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

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ABSTRACT

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 0.1µm Standard Reference Material (SRM) Particles for well over a decade [2,3]. Lately, 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 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. Applications of electrical mobility technique in nanotechnology are discussed.

Keywords: electrical mobility, Scanning Mobility Particle Sizer™ spectrometer, nanaoparticle size, real-time data, online analysis.

1 INTRODUCTION

Electrical mobility techniques have been used to measure size distribution of aerosols since the work of Rohman [4]. Originally, the technique was mainly applied to classify polydisperse aerosols to provide a size calibrated monodisperse aerosol stream [5]. Now, it is routinely used as part of sizing systems like Scanning Mobility Particle Sizer™ spectrometer (SMPS, TSI Incorporated, Shoreview, MN) to measure in-situ aerosol size distributions in real-time for a wide variety of applications, including nanotechnology research.

Nowadays, more and more technologies for engineered nanoparticle manufacturing are utilizing aerosol based processes. Nanoparticle size is an important parameter affecting material properties and thus functionality of the final nanotechnology product. Agglomeration in aerosol systems should be prevented and number concentrations should be tightly controlled to regulate optimum size. This requires that the rate of new particle formation be quantitatively determined. Real-time measurements of particle size distributions offered by the SMPS are thus an enabling technology for quality control in industrial nanotechnology processes as well as in nanomaterial synthesis research.

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 exist to limit exposure to nanoparticles. Nanoparticle size governs their deposition pattern in various parts of the lung and their ultimate fate within a human body. Thus, ambient measurements of nanoparticle size distributions provided by the electrical mobility technique is a powertool in understanding adverse health effects associated with nanoparticle related exposure.

This paper provides a brief overview of the technology as integrated in the SMPS spectrometer and investigates the applications in nanoparticle synthesis and exposure research.

1.1 Scanning Mobility Particle Sizer™ Spectrometer

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 establishes bipolar charge equilibrium on the particles. This defined charge condition is necessary for the size classification using electrical mobility. The electrical mobility of a particle is defined as:

$$Z_p = \frac{\text{ParticleVelocity}}{\text{ElectricFieldStrength}} = \frac{v}{E} = \frac{n_p e C}{3\pi\mu D_p} \qquad (1)$$

Where, 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

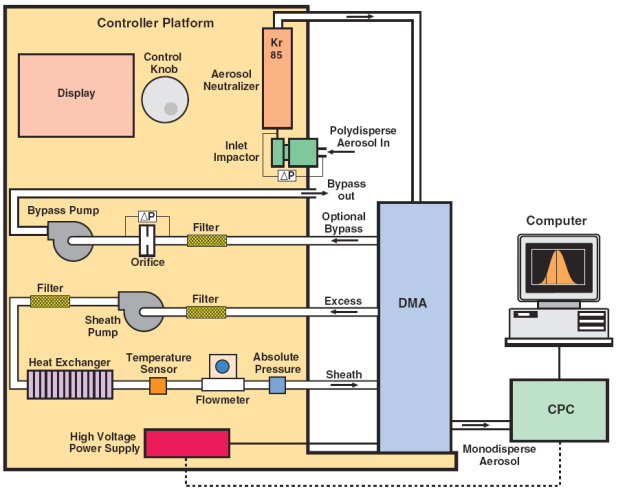

Fig. 1: Schematic of an SMPS spectrometer

Particles are size classified in a Differential Mobility Analyzer (DMA). A DMA utilizes the fact that a particles' electrical mobility is inversely proportional to particle diameter (eq. 1). Figure 2 shows a schematic of a DMA for nanoparticles [6] (Nano DMA or NDMA). The NDMA consists of a center cylindrical electrode that is typically at a positive voltage surrounded by a grounded concentric outer electrode. The aerosol to be analyzed is pulled into the cylindrical DMA at the top and introduced at the inside wall of the outer electrode. Sheath flow is introduced from the bottom of the NDMA and routed to the top of the instrument to surround the inner electrode with laminar flowing 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.

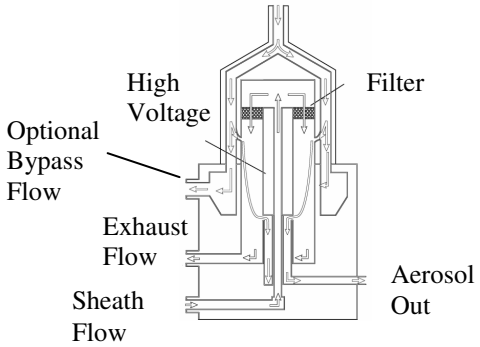

Figure 2: Schematic of Nano DMA

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.

2 TYPICAL APPLICATIONS IN NANOTECHNOLOGY

2.1 Sizing of Nanoparticles in 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 3 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 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.

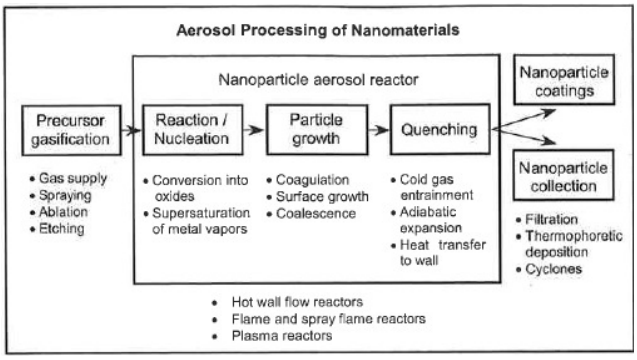

Figure 3: Aerosol processes for synthesis of nanomaterials

SMPS has been increasingly employed in nanotechnology research. In 1991, Akhtar et al. [8] used an SMPS system 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. Recently, Zhang et al. (2007) [15] studied temperature effects on Tellurium dioxide synthesis by spray pyrolysis. SMPS data from this reactor (figure 6) clearly shows transition of precursor droplets to product droplets as the temperature increases.

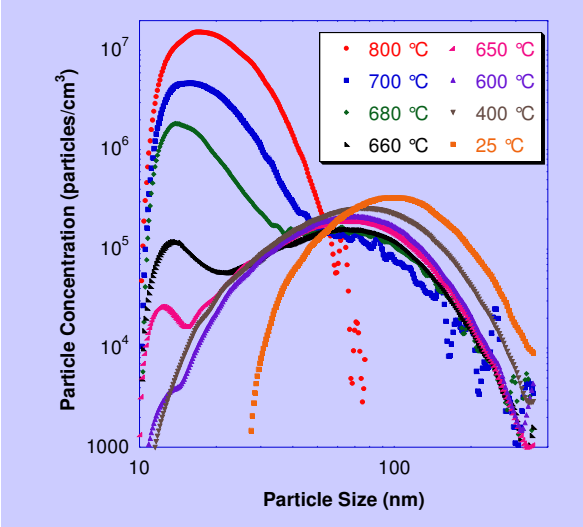

Figure 6: Particle size distributions as measured by SMPS at different furnace temperatures.

2.2 Sizing of Nanoparticles suspended in Colloids

When combined with electrospray dispersion, the electrical mobility technique has been shown to accurately size nanoparticles suspended in colloids [16]. Figure 3 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 a SMPS (TSI Model 3936-N25).

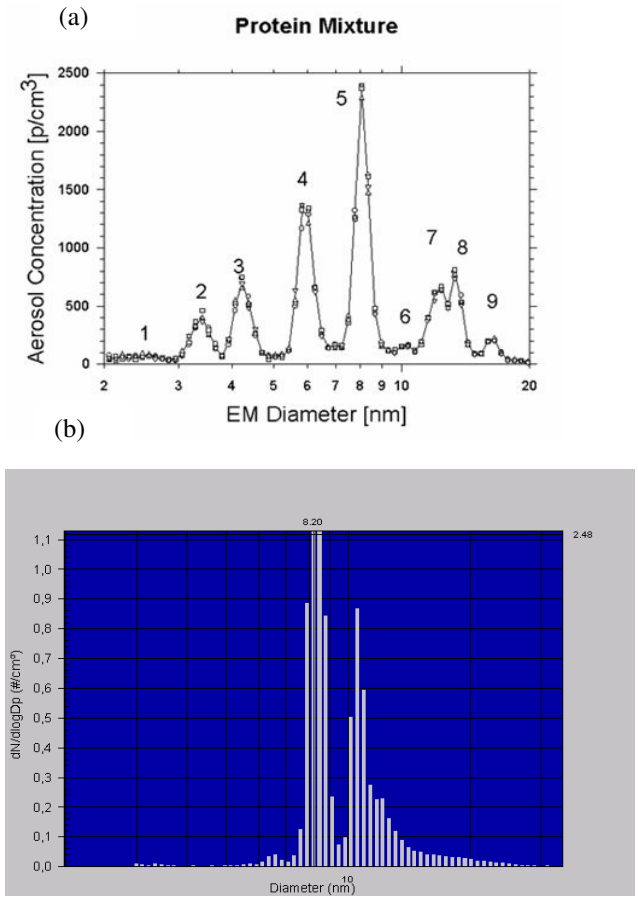

Figure 7: Size distributions of electrosprayed nanoparticles measured with SMPS. (a) Mixture of 9 different proteins; (b) BSA nanoparticles

2.3 Naonoparticle 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 surface and particle volume distributions. Figure 5 shows an example [17]: the measurements were taken during emptying an ultrafine Titanium dioxide baghouse into a powder collection bucket. Besides the SMPS data (number median diameter), the figure 5a shows total number concentration measured with a Condensation Particle Counter (CPC) and total alveolar deposited surface area concentration measured with a Nanoparticle Surface Area Monitor (TSI NSAM Model 3550). Figure 5 b depicts 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.

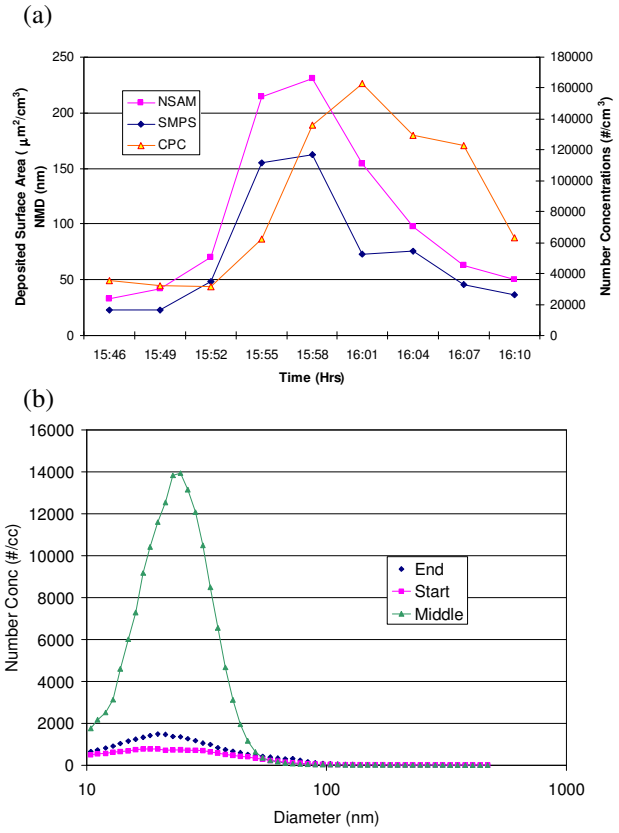

Figure 8: Titanium dioxide concentrations (a) counts, deposited surface area and number median diameter; (b) SMPS size distributions.

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