

Measuring Nanoparticle Size Distributions in Real-Time: Key Factors for Accuracy

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ABSTRACT

The benefits of sizing aerosolized submicrometer particles using an electrical mobility sizing technique have been well documented. The National Institute of Standards and Technology (NIST) has been using this method to measure 0.1 μm Standard Reference Material (SRM) Particles for well over a decade [1][2]. Mullholland and Pui (2006) measured 60 and 100nm SRM using electrical mobility and calculated the uncertainty to be approximately 1% of the particle size [3]. Vasiliou (2005) evaluated the measurement from an SMPS spectrometer using Duke Scientific NIST-traceable particle size standards from 14.5 to 100.2nm, and compared these results to both TEM and DLS techniques. In all cases, for all sizes the SMPS mean diameter fell within the uncertainty of the reference standard [4]. In this paper, key factors which play a significant role in accuracy for real-time on-line measurement of aerosolized nanoparticles using an electrical mobility technique will be discussed.

1 INTRODUCTION

The end of the 20th century and the beginning of the 21st century have been marked with a flood of interest in nanotechnology and nanoparticle manufacturing. Researchers and process engineers require accurate nanoparticle size measurement tools because particle size is a critical metric affecting the material properties of the final nanotechnology product. The Scanning Mobility Particle SizerTM spectrometer is being used to size nanoparticles for a number of reasons, including: excellent submicron size resolution, complete size distributions can be measured in real time, and the spectrometer can be used to make on-line measurements. Much early sizing work was done on titanium dioxide. Akhtar et al (1991) [5] used an SMPS to study the vapor synthesis of titania particles, and in Somer et al (1994) [6] used the technique to study TiO₂ agglomeration in high intensity sound fields. Since then, many other researchers have used SMPS to study the output produced by nanoparticle reactors [7]. The SMPS has also been used widely to study the size distribution of nanoparticles produced by a variety of other techniques [8] and to evaluate nanoparticle emissions.

Originally, the SMPS spectrometer was a tool of the aerosol research scientist. As the spectrometer has gained broader use, it now becomes necessary to detail key factors that are integral for measurement accuracy to ensure users produce the high quality measurement data that is achievable.

1.1 Differential Mobility Analysis Theory

The SMPS spectrometer uses a DMA to size classify the particle stream and a condensation particle counter to determine the concentration at each size. A DMA utilizes the fact that a particles' electrical mobility (Z_p ; ability of a charged particle to move in an electric field) is roughly inversely proportional to particle diameter.

$$Z_p = \frac{\text{Particle Velocity}}{\text{Electric Field Strength}} = \frac{v}{E} = \frac{n_p e C}{3\pi\mu D_p} \quad (1)$$

Z_p = electrical mobility; n_p = number of charges/particle; e = elementary unit of charge; μ = viscosity of gas; D_p = particle diameter; C = Cunningham slip correction. Note: C is also a function of D_p .

The nano Differential Mobility Analyzer (NDMA) was specifically designed to improve nanometer size resolution and engineered to increase transmission efficiency of nanometer particles by minimizing diffusion broadening and particle losses due to diffusion and electrostatic forces [9]. The design was optimized using numerical modeling and underwent extensive experimental validation to ensure a highly repeatable and consistent measurement. The NDMA consists of a center cylindrical electrode that is typically at a negative voltage surrounded by a grounded concentric outer electrode. The aerosol to be analyzed is pulled into the cylindrical NDMA at the top and introduced at the inside wall of the outer electrode. As shown in the schematic below, sheath flow is introduced from the bottom of the NDMA and routed to the top of the instrument to surround the inner electrode with a laminar flow of particle free air. When a negative voltage is applied to the center electrode, positively charged particles migrate toward the inner electrode and follow different trajectories according to their electrical mobility. Particles with a given narrow mobility range will exit the DMA through the exit slit.

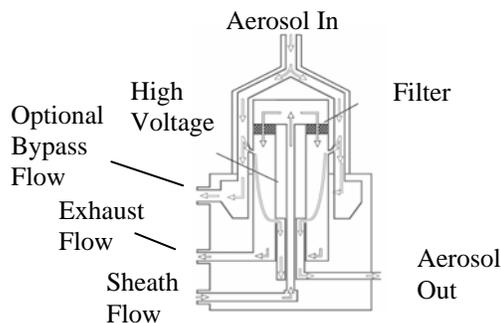


Figure 1: Schematic of Nano DMA

Originally, the size distribution of a static aerosol was measured by stepping the voltage and recording readings at a variety of particle sizes. Wang and Flagan (1990) introduced the concept of scanning the voltages exponentially to decrease the time of measurement, cover the entire size range, and allow in situ real-time sizing of aerosols [10].

1.2 Condensation Particle Counter Theory

CPCs work by condensing a working fluid on small particles to grow them to a size which is easily detected by optical methods. CPCs consist of three basic components: 1) saturator, 2) condenser, 3) optics & detector. The smallest non-evaporating particle (D_{kelvin}) is determined by the properties of the working fluid and the supersaturation ratio of the vapor. Particle surface characteristics play a role as well.

$$D_{\text{Kelvin}} = \frac{4\delta_s M}{\rho_L RT \log S} \quad (2)$$

D_{kelvin} = Kelvin Diameter; δ_s = Surface Tension of Working Fluid; M = Molecular Weight of Working Fluid; ρ_L = Density of Working Fluid; R = Gas Constant; T = Temperature; S = Supersaturation Ratio

$$S \equiv \frac{P_v}{P_{\text{Saturation}}(T)} \quad (3)$$

S = Supersaturation Ratio; P_v = Vapor Pressure; $P_{\text{saturation}}(T)$ = Saturation Vapor Pressure

CPCs are capable of detecting particles down to 2.5nm with 50% efficiency.

2 SMPS: KEY FACTORS FOR ACCURACY

The elegance of the electrical mobility technique to size aerosols is that the instrument is a first principle device. In order to accurately provide size and concentration information, no classical calibration needs to be done. However, in an SMPS spectrometer, the raw data stream from the CPC must be processed by a relatively complex data inversion to convert the data into a size distribution. This data inversion takes into account the following variables:

- 1) DMA voltage
- 2) CPC & DMA flow
- 3) Scan time
- 4) Charge distribution
- 5) Efficiency curve of the CPC
- 6) DMA transfer function
- 7) Parameters of working gas
- 8) Diffusion loss

In addition to these considerations, a well thought out sampling scheme is another important factor in achieving a highly accurate on-line aerosol measurement. Nanotechnology sampling techniques may have to be tailored to specific applications.

2.1 DMA Voltage

As mentioned above, the electrical mobility technique is first principle, but the technique relies on accurate voltage and flow measurements. The TSI SMPS

has an accurate and reliable high voltage scheme, which is calibrated with NIST traceable meters.

2.2 CPC & DMA flow rates

Flow accuracy is extremely important for high quality measurements. The SMPS utilizes a recirculating flow scheme so that the inlet sheath flow precisely matches the exit sheath (exhaust) flow. This is important to ensure laminar flow in the DMA, minimize flow disturbances which can result in decreased resolution, and ensure that the exiting monodisperse aerosol flowrate precisely matches the incoming aerosol flowrate. The flowmeters which control the sheath and bypass flow are NIST traceable, micro-processor controlled, and adjust for atmospheric pressure and temperature differences. Since recirculation of the excess air/sheath air is used, incoming aerosol flow is equal to exiting monodisperse aerosol flow, which is typically controlled by the flowrate of the CPC. The accuracy of the sheath flow should be periodically checked using an independent volumetric flow measurement, as should the aerosol flow and CPC inlet flow. Errors in flow can greatly reduce the measurement accuracy.

2.3 Scan Time

The duration of the scan is used in the data inversion to map particle counts to a corresponding size. It is also important to note that a longer scan time will result in more accurate measurement. Russell et al (1995) first noted the scan time effect which develops during short scans [11]. This results in a tail toward large particles sizes most likely resulting from turbulent mixing in the plumbing between the DMA and the CPC. For the greatest accuracy 300 second scans are recommended, if the incoming aerosol remains stable for that long.

2.4 Bipolar Charge Distribution

In the SMPS data inversion, the size distribution and concentration accuracy are dependent on knowledge of the charge distribution of the incoming aerosol. The incoming aerosol must have a predictable charge distribution. For this reason, a radioactive ionizer is used to induce a bi-polar charge distribution. TSI uses the beta-emitter Krypton-85 for safety, convenience and the legacy of aerosol research. For safety, Kr-85 is an inert gas that is not absorbed by the body. When used with the SMPS, it is sealed in an air tight stainless steel container. In the US, the amount used for the SMPS is classified as a "non-biological health hazard". In terms of convenience, it has a relatively long half-life of more than 10 years, and it is well researched and documented in technical literature. The charge distribution used in the TSI data inversion was taken from the work of Wiedensohler et al (1988) [12]. For most applications, it is best to use a 10 mCi Kr-85 source to ensure the incoming aerosol has the correct bi-polar charge distribution.

2.5 Efficiency Curve of the CPC

The minimum particle size specification of the CPC is determined from the CPC counting efficiency curve.

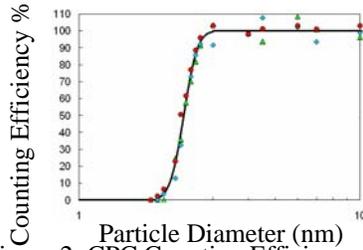


Figure 2: CPC Counting Efficiency Curve

The minimum specification is the size at which the CPC can see 50% of the challenge particles. A file of the efficiency curve for the specific CPC used is included in the software, so the correct size distribution can be built. The efficiency curve of the CPC can become very important if there are a lot of aerosol particles at the minimum size detection limit of the CPC.

Several factors can affect the CPC efficiency curve.

1) Instrument to instrument variation: there will be slight differences in the efficiency curves of each instrument. 2) Working fluid: all working fluids exhibit some material dependence. 3) Carrier gas: The gas used that carries the particles affects the CPC efficiency curve. All of the default curves in the software were taken using air as the aerosol carrier gas. Niida et al (1988) investigated the counting efficiency of CPCs using N_2 , Ar, CO_2 and He and noted slight efficiency curve differences [13].

It is possible to use a custom efficiency curve file in the software. To achieve the most accuracy possible, generating a custom efficiency curve using the calibration procedure outlined by Liu et al [14] may be necessary.

2.6 DMA Transfer Function

Knutson and Whitby (1975) developed DMA theory based on particle trajectory equations [15]. Out of this came the concept of the transfer function of a DMA, which is defined as the probability that an entering particle with an electrical mobility of Z will have the correct trajectory to exit through the exit slit with the classified aerosol. An ideal DMA with an ideal transfer function would produce only one size of aerosol when set at a constant voltage. In reality, there is a narrow distribution of sizes which exit the DMA at a set voltage. The width of this distribution can be controlled by the ratio of sheath air to sample aerosol. The higher the ratio of sheath to sample air, the more monodisperse the classified aerosol will be. TSI recommends a sheath to aerosol ratio of 10:1 for optimum performance. Figure 3 illustrates the effect of the transfer function on resolution. In an optimized DMA, the transfer function is triangular in shape. At flow ratios of 10:1 or higher, each bin of data totally represents the size data at each voltage (Figure 3a). In Figure 3b, the sheath to air ratio is lower, and the transfer function is wider. Even though the

displayed resolution is the same, the actual resolution of the data is no better than the width of the transfer function, because it is impossible to determine whether particles from adjacent bins actually have differing sizes.

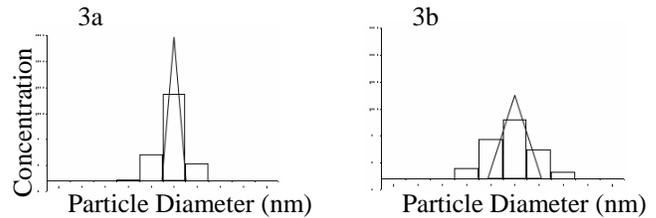


Figure 3a & b: Effect of transfer function on resolution.

Another important note on DMA flow is that if the total flowrate inside the DMA is too high, or if the flow ratio is too high, non ideal flow can develop and adversely affect the resolution. The SMPS system can measure size resolution with σ_g of 1.05, or even lower.

2.7 Parameters of the Working Gas

The particle velocity is a function of the working gas used with the DMA. The TSI software allows input of gas viscosity and mean free path. But, when switching working gases, other variables need to be considered as well. The internal flowmeters are calibrated using air. So, if other gases are used, it is important that the flows of the DMA and CPC be calibrated using an independent volumetric flowmeter. Karg et al (1992) studied the effect of relative humidity and gas composition on the performance of a DMA [16]. Schmid et al (2002) also investigated DMA accuracy using He, Ar, H_2 , CO_2 and N_2O and concluded that when properly calibrated, there was no effect of gas type on the accuracy of the DMA [17]. There is however, an issue concerning electrical breakdown. At high voltages, electrical arcing can occur within the DMA which limits the upper range of the DMA. Meek and Craggs (1978) looked at breakdown voltage (V_b) for different gas types [18]. Schmid found that noble gases have V_b of about an order of magnitude smaller than air. This will limit the upper size range of the measurement.

2.8 Diffusion Loss

The largest force by far, acting on nanoparticles is diffusion. Gormley and Kennedy (1949) derived an equation for circular tube penetration efficiency for aerosols [19]. These transport losses will be significant for all aerosol nanoparticle applications, but since the diffusion losses are size dependent (the smaller the particle, the more susceptible it is to diffusion), it is important to roughly quantify these losses when sizing nanoparticle aerosols on-line. TSI software currently includes a useful algorithm that can estimate the diffusion losses through the SMPS spectrometer.

It is important to calculate size dependent losses through transport tubing. Note that the primary factor

affecting diffusion losses is residence time, not tubing diameter. Higher flows to the instrument will result in less diffusion losses.

2.9 Nanoparticle Sampling Techniques & Challenges

Nanoparticle manufacturing and research can present some challenging sampling issues. Many processes use a variety of gas compositions, pressures, temperatures, and produce high aerosol concentrations. Gas composition issues were briefly discussed above, but introduction of inert sampling gases (preferable N₂ because it is closest to air in its material properties) to carry samples into the SMPS should be considered. This minimizes measurement variables, and also minimizes safety problems derived from hazardous or explosive gases. Many nanoparticle reactors operate at low pressure, which can present a problem since the SMPS was designed to operate at atmospheric pressure. Ober et al (2002) designed and experimentally validated a low pressure sampling system specifically for use with an SMPS spectrometer [20]. Wang et al. (2005) designed a diagnostic system to measure particle size from low pressure high temperature environments [21]. Many other published researchers have successfully sampled from nanoparticles reactors. For high concentration aerosols, care must be taken to properly dilute the sample to minimize the effects of evaporation and coagulation, and to effectively freeze the size distribution as it was in the process stream.

3 CONCLUSION

With an understanding of key measurement factors, the SMPS can be used successfully for highly accurate on-line nanoparticle measurements. Many of the factors noted can be automatically adjusted in the software. An awareness of the importance of voltage and flow accuracy, scan time, bi-polar charge distribution, CPC efficiency curve, DMA transfer function, working gas, diffusion losses, and sampling and conditioning issues will enable the user to achieve the resolution and accuracy the SMPS is capable of.

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