Nano-Particle Standards and their use for Particle Counter Calibration
and Particle Deposition Studies

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A particle standard is an aqueous suspension of particles of known size and ideally known concentration. The ability to make a particle of known size is restricted to particles composed of polystyrene latex (PSL), colloidal gold and recently colloidal silica.
Particle standards have recently been used for particle deposition studies (ref needed), but their primary use has been to calibrate particle counters.

Optical Particle Counters (OPC) or Liquid Particle Counters (LPC) has exclusively used polystyrene latex (PSL) particles for calibration. The reason is obvious: they were readily available in a variety of sizes, had a low standard deviation, were inexpensive and their size could be traced to NIST available standards. However, PSL particles are white, spherical and have a refractive index different from particles found in semiconductor process chemicals and pharmaceutical waters for example. Hardly an ideal calibration material. So when an OPC/LPC reports a particle count it is reporting an equivalent PSL size that can be quite different form the particle's actual physical size. In spite of this short coming OPCs/LPCs have provided valuable information for reporting "particle incidences or excursions".

The development of OPCs/PLCs technology has been driven by the semiconductor industry. With ever decreasing line-width, semiconductor process engineers have been demanding OPCs/PLCs with smaller and smaller particle size detection. The current most sensitive OPC/LPC offers 20nm detection. However, the industry needs a particle size detection of 7nm to make today's most advanced semiconductor, and even the 20nm particle counter has a detection efficiency of <3%. To make matters worse the ability to make PSL calibration particles becomes increasingly difficult below 50nm and virtually impossible at 20nm. As shown by Van Schooneveld (ref required) in figure 1 the standard deviation of PSL size distributions dramatically increase as sizes get smaller and smaller.

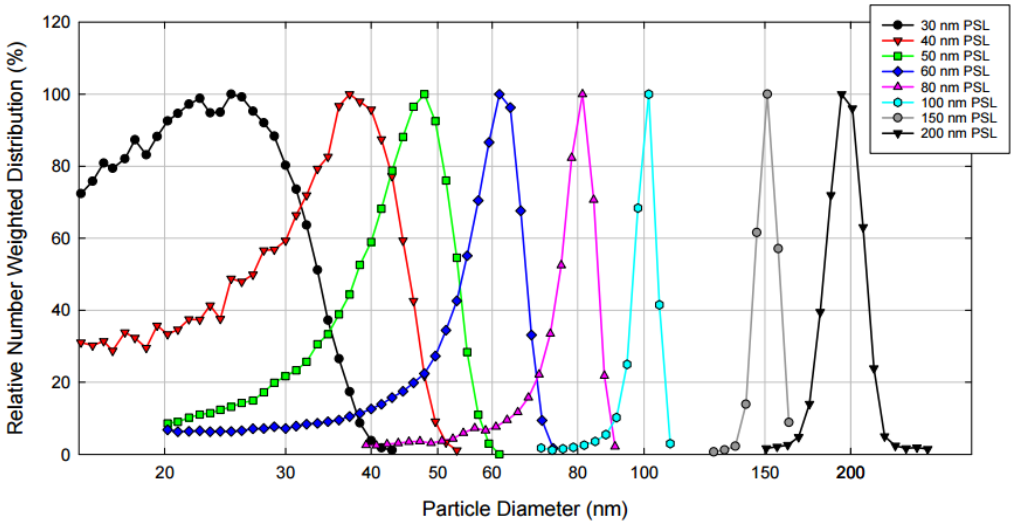

Figure 1 Size and relative number concentration of a range of PSL calibration standards

In an effort to overcome this shortcoming CT Associates and Kanomax FMT have developed a "cocktail" of PSL sizes, of known concentration, ranging in size from 20nm to 125nm. The slope of this cocktail has been adjusted to approximately minus 3 to mimic the naturally occurring incidence of increased concentration of smaller particles observed in nature. The size and concentration of this unique PSL standard is shown in figure 2. This data was obtained using a PMS M50e OPC, a Lighthouse NC30^{+} OPC and a Kanomax Liquid Nanoparticle Sizer (LNS). This cocktail of PSL sizes has the added advantage of allowing an OPC manufacturer to adjust size detection (or binning) at one size and observe/adjust the size detection in an adjacent channel or size bin. Lighthouse has now standardized using this PSL cocktail to calibrate its most sensitive OPC.

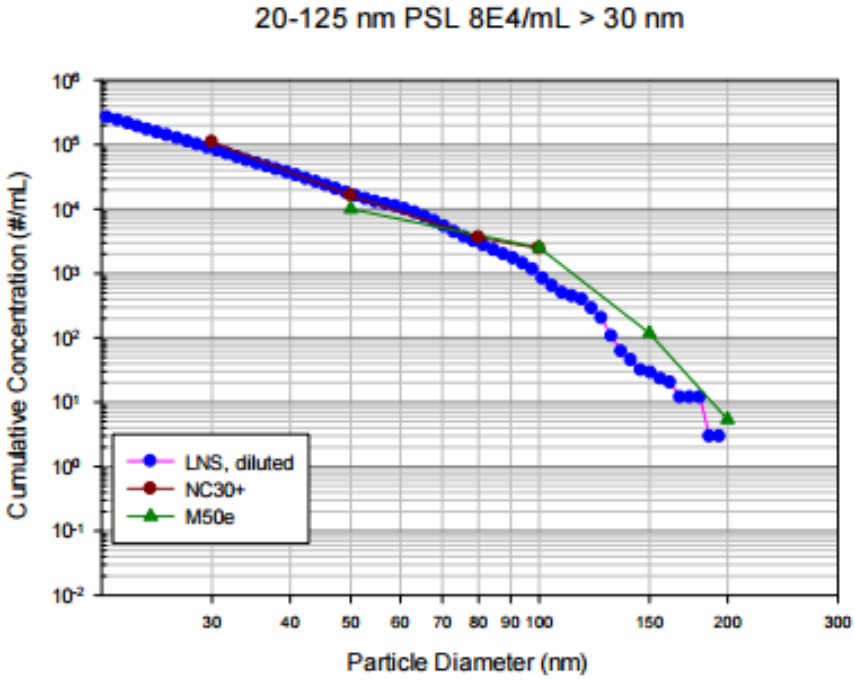

Figure 2. Size distribution and concentration of a cocktail of PSL particles measured by three different sizing instruments.

Ideally a new material is need for calibrating the next generation of particle counter at 10nm and below. It is the author's opinion that this next generation of particle counters will not be based on light scattering as this technique has essentially reached to end of its capability (the laws of physics tells us so). New non-optical particle counters are being developed. The Scanning Threshold Particle Counter (sTCP) has a lower detection efficiency of 10nm and is calibrated using colloidal silica particle standards. Colloidal silica particles represent a much more realistic material for calibrating particle counters as we believe a significant proportion of naturally occurring particles in Ultrapure Water (UPW) are silica. Colloidal silica particles are also readily available, come in sizes form 7nm to 90nm, have a narrow size distribution (at even the smallest sizes), are inexpensive and are size traceable to a European Reference Material (ERM) standard. The size distribution for three colloidal silica standards are shown in Figure 3 (reference needed)

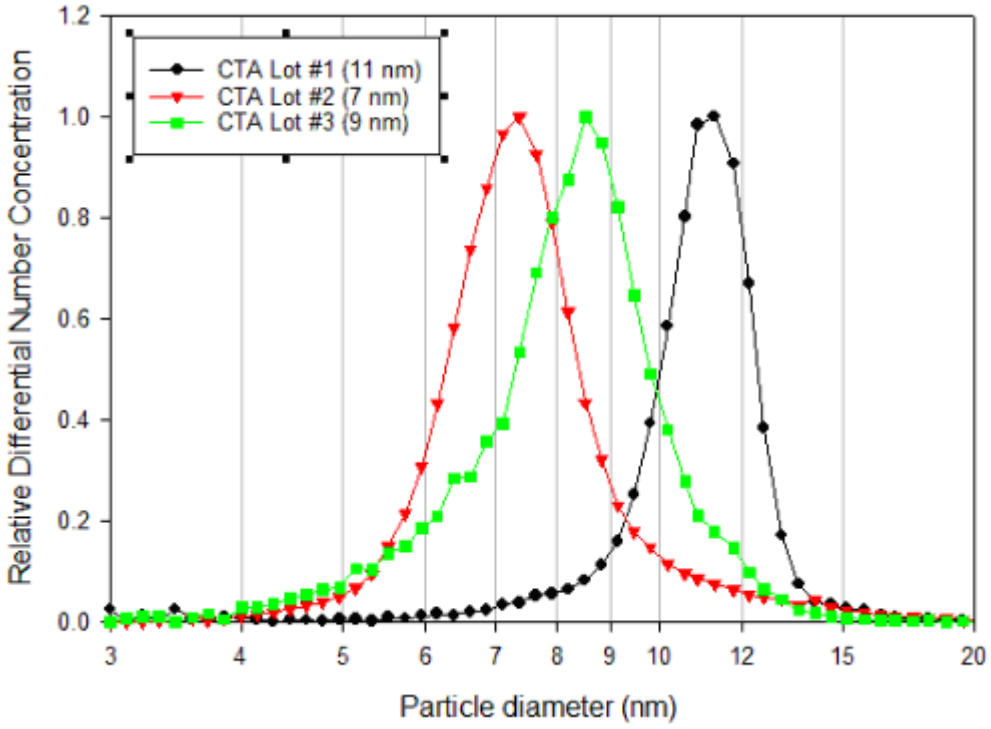

Figure 3. Size distribution and relative number concentration of 7, 9 and 11nm colloidal silica standards.

An alternative to colloidal silica is colloidal gold, which can be purchased with a very narrow size distribution and has NIST and ERM traceability (?). However, colloidal gold is far from ideal. It is hardly representative of the material of particles found in UPW, including a very high refractive index, it's expensive and comes with a significant amount of non-volatile residue. The non-volatile residue can be seen in Figure 4 as an increasing tail of smaller sizes quite distinct from the 30nm colloidal gold particles.

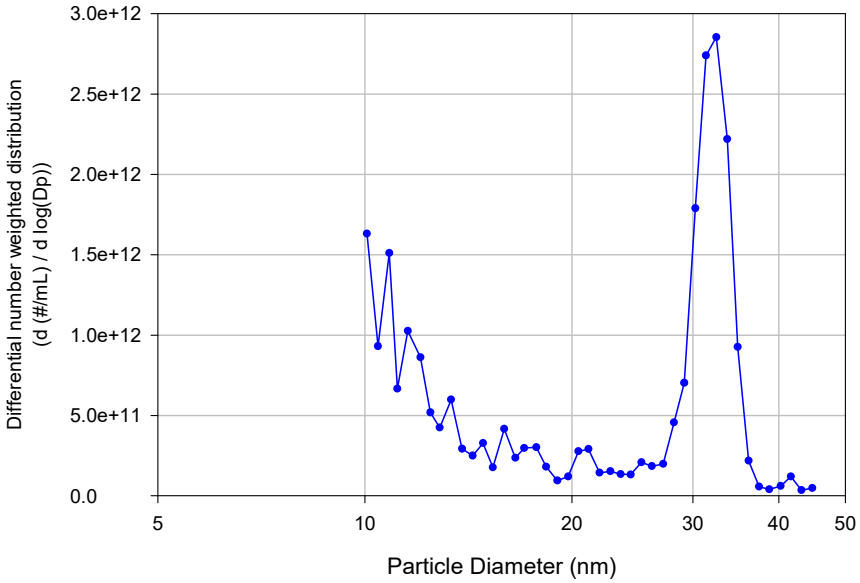

Figure 4 Size distribution and number concentration of colloidal gold as measured by the LNS

Colloidal gold also has significant surface characteristics (notably surface charger) that may require modification before it can be used.

CT Associates and Kanomax FMT have developed a technique they call Diafitration that can preferentially remove the non-volatile residue material from colloidal gold and other aqueous particle suspensions. Diafiltration is essentially the same as desalination of sea water or dialysis of blood to remove impurities. A schematic of the Diafiltration system is shown in Figure 5. A sample of the aqueous particle suspension in placed in the stirred cell at the bottom of which is a small ultrafilter. UPW continuously flows through the cell and ultrafilter and essentially washes away the non-volatile residue, leaving the particle suspension virtually intact.

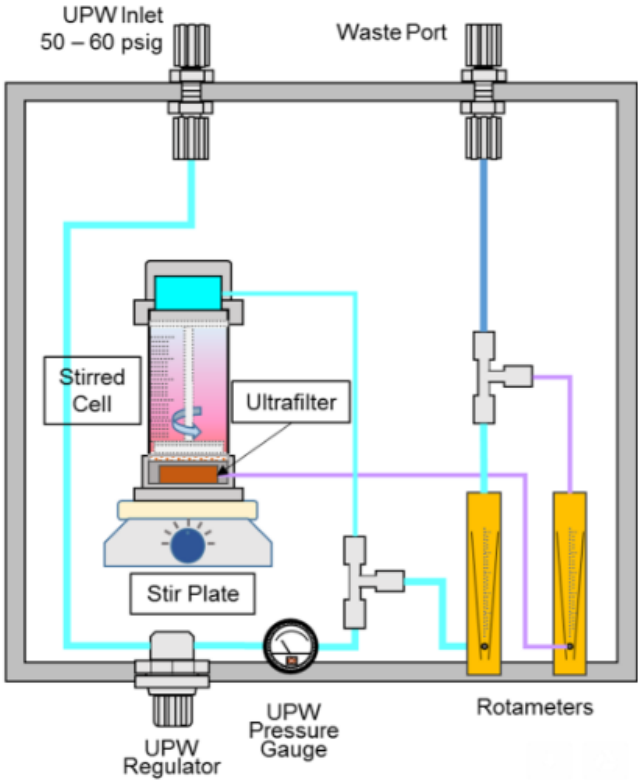

Figure 5. Schematic of the Diafiltration system

One problem associated with all these particle standards is what bottle to put them in. There is no such thing as a clean bottle. A paper by Blackford et al showed how the meniscus created by the liquid/air boundary as it moves up and down the walls of very bottle tested released 1000s of nanometer sized articles. This particle release hardly diminished as any bottle is repeatedly turned up side down. The solution to this is not to over clean bottles, but to find a relatively clean bottle and fill it with a high concentration of particles. A precise concentration of 4E7 particles per mL has been found to be optimal. In order to dilute this high concentration a Precision Dilution System (PDS) was developed by CT Associates and Kanomax FMT. The PSD is capable of achieving accurate dilutions as high as 20,000 to 1.

Particle deposition studies.
Libman et al. (2016) reported the results of an ITRS-sponsored particle deposition study. Known concentrations (3,000/mL to 10,000/mL) of 60nm SiO_2, 80nm NH_2SiO_2 and 200nm PSL were deposited onto a rotating 200mm SiO_2 wafer. From this study it was concluded:

- Positively charged particles have a higher tendency to deposit
- Particles of PSL deposit at the same rate, regardless of size
- Particle and wafer properties (charge and hydrophobicity) significantly affect deposition
- Drying effect is likely responsible for the deposition of negatively charged particles.
- Attraction mechanisms seem to play an important role for positively charged particles

Front End Processing (FEP), requires that no more than 12 particles should be detected on a 300 mm wafer (see ITRS2.net 2013 FEP table). The deposition study concluded that to meet this particle level on the wafer the UPW used to wash the wafer must contain no more than 36.6 particles per mL. This number is much higher than is currently reported (1 particle per mL) in the latest roadmap for semiconductor manufacture.

References:

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