Validating the Counting Efficiency of Liquid Optical Particle Counters below 100 nm

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Introduction

- Semiconductor manufacturing requirements continuously challenge the particle measurement supply base to provide instruments capable of detecting and sizing increasingly smaller particles.
- A number of manufacturers have or are introducing new liquid optical particle counters (OPC) able to size and count smaller particles.
- It is important that instrument users understand the particle counting efficiency of these instruments relative to particle size when making process measurements.
- SEMI recently released C77-0912, Test Method for Determining the Counting Efficiency of Liquid-borne Particle Counters for which the Minimum Detectable Particle Size is between 30 and 100 nm.
- This paper will examine the particle size distributions (PSD) of 30 to 100 nm polystyrene latex (PSL) particles, discuss the implications of the PSL PSD on SEMI C77 and present counting efficiency data on two commercially available OPC's.

Outline

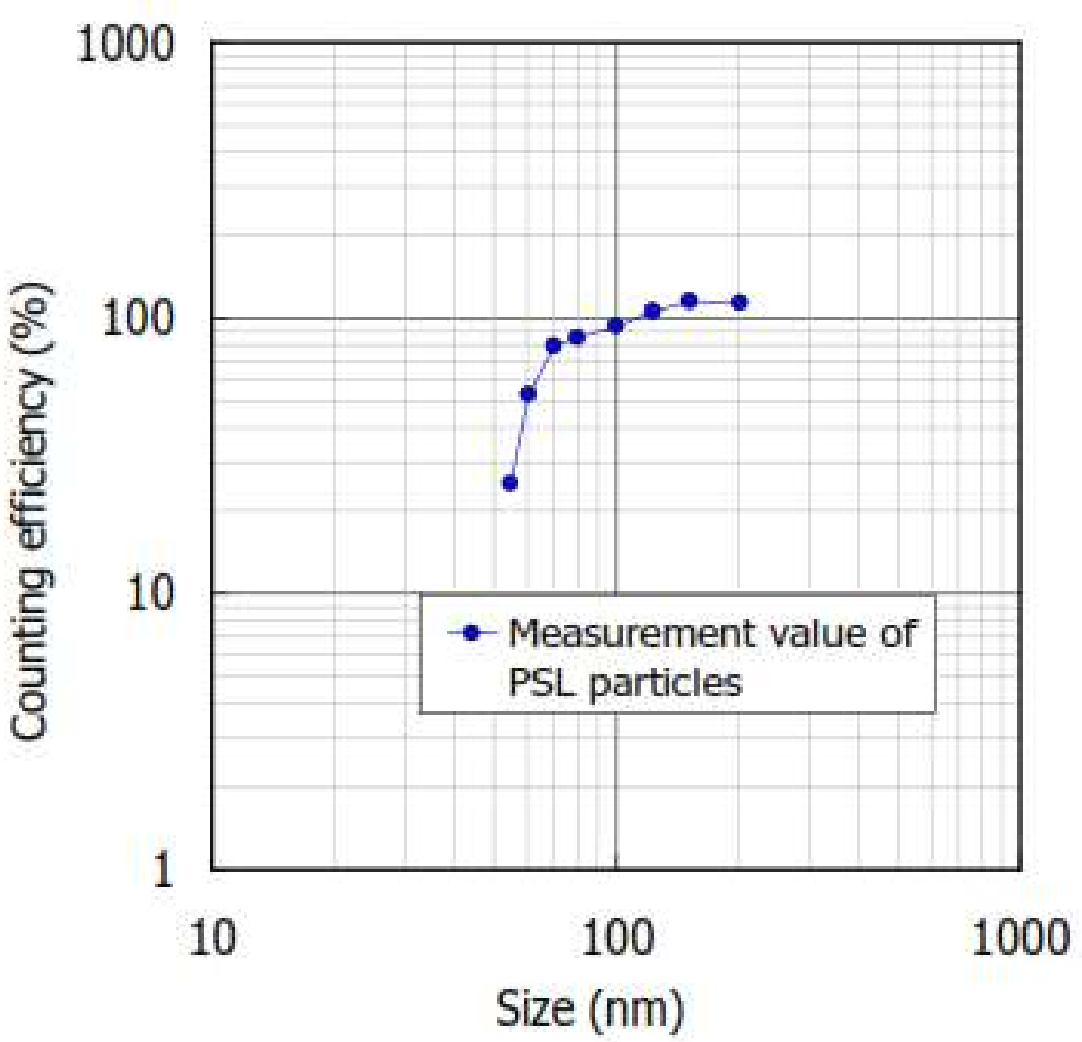
- Overview of the SEMI C77 methodology.
- Examination of polystyrene latex (PSL) particle size distributions (PSDs).
- Discuss the implications of PSL PSDs on SEMI C77.
- Test details
  - Procedures
  - Instrumentation
- Test results
- Summary

SEMI C77-0912 Overview

- Approved in 2012 by the Global Liquid Chemicals Technical Committee.
- Minimum OPC detection limit of 30 – 100 nm.
- Monodispersed polystyrene latex beads are specified as the challenge particles.
- Multiple sizes of PSL are run.
- Particles are to be size traceable to an international standard of length.
- Standard sizing uncertainty must be $\leq \pm 2.5\%$
- Challenge concentration to be > 1,000/mL and less than the coincidence limit of the OPC.
- Number concentration of the PSL before dilution is calculated using the stated mean diameter and % solids concentration. *(See note)*
- Counting efficiency as a function of size is presented.

(Note: Variability in solids concentration will effect the number concentration calculations. Solids concentration is provided as a nominal value without uncertainty. In addition to the PSL, there are dissolved solids present that make up the total. This potential source of error was not evaluated but prior experience suggests that % solids variability should be considered.)

SEMI C77-0912 Overview



Source: SEMI C77-0912

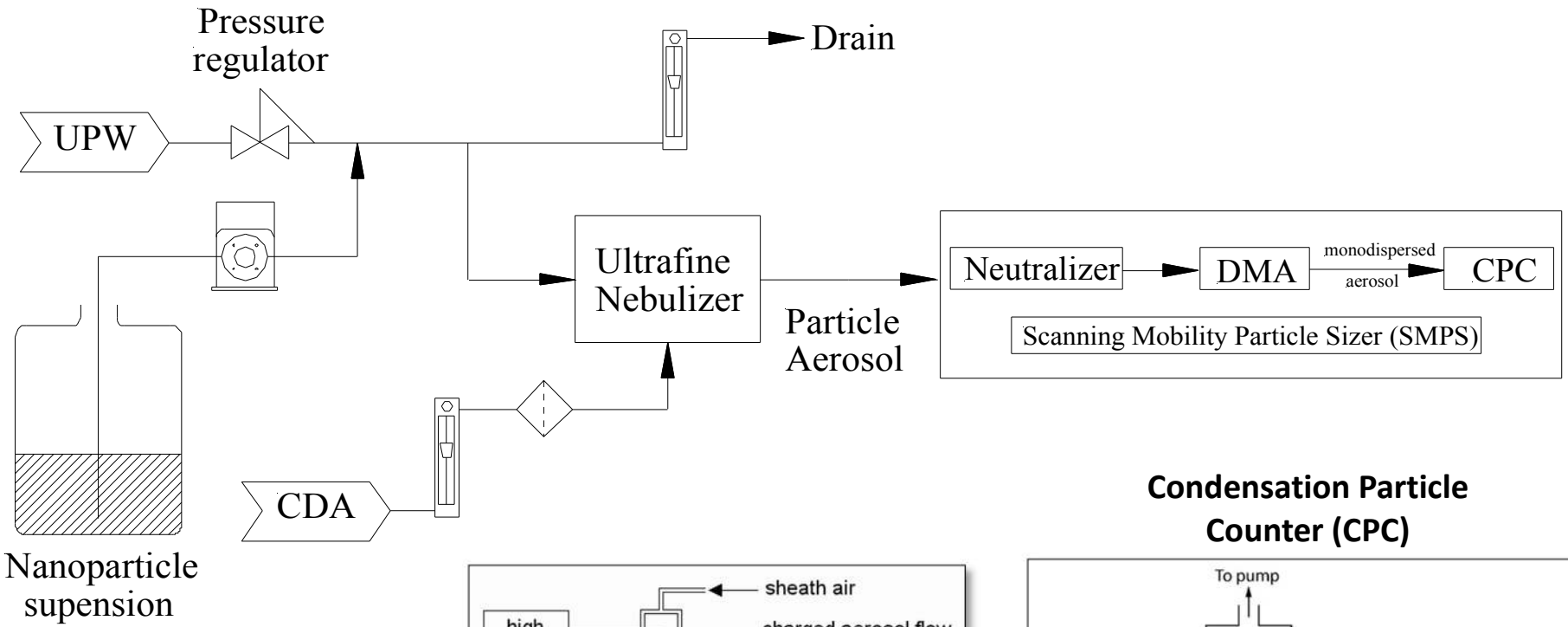
PSL Particle Size Distribution Data

(Thermo Scientific Nanosphere™ Size Standards)

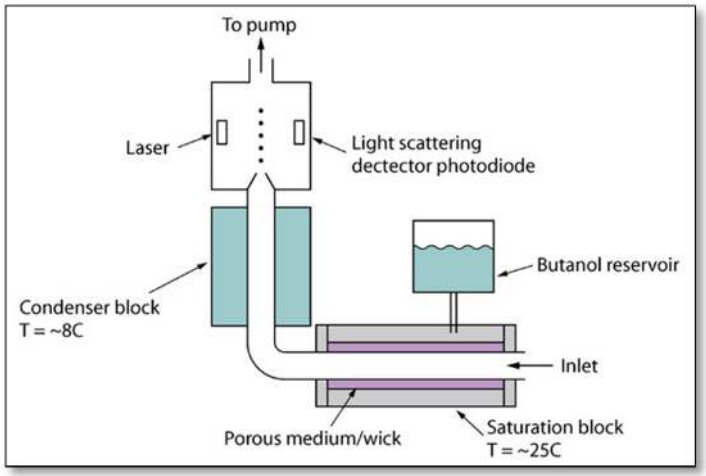
PSL Sizing Techniques

- Photon Correlation Spectroscopy (PCS) or Dynamic Light Scattering (DLS)
  - Thermo 20, 30, 40 nm PSL
- Transmission Electron Microscopy (TEM).
  - Thermo 50 nm to 1 μm
- Nebulization/Dynamic Mobility Analysis (N/DMA)
  - NIST 60 and 100 nm PSL SRM
  - NIST 10 and 30 nm GNP SRM

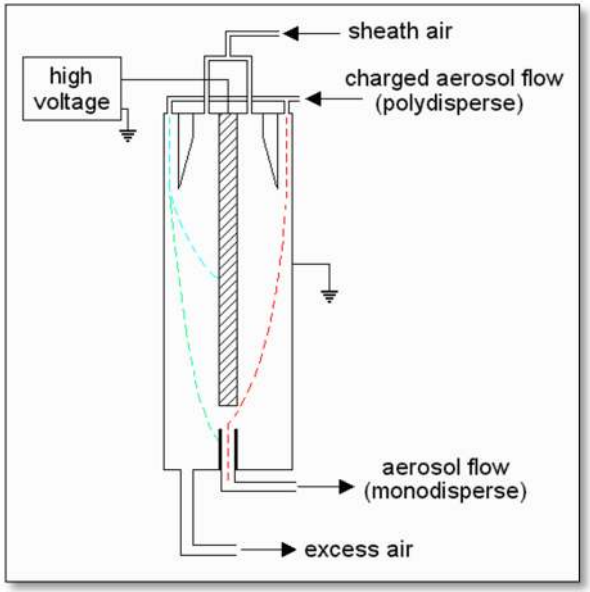
Schematic of the Liquid Nanoparticle Sizing (LNS) System



Condensation Particle Counter (CPC)



Dynamic Mobility Analyzer (DMA)



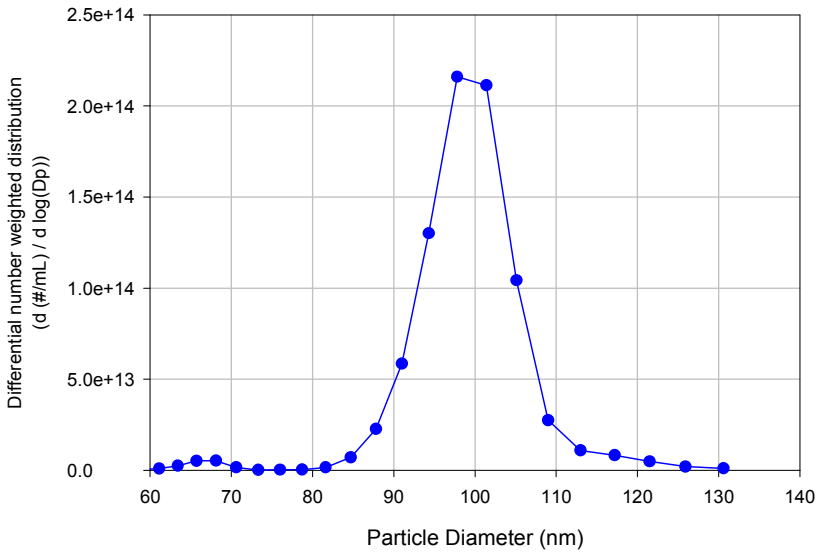
Van Schooneveld, et al. Ultrapure Water - Micro 2013
(CTA Publication 120)

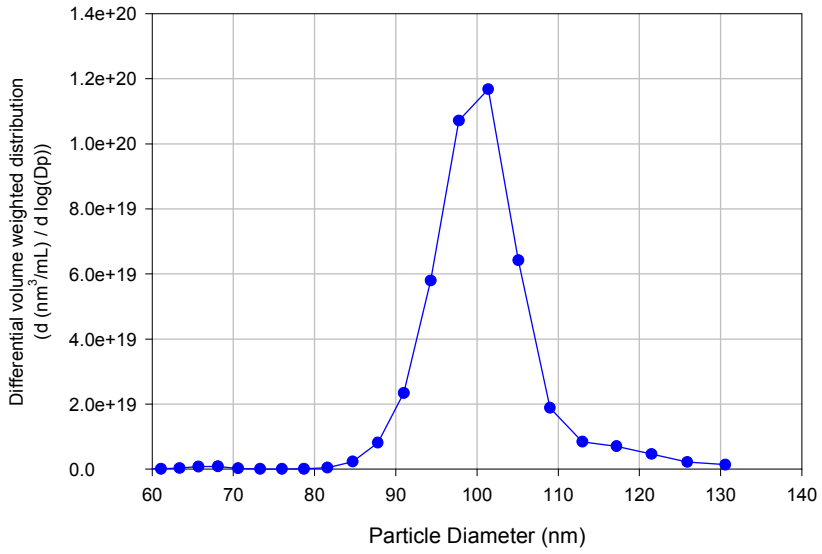
Comparison of Sizing Calculations (NIST Data)

Sample	Certified Diameter – Modal (nm)	Number mean diameter (nm)	Volume mean diameter (nm)	DLS mean diameter (nm)
100 nm PSL SRM 1963a	101.5	100.6	101.0	101.3
60 nm PSL SRM 1964	60.55	55.70	58.49	59.72

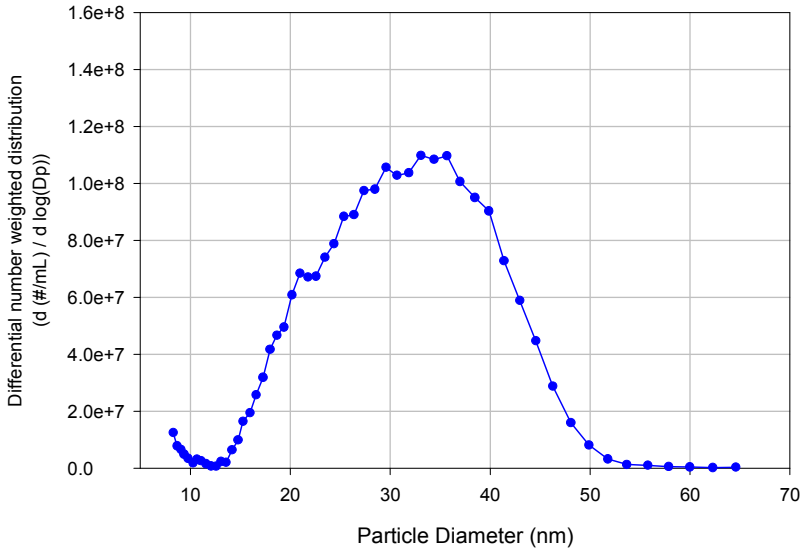
Particle Size Distribution of Polystyrene Latex

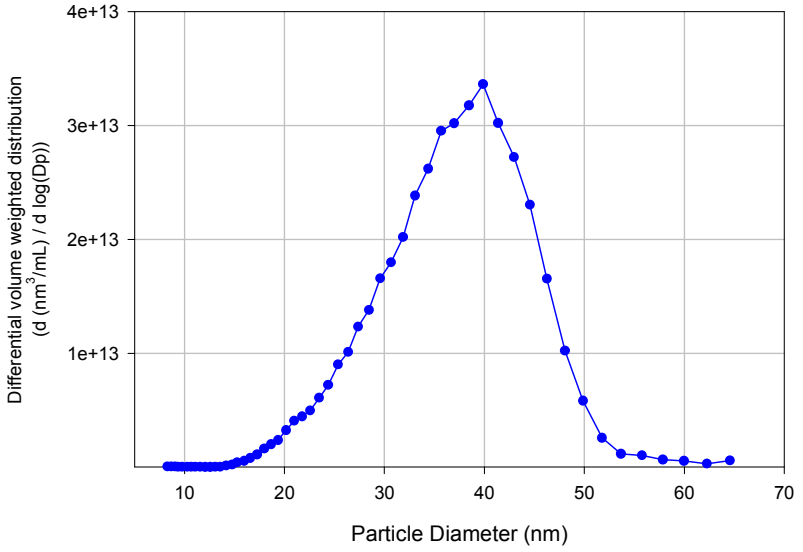
Thermo 100 nm PSL - Lot number 38647
(102 ± 3 nm) - 07/15/20103





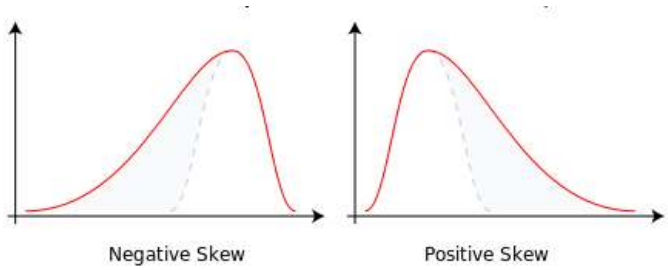
Thermo 40 nm PSL - Lot Number 40718
(40 ± 1 nm)





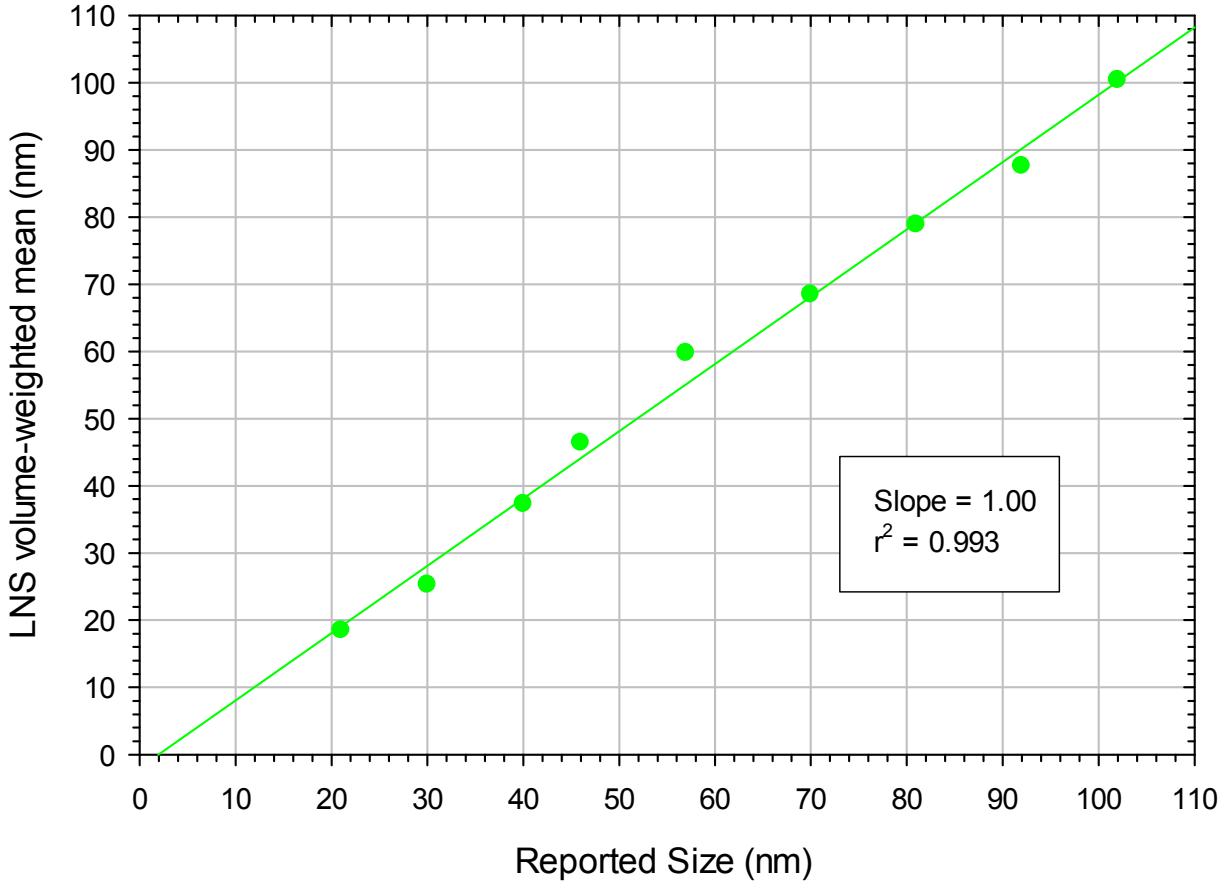
PSL Analysis Method

- Measured particle size distribution of 9 batches of Thermo Nanosphere™ Size Standards (20 to 100 nm).
- Used CTA's Liquid Nanoparticle Sizing System (LNS) to measure the PSL particle size distributions (particle diameter vs concentration).
- Analyzed each size for:
  - Number mean diameter
  - Volume mean diameter
  - Number standard deviation
  - Coefficient of skewness ($S_k = \frac{\sum f(X-\overline{X})^3}{s^3}$)



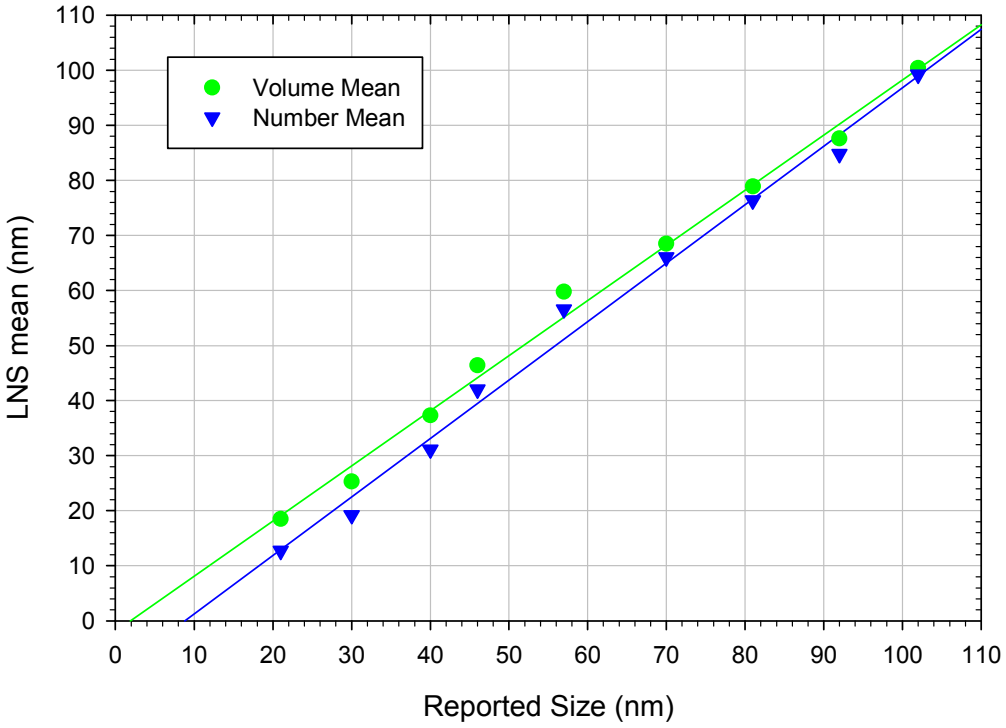
Source: Wikipedia.org

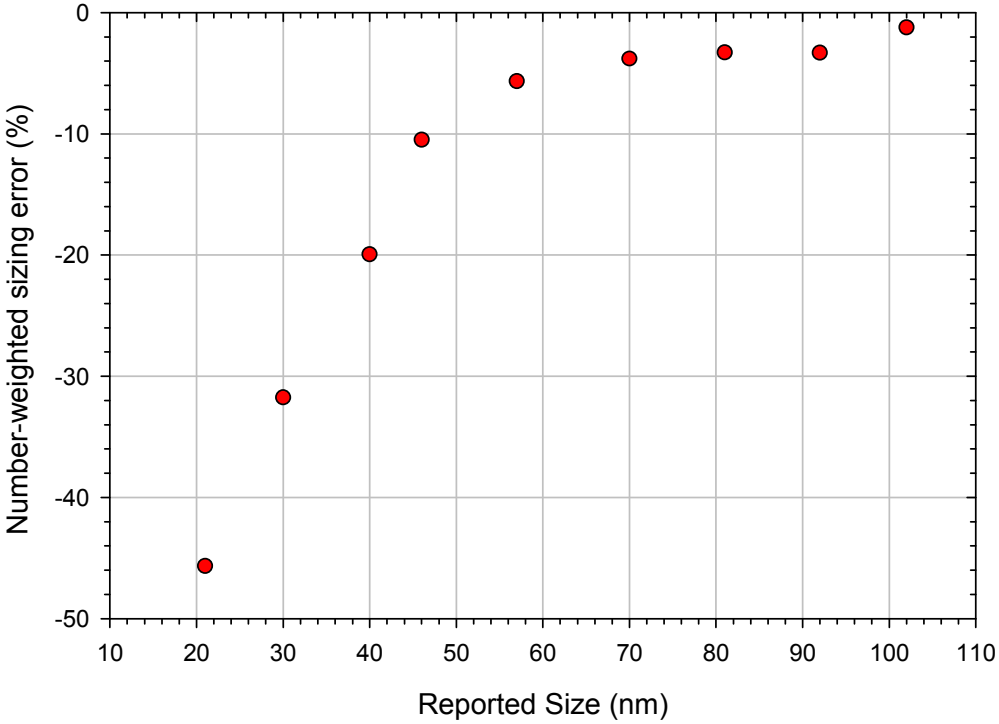
PSL Sizing Comparisons



Excellent correlation was found between volume weighted LNS data and Thermo published sizing data.

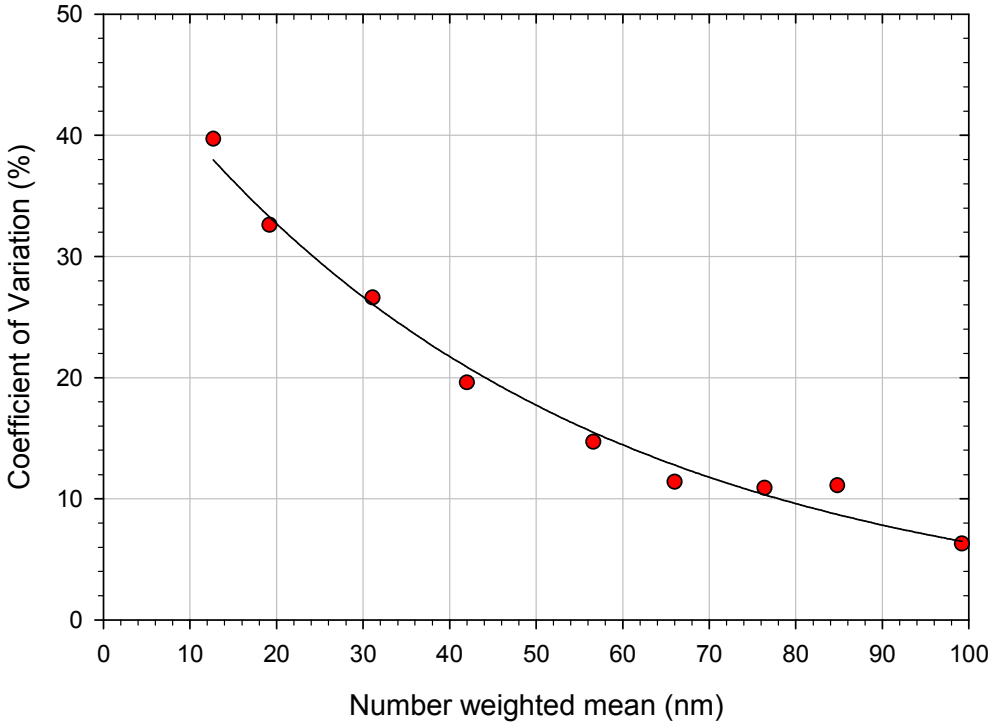
PSL Sizing Comparisons

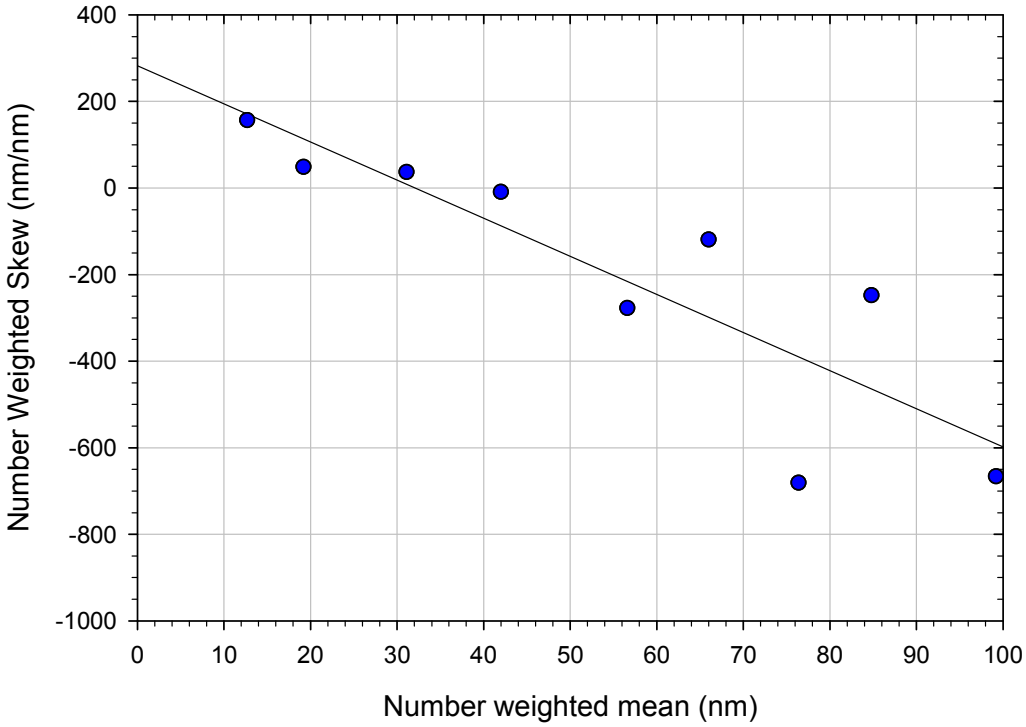




- *Because the particles are not monodispersed, the number weighted mean is smaller than the volume weighted mean.*
- *The difference between volume weighted mean and number weighted mean is > 2.5% for the 90 nm PSL and smaller.*
- *The difference becomes very significant below 50 nm (> 10% error).*

PSL Distribution Statistics





- *Standard deviation increases as mean particle diameter decreases.*
- *Number Cv > 15% at < 50 nm*

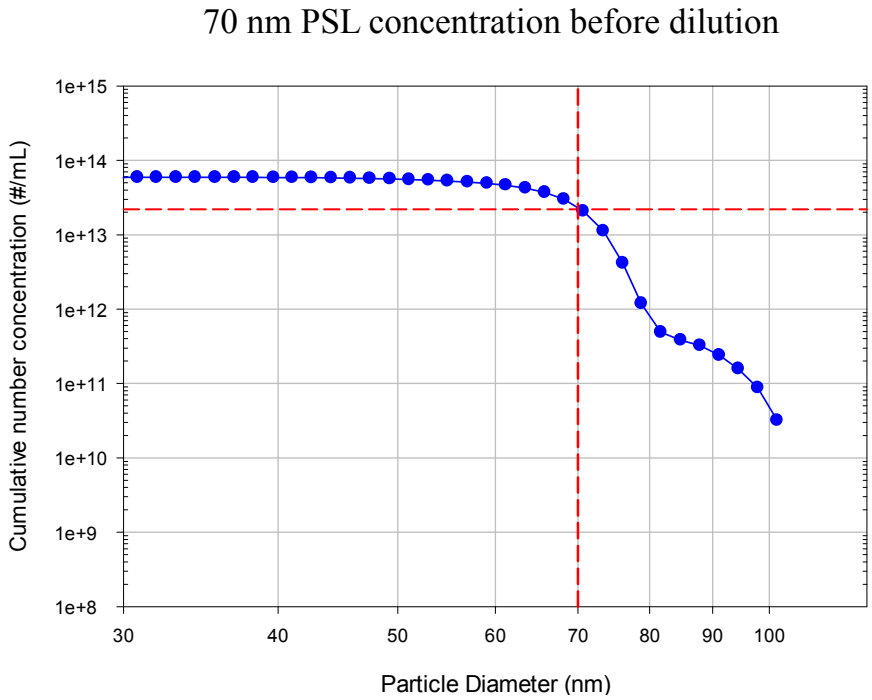
- *Number weighted skew becomes more negative with increasing particle size.*
- *Note: Thermo 100 nm PSL is tri-modal resulting in negative skew calculation. Primary mode only has a slight positive skew.*

Implications of the PSL PSD on SEMI C77

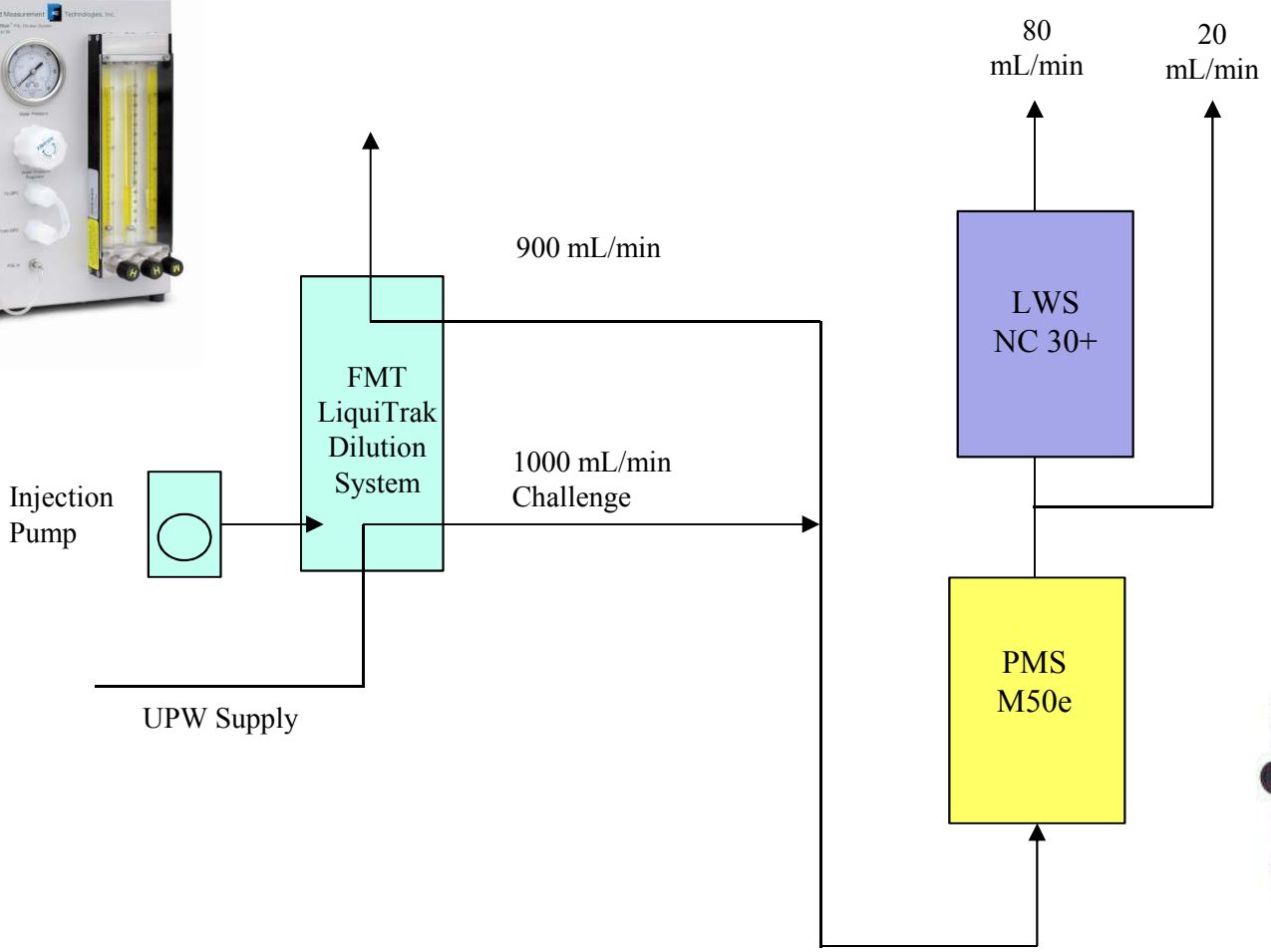
- The PSL below 100 nm used in for this study were not monodispersed.
  - Coefficient of variation (standard deviation divided by the mean) are > 10%.
  - PSD are skewed, not normal distributions.
- Volume weighted mean diameter is larger than the number weighted mean diameter with > 2.5% difference for 60, 70,80, 90 nm PSL and > 10% for 50 nm and smaller.
- Potential error from % solids variability needs to be considered during the analysis.
- *An alternative to the approach specified in SEMI C77 is needed to accurately measure the counting efficiency when the PSL is polydispersed and the accuracy of the % solids is unknown.*

Measurement Approach

- Utilize the LNS-measured particle size distribution to determine the actual particle size distribution of the undiluted PSL challenge.
- Use the cumulative number concentration ≥ the nominal particle size (30 nm, 40 nm, 50 nm, etc.) to determine the pre- dilution concentration.
- Calculate the counting efficiency for each PSL size at the nominal particle diameter.



Test Details - Apparatus



Optical Particle Counters Tested

- Particle Sizing Systems M-50e
  - *HSLIS M50e*
  - *Serial #35008-0496-432*
  - 50, 100, 150, 200 nm channels
  - Coincidence limit – 20,000 particles/mL

- Lighthouse NC30+
  - *Part #403010210-1*
  - *Serial #130143001*
  - 30, 50, 80, 100 nm channels
  - Coincidence limit – 1,000,000 particles/mL

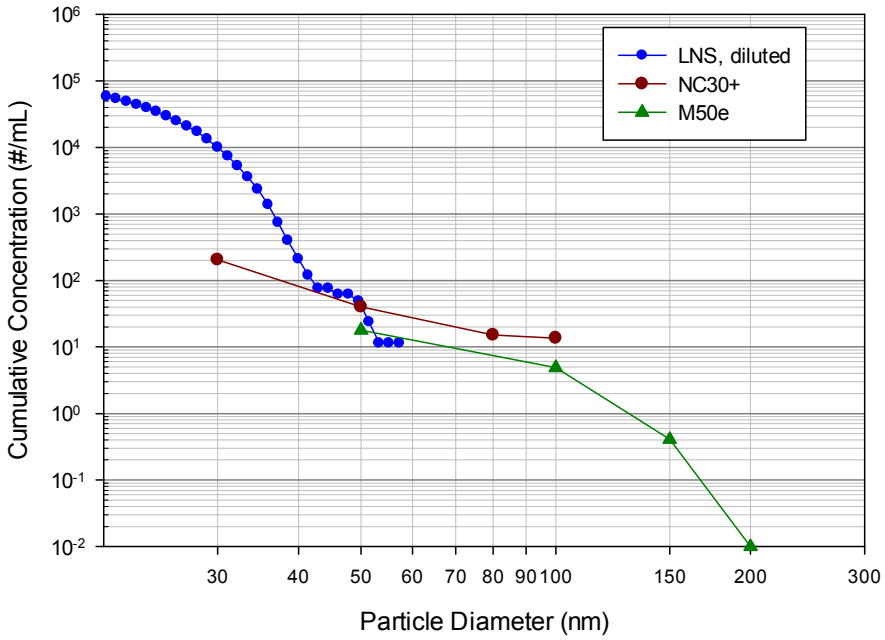
Both counters were factory calibrated less than one month prior to testing.

Test Details - Procedure

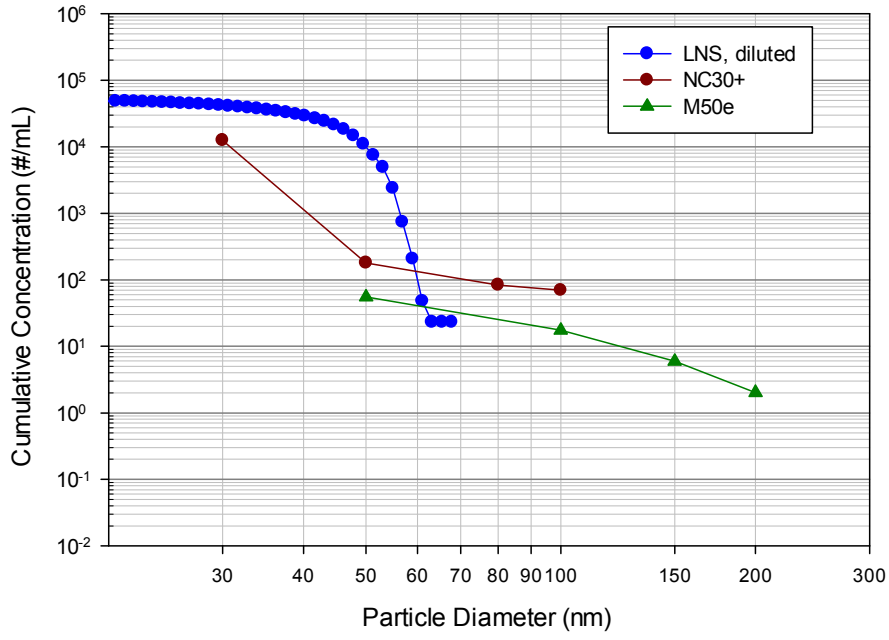
- Rinse system to background levels overnight.
- Adjust flow to specified rate for each instrument.
- Inject particle standards via FMT LiquiTrak Dilution System
  - "Monodispersed" PSL : 10,000 particles/mL
    (30, 40, 50, 60, 80, 100 nm)
  - Polydispersed PSL: 80,000 particles/mL ≥ 30 nm with a target PSD slope (log/log) of -3 (20- 125 nm and 20 – 300 nm)
- Measure particle concentrations for at least 10 minutes or until a steady measurement is achieved.
- Stop injecting particle standard and purge injection line.
- Wait until system background recovers and start next measurement.

Monodispersed PSL results

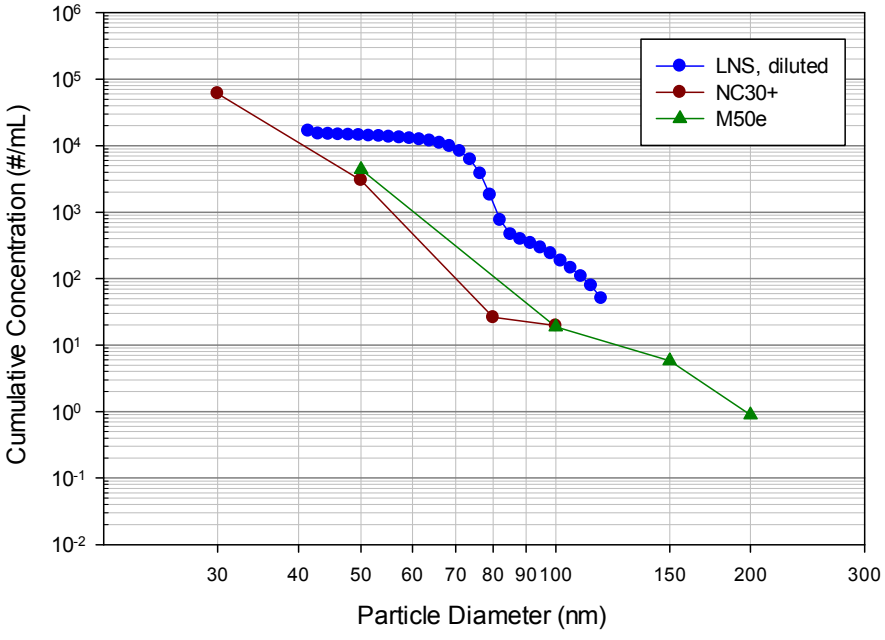
30 nm PSL 1E4/mL



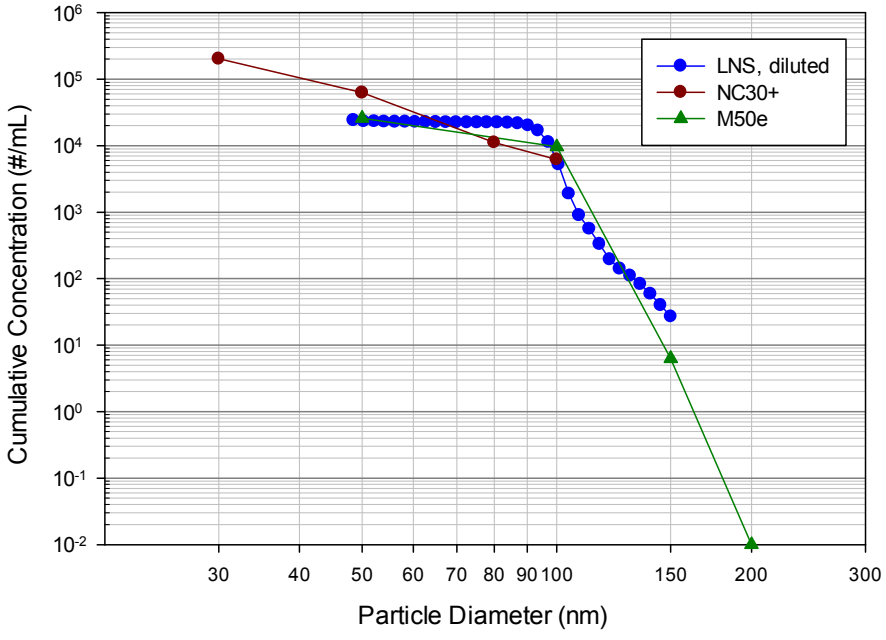
50 nm PSL 1E4/mL



70 nm PSL 1E4/mL



100 nm PSL 1E4/mL



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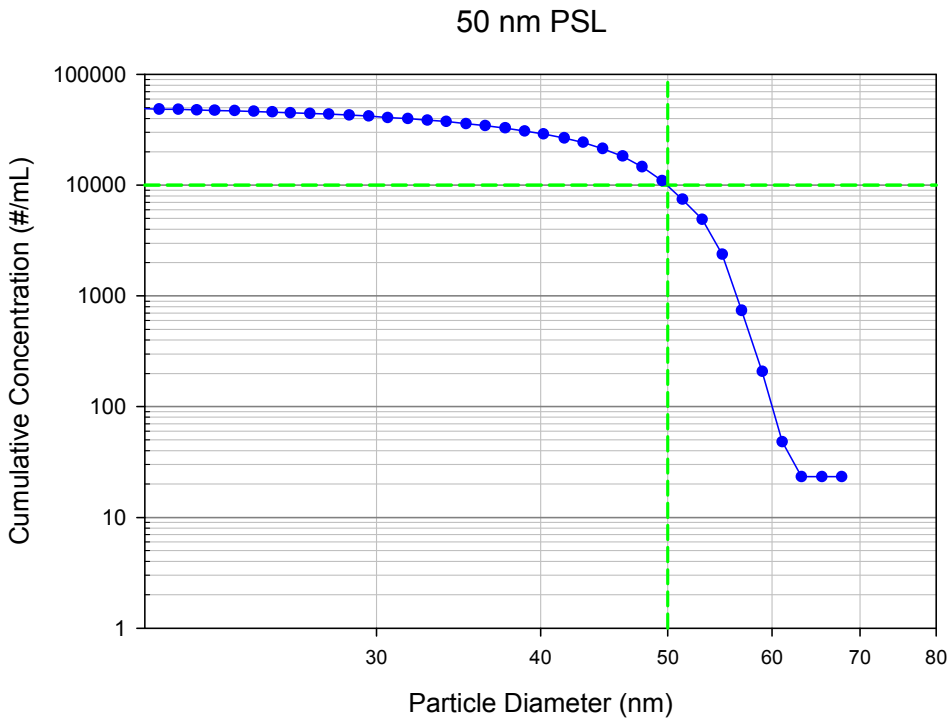
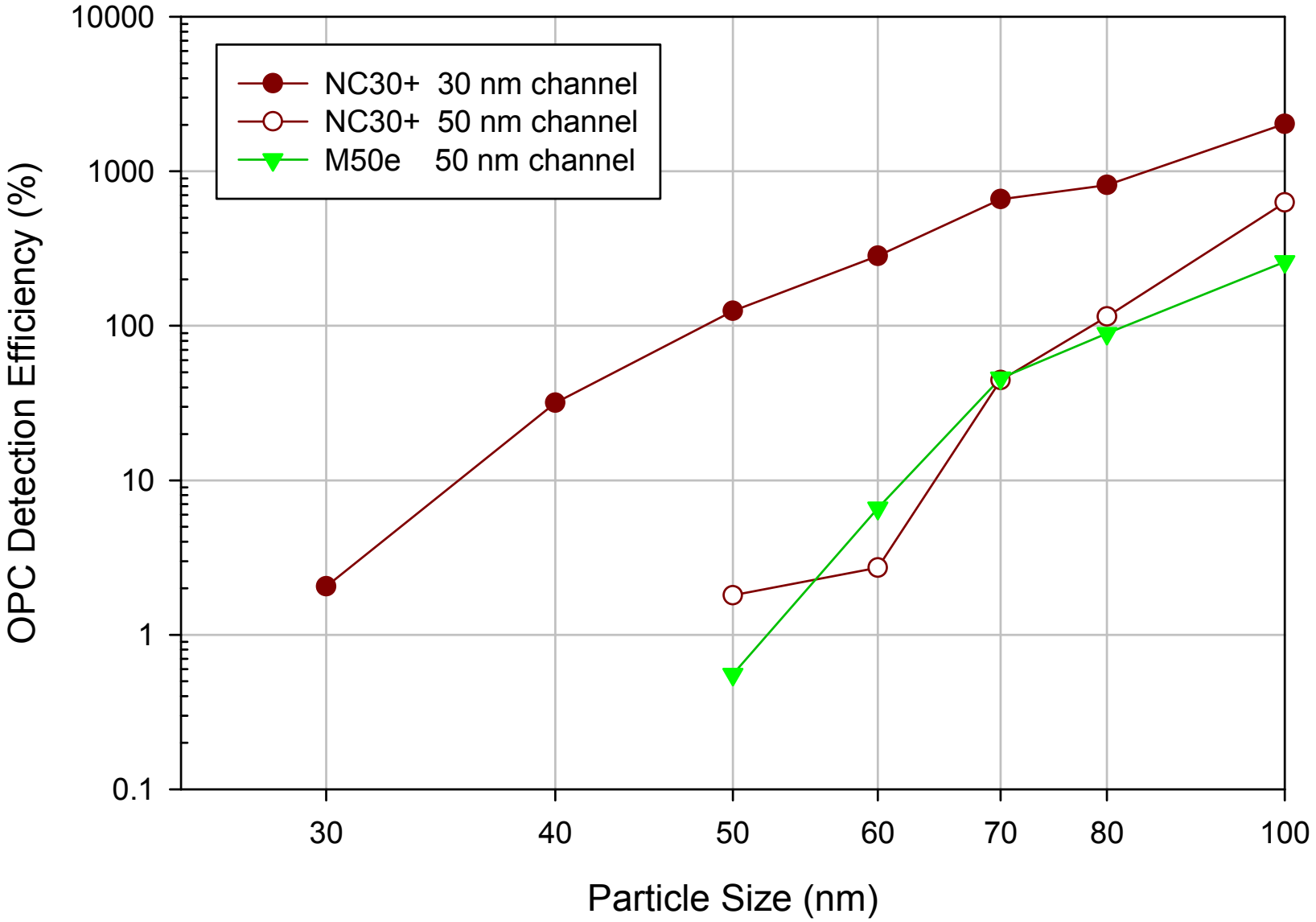
Counting Efficiency Calculations

- Using the LNS generated data, determine the cumulative particle concentration ≥ the nominal PSL particle size in the concentrate.
- Divide by the appropriate dilution ratio to calculate the concentration at the OPC.
- Counting efficiency @ nominal size =

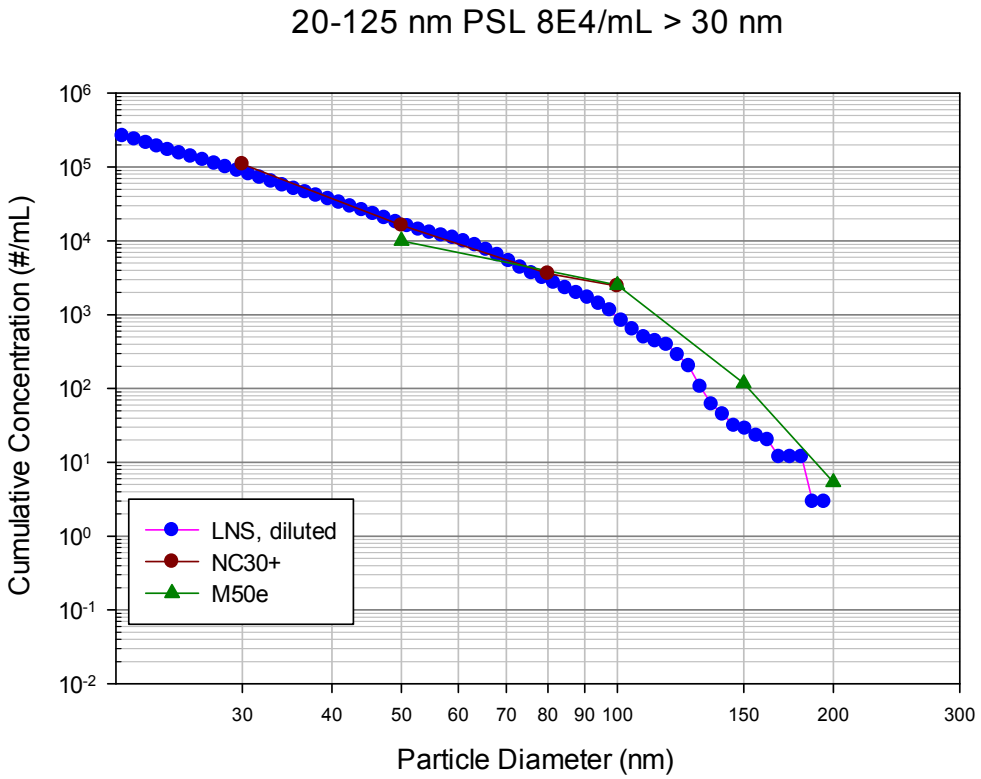
$$\frac{\text{Cumulative concentration measured by the OPC}}{\text{Cumulative concentration measure by the LNS}}$$

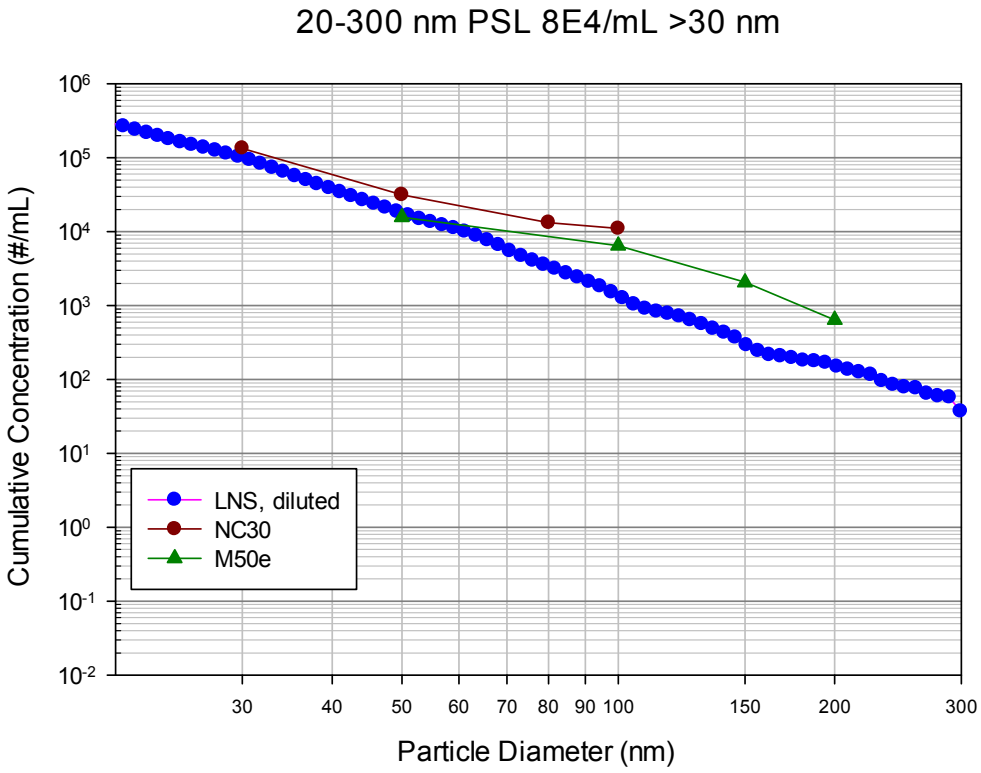


Counting Efficiency



Polydispersed PSL Results





- *Both the Lighthouse NC30+ and PMS M50e correlated well to the polydispersed PSL challenge particularly with the 20 – 125 nm challenge.*
- *Over counting was observed with both counters using the 20 -300 nm challenge.*

Summary

- The PSL particle size distributions (PSDs) of the polystyrene latex (PSL) specified in SEMI C77-0912 were not mono-dispersed or normally distributed at sizes smaller than 100 nm.*
- A true monodispersed PSL or alternate monodispersed nanoparticle is need to effectively utilize the specification as written.
- Measuring the PSDs (size and concentration) of the polydispersed PSL is necessary to accurately interpret the sizing results.
- Refinements to SEMI C77-0912 are needed to address the issues associated with variability in PSL PSD.

** Only Thermo Scientific Nanosphere™ PSL has been measured using the LNS at the time of preparing this paper.*

Acknowledgements

- Chris Howe (CTA) – Particle measuring and data analysis
- Don Grant (CTA) – Data analysis and interpretation
- David Blackford (FMT) – LiquiTrak Dilution system
- Michael Thomas (LWS) – NC30+ instrument startup and support
- WL Gore – Equipment Support (PMS M50e)

Thanks for your attention!