external dilution due to use of a flow equalizer, is the responsibility of the user.
- For users conducting fieldwork, or who may have other physical constraints to their experiment, it may be important to remember that the Model 3777 Nano Enhancer is designed to be used with an external vacuum source.

Conclusions

You can see that these two non-standard configurations of the 1nm SMPS system are able to measure and count particles nearly all the way down to 1 nm with a high degree of accuracy. It is notable that one of the non-standard configurations uses a water-based CPC instead of the standard butanol CPC. This means:

- Customers conducting SMPS measurements can fully utilize the modular aspect of the Model 3938 SMPS system as they can
  - use a CPC they already own as component in a 1nm SMPS system, and/or
  - use a water-based CPC in a 1nm SMPS system
- Customers conducting CPC-based measurements can add a Model 3777 Nano Enhancer in front of a Model 3775 or Model 3788, thus enabling them to accurately count particles substantially below the original D50 cutpoint sizes of their CPC.
- Characterizing the counting efficiency curve of the Model 3777 coupled with an alternate CPC is not necessary, since the Model 3777 grows the particles with DEG to a size that is counted with 100% efficiency by the alternate CPC. Thus, customers do not need any different software tools in order to use their alternate CPC in this manner.

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