

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



Application Note SMPS-003 (A4)

Introduction

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 decades [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 Scanning Mobility Particle Sizer (SMPS) spectrometer 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 measurement of aerosolized nanoparticles using an electrical mobility technique will be discussed.

Recent years have been marked with a flood of interest in nanotechnology and nanoparticle-based 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 SMPS 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 continuous 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 TiO_2 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 increasingly broader use, it is useful to detail key factors that are integral for measurement accuracy to ensure users produce the high-quality measurement data that is achievable.



Differential Mobility Analysis Theory

The SMPS spectrometer uses a Differential Mobility Analyzer (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 particle's electrical mobility (Z_p , or the ability of a flowing charged particle to move in an electric field) is approximately 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.

This relationship is only approximately inversely proportional because C is itself also a function of D_p .

There are four models of DMA available to use in the SMPS, depending on application. One of these is the nano Differential Mobility Analyzer (NDMA), which 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 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 voltage is applied to the center electrode, particles of the opposite polarity 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.

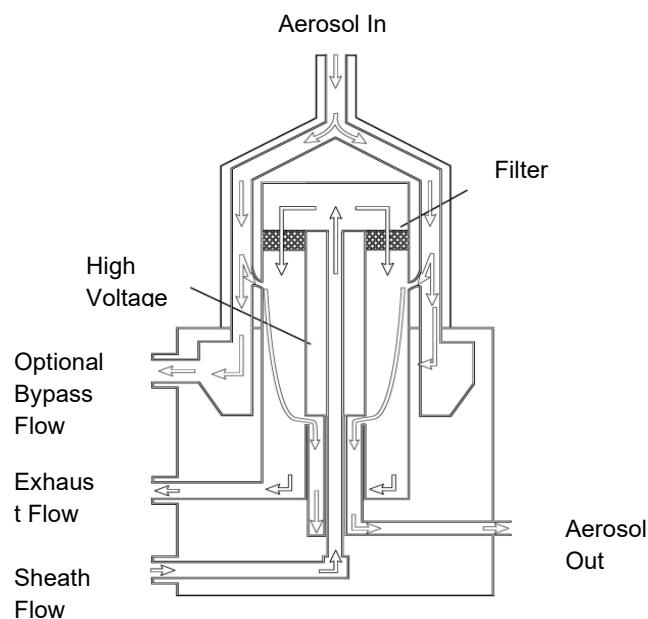


Figure 1. Schematic of Nano DMA

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].

Condensation Particle Counter Theory

Condensation Particle Counters (CPCs) work by condensing a working fluid on small particles to grow them to a size which is easily detected by simple optical methods. The basic CPC design consists of three basic components: 1) saturator, 2) condenser, and 3) optical detector. The smallest non-evaporating particle that can be detected, described by the Kelvin Diameter (D_{kelvin}), is determined by

the properties of the working fluid and the supersaturation ratio S of the vapor. Particle surface characteristics play a role as well, but these will not be discussed in this paper.

$$D_{Kelvin} = \frac{4\delta_S M}{\rho_L R T \log S} \quad (2)$$

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

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

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

In the CPC, the saturator fills the carrier gas with the vapors from a working fluid, n-butanol being a very common choice. The condenser drives the supersaturation ratio to a high level, such that the vapor preferably condenses onto the aerosol particles in a process called heterogeneous nucleation. The particles grow to a size easily detectable with simple lasers and optics, where they are counted individually.

Depending on the design, CPCs are capable of detecting particles down to about 1nm with 50% efficiency.

SMPS: Key Factors for Accuracy

The elegance of using the electrical mobility technique to size aerosols is that the instrument using the technique can be a first-principles device. In order to accurately provide size and concentration information, no classical calibration needs to be done, i.e., “correcting” the diameters to a reference via a curve or similar. If the core operational parameters, discussed next, are accurate, then the measurement will also be accurate. 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 could take into account the following variables, and potentially others, depending on the specific inversion model:

- | | |
|------------------------|--------------------------------|
| 1) DMA voltage | 6) Efficiency curve of the CPC |
| 2) CPC & DMA flows | 7) DMA transfer function |
| 3) Scan time | 8) Parameters of carrier gas |
| 4) Delay time | 9) Diffusion losses |
| 5) Charge distribution | |

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.

DMA Voltage

As mentioned above, the electrical mobility technique can be implemented in a first-principles way, but the technique relies on accurate voltage and flow measurements. The TSI® SMPS has an accurate and reliable high voltage control scheme, which is calibrated with National Institute of Standards and Technology (NIST, the United States’ national metrology laboratory) traceable reference equipment.

Figure 2 shows the theoretical DC voltage applied to the DMA high voltage rod (the voltage setting that the instrument calls for, based on calculation from the theory) and the DMA voltage directly measured using a reference for the same scan. The measured and theory lines agree very well across the scan. The percent difference is also plotted, showing error of less than 1% across the scanned voltage range (0 – 10 kV).

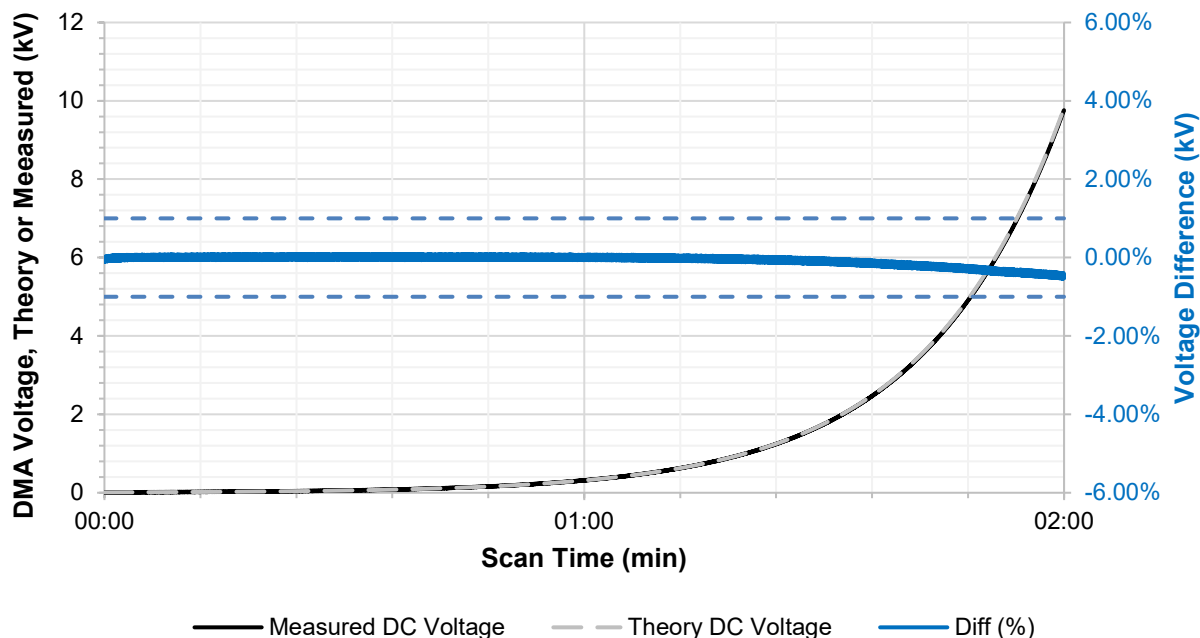


Figure 2. Measured vs theoretical DMA voltage for a typical 2-minute SMPS scan.

The difference between the two is also plotted as the % Difference. The blue dashed lines represent $\pm 1\%$ error.

CPC and 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 for ensuring laminar flow in the DMA, minimizing flow disturbances and particle migration, which can result in decreased size resolution, and ensuring that the exiting monodisperse aerosol flow rate precisely matches the incoming polydisperse aerosol flow rate. The flowmeter which controls the sheath flow loop has a NIST traceable calibration, is micro-processor controlled, and adjusts for atmospheric pressure and temperature differences. Since recirculation of the sheath air is used, incoming aerosol flow is equal to exiting monodisperse aerosol flow, as mentioned previously, which is typically controlled by the flow rate of the detector, most often a CPC. The accuracy of the sheath flow should be periodically checked using an independent volumetric flow measurement, as should the polydisperse aerosol inlet flow and CPC inlet flow. Errors in flow can greatly reduce the measurement accuracy.

Scan Time

The DMA voltage continuously changes during a scan, and therefore also the size of particle eluted from the DMA. The overall length of the scan then determines how much time is spent at each particle size, and how long the particles have to transit the DMA. A longer scan time will in general result in more accurate measurements, because of the increased time allowed for particles to be classified and counted by the CPC. Russell et al. (1995) first noted a scan time dependency which develops during short scans [11]. This results in a tail in the size distribution forming toward large particle sizes, most likely resulting from turbulent mixing in the plumbing between the DMA and the CPC. For the greatest accuracy, 300 second or longer scans are recommended, if the incoming aerosol remains stable for that long.

Delay Time

In addition to the total scan duration, the accuracy of the start and stop times of the scan and the measurement time itself become important. As discussed in the previous section, this is due to the necessary transit time of the particles as they pass through the various system components: the DMA inlet to the exit; the DMA exit to the CPC inlet; and the CPC inlet to the detector of the CPC. This total offset from the time of sizing to the time of counting needs to be accounted for. An additional source of delay is the dwell time, or, the difference between the start of the measurement command until the voltage ramp begins within the instrument. Using an accurate delay time is essential for sizing accuracy in shorter scans in particular.

In order to account for all delays in the system, it is recommended to perform an upscan/downscan offset measurement. In other words, perform a measurement of a known aerosol (typically a monodisperse aerosol such as Polystyrene Latex, or PSL), by scanning the voltage both up from low to high absolute voltage, and then in reverse, from high absolute voltage to low. The offset in the size distributions, usually quantified as a difference in the diameter of the measured peak, can be used as a measure of the amount of unaccounted for delay time within the system. This time can then be calculated and input into the software as an additional offset in order to correct for these sources of delay.

Bipolar Charge Distribution

In the SMPS data inversion, the sizing accuracy is dependent on knowledge of the charge distribution of the incoming aerosol. The incoming aerosol must have a stable and predictable charge distribution that is well-described mathematically, and ideally, one that is in equilibrium. For this reason, a charge conditioner (sometimes also called a “neutralizer”) is used to induce a bi-polar charge distribution.

Radioactive Neutralizers

TSI has several options for using different charge conditioners, depending on the needs of the user. The radioactive source-based Models 3077 and 3077A use the beta-emitter Krypton-85 for safety and convenience. This source has a long and established legacy in aerosol research. In terms of safety, Kr-85 is a chemically 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. Another radioactive option is the ACC-EL2-63 charge conditioner. It uses an optimized flow path with a < 100 MBq Nickel-63 beta source and a 10 year service life to deliver safe but predictable particle charging. This approach significantly reduced regulatory burden in many locales compared to traditional radioactive charge conditioners.

Non-Radioactive Neutralizers

For users who want a non-radioactive alternative, the Model 3088 uses “soft” (< 9.5 keV) x-ray charge conditioning. This option produces no radiation when power is not applied, and the design makes emissions close to background in the vicinity of the source. As local, state, and national regulations become increasingly stringent, obtaining licenses to acquire and use radioactive sources can be difficult and, in some cases, prohibited. Fully compliant with U.S. FDA CDRH (Food and Drug Administration, Center for Devices and Radiological Health) standards, the Model 3088 provides an attractive alternative, with particle sizing performance virtually identical to TSI’s Aerosol Charge Conditioner Model 3077A [12].

The charge distribution used in the TSI data inversion was taken from the work of Wiedensohler et al. (1988) [13].

Efficiency Curve of the CPC

The minimum particle size specification of the CPC is determined from the CPC counting efficiency curve. This curve is generated by producing a small monodisperse aerosol at various sizes and comparing to a reference detector, like the Model 3068B aerosol electrometer.

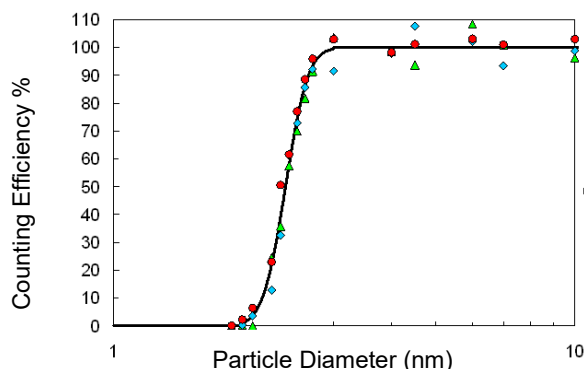


Figure 3. CPC Counting Efficiency Curve

The minimum specification is usually the size at which the CPC can detect 50% of the challenge particles compared to the reference, called the D_{50} . Files of the efficiency curves for all compatible CPCs used in SMPS systems are included in the Aerosol Instrument Manager software, so the correct size distribution can be built. The efficiency curve of the CPC can become very important if there are many aerosol particles around the ascending portion of the CPC counting efficiency curve.

Several factors can affect the CPC counting efficiency curve, including:

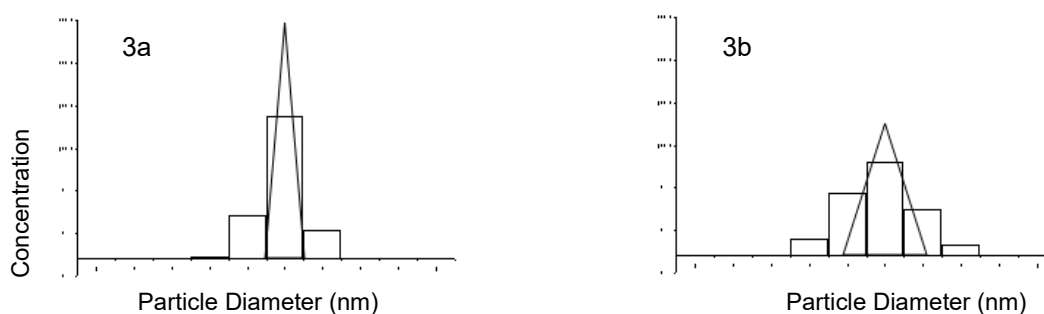
- 1) Instrument to instrument variation: there will be slight differences in the efficiency curves of each instrument.
- 2) Working fluid- aerosol material dependence: all working fluids exhibit some material dependence, and vice versa.
- 3) Carrier gas: The gas used that carries the particles affects the CPC efficiency curve.

All of the default counting efficiency curves in the AIM software were generated 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 [14].

It is possible to use a custom efficiency curve file in the software. To achieve the best accuracy possible, generating a custom efficiency curve using the calibration procedure outlined by Liu et al. [15] may be necessary.

DMA Transfer Function

Knutson and Whitby (1975) developed the first practical DMA theory based on particle trajectory equations [16]. Out of this came the concept of the transfer function of a DMA, which encapsulates the probability that an entering particle with an electrical mobility of Z_p will have the correct trajectory to exit through the exit slit with the classified aerosol. A DMA with an ideal transfer function would produce only one size of aerosol (i.e., a perfectly monodisperse 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 flow to sample aerosol flow. The higher the ratio of sheath to sample air flow, the more monodisperse the classified aerosol will be. TSI® recommends a sheath to aerosol ratio of 10:1 as rule of thumb to start, after which it can be adjusted based on the needs of the application. Figure 3 illustrates the effect of the transfer function on resolution. In an ideal DMA with no diffusion broadening, 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 4a). In Figure 4b, 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 deterministically know whether particles from adjacent bins actually have different sizes, i.e., if particles are placed in the correct size bin. There would be some statistical proportioning of particles into the bins based on the shape (area) of the transfer function in this case.



Another important note on DMA flow is that if the total flow rate inside the DMA is too high, or if the flow ratio is too high, transitional or turbulent flow can develop and adversely affect the resolution. The SMPS system can measure size resolution with Geometric Standard Deviation, σ_g of 1.05, or even lower, when this is not the case.

Since 1975, there have been several improvements to the inversion models developed and tested by various authors. The reader is recommended to perform a search of the literature to learn about the latest developments, and the benefits and drawbacks of the various approaches. Raw count data and the parameters that define the scan are always available to the user in the AIM software, so the raw data can be processed as desired with user-implemented analysis codes if the standard TSI inversion is not sufficient for the user's needs.

Parameters of the Carrier Gas

The particle velocity is a function of the carrier gas used with the DMA. The TSI® software allows measurement or specification of sheath gas temperature and pressure, which are used to compute gas viscosity and mean free path. But, when changing the carrier gas, other variables need to be considered as well. The internal flowmeter is 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 [17]. Schmid et al. (2002) also investigated DMA accuracy using He, Ar, H₂, CO₂ and N₂O and concluded that when properly calibrated, there was no effect of gas type on the accuracy of the DMA for an applicable size range [18]. There is, however, the possibility high voltage electrical breakdown depending on carrier gas properties. At high voltages, electrical arcing can occur within the DMA, which limits the upper sizing range of the DMA. Meek and Craggs (1978) examined breakdown voltage (V_b) for different gas types [19]. Schmid found that noble gases have V_b of about an order of magnitude smaller than air.

Diffusion Losses

The most significant transport mechanism by far driving nanoparticle motion in the absence of external fields is diffusion. Brownian motion will cause particles to migrate, often in undesirable ways, leading to losses to tubing walls or broadening of the transfer function. As a first step to quantify losses mathematically, Gormley and Kennedy (1949) developed an equation for circular tube penetration efficiency for aerosols [20], normalized so different dimensions and flow rates could be accounted for. The primary factor affecting diffusion losses is residence time, not tubing diameter. Higher flows to and through the instrument will result in lower diffusion losses, assuming the flows remain laminar. Since these transport losses are significant for all practical aerosol nanoparticle measurement applications, and because the diffusion losses are particle size dependent (the smaller the particle, the more susceptible it is to diffusion loss), it is important to quantify and correct for these losses experimentally or theoretically when sizing nanoparticle aerosols. TSI® software currently includes a diffusion loss correction algorithm that can estimate the diffusion losses through the SMPS spectrometer.

Nanoparticle Sampling Techniques and 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 (oftentimes preferably N₂ because it is closest to air in its physical properties) to carry samples into the SMPS should be considered. This minimizes deviations in system process variables from air, 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 [21]. Wang et al. (2005) designed a diagnostic system to measure particle size from low pressure, high temperature environments [22]. Many other published researchers have successfully sampled from nanoparticle reactors. For high concentration aerosols, care must be taken to properly dilute the sample to minimize the possibility of the aerosol changing from the point of production to the point of sampling through processes such as evaporation and coagulation, and to effectively freeze the size distribution as it was in the process stream.

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.

References

- [1] P. Kinney, D. Pui, G. Mulholland, N. Bryer, "Use of the Electrostatic Classification Method to Size 0.1 μm SRM Particles – A Feasibility Study" *J. of NIST* **96**:147, 1991.
- [2] G. Mulholland, N. Bryner, C. Croarkin, "Measurement of the 100nm NIST SRM 1963 by Differential Mobility Analysis," *Aerosol Sci. & Tech.*, **31**:39-55, 1999.
- [3] G. Mulholland, M. Donnelly, C. Hagwood, S. Kukuck, V.A. Hackley, "Measurement of 100nm and 60nm Particle Standards by Differential Mobility Analysis," *J. of Research of the NIST*, **111**:4,257-312, 2006.
- [4] J. Vasiliou, "An Evaluation of a Scanning Mobility Particle Sizer with NIST-Traceable Particle Size Standards," *NSTI-Nanotech*, **2**:691-693, 2005
- [5] M. Akhtar, X. Yun, P. Sotiris, "Vapor synthesis of titania powder by titanium tetrachloride oxidation," *AIChE Journal*, **37**(10):1561-1570, 1991.
- [6] J. Somers, P. Caperan, K. Richter, S. Fourcaudot, "Agglomeration of a titanium dioxide aerosol in a high intensity sound field," *J. of Aer. Sci.*, **25**(S1):355-356, 1994.
- [7] J. Hyun, T. Lee, "Structural effect of the in situ generated titania on its ability to oxidize and capture the gas-phase elemental mercury," *Chemosphere*, **62**(1):26-33, 2006.
- [8] L. Hsu, H. Chein, "Evaluation of nanoparticle emission for TiO₂ nanopowder coating materials," *J. of Nanoparticle Research*, **9**(1):157-163, 2007.
- [9] D. Chen, D. Pui, D. Hummes, H. Fissan, F. Quant, G. Sem, "Design and Evaluation of a Nanometer Aerosol Differential Mobility Analyzer (Nano-DMA)," *Journal of Aerosol Science*, **29**(5-6):497-509, 1997
- [10] S. Wang, R. Flagan, "Scanning Electrical Mobility Spectrometer," *Aerosol Sci. & Tech.*, **13**:230-240, 1990.
- [11] L. Russell, R. Flagan, J. Steinfeld, "Assymmetric instrument response resulting from mixing effects in accelerated DMA-CPC measurements," *Aerosol Sci. & Tech.*, **23**:4, 491-509, 1995.
- [12] TSI Incorporated. *Advanced Aerosol Neutralizer Model 3088*; [P/N 5001285](#), Rev. G; TSI Incorporated: Shoreview, MN, 2025.
- [13] A. Wiedensohler, "An Approximation of the Bipolar Charge Distribution for Particles in the Submicron Size Range," *J. of Aerosol Sci.*, **19**(3):387-389, 1988.
- [14] T. Niida, H Wen, R. Udischas, G. Kasper, "Counting Efficiency of Condensation Nuclei Counters in N₂, Ar, CO₂ and He," *J. Aerosol Sci.* **19**:7,1417-1420, 1988.
- [15] W. Liu, S. Kaufman, B. Osmondson, G. Sem, F. Quant, D. Oberreit, "Water-based Condensation Particle Counters for Environmental Monitoring of Ultrafine Particles," *J. of Air & Waste Management Assoc.*, **56**(4):444-455, 2006.
- [16] E. Knutson and K. Whitby, "Aerosol Classification by Electric Mobility: Apparatus, Theory, and Applications," *J. of Aerosol Science*, **6**:443-451, 1975.
- [17] E. Karg, S. Dua, G. Ferron, "Performance of a Differential Mobility Analyzer at Different Gas Compositions," *Aerosol Science*, **23**(S1):S389-S392, 1992.
- [18] O. Schmid, M. Tureblood, N. Gregg, D. Hagen, P. Whitefield, "Sizing of Aerosol in Gases Other Than Air Using a Differential Mobility Analyzer," *Aerosol Sci. & Tech.* **36**:351-360, 2002.
- [19] J.M Meek, J.D. Craggs, "Electrical Breakdown of Gases," John Wiley, Chichester, 1978.
- [20] P. Gormley, M. Kennedy, "Diffusion from a stream flowing through a cylindrical tube". *Proceedings of the Royal Irish Academy*, **52A**, 163-169, 1949.

- [21] F. Ober, M. Mayer, H. Buttner, F. Ebert, "Aerosol Measurement in Low-Pressure Systems with Standard Scanning Mobility Particle Sizers," *Part. Part. Syst. Char.* **19**, 229-239, 2002.
- [22] X. Wang, J. Hafiz, R. Mukherjee, T. Renault, J. Heberlein, S. Girshick, P. McMurry, "System for In Situ Characterization of Nanoparticles Synthesized in a Thermal Plasma Process," *Plasma Chemistry and Plasma Processing*, Volume **25**(5):439-453, 2005.



Knowledge Beyond Measure.

TSI Incorporated – Visit our website www.tsi.com for more information.

USA	Tel: +1 800 680 1220	India	Tel: +91 80 67877200
UK	Tel: +44 149 4	China	Tel: +86 10 8219 7688
459200		Singapore	Tel: +65 6595 6388
France	Tel: +33 1 41 19 21		
99			
Germany	Tel: +49 241 523030		

TSI and TSI logo are registered trademarks of TSI Incorporated in the United States and may be protected under other country's trademark registrations.