

An Evaluation Of A Scanning Mobility Particles Sizer With NIST-Traceable Particle Size Standards

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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, electrospray 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.

Keywords: particle, standard, size, nist, smps

1 INTRODUCTION

A Scanning Mobility Particle Sizer (SMPS) manufactured by TSI incorporated is used for sizing particles from 5 nanometers (nm) to 1 micron (μm) 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).

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. Following is a short description of the components used in this evaluation:

- TSI Model 3480 Electrospray Aerosol Generator
2-100nm particle size range
- TSI Model 3085 Nano DMA
2-150nm particle size range
- TSI Model 3081 Long DMA
10-1000nm particle size range
- TSI Model 3025 Ultrafine CPC
Concentration range from 0 to $\sim 1 \times 10^5 \#/\text{mL}$

This report describes some of the instrument operating conditions that optimize the performance of the SMPS system when measuring polystyrene microspheres. It

discusses 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.

2 EXPERIMENTAL SETUP

2.1 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 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.

2.2 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 μL 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.

2.3 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.

Anionic 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.

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, there should not be any visible inhomogeneity in the solution. 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.

2.4 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 electrospray 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.

3 DATA COLLECTION

Outside of the Electrospray 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.

4 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.

Figure 1 (on the following page) 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.

5 CONCLUSION

The SMPS system can give very accurate and repeatable results if it is operating correctly. In our setup, the Electrospray was the most critical component for achieving accurate results. A newer and cheaper capillary design from the manufacturer has allowed the electrospray 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.

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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

Table 1: SMPS Mean Diameters vs. Reference Standards

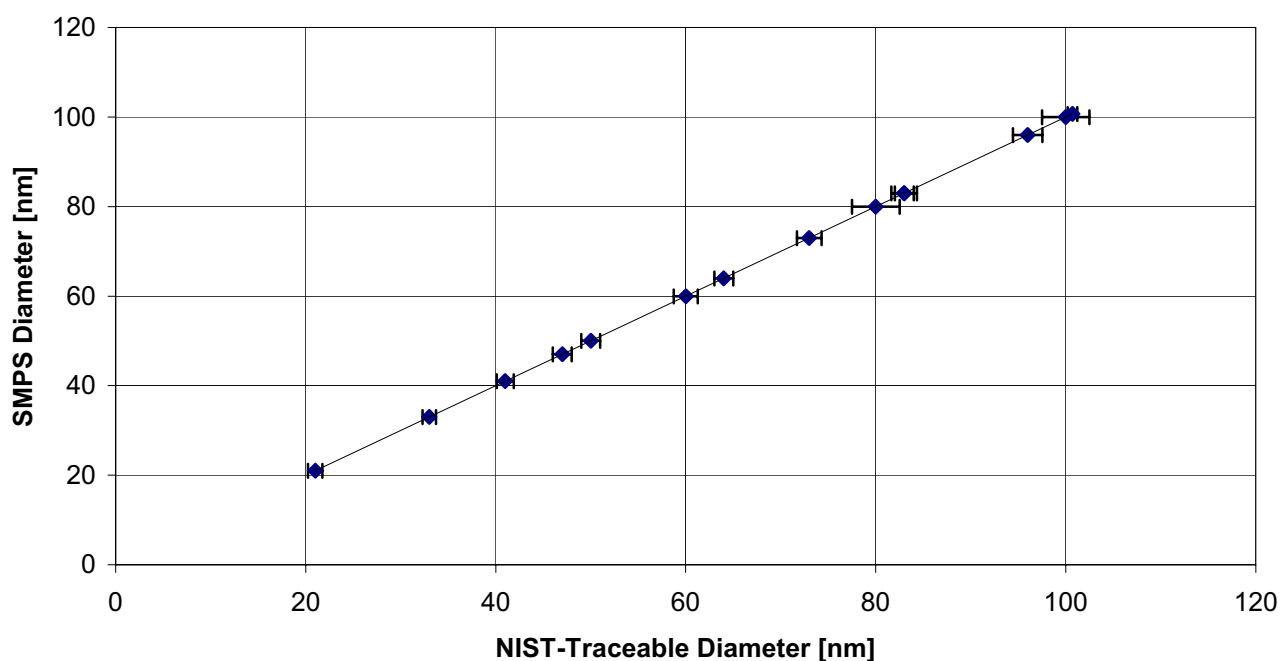


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