

## AN EVALUATION OF A SCANNING MOBILITY PARTICLE SIZER WITH NIST TRACEABLE PARTICLE SIZE STANDARDS

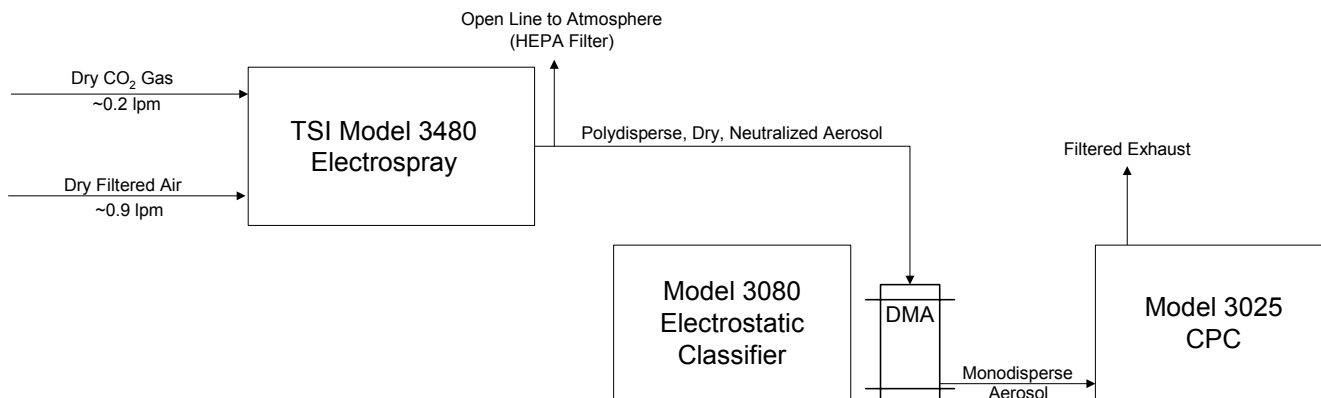
### ABSTRACT

A scanning mobility particle sizer (SMPS -- TSI Model 3936-Series) was evaluated using Duke Scientific NIST traceable particle size standards and Standard Reference Materials from the National Institute of Standards and Technology (NIST SRM's). The importance of instrument setup, electro spray operation and sample preparation for polystyrene spheres are discussed as well as the results from 14 different size reference standards. Correlations between the SMPS system and established electron microscopy and dynamic light scattering methods are also shown in tabular and graphical forms. Results show that with proper operation, the SMPS results fall within the uncertainty of the NIST traceable diameters in the range that was evaluated — 20 to 100 nanometers.

### INTRODUCTION

A Scanning Mobility Particle Sizer (SMPS) manufactured by TSI incorporated<sup>1</sup> is used for sizing particles from 5 nanometers (nm) to 1 micron ( $\mu\text{m}$ ) in size. The entire sizing system can be made up from many different components depending on the end-user's requirements. The three basic parts to the system include an aerosol nebulizer, a differential mobility analyzer (DMA) and a condensation particle counter (CPC).

Figure 1. Schematic Diagram of the SMPS System



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Duke Scientific's interest lies in the smaller size ranges, therefore, we have selected the components that optimize the precision and accuracy of the measurement data in the smallest range. The following is a short description of the components used in this evaluation:

Table 1. Major Components of the SMPS System

Model Number	Description	Specifications
3480	Electrospray Aerosol Generator	2-100nm particle size range with a generation rate of up to $10^7$ particles / $\text{cm}^3$ .
3085	Nano DMA	2-150nm particle size range
3081	Long DMA	10-1000nm particle size range
3025	Ultrafine Condensation Particle Counter	90% detection at 5nm particle size. Concentration range: 0 to $9.99 \times 10^4$ particles / $\text{cm}^3$

This report describes some of the instrument modifications and operating conditions that optimize the performance of the SMPS system when sizing polystyrene microspheres. It discusses nebulizer stability, sample preparation and data collection. The SMPS system was also evaluated using NIST traceable particle size standards and the results are compared to other methods including transmission electron microscopy (TEM) and Dynamic Light Scattering.

## EXPERIMENTAL AND INSTRUMENT SETUP<sup>2</sup>

### Electrospray

Almost all commercial particles below one micron are packaged in an aqueous suspension. To suspend these particles into air requires some type of nebulizer. The electrospray generates an aerosol through a combination of a pressure differential and an electric field. The instrument runs on a mixture of  $\text{CO}_2$  and air. The gases are filtered and dried. A small (1.5 mL) vial of a mixture of the suspension and an electrolyte is placed into the electrospray chamber and pressurized. The liquid travels through a capillary under approximately 3 PSIG of positive pressure and an electric field. At the other end of the capillary the droplets form a cone-jet that creates a uniform distribution of fine liquid droplets. The cone-jet is controlled by varying the strength of the electric field. The droplets evaporate almost immediately and the non-volatile material inside the droplets remain. These particles are highly charged and must be neutralized before they can be used by the DMA. A radioactive source of ions (Polonium-210) is used to bring the particles to a neutral state called Boltzman Equilibrium. By the time the aerosol has left the electrospray, it is dry and neutrally charged.

### Electrospray Capillary

The original capillary used in the electrospray had a 25 micron inner diameter. Each capillary was housed in a semi-rigid, plastic sheath. These capillaries worked well, but they were expensive and had a tendency to clog.

A second generation of capillaries is offered by TSI in packs of 25. These consist of just the capillary, along with a modification kit for the electrospray. The kit contains sleeves for the capillary, ferrules and

<sup>2</sup> Detailed theory on the Electrospray, DMA or CPC is beyond the scope of this paper. The interested reader is referred to the instrument manuals, which contain theoretical descriptions as well as extensive bibliographies and are available online at [www.tsi.com](http://www.tsi.com).

fittings. Three sizes of capillaries are offered: 25  $\mu\text{m}$ , 30  $\mu\text{m}$  and 40  $\mu\text{m}$  inner diameter. All of our analyses were performed on the 30  $\mu\text{m}$  inner diameter capillary. Following is a table of operating procedures that deviate from the original instrument manual, but reflect the way we operated the new, second generation capillary in the Electropray.

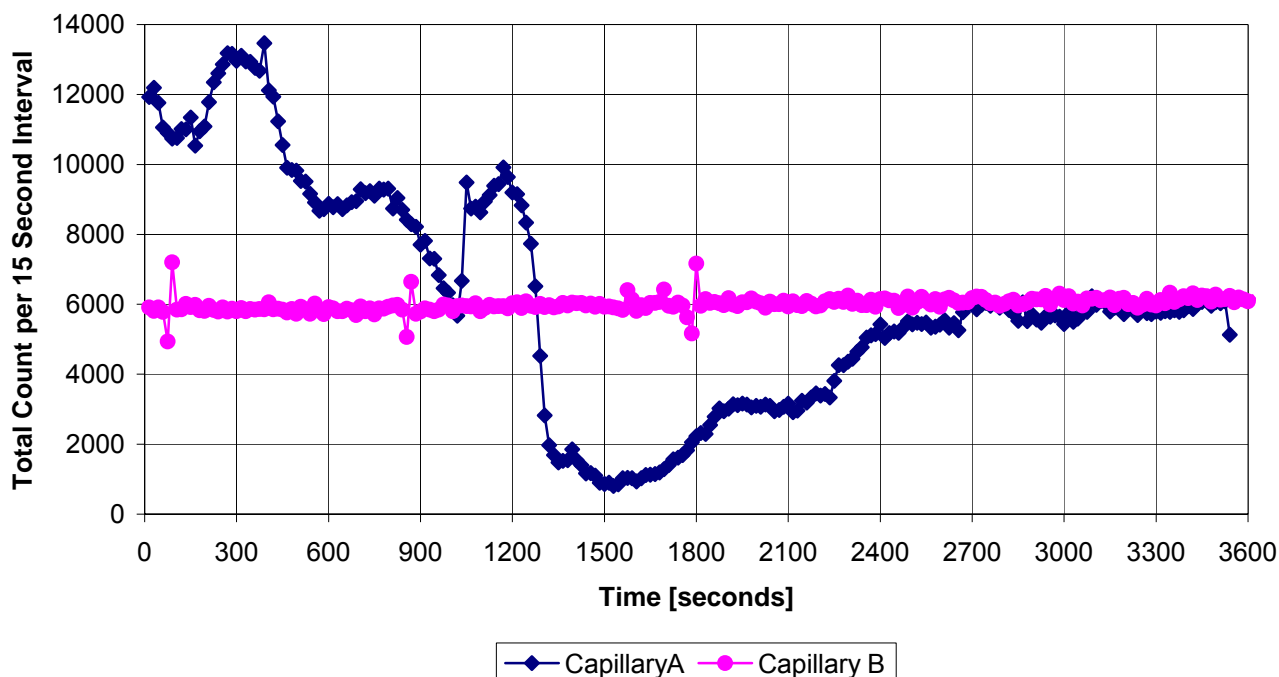
Table 2. Recommended Operating Specifications for the 30 $\mu\text{m}$  Capillary

Specification	Original	Revised	Comments
<b>Buffer Solution</b>	20 mM Ammonium Acetate	20-50 mM Ammonium Acetate	There is some indication from the manufacturer that larger diameter capillaries may perform better with a higher liquid conductivity.
<b>Air/CO<sub>2</sub> Flow Rate</b>	1.0 Lpm air 0.1 Lpm CO <sub>2</sub>	0.9 Lpm air 0.2 Lpm CO <sub>2</sub>	The larger capillary may produce a larger primary droplet size which is more susceptible to corona discharge. The increased CO <sub>2</sub> flow will inhibit the corona discharge.
<b>Pressure</b>	3.7 psi	1.5-3.0 psi	The increased inner diameter of the capillary requires less pressure to drive the flow.

Even under optimal operating conditions, capillary plugging can cause problems. Since most standard SMPS scans range from 120 to 300 seconds in duration, the electropray stability usually isn't an issue. However, it is always a good idea to monitor the capillary performance. The digital current readout on the Electropray as well as the viewing window for the capillary tip are both excellent tools for determining the stability of the aerosol being generated. The tip of the capillary should always show a static sharp point as described in the manual. There should not be any motion in the viewing window. Also, the current reading should be stable, with a constant voltage setting. If the current reading fluctuates, or the view of the capillary tip changes over time, it is very likely that the output of the electropray is also changing.

Electropray stability is more important when the scan times run longer. Manual scans can run for over one hour. A stable output from the Electropray is absolutely required for accurate aerosol size and distribution measurements. Figure 1 shows a graph of the performance of two different capillaries. Capillary A had been in use for 6 to 9 months and showed signs of partial clogging. Even after repeated washing with 20 mM potassium hydroxide, the fluid flow through the capillary seemed erratic. The electropray current fluctuated during use and even though the capillary tip didn't always indicate problems, it was clear that the output of the electropray was erratic. Capillary B was a new capillary that had just been installed and cleaned. The orifice in the electropray had also just been cleaned. Both capillaries were running the same suspension of 20 nm polystyrene particles.

Figure 1. Aerosol Output from Two Different Electrospray Capillaries



It is clear from this figure that the aerosol output from the older capillary (Capillary A) is unstable. Determining an accurate size distribution with a longer, manual scan would be difficult. It is always important to verify the stability of the aerosol output over the desired scan period.

#### Sample Preparation

Small polystyrene latex microspheres can be easily nebulized in the electrospray. The typical sizes range from 150 nanometers and below. It is possible to generate droplets as large as 500 nanometers in diameter including the latex particle. However, as the particle size increases, so does the chance of forming partial or complete blocks of the capillary tube and, in most instances, ruining the capillary.

In general, from 20  $\mu\text{l}$  up to one or two drops of a standard 1% suspension of particles in the standard buffer solution (1.5 mL of 20 mM ammonium acetate) will suffice for running on the SMPS system. However, there are some added steps to the sample preparation that may give better results.

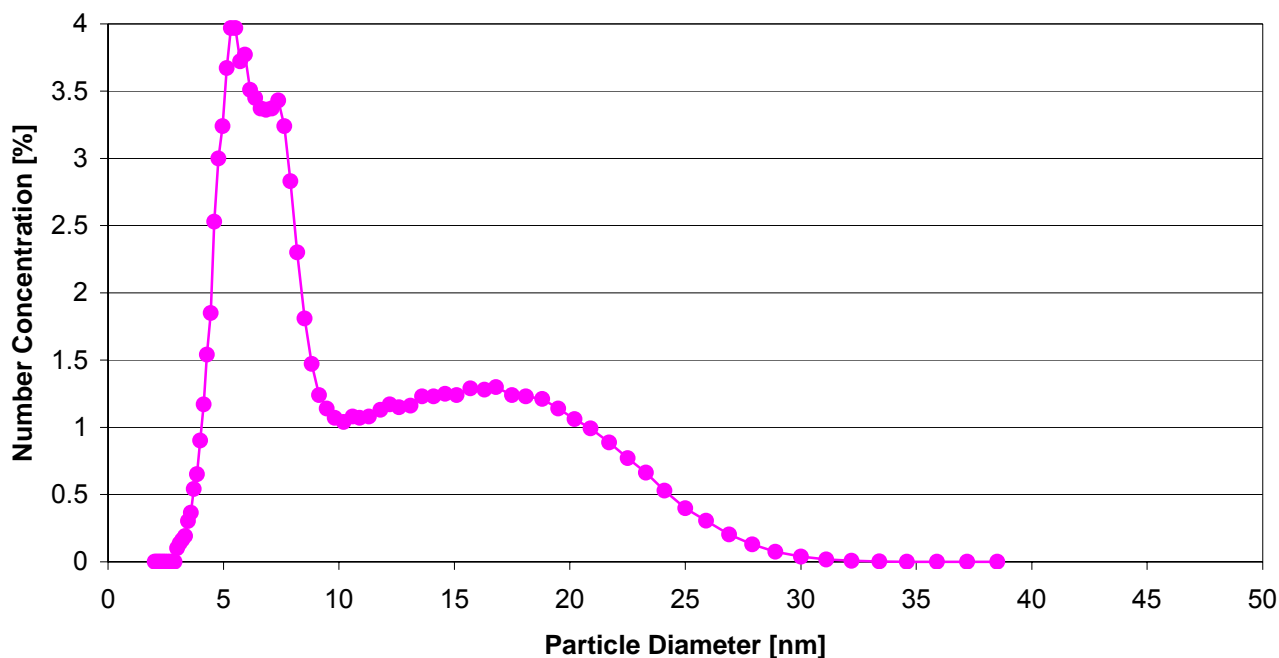
#### Surfactant Removal from the Sample

Surfactant exists in almost all general purpose, aqueous-suspended, polystyrene products. The surfactant is usually negatively charged, and is added to stabilize the small particles and keep them from agglomerating. The amount of surfactant added varies quite a bit and is usually also a function of particle size. The smaller particles require more surfactant to remain stable.

The presence of surfactant is generally not a concern for most applications, however, in aerosol applications it can cause problems. The surfactant is non-volatile, so when the droplets exiting the electrospray evaporate, there will be two possible results. First, any liquid droplets that do not contain polystyrene particles will evaporate, leaving a small surfactant particle. Second, any liquid droplets that do contain a polystyrene particle will evaporate and leave a surfactant shell around the PSL particles, thus, increasing their size. Whether the surfactant will actually affect the particle size measurement is a function of the surfactant concentration, particle size, sample concentration, and

electrospray droplet output. The following illustration is a common result from a SMPS system using small particles containing a significant amount of surfactant.

Figure 2. PSL Particles Containing Surfactant



From this example, a bi-modal distribution is observed. The larger, narrow peak is assumed to be surfactant particles formed from droplets containing no PSL particles. The wider peak is assumed to be the particles. From this scan, it is impossible to determine the actual number mean diameter or the distribution of the particles due to the surfactant interference.

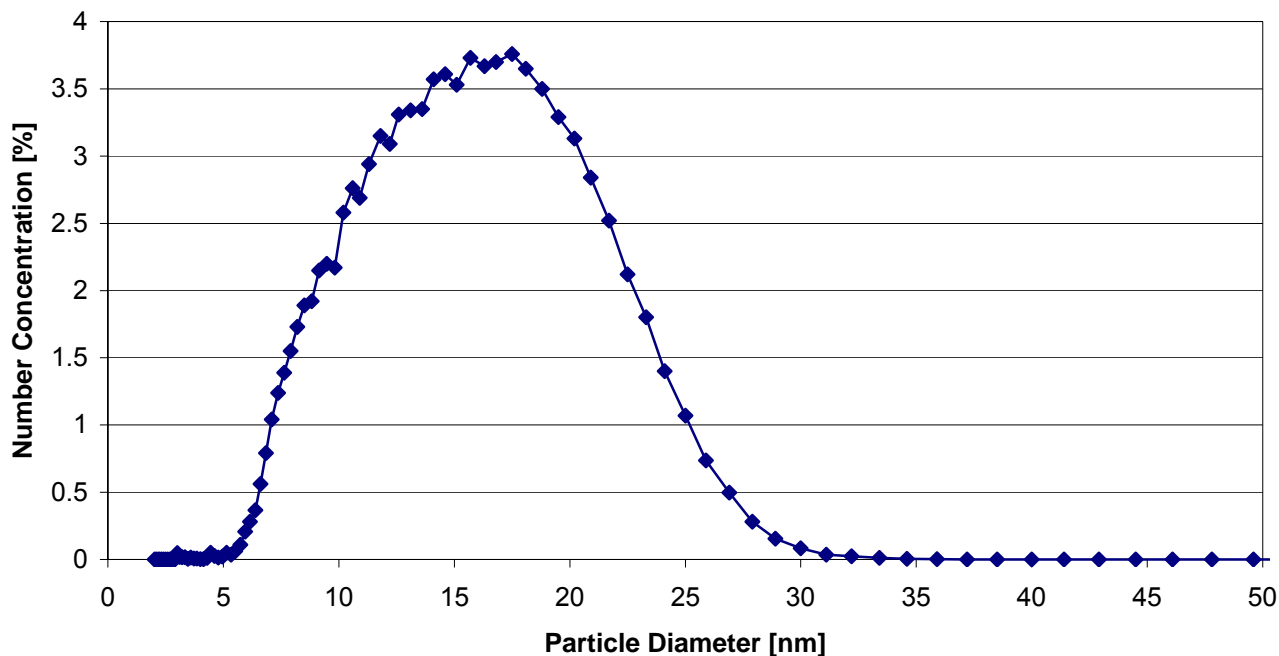
In a second experiment, the surfactant was removed from the sample and the scan was repeated. Anionic (or cationic) surfactant can be removed with a procedure called ion-exchange. The method is simple and effective and can be conducted on small samples. Our procedure is outlined below:

1. Obtain some ion-exchange resin (we have used Bio-Rad AG501-X8)
2. For a 15 mL bottle of particles at 1% solids use 3 to 4 grams of resin
3. Wash the resin thoroughly to remove potential contaminants
  - a. Wash resin with five portions of 200 mL DI water
  - b. Allow the resin to settle, and pour off the water
4. Add the particle suspension to the resin in a small bottle. You can add extra water if needed.
5. Roll the mixture for 4 to 6 hours and filter through washed glass wool to remove the resin
6. Alternatively you can let the resin settle and you can pour off the suspension into another clean bottle.
7. The suspension should be surfactant free and ready to use.

For applications involving the electrospray, just 1 mL of a suspension can be ion-exchanged and diluted with water to form 15 mL's of liquid. Generally, a 1% solution of particles below 100 nm is too concentrated, so a 15:1 dilution is reasonable and saves the other 14 mL of particles in a more stable form. Ion-exchanged particles can be unstable and shouldn't be stored for more than a few days.

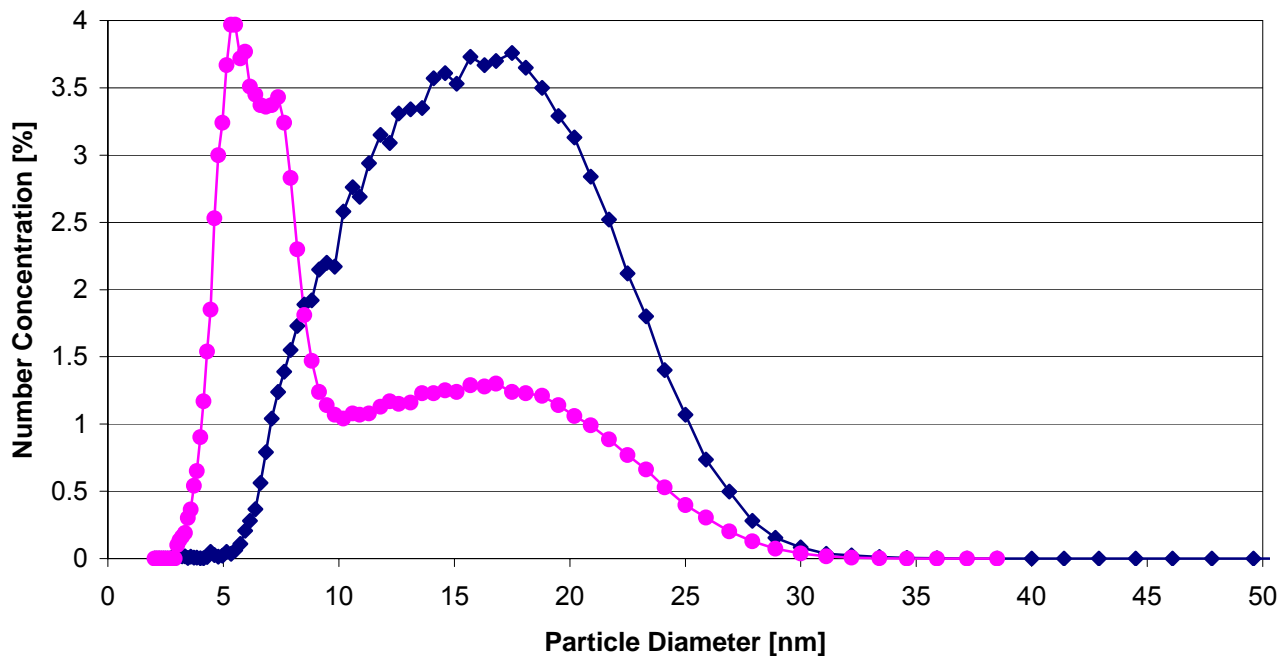
The results of the SMPS scan with the ion-exchanged material are shown in Figure 3.

Figure 3. PSL Particles with Surfactant Removed



The difference between these two runs can best be seen with an overlay:

Figure 4. PSL Particles With and Without Surfactant



Since the electrospray has such a small droplet diameter, the surfactant peaks generally range from 4 to 10 nanometers in diameter. This interference does not cause a significant error for particles 50 nm and larger. At those sizes, the two peaks have no overlap, and the statistics can be performed only on the PSL distribution.

It is also important to note that the surfactant shell around small particles can artificially increase the apparent size of the PSL particles. Usually this contribution is insignificant, but if the surfactant concentration is high or the PSL size is very small, it may be worth taking the time to ion-exchange the sample to avoid this problem.

One last note about sample preparation concerns particle stability. Generally, PSL particles have been found to be stable in a 20 mM ammonium acetate buffer solution, but there have been instances where the particles immediately flocculate to the point of settling out of suspension. It is important to test a small amount of the sample in the standard 1.5 mL container with the buffer solution. After shaking the suspension, the solution should be homogeneous. This simple test can avoid having to replace the capillary due to clogging. Flocculated material will immediately, and in almost all cases, permanently clog the capillary.

### DMA and CPC Instruments

Both the 3080 Electrostatic Classifier and the 3025 Ultrafine CPC were operated according to the instrument manual. In all particle analysis below 60 nanometers, the nanoDMA was used in conjunction with the 3080 classifier. For particles larger than 60 nanometers, the long DMA was used. The flow rates on the 3080 were verified using a Gilibrator bubble flow calibrator. The voltage regulator was assumed to be correct. In all scans, the sheath flow rate was as high as allowable—generally between a 10:1 and 12:1 sheath/aerosol flow ratios.

The CPC was operated in its high flow mode of 1.5 Lpm of aerosol. With the electropray output of approximately 1.1 Lpm, 0.4 Lpm of make-up air was provided upstream of the DMA. This corresponds to running the SMPS system in a slight underpressure mode as outlined in the instrument manuals.

## DATA COLLECTION

Outside of the Electropray stability tests, all data was collected using TSI's Aerosol Instrument Manager (AIM) version 4.3. This software computes a particle's mean size and geometric distribution by rapidly stepping up the voltage across the DMA from 1 to 10,000 volts. The software uses algorithms to convert from a voltage to a particle size taking into account all of the variables associated with the DMA transfer function and operating parameters.

Scan times ranged from 120 seconds to 300 seconds for an upscan from 1 to 10,000 volts. A 15 second downscan (from 10,000 to 1 volt) is also performed with this software, but the data is not used. The data is corrected for multiple charged particles and the information is presented graphically and in table format.

Tabular data including particle diameter and number % were extracted from the AIM program and copied into an Excel worksheet. This data was incorporated into a statistics worksheet to allow comparisons between different sizing methods that measured different moment weighted diameters.

## RESULTS AND DISCUSSION

Thirteen NIST traceable particle size standards and one NIST SRM were evaluated on the SMPS system. The results were in good agreement with the TEM measurements as well as measurements made with Dynamic Light Scattering (DLS) Instruments. DLS instruments report an intensity weighted

mean diameter, so the SMPS number mean values were converted to intensity weighted values for comparison purposes.<sup>3</sup>

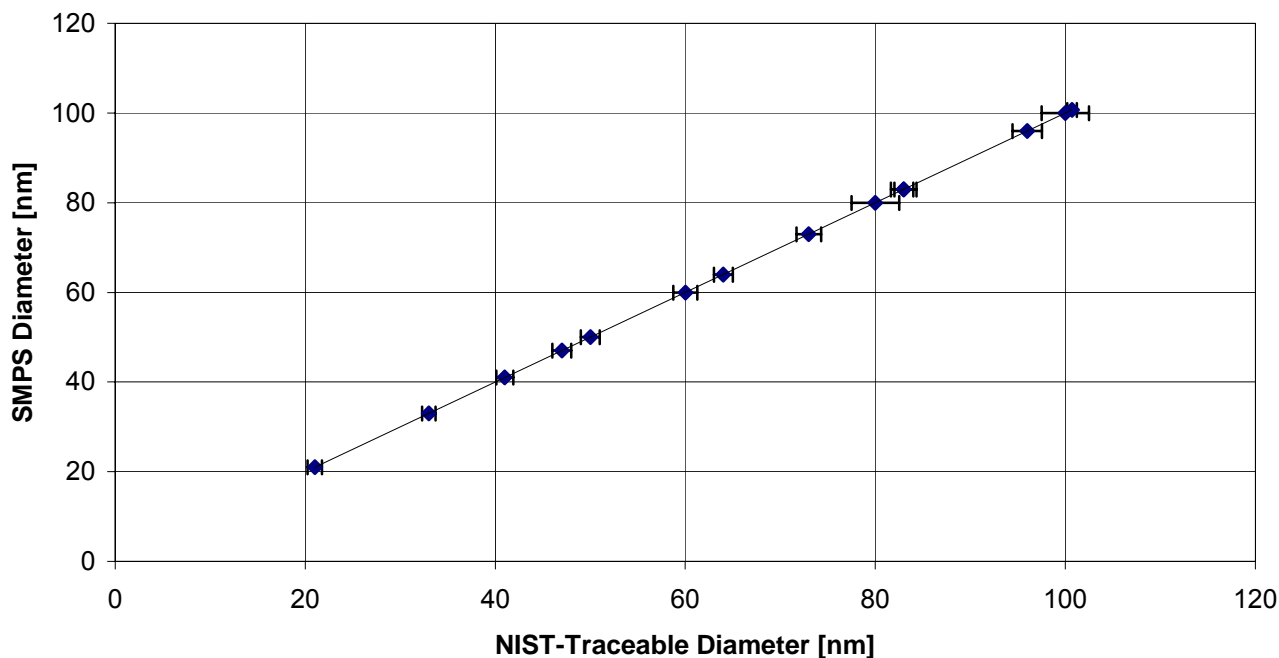
Table 3. SMPS Mean Diameters vs. Reference Standards

Catalog PN Tested	TEM Diameter* [nm]	SMPS Diameter [nm]	SMPS Intensity** Weighted [nm]	DLS/PCS Diameter [nm]
3020A	N/A	14.5 nm	21 nm	21 nm ± 1.5 nm
3030A	N/A	23.0 nm	33nm	33 nm ± 1.4 nm
3040A	N/A	30.2 nm	41 nm	41 nm ± 1.8 nm
PD-047	47 nm ± 2 nm	46 nm	49 nm	50 nm
3050A	50 nm ± 2.0 nm	51 nm	54 nm	54 nm
3060A	60 nm ± 2.5 nm	58 nm	62 nm	64 nm
PD-064	64 nm ± 2 nm	63 nm	65 nm	64 nm
3070A	73 nm ± 2.6 nm	73 nm	76 nm	76 nm
PD-080	80 nm ± 5 nm	82 nm	85 nm	83 nm
3080A	83 nm ± 2.7 nm	81 nm	83 nm	86 nm
PD-083	83 nm ± 2 nm	83 nm	85 nm	84 nm
3090A	96 nm ± 3.1 nm	97 nm	100 nm	97 nm
PD-100	100 nm ± 5 nm	100 nm	101 nm	102 nm
NIST1963	100.7 nm ± 1 nm	100.2 nm	101 nm	101 nm

\* Diameter calculated as  $\sum nd/\sum n$

\*\* Diameter calculated as  $\sum nd^6/\sum nd^5$

Figure 5. SMPS Values vs. Reference Standards



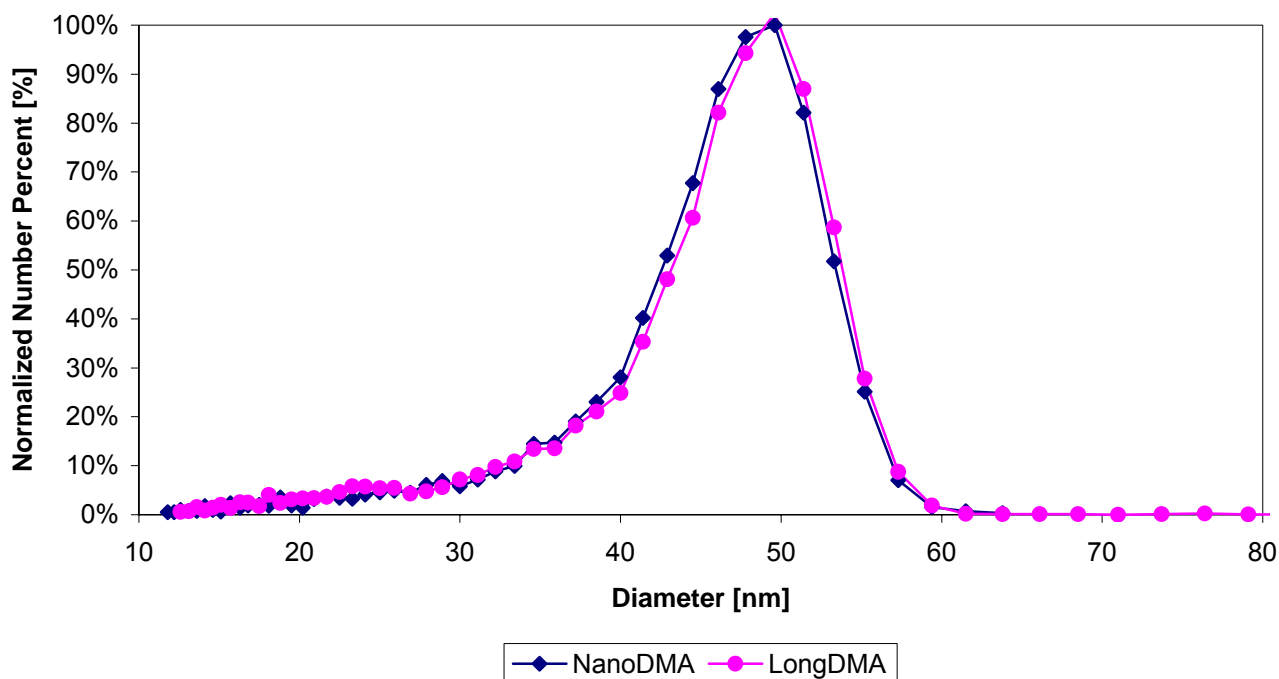
<sup>3</sup> For a discussion of moment averages and weighted distributions the reader is referred to the Hinds' book listed in our bibliography. DLS instruments report a  $\sum nd^6/\sum nd^5$  weighted mean, while the SMPS and TEM methods report a standard number mean diameter.

Figure 5 shows excellent agreement between the SMPS measured diameter and the reference standards. Horizontal error bars indicate the uncertainty of the reference standard measurement. In all cases, the SMPS mean diameter (or calculated intensity weighted mean diameter) fell within the uncertainty of the reference standard.

An analysis of the width of the distribution for each particle size has been omitted from this paper due to complications arising from the different measurement techniques. Actual mean diameters calculated from 100% of the SMPS data will not correctly correlate with TEM data for the following reasons: TEM data is difficult to obtain below 40 nanometers, so a low-end tail of a distribution will not be seen with TEM data; surfactant crystals and multiply-charged doublets can cause extra counts on the low side of a distribution in the SMPS analysis. For the SMPS values listed above, the mean diameter was calculated using as range similar to, or slightly larger than, the TEM measurements. Obvious outliers and multiply charged particles were also excluded. In general, it seems that the SMPS system tends to broaden the distribution very slightly, although that may have more to do with the limitations of the software rather than the physical instrument.

SMPS measurement repeatability has also been measured with single samples, multiple samples, and multiple setups. Figure 6 represents typical overlay data from a single sample run under varying conditions. The first run was performed using the nanoDMA setup with a 15 Lpm sheath flow rate and a 1.5 Lpm aerosol flow rate. The AIM software scan time was 300 seconds. The second run was performed on the same sample using the long DMA setup with a 17 Lpm sheath flow rate and a 1.5 Lpm aerosol flow rate. The AIM software scan time was also 300 seconds. With a properly cleaned and operating SMPS system, the results of multiple runs on a single sample is typically very consistent over time and using different instrument configurations.

Figure 6. SMPS Consistency Chart



## CONCLUSION

The SMPS system can give very accurate and repeatable results if it is operating correctly. In our setup, the Electropray was the most critical component for achieving accurate results. A newer and cheaper capillary design has allowed the electropray to provide a constant aerosol output over most ordinary scan times. Clean, unobstructed capillaries can deliver consistent concentrations of polystyrene particles for an accurate measurement. In addition, difficulties due to surfactant and additives can be eliminated through the use of dilution or ion-exchange methods.

Dynamic Light Scattering, Transmission Electron Microscopy and the SMPS methods all correlate very well. The standard AIM software with a 300 second scan was used for the SMPS method. Better resolution can be obtained using a manual scan, but that is not within the scope of this paper. It is clear from the results in this paper that a properly operated and maintained SMPS instrument can accurately and precisely measure small particles with a reliability similar to other established methods.

## BIBLIOGRAPHY

Aerosol Instrument Manager® Software Ver. 4.3, TSI Incorporated, St. Paul, MN.

Hinds, W. C. (1982). *Aerosol Technology: Properties, Behaviour, and Measurement of Airborne Particles*. John Wiley & Sons, inc., New York.

TSI Incorporated. (2000). *Model 3080 electrostatic classifier: instruction manual (revision C)*. St. Paul, MN: TSI, Inc.

TSI Incorporated. (2001). *Model 3936 SMPS (scanning mobility particle sizer: instruction manual (revision F)*. St. Paul, MN: TSI, Inc.

TSI Incorporated. (2000). *Model 3025A ultrafine condensation particle counter: instruction manual (revision H)*. St. Paul, MN: TSI, Inc.

TSI Incorporated. (2000). *Model 3062 diffusion dryer: instruction manual (revision E)*. St. Paul, MN: TSI, Inc.

TSI Incorporated. (2000). *Model 3077 aerosol neutralizer: instruction manual (revision K)*. St. Paul, MN: TSI, Inc.

TSI Incorporated. (2000). *Model 390081 CPCCount software: instruction manual (revision E)*. St. Paul, MN: TSI, Inc.

TSI Incorporated. (2001). *Aerosol instrument manager software: instruction manual (revision A)*. St. Paul, MN: TSI, Inc.

TSI Incorporated. (2000). *Model 3480 electrospray aerosol generator: instruction manual (revision A)*. St. Paul, MN: TSI, Inc.