

# **Device and Method for Sizing and Counting 5-500-nm Particles in Colloidal Suspensions**

DC Grant<sup>1</sup>, MR. Litchy<sup>1</sup>, HG Van Schooneveld<sup>1\*</sup>, and J Farnsworth<sup>2</sup>

<sup>1</sup>CT Associates, Inc., 7121 Shady Oak Road, Eden Prairie, MN 55344, U.S.A.,

<sup>2</sup>TSI, Inc., 500 Cardigan Road, Shoreview Rd, MN 55126, U.S.A.

\* - Presenting author

## **ABSTRACT**

Measurement of the sizes and concentrations of particles in colloidal suspensions has historically been a challenge, particularly for suspensions with particles smaller than 100 nanometers. A newly developed measurement device, a Liquid Nanoparticle Sizer (LNS), allows sizing and counting of particles as small as 5 nanometers in these suspensions.

The LNS consists of an ultrafine nebulizer and a scanning mobility particle sizer (SMPS). A colloidal suspension undergoing analysis is diluted on line in ultrapure water (UPW) and injected into the nebulizer. The nebulizer generates a droplet distribution in filtered air which is subsequently dried to form an aerosol containing the particles originally in the colloidal suspension. The size distribution (PSD) of the aerosol particles is measured using an SMPS capable of measuring particles as small as 5 nm in size.

This paper describes the LNS measurement technique in detail and shows examples of its use in measurement of particle size distributions in colloidal suspensions such as chemical/mechanical planarization (CMP) slurries and measurement of the retention of particles and macromolecules as small as 5 nanometers by microporous membrane filters and ultrafilters.

## **KEYWORDS**

Nanoparticle Measurement, Particle Size Distribution Measurement, Particle Counters, Online Particle Analysis, Microfiltration, Nanofiltration

## 1. Introduction

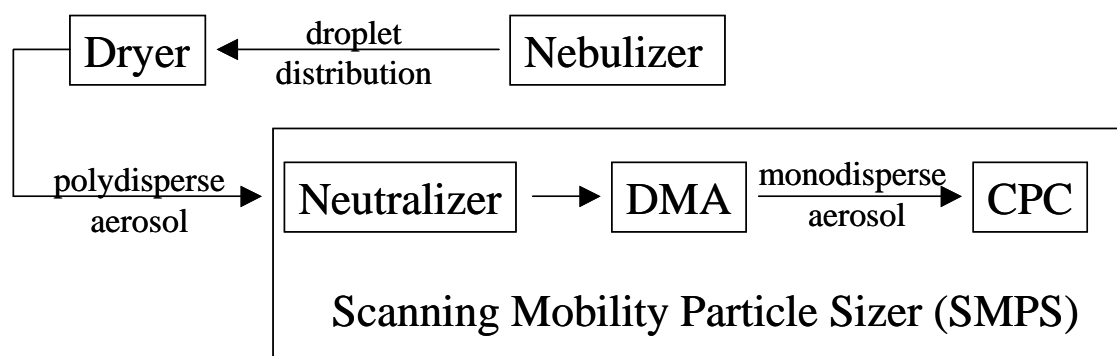
The particle size distribution (PSD) of particles in a colloidal suspension can strongly influence the efficacy of the suspension in its intended use. For example, the PSD of particles in chemical/mechanical planarization (CMP) slurries used in semiconductor chip manufacturing has a significant effect on the rate of material removal during planarization steps. The removal rate is affected by both the size and concentration of the particles in the suspension.

Techniques presently used to measure colloidal suspension PSDs include dynamic light scattering (DLS), Fraunhofer diffraction and differential sedimentation. However, these techniques suffer from a number of limitations. They measure the relative numbers of particles of different sizes rather than actual number concentrations. Also, these are ensemble techniques which measure the properties of numerous particles simultaneously then calculate their size distribution using a complex mathematical algorithm. The algorithms often require that a shape for the PSD be assumed and the data are forced to fit that shape. For example, DLS instruments often assume that the particles are log-normally distributed. In addition, rather than measuring the number concentration, these techniques measure either the volume-weighted concentration (proportional to the particle diameter cubed) or the intensity-weighted distribution (proportional to the particle diameter to the sixth power). Finally, the measurement is often affected by the density and optical properties of the particles.

The LNS measurement technique described in this paper allows direct measurement of the number-weighted particle size distribution. Both the size and number concentration of individual particles are measured. No assumption as to the shape of the distribution is made and the measurement is independent of particle density and optical properties.

## 2. Method

The Liquid Nanoparticle Sizer (LNS) measurement technique, shown schematically in Figure 1, combines proven technologies used for measuring aerosol PSDs to measure particle concentrations in highly concentrated liquid suspensions. The technique consists of two major components: a nebulizer and a scanning mobility particle sizer (SMPS) [1,2].

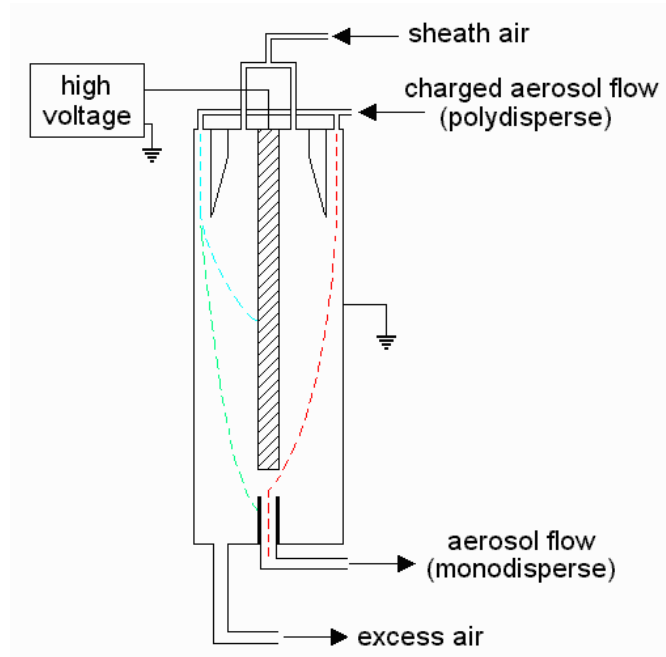


**Figure 1. Schematic of the Liquid Nanoparticle Sizer**

In the LNS, a colloidal suspension or slurry sample is injected into the nebulizer. The nebulizer converts the suspension into ultrafine droplets dispersed in essentially particle-free air. The resultant droplets are then dried to form an aerosol. The aerosol PSD is measured using the SMPS, which consists of an aerosol neutralizer, differential mobility analyzer (DMA), whose main component is an electrostatic classifier [3,4], and a condensation particle counter (CPC) [5-7]. In the SMPS, the aerosol first passes through the aerosol neutralizer, which exposes the particles to a high concentration of bipolar ions generated by a low energy soft X-ray source. Through this bipolar diffusion charging process, any excess charges on the particles are neutralized resulting in a steady-state charge distribution – the Boltzmann equilibrium distribution [8]. The aerosol then passes through the electrostatic classifier in the DMA, which separates the particles according to their electrical mobility. Finally, the CPC counts the monodispersed particles exiting the DMA.

The key to making this measurement approach work for colloidal suspensions containing sub-100-nm particles is the nebulizer. The droplets produced by the nebulizer must be sufficiently small and uniformly sized that particles formed from dissolved materials in the droplets do not form detectable “residue” particles when the liquid is evaporated. In addition, the particle suspension must be sufficiently dilute so that no more than one particle is present in each droplet. If more than one particle is present, the particles will be counted as one particle with a larger diameter. This results in a decrease in the measured total particle concentration and a shift in the PSD to larger particle sizes. A similar error occurs with optical particle counters when the coincidence limit of the sensor is exceeded. The droplets produced by the nebulizer in the LNS have a median diameter of approximately 300 nm and a geometric standard deviation of approximately 1.4.

The electrostatic classifier in the LNS consists of two concentric cylinders with an annular air gap as shown in Figure 2. Particle free sheath air enters the classifier on an inner annular ring at the top of the classifier while the polydisperse aerosol enters at the outer annular ring of the device. The outer cylinder is grounded while the voltage on the inner cylinder is varied from 0 to -10,000 volts. As the polydisperse aerosol and particle free sheath gas flow towards the bottom of the cylinder, particles with a positive charge are drawn across the sheath gas towards the negatively charged inner cylinder. For a given voltage, particles with high electrical mobility (small particle size or high particle charge) deposit on the upper portion of the inner cylinder (blue particle trajectory) while particles with low electrical mobility deposit on the lower portion of the inner cylinder (green particle trajectory) or exit the instrument through the excess flow. However, particles of a specific, monodispersed size (red particle trajectory) exit through a small slit in the inner cylinder. The dynamic range of particle sizes that can be separated with this instrument, that is the ratio of the largest measurable particle size to the smallest measurable particle size, is approximately a factor of 80, from 5 to 400 nm. The instrument has 64 channels of resolution per decade of particle size.

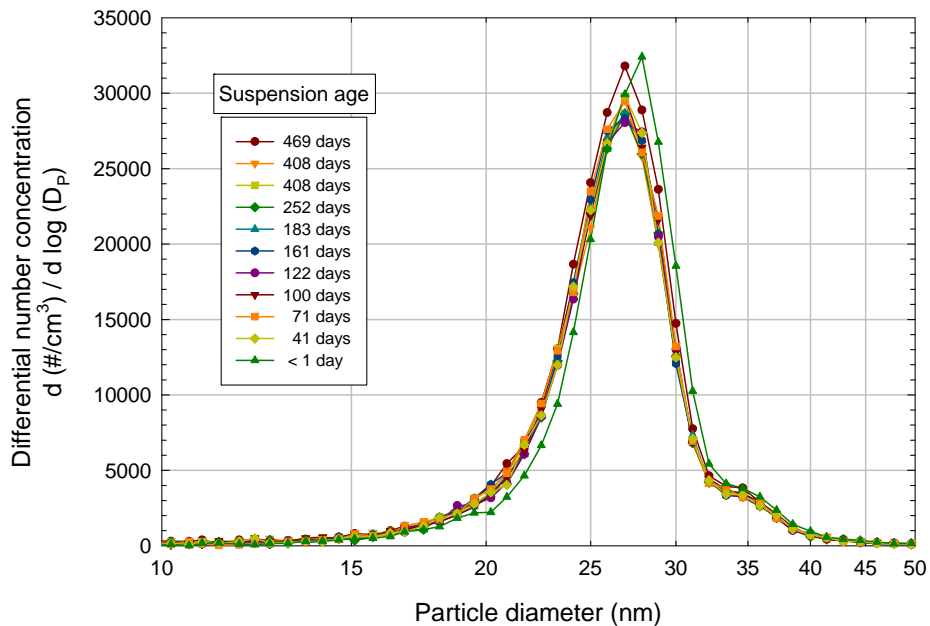


**Figure 2. Schematic of electrostatic classifier**

The CPC counts the monodisperse particles exiting the classifier by growing the particles to a size easily detected using relatively simple optics. The CPC consists of a conditioner, growth tube and optics. The aerosol enters a conditioner which conditions the aerosol temperature and increases the relative humidity to approximately 100%. The aerosol then passes through a growth tube which condenses water vapor onto the particles using a tube with wetted walls that are warmer than the incoming aerosol. The particles (now droplets) increase in size as the water vapor condenses. All particles larger than a certain size, regardless of their initial size, quickly form water droplets that grow to approximately 10  $\mu\text{m}$  in diameter. At this large size, the particles are easily counted in the optics region of the CPC by passing them through a laser beam where they scatter light onto a photo detector. By controlling the conditions in the conditioner and growth tube, the minimum particle size on which condensation takes place can be controlled [5-7]. In the CPC presently used in this instrument that size is 5 nm.

In order to measure number concentrations rather than relative concentrations of particles, the LNS must be calibrated to determine the volume fraction of the suspension converted to aerosol. Calibration is achieved by measuring instrument response to injection of a colloidal suspension with a known concentration of silica particles having a median diameter of 28 nm. In order for the calibration to be accurate, the reference standard must be stable over time. Figure 3 presents PSDs of reference standards prepared over a 15-month period and measured at the same time. No change in the distribution is evident over the 15-month age range of the standards tested.

Once an accurate measurement of the number distribution is obtained it is straightforward to calculate distributions with different weightings (e.g. volume-weighted, area-weighted) using straightforward mathematical transformations [9].



**Figure 3: PSDs of aged calibration standards.**

### 3. Main Results

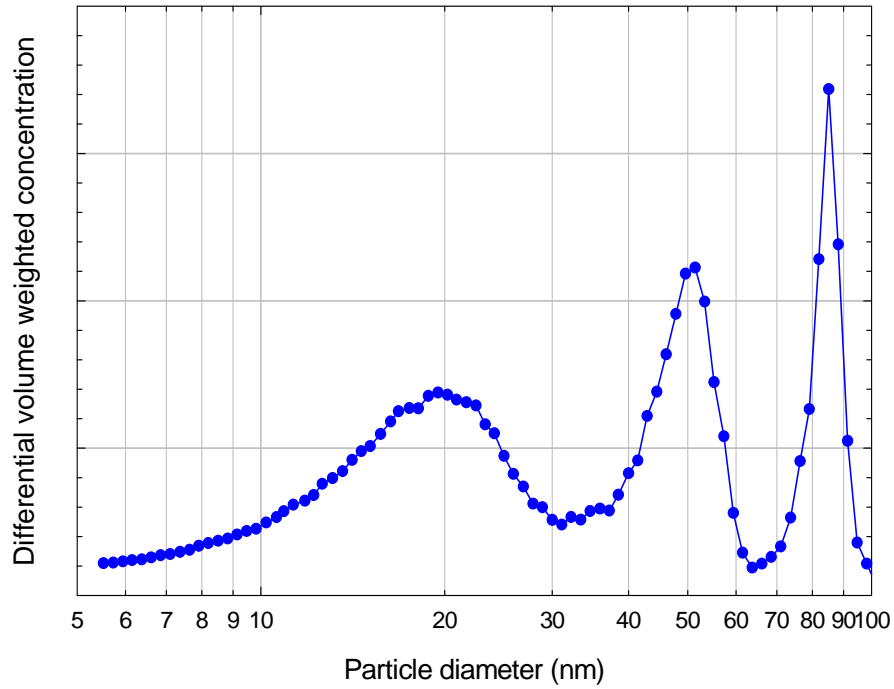
#### 3.1 Measurement of colloidal dispersions with narrow particle PSDs

The LNS technique has been used to measure commercially available particles with narrow size distributions and NIST traceable sizes to verify the sizing accuracy of the technique. Both polystyrene (PSL) latex spheres and gold colloidal nanoparticles have been measured. An example showing sizing of a mixture of three sizes of PSL spheres (20, 50, and 80 nm), is shown in Figure 4 [1]. The instrument is able to easily resolve the sizes of the three PSL spheres.

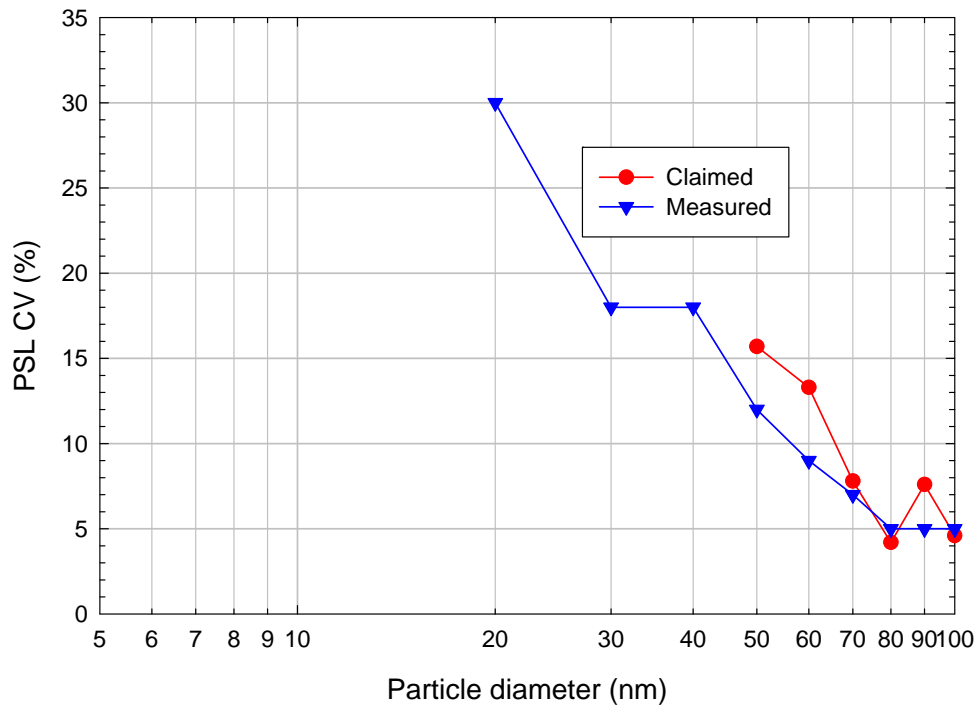
Although the PSL spheres have fairly narrow size distributions, they are not monodispersed. Figure 5 shows the diameter coefficient of variation (CV) claimed by the manufacturer of the spheres and the CV measured using the LNS for several PSL sizes. Since the measured and claimed CVs are essentially identical, the spread in the PSL distributions shown in Figures 4 and 5 is largely due to variation in sphere diameter with no detectable variation due to the instrument.

Measurement of colloidal gold particles by the LNS is shown in Figure 6 [10]. Sizing of three gold colloids (BBI Research, Madison, WI) measured individually is shown. The Figure shows that the particles have narrow size distributions. The LNS measurements correlate well with the manufacturer's sizing claims made using TEM (Table 1).

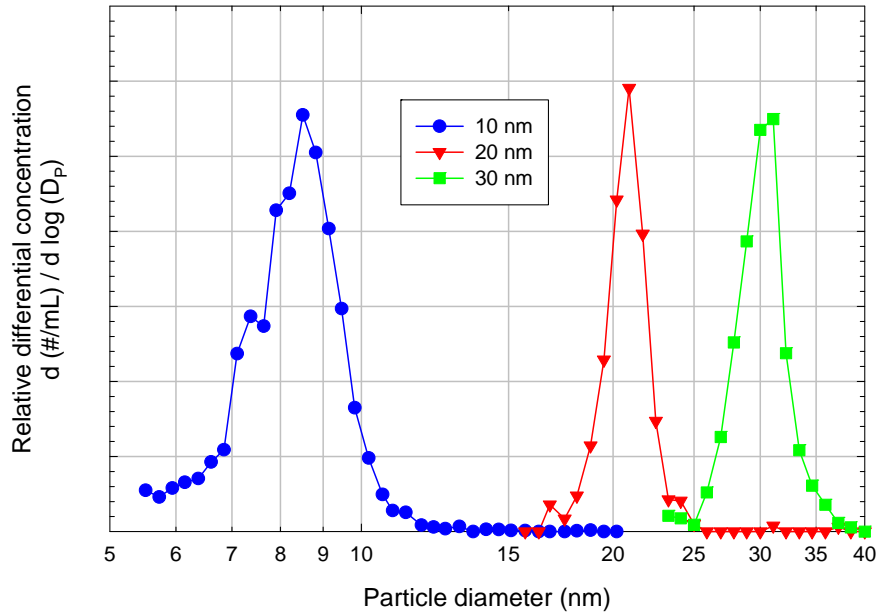
The instrument has also been used to measure the size of macromolecules. Sizing of five dextran molecules with molecular weights ranging from 10,000 to 670,000 is shown in Figure 7 [11].



**Figure 4. Sizing of a mixture of 3 sizes of PSL spheres**



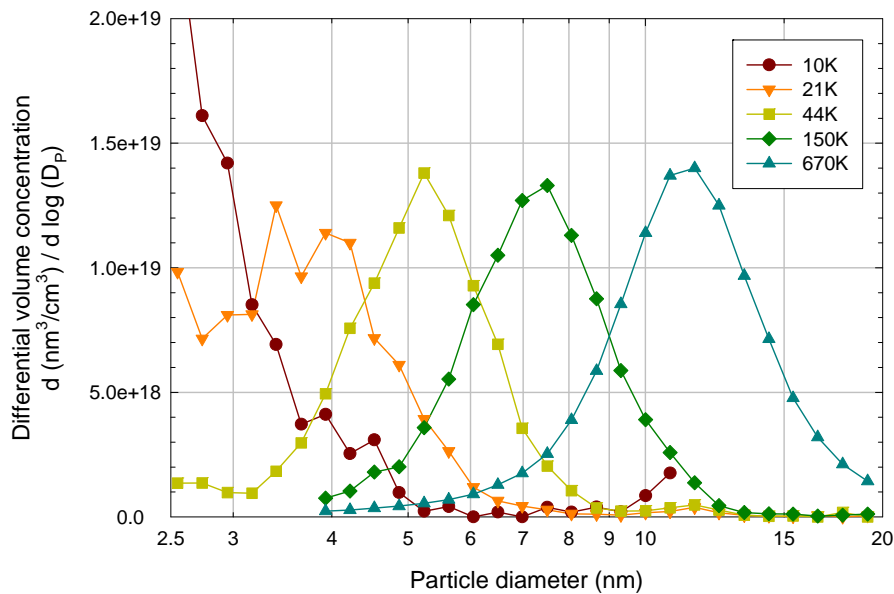
**Figure 5. PSL size variation as claimed by the manufacturer and as measured using the LNS technique**



**Figure 6. Measurement of BBI gold nanoparticles**

Nominal Size (nm)	Claimed size		Measured size	
	Mean (nm)	CV (%)	Mean (nm)	CV (%)
10	9.3	< 15	8.4	13
20	20.3	< 8	20.8	7.4
30	30.3	< 8	30.5	7.3

**Table 1. Gold nanoparticle size distributions claimed by the manufacturer and measured by the LNS technique**



**Figure 7: Measurement of dextran molecular size by the LNS**

### 3.2 Measurement of commercially available dispersion PSDs

The LNS has been used to measure PSDs of particles in numerous colloidal dispersions containing numerous types of particles [12-13]. Figure 8 shows examples of PSDs measured in CMP slurries used in semiconductor manufacturing that contain alumina (Figure 8A), ceria (Figure 8B) and silica (Figure 8C) particles. Figures 8A and 8B present measured concentrations and indicate that the particles in the two slurries had median particle sizes of 75 nm (volume weighted) and 110 nm (number weighted). Figure 8C presents a normalized volume weighted distribution measured by the LNS compared to that measured by DLS. The distributions measured by the two techniques were similar.

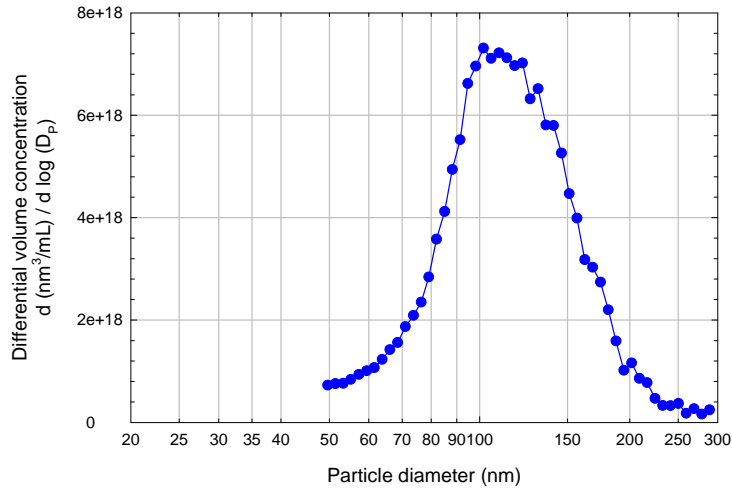
Figure 9 shows a scanning electron microscopy (SEM) image of particles in a commercially available polishing slurry (Figure 9A) along with volume-weighted PSDs measured using the LNS (Figure 9B), DLS (Figure 9C), and Fraunhofer diffraction (Figure 9C). The SEM and LNS measurements indicate that the slurry contains three distinct particle sizes with approximately equal volumes of the three sizes. The DLS and Fraunhofer measurements indicated similar distributions, but were unable to distinguish the three particle sizes. The peak of the distributions measured by these techniques was between the sizes of the two larger particles measured using the LNS.

### 3.3 Measurement of the effect of handling on dispersion PSDs

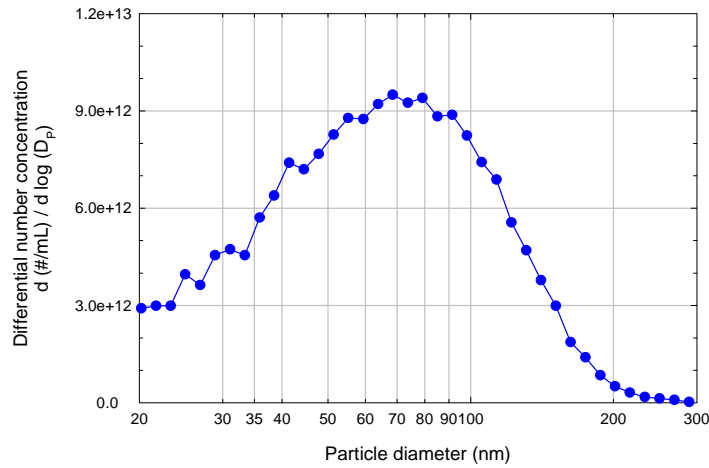
The LNS has also been used to measure changes in slurry PSDs over time. For example, experiments have been performed in which slurries were handled in ways that might occur in a typical semiconductor fabrication facility. During these tests, the PSDs of the slurries were monitored over time. In some slurry handling tests, relatively little change in the particle size distribution was observed while in some cases significant changes were evident [12].

Figure 10 shows an example of changes in PSD measured during circulation of a slurry containing colloidal silica particles. Graphs showing number- and volume-weighted distributions measured using the LNS (Figures 10A and 10B) and volume-weighted distributions measured using DLS (Figure 10C) are shown. The LNS measurements indicate that concentrations of the small particles decreased while the concentrations of larger particles increased as the slurry was circulated; an observation that is consistent with increasing agglomeration of the particles. The DLS measurements indicate that the median particle size decreased and the distribution broadened as the slurry was circulated. Clearly the LNS measurements provided a better indication of the effect of circulation on the PSD of this slurry.

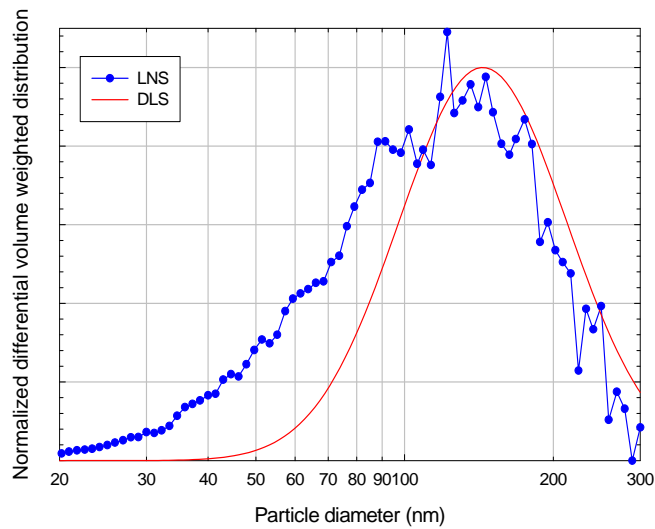




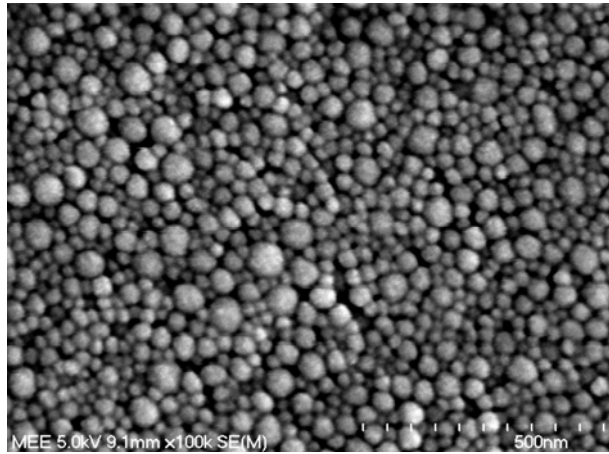
**Figure 8A: PSD of alumina particles in a CMP slurry**



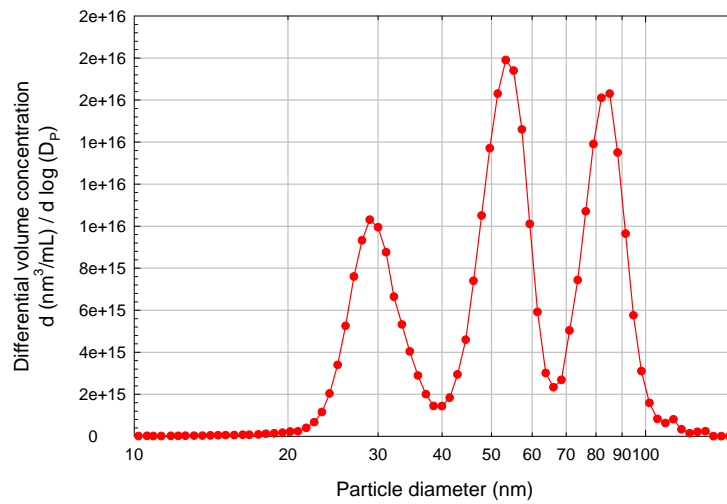
**Figure 8B: PSD of ceria particles in a CMP slurry**



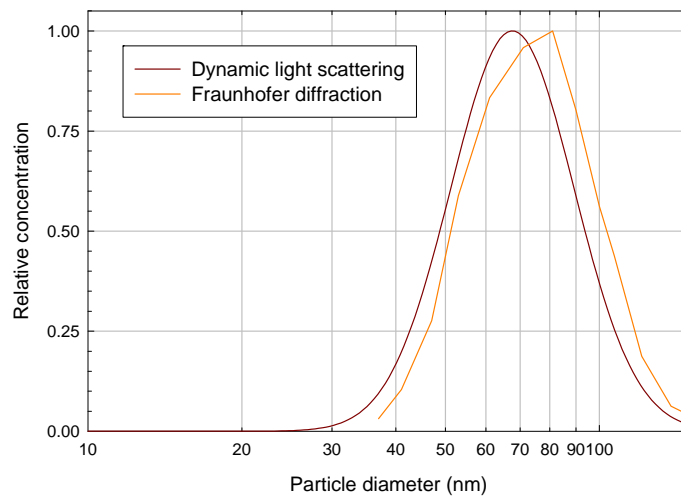
**Figure 8C: PSDs of silica particles in a CMP slurry measured by LNS and DLS**



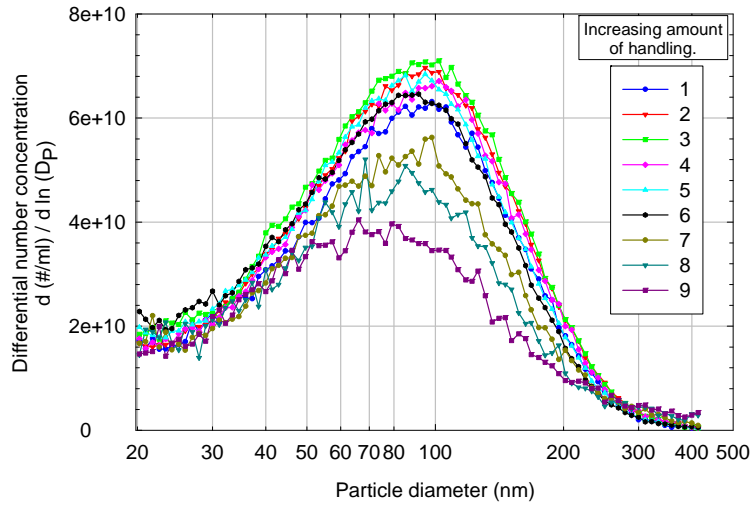
**Figure 9A. Scanning electron micrograph of slurry particles**



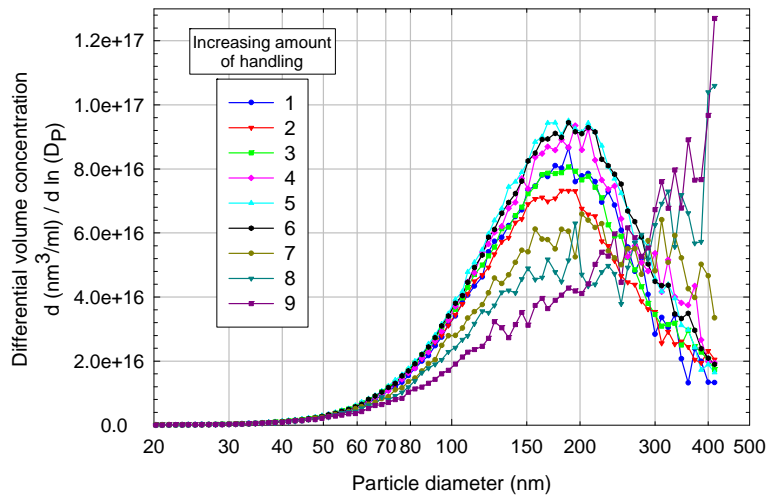
**Figure 9B. PSD measured using the LNS technique**



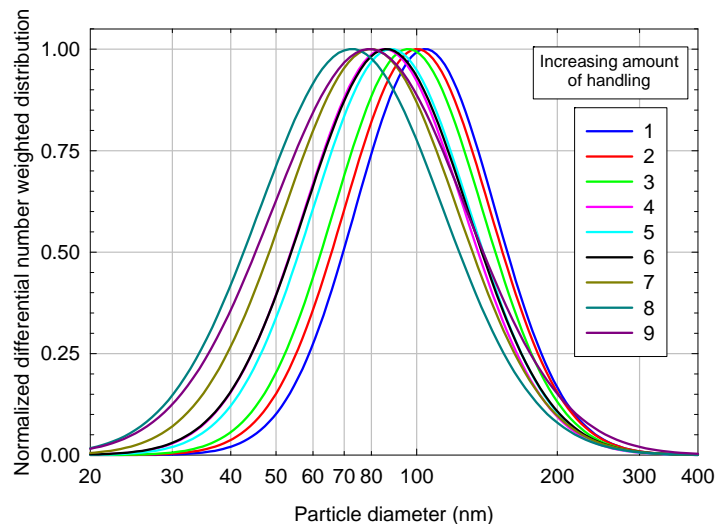
**Figure 9C. PSDs measured using DLS and Fraunhofer diffraction**



**Figure 10A: Number-weighted distributions during handling of a silica slurry**



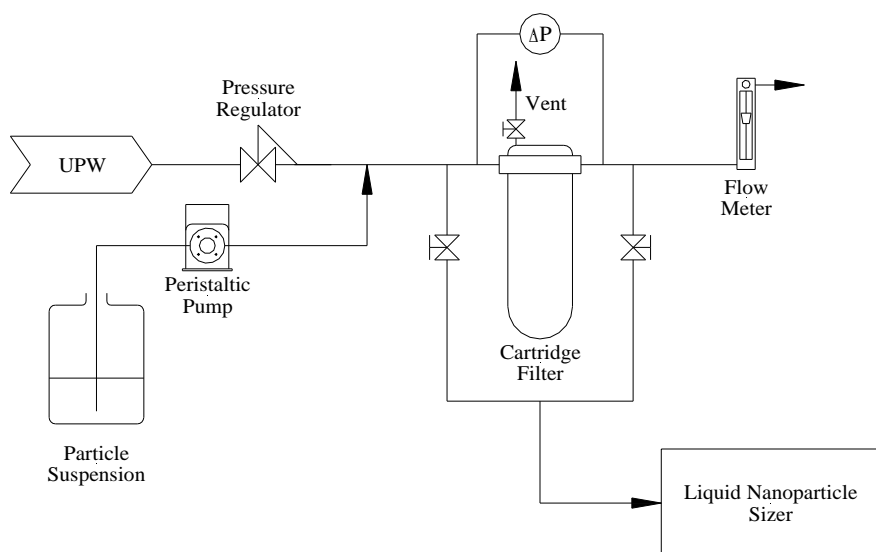
**Figure 10B: Volume-weighted distributions during handling of a silica slurry**



**Figure 10C: Volume-weighted distributions measured by DLS during handling of a silica slurry**

### 3.4 Measurement of particle retention by filters

The LNS has also been used to measure the removal of sub-100-nm particles from ultrapure water (UPW) by microporous membrane filters using the system shown in Figure 11. In this system, UPW is passed through the test filter at a controlled pressure and flow rate. Particles are injected into the UPW upstream of the filter using a peristaltic pump. Measurements of both upstream and downstream particle concentrations are performed.



**Figure 11: Filter challenge test system schematic**

Testing has been performed with various types and sizes of particles including mixtures of PSL spheres and silica particles with narrow size distributions. In one study the retention characteristics of four types of filters with retention ratings between 20 nm and 100 nm were compared by challenging the filters with a mixture of PSL spheres [14, 15]. An example comparing PSDs measured downstream of these filters (the filtrate) with the incoming concentration (the feed) when the filters had been heavily loaded with particles is shown in Figure 12A. Figure 12B shows the retention characteristics of the four filters based on the PSDs shown in Figure 12A. Clear differences among the filters abilities to remove these particles are evident.

Another study compared the efficiencies of four types of microporous membrane filters at removing 28-nm silica particles from high purity water [16, 17]. Filter removal efficiencies as a function of filter loading are shown in Figure 13. Clear differences among the filters are shown.

Removal of macromolecules by an ultrafiltration membrane has also been measured using the LNS [18]. In this study, an ultrafiltration (UF) membrane with a 30,000 molecular weight cutoff was challenged with a mixture of dextran molecules in a dead-headed operational mode. Retention of the macromolecule over time was measured. Retention decreased with decreasing molecular size and increasing loading as shown in Figure 14.

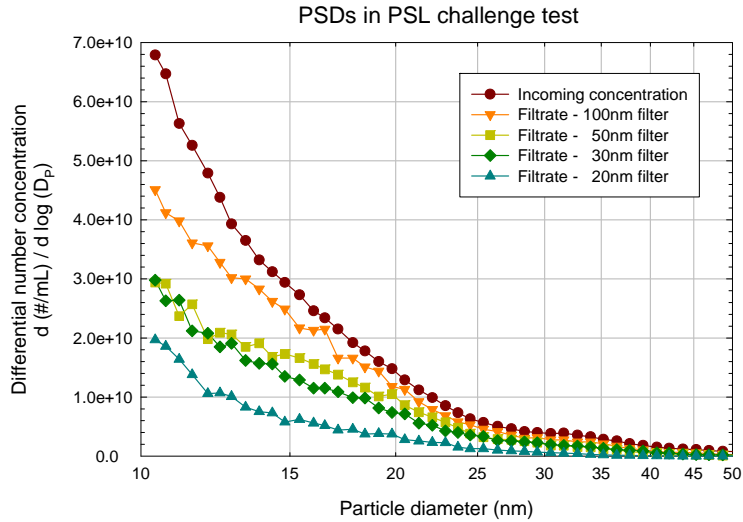


Fig 12A: Comparison of filtrate PSDs during PSL particle removal test

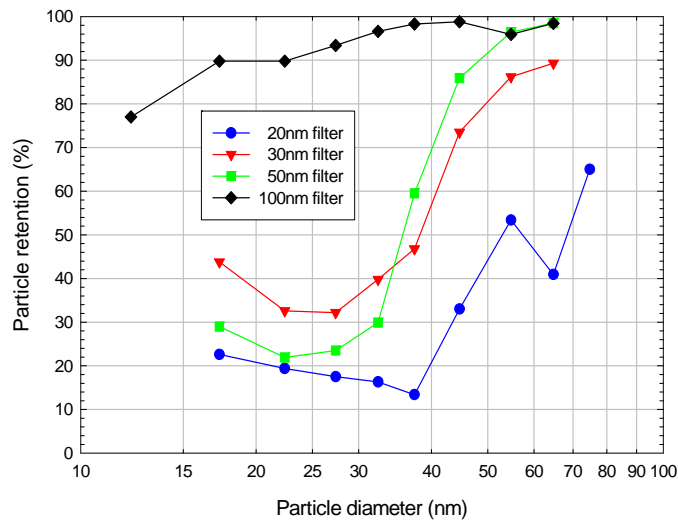


Fig 12B: Retention of PSL particles by four types of filters

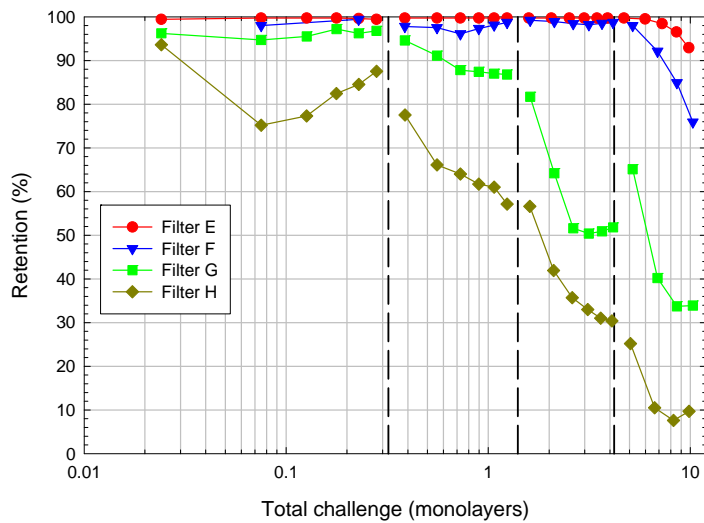
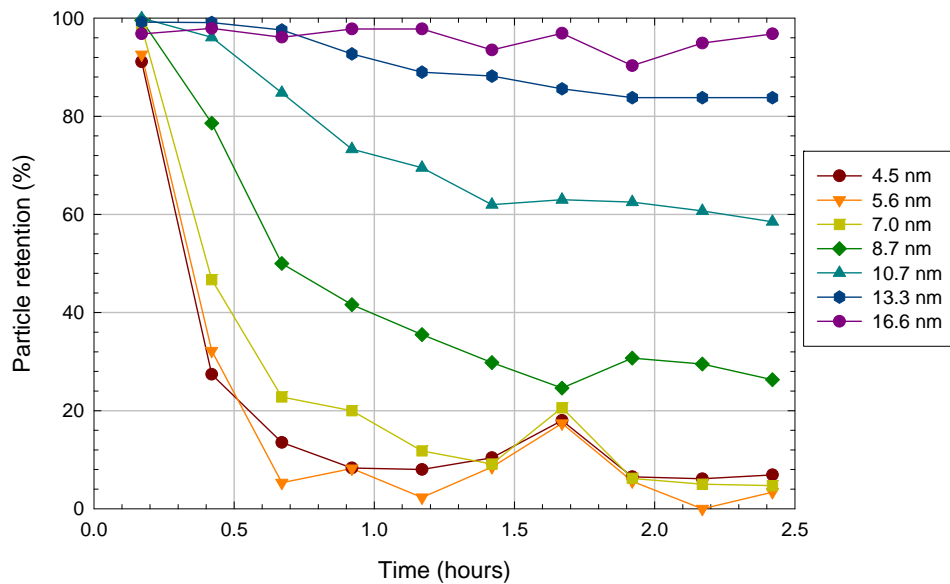


Figure 13: Retention of 28-nm silica particles by 4 types of membrane filters



**Figure 14: Dextran retention by a 30,000 molecular weight cutoff UF membrane**

#### 4. Summary

A liquid nanoparticle sizing (LNS) system capable of measuring the sizes and concentrations of particles in colloidal suspension has been developed. The method is capable of measuring sizes and concentrations of particles as small as 5 nm. It is capable of detecting small differences between particle size distributions in colloidal suspensions and macromolecule solutions. It allows measurement of retention of particles as small as 5 nm by filters and ultrafilters.

#### 5. References

1. Grant DC (2008). "A New Method for Determining the Size Distribution of the Working Particles in CMP Slurries," presented at the 2008 CMP Users Conference, sponsored by Levitronix.
2. Grant DC (2008). "A New Method for Determining the Size Distribution of Particles in Colloidal Suspensions," presented at the Particle Society of Minnesota annual meeting, March 19, 2008.
3. Knutson EO and KT Whitby (1975). "Aerosol Classification by Electric Mobility: Apparatus, Theory and Applications," *Journal of Aerosol Science*, 6:443.
4. Wang SC and RC Flagan (1989). "Scanning Electrical Mobility Spectrometer," Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA 91125, pp. 138-178.
5. Bricard J, P Delattre, G Madelaine, and M Pourprix (1976). "Detection of Ultrafine Particles by Means of a Continuous Flux Condensation Nucleus Counter," *Fine Particles*, B.Y.H. Liu, ed., Academic Press, New York, pp.565-580.
6. Sinclair D and GS Hoopes (1975). "A Continuous Flow Nucleus Counter," *Journal of Aerosol Science*, Vol. 6, pp.1-7.

7. Hering SV, MR Stolzenburg, FR Quant, DR Oberreit, and PB Keady (2005). "A Laminar-Flow, Water-Based Condensation Particle Counter (WCPC)," *Aerosol Science and Technology*, 39:659–672.
8. Wiedensohler A (1988). "Technical Note: An Approximation of the Bipolar Charge Distribution for Particles in the Submicron Range," *Journal of Aerosol Science*, 19:3 (387-389).
9. Hinds WC (1982). Chapter 4: Particle Statistics, *Aerosol Technology*, John Wiley & Sons, New York,
10. Van Schooneveld HG, M Litchy, and D Grant (2011), "A Novel Method of Measuring Sizes and Concentrations of 5-500 nm Particles in Colloidal Suspensions," *TechConnect World 2011*, Boston, MA.
11. Farnsworth J, DC Grant, G Van Schooneveld, MR Litchy, J Scheckman, B Osmondson and R Caldwell (2011), "Device and Method for Counting and Sizing Nanoparticles in Colloidal Suspensions," AAAR 30th Annual Conference.
12. Van Schooneveld, G, M Litchy, and D Grant (2010). "A New Method for Determining the Size Distribution of Particles in CMP Slurries", *Proceedings of the 2010 International Conference on Planarization/CMP Technology*, Phoenix, AZ , pp. 348-351.
13. Farnsworth JE, DC Grant, HG Van Schooneveld, MR Litchy, BL Osmondson, and R Caldwell (2011), "Ultrafine Nebuliser for Aerosolization of Nanoparticles in Colloidal Suspensions", presented at *European Aerosol Conference 2011*, Manchester, England.
14. Grant D and U Beuscher (2009), "Measurement of Sub-50 nm Particle Retention by UPW Filters", *Ultrapure Water Journal*, 26(11):34-40.
15. Grant DC and U Beuscher (2009). "Measurement of Particle Removal from High-Purity Liquids Down to 10nm," presented at the 2009 Ultra Pure Fluid and Wafer Cleaning Conference, sponsored by Levitronix.
16. Grant, DC (2010). "Measurement of 28 nm Particle Removal from Liquids by High Purity Filters, Poster presented at the North American Membrane Society 2010 Conference, Washington, DC.
17. Grant DC and G Van Schooneveld (2011). "Measuring sub-50nm Particle Retention of UPW Filters," presented at the 2011 CMP and Ultrapure Conference, sponsored by Levitronix.
18. G Van Schooneveld and DC Grant (2010). "Measurement of sub-50 nm Particle Removal from UPW," presentation at the Executive Forum at ULTRAPURE WATER Micro 2010, ITRS subcommittee for UPW quality, Phoenix, AZ, November 16, 2010