

Real-Time Measurement of Nanoparticle Size Distributions using Electrical Mobility Technique

Application Note SMPS-004

Introduction

The benefits of sizing aerosolized submicrometer particles using an electrical mobility sizing technique have been well documented. The technique is highly accurate and has been shown to size 60 nm and 100 nm Standard Reference Material (SRM) with an uncertainty of only 1% [1]. The National Institute of Standards and Technology (NIST) have been using electrical mobility to measure its 0.1 μm Standard Reference Material (SRM) Particles for well over a decade [2,3]. Lately, the electrical mobility technique is finding increased use in the in-situ near real-time sizing of engineered nanoparticles synthesized by a variety of aerosol-based processes like diffusion flame synthesis, spray pyrolysis, thermal plasma etc. When combined with electrospray and other dispersion methods, the electrical mobility technique has been shown to accurately size nanoparticles suspended in colloids as well.

With the commercialization of nanotechnology, occupational health risks associated with manufacturing and handling of nanoparticles is a growing concern. Workers may be exposed to nanoparticles through means of inhalation, at levels that greatly exceed ambient concentrations; and no workplace standards currently exist to limit exposure to nanoparticles. Nanoparticle size governs their deposition pattern in various parts of the lung and their ultimate fate within the human body. Thus, ambient measurements of nanoparticle size distributions provided by the electrical mobility technique is a powerful tool in understanding adverse health effects associated with nanoparticle related exposure.

This application note provides a brief overview of the electrical mobility technology as integrated in TSI Scanning Mobility Particle Sizer™ (SMPS) spectrometer followed by a discussion on applications in nanoparticle synthesis and exposure research.

Scanning Mobility Particle Sizer™ Spectrometer

The Scanning Mobility Particle Sizer™ (SMPS) spectrometer consists of a sample preconditioner, a bipolar charger, a nanoparticle size classifier and a nanoparticle detector. Figure 1 depicts a schematic of the entire system. The pre-conditioner (typically an impactor or a cyclone) eliminates large micrometer sized particles. The bipolar charger (also referred to as neutralizer) establishes bipolar charge equilibrium on the particles. This defined charge condition is necessary for the size classification using electrical mobility. Particles are size classified in a Differential Mobility Analyzer (DMA). The charged aerosol passes from the neutralizer into the main portion of the DMA. The

Scanning Mobility Particle Sizer and SMPS are trademarks of TSI Incorporated.



TRUST. SCIENCE. INNOVATION.

DMA shown in the figure is a nano-DMA which is specifically designed for sizing nanoaerosols in the size range of 2 nm to 150 nm. The nano-DMA contains an outer, grounded cylinder and an inner cylindrical electrode that is connected to a negative power supply (0 to 10 kVDC). The electric field between the two concentric cylinders separates the particles according to their electrical mobility which is inversely related to the particle size. Particles with negative charge(s) are repelled towards and deposited on the outer wall. Particles with neutral charge exit with the excess air. Particles with positive charge(s) move rapidly towards the negatively-charged center electrode. Only particles within a narrow range of electrical mobility have the correct trajectory to pass through an open slit near the DMA exit. The electrical mobility of these selected particles is a function of flow rates, geometric parameters and the voltage of the center electrode.

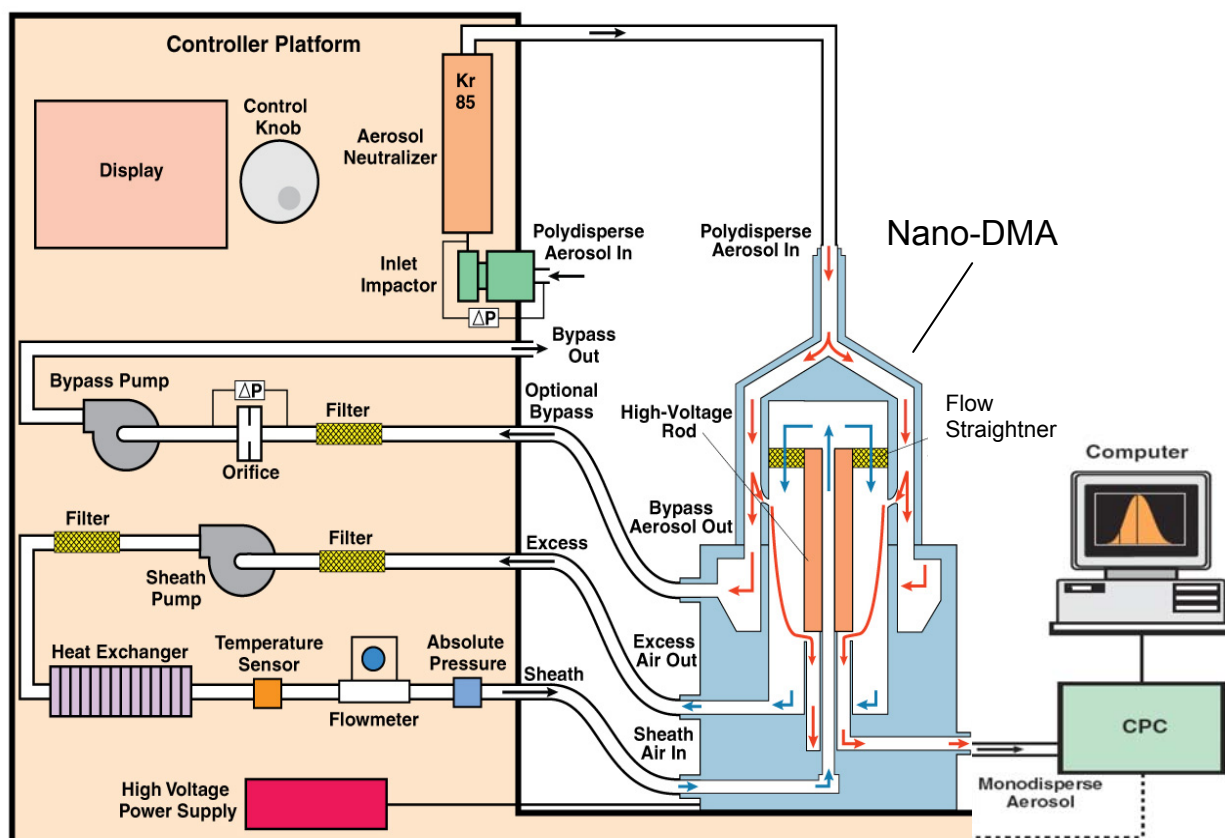


Figure 1: Schematic of an SMPS spectrometer

The monodisperse particle stream exiting the DMA is counted by a Condensation Particle Counter (CPC). In the CPC, single particles larger than 2 nm are grown to micrometer size by means of condensation of a working fluid (alcohol or water) on the particles. The CPC then optically counts these particles. Particle size distributions are measured by changing the applied high voltage in the DMA, which changes the electrical field, thus scanning the whole size distribution.

TYPICAL APPLICATIONS IN NANOTECHNOLOGY

Sizing of Nanoparticles in Dry-Synthesis Reactors

The electrical mobility technique is finding increasing use in the in-situ near real-time sizing of engineered nanoparticles synthesized by a variety of aerosol-based processes. The near real-time measurement offered by electrical mobility technique accelerates the research and development process of nanoparticle synthesis since it enhances the understanding of the mechanisms of particle

formation and growth. An in-situ measurement eliminates the need for sample collection for off-line methods thus minimizing operator error and providing more consistent repeatable results. Figure 2 gives an overview of important steps in synthesis of nanomaterials in an aerosol based reactor [7]. Real-time sizing of nanoaerosols in these reactors permits the user to follow dynamics of particle formation and growth in highly reacting flows. A precise control of particle size is key; real-time measurement of particle size distributions in the reactor provides the necessary feedback to control reactor conditions to achieve high quality control.

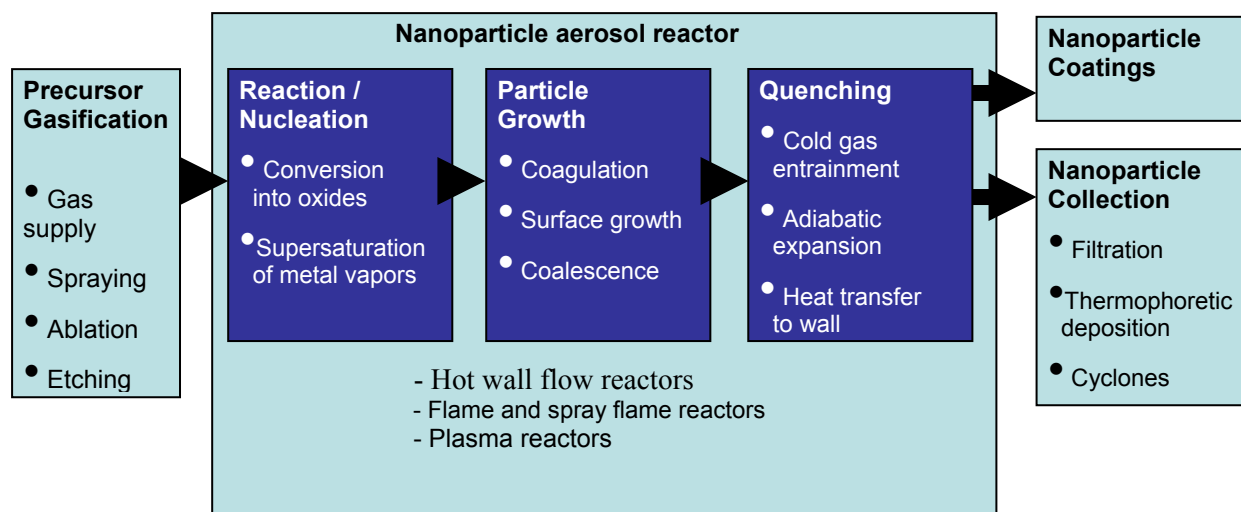


Figure 2: Aerosol processes for synthesis of nanomaterials

SMPS has been increasingly employed in nanotechnology research. In 1991, Akhtar et al. [8] used an SMPS spectrometer to study vapor synthesis of Titania powder, specifically, the effect of process variables (reactor residence time, temperature, and reactant concentration) on powder size and phase characteristics. The SMPS measured particle size distributions were used to validate particle coagulation model. Somer et al. (1994) [9] used SMPS to study agglomeration of Titanium dioxide aerosol in high intensity field. Ahn et al. (2001) [10] studied silica particle growth characteristics in H₂/O₂/TEOS diffusion flame. They found close agreement of SMPS measured size as compared to the Transmission Electron Microscope (TEM) image processed size data. Ullman et al. (2002) [11] studied properties of nanoparticle aerosols of size 4.9-13 nm, generated by laser ablation. Measurements of eight materials including Silica, Carbon, Titania, Iron oxide, Tungsten oxide, Niobium oxide, Carbon and Gold were successfully achieved. Other SMPS assisted studies of nanoparticle reactors include liquid flame spray (silver-titania deposit nanoparticles) [12], ethylene flame (soot nanoparticles) [13] and thermal plasma reactors (Si, Ti particles) [14] to name a few. More recently, Zhang et al. (2007) [15] studied temperature effects on Tellurium dioxide synthesis by spray pyrolysis. SMPS data from this reactor (figure 3) clearly shows transition of precursor droplets to product droplets as the temperature increases.

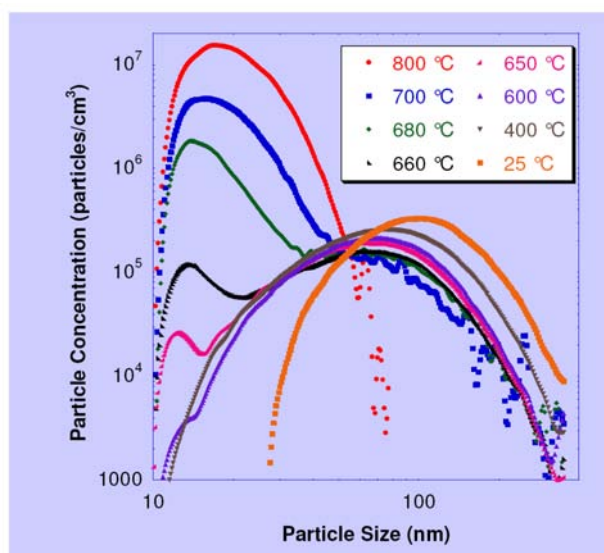


Figure 3: Particle size distributions as measured by SMPS at different furnace temperatures.

The discussion on nanotechnology is incomplete without the mention of carbon nanotubes (CNTs). Several investigations of gas-phase synthesis of carbon nanotubes (CNTs) have utilized the electrical mobility analysis. For example, Moisala et al. (2005) [16] used the on-line detection of single-walled (SW) CNT formation during aerosol synthesis method using a differential mobility analyzer. Despite the different product morphology and concentration, the authors report that the on-line measurement was able to distinguish SWCNT formation in each experimental set-up as an increase in the geometric mean particle diameter and as a decrease in the total particle number concentration. Furthermore, information regarding the relative SWCNT concentration was also obtained from the DMA measurement. The authors have developed a theoretical approach to the mobility of nonspherical particles in the electric field in order to convert the electrical mobility size of the high aspect ratio SWCNTs measured with DMA to the physical size of the product. The authors studied size-selected SWCNTs with transmission electron microscopy in order to find the correlation between the on-line DMA measurement data and the SWCNT morphology.

DMA data analysis for carbon nanotubes is discussed in detail in a paper by Kim and Zachariah (2005) [17] and has been used in subsequent works by the same group [18] and other investigations of carbon nanotubes [19]. Using the analysis described in this paper, it is possible to calculate the length distribution of nanotubes on the basis of the mobility size distribution curve obtained from SMPS. Chiang and Sankaran (2007) used this methodology for gas-phase studies of catalyzed carbon nanotube growth [19]. Figure 4 shows the temperature dependent aerosol size distributions of carbon nanostructures grown on nickel catalysts using microplasma induced synthesis [19].

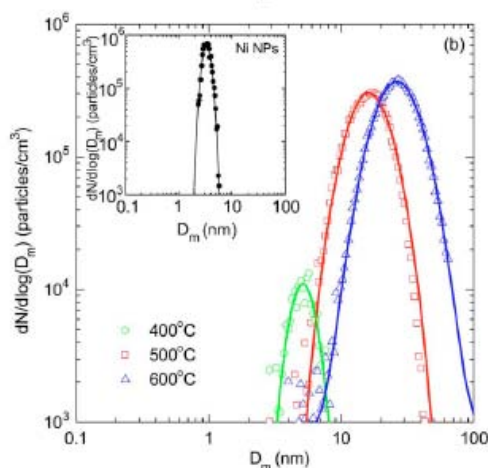


Figure. 4 Temperature-dependent aerosol size distributions of carbon nanostructures grown on Ni catalysts.

Sizing of Nanoparticles Suspended in Colloids

Many wet synthesis methods eg. sol-gel, microemulsion etc. are now available for producing nanoparticles as colloidal dispersions. The stability of dispersion is a desired trait that ensures nanoparticles are not agglomerating; the level of dispersity can be judged from measured particle size distributions. When combined with electrospray dispersion, the electrical mobility technique has been shown to accurately size nanoparticles suspended in colloids [20, 21]. Figure 5 demonstrates the high size resolution of SMPS. The size distributions of a mixture of nine different proteins and of electrosprayed bovine serum albumin (BSA) nanoparticles were measured with an SMPS (TSI Model 3936-N25) [21]. The x-axis denotes electrical mobility based diameter and y-axis denotes particle concentrations in units of counts per cm³ of carrier gas.

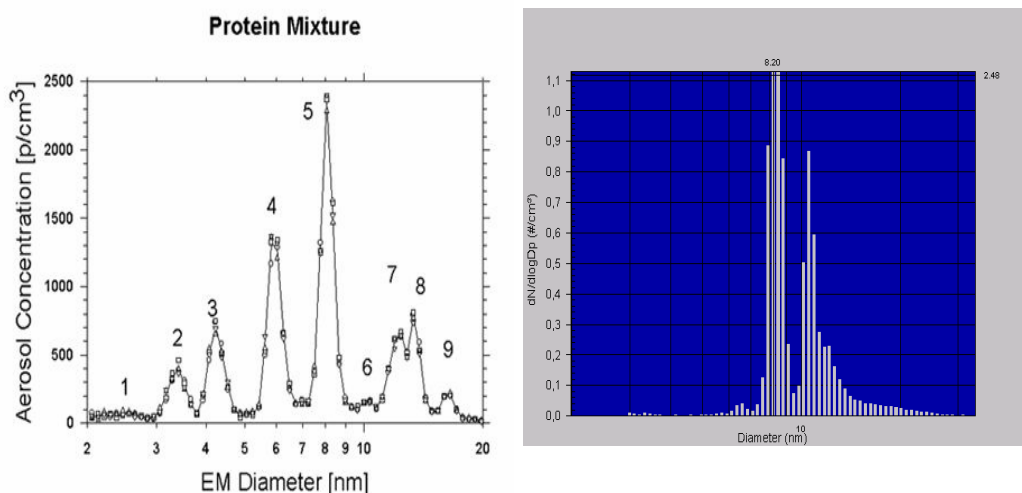


Figure 5: Size distributions of electrosprayed nanoparticles measured with SMPS. Left: Mixture of 9 different proteins; right: BSA nanoparticles

Figure 6 shows the SMPS measured size distribution of zirconium oxide nanoparticle colloids for tests conducted at TSI. The colloidal particles were prepared in a 20mM ammonium acetate solution in water adjusted to pH 3.8. Plot (a) shows size distribution for a suspension concentration of 20 µg/ml; the plot (b) shows the size distribution of a diluted suspension with a concentration of 10 µg/ml. Note that the size distribution remains same, however the relative counts of particles of different sizes is scaled down in proportion to the amount of dilution. This test confirms that the particle size distributions are representative of single particles and not multiplets.

Zirconia Hydrosol

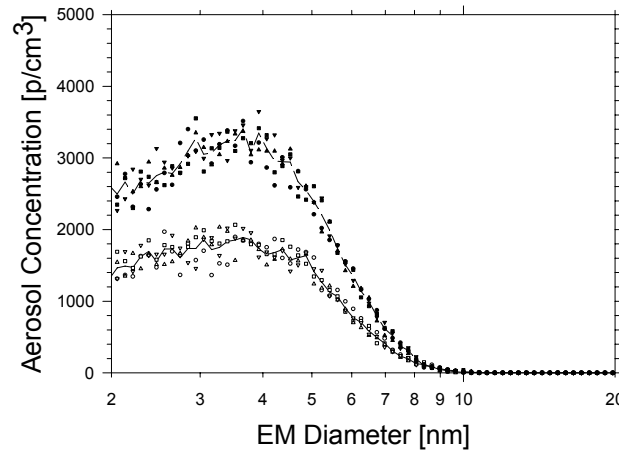


Figure 6: Zirconia nanoparticle size distributions for suspension concentrations of (a) 20 µg/ml (b) 10 µg/ml.

Nanoparticle Exposure Analysis

Besides the near real-time analysis related to nanoparticle processes discussed above, electrical mobility analysis with SMPS can also be used to monitor process related nanoparticle exposure. The high size resolution allows the calculation of particle area distributions. Figure 7 shows an example [22]: the measurements were taken during emptying an ultrafine Titanium dioxide baghouse into a powder collection bucket. Besides the SMPS data the figure 7 a shows total number concentration measured with a CPC and total alveolar deposited surface area concentration measured with a Nanoparticle Surface Area Monitor (TSI NSAM Model 3550). Figure 7 b depicts alveolar deposited surface area distribution calculated from SMPS measured particle size distribution in the ambient air close to the material handling operation. A peak in concentrations during middle of process coincided with dumping of a drum of Titania powder in a reservoir.

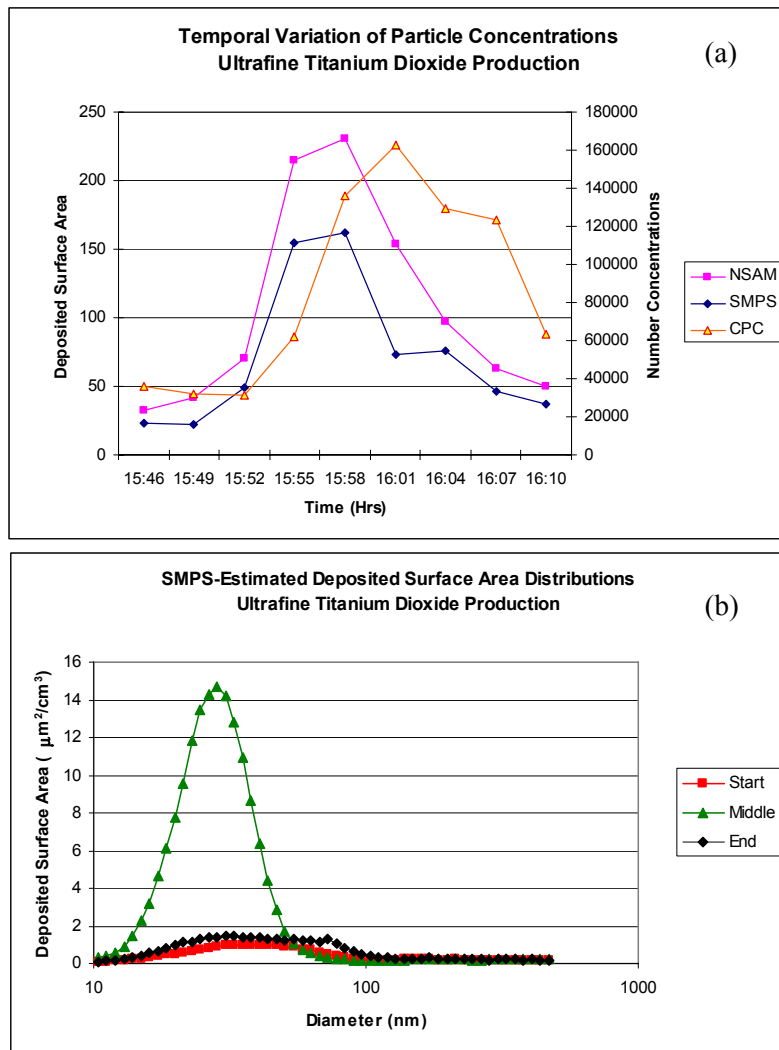


Figure 7: Nanoparticle exposure measurement (alveolar deposited particle surface area) in an ultrafine TiO₂ facility. Filling process monitored with SMPS, NSAM and CPC[17].

References

- [1] 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.
- [2] P. Kinney, D. Pui, G. Mullholland, N. Bryner, "Use of the Electrostatic Classification Method to Size 0.1 μm SRM Particles – A Feasibility Study" *J. of NIST* **96:147**, 1991.
- [3] G. Mullholand, N. Bryner, C. Croarkin, "Measurement of the 100nm NIST SRM 1963 by Differential Mobility Analysis," *Aero. Sci. Technol.*, **31**:39-55, 1999.
- [4] Rohmann, H. [1923] *Z. Phys.* **18:188**.
- [5] D. Pui, B. Liu. Technical paper: "Aerosol Generation and Calibration of Instruments," Mechanical Engr. Dept. Univ of MN, May/June, 1979.
- [6] D. Chen, D. Pui, D. Hummes, H. Fissan, F. Quant, G. Sem, "Design and Evaluation of a Nanometer Aerosol Differential Mobility Analyzer (Nano-DMA)," *J. of Aer. Sci.*, **29(5-6)**:497-509, 1997.
- [7] C. Wang, S. Friedlander, L. Madler, "Nanoparticle aerosol science and technology: an overview," *China Particology*, **3**: 243-254, 2005.

- [8] M. Akhtar, X. Yun, P. Sotiris, "Vapor synthesis of titania powder by titanium tetrachloride oxidation," *AIChE Journal*, **37(10)**:1561-1570, 1991.
- [9] 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.
- [10] K. Ahn, C. Jung, M. Choi, J. Lee, "Particle Sampling and Real Time Size Distribution Measurement in H₂/O₂/TEOS Diffusion Flame," *J. of Nanoparticle Res.*, **3**:161-170, 2001.
- [11] M. Ullman, S. Friedlander, S. Andreas, "Nanoparticle formation by laser ablation," *J. of nanoparticle Res.*, **4**:499-509, 2002.
- [12] H. Keskinen, J. Makela, M. Aromma, J. Ristimaki, T. Kanerva, E. Levanen, T. Mantyla, "Effect of silver addition on the formation and deposition of titania nanoparticles produced by liquid flame spray," *J. of Nanoparticle Res.*, DOI 10.1007/s11051-006-9073-x., 2007.
- [13] B. Zhao, Z. Yang, J. Wang, M. Johnston, H. Wang, "Analysis of Soot Nanoparticles in a Laminar Premixed Ethylene Flame by Scanning Mobility Particle Sizer," *Aero. Sci. Technol.*, **37**:611-620, 2003.
- [14] 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 Chem. and Plasma Process.*, Volume **25**: 439-453, 2005.
- [15] H. Zhang H., M. Swihart, "Synthesis of Tellurium dioxide nanoparticles by spray pyrolysis. Presented at the International Aerosol Conference, September 10-15, 2006, St. Paul, MN.
- [16] Moisala, Anna; Nasibulin, Albert G.; Shandakov, Sergei D.; Jiang, Hua; Kauppinen, Esko I., "Online detection of single-walled carbon nanotube formation during aerosol synthesis methods," *Carbon*, **43** (10): 2066-2074, 2005.
- [17] Kim, S.H.; Zachariah, M.R., "In-flight size classification of carbon nanotubes by gas phase electrophoresis," *Nanotechnology* **16**, 2149-2152, 2006.
- [18] Kim, S.H.; Zachariah, M.R., "In-Flight Kinetic Measurements of the Aerosol Growth of Carbon Nanotubes by Electrical Mobility Classification," *J. of Phys. Chem. B*, **110**, 4555-4562, 2006.
- [19] Chiang, Wei-Hung; Sankaran, R. Mohan, "Microplasma synthesis of metal nanoparticles for gasphase studies of catalyzed carbon nanotube growth," *Appl. Phys. Letts.*, **91**, 121503, 2007.
- [20] Bottger, PHMichael; Bi, Zhaoxia; Adolph, David; Dick, Kimberly A; Karlsson, Lisa S, "Electrospraying of colloidal nanoparticles for seeding of nanostructure growth," *Nanotechnology*, **18** 105304 (6pp) doi:10.1088/0957-4484/18/10/105304, 2007.
- [21] Laschober C., Kaufman S.L. Reischl G., Allmaier G. and Szymanski W. (2006). Comparison Between an Unipolar Corona Charger and a Polonium-Based Neutralizer for the Analysis of Nanosized Particles and Biopolymers. *J. of Nanosci and Nanotechnol.* **6**: 1474.
- [22] M. Hoover, B. Stefaniak, M. Methner, B. Ku, C. Geraci, T. Maher, M. Singh, "Evaluation of a Real-Time Surface Area Monitor in a Nanotechnology Workplace", International Conference on Nanotechnology Occupational and Environmental Health and Safety: Research to Practice. Cincinnati, OH. Dec 4-7, 2006.

TSI Incorporated - 500 Cardigan Road, Shoreview, MN 55126-3996 USA

USA	Tel: +1 800 874 2811	E-mail: fluid@tsi.com	Website: www.tsi.com
UK	Tel: +44 149 4 459200	E-mail: tsiuk@tsi.com	Website: www.tsiinc.co.uk
France	Tel: +33 491 95 21 90	E-mail: tsifrance@tsi.com	Website: www.tsiinc.fr
Germany	Tel: +49 241 523030	E-mail: tsigmbh@tsi.com	Website: www.tsiinc.de
Sweden	Tel: +46 8 595 13230	E-mail: tsiab@tsi.com	Website: www.tsi.se
India	Tel: +91 80 41132470	E-mail: tsi-india@tsi.com	
China	Tel: +86 10 8260 1595	E-mail: tsibeijing@tsi.com	

Contact your local TSI Distributor or visit our website www.tsi.com for more detailed specifications.



TRUST. SCIENCE. INNOVATION.