Measuring the Particle Retention of Liquid Filters below 100 nanometers

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Introduction

- Industrial requirements have driven the particle retention capabilities of liquid microfiltration and ultrafiltration processes to near or below 10 nanometers.
- International Technology Roadmap for Semiconductors (ITRS) has defined a critical particle size of 20 nm for 2013, and projects that in 2019, the critical particle size will be 10 nm.
- Optical particle counters traditionally used for measuring retention of ultrahigh-purity water (UPW) and chemical filters are beginning to reach their lower limits, and are currently not able to measure below 30-40 nanometers.
- Selection of an appropriate test particle (such as polystyrene latex (PSL), gold, and silica) is challenging due to size variability, and the possible interaction between the test particles used for the challenge and the filter media.
- This presentation will review and discuss a number of test methods being used or considered for measuring the removal of particles less than 100 nm.

Outline

- Available test methods
  - Strengths and limitations
  - Particles used
  - Instrumentation
  - Test examples and sampling of test data (as available)
- Summary

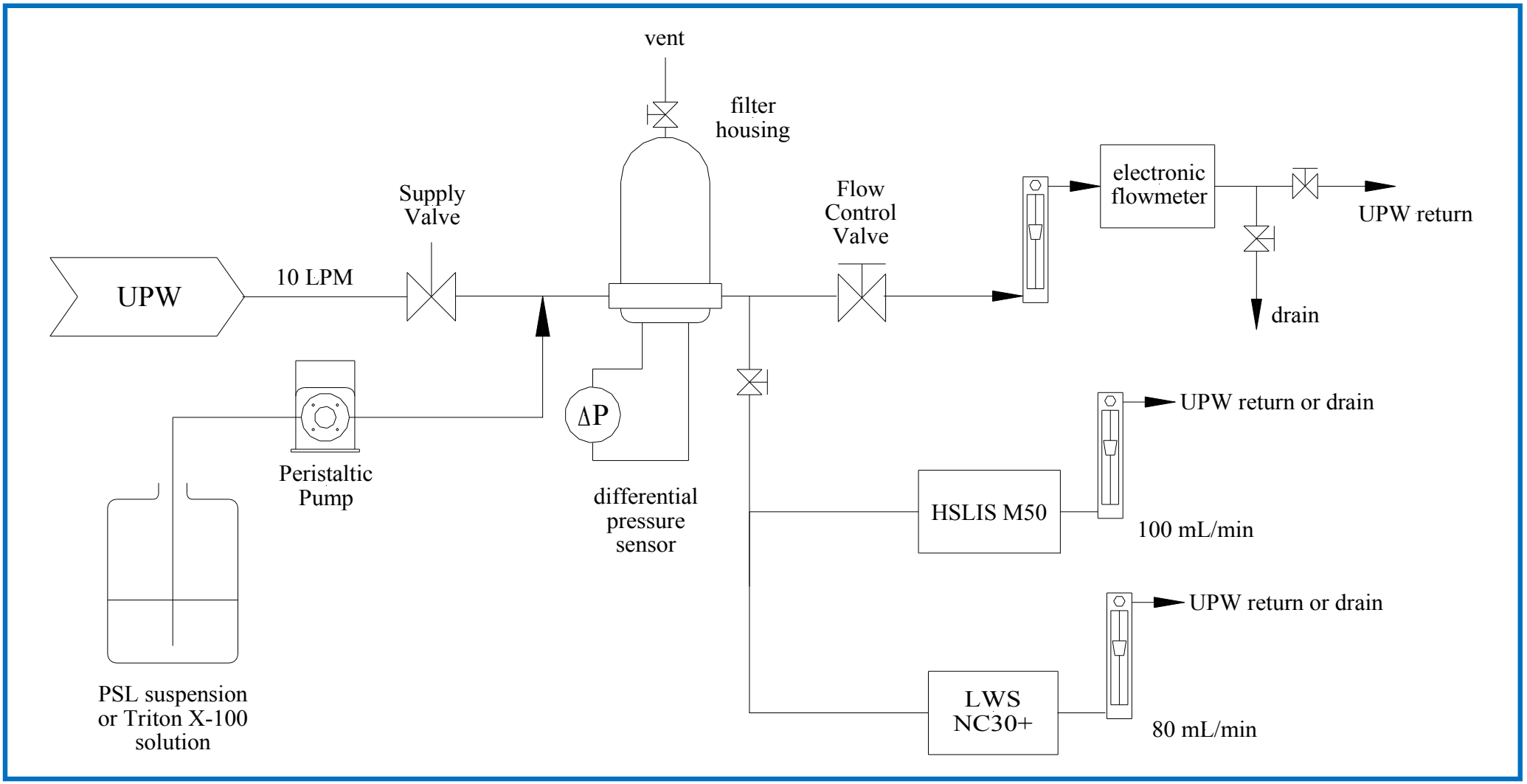
Test Methods

Method 1. SEMATECH Provisional Filter Test*

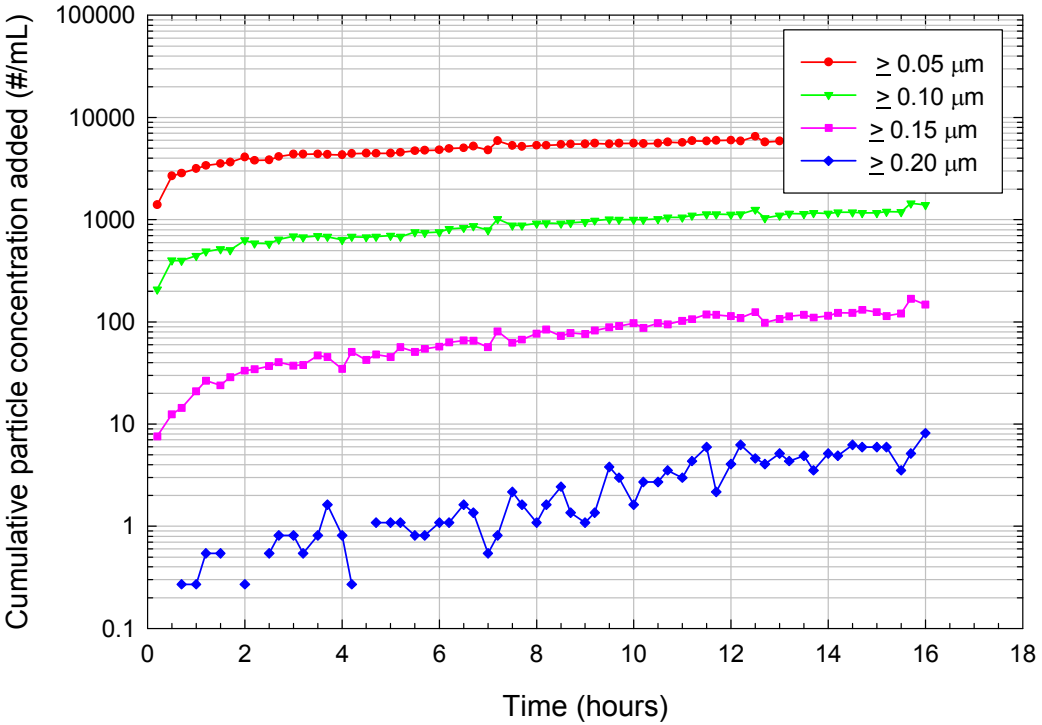
- Generally used for testing a 10-inch cartridge filter.
- Test flow rate of 10 liters per minute.
- Challenge solution:
  - Polydispersed polystyrene latex bead solution (11 bead sizes ranging from 0.055 to 0.502 μm)
  - Slope of concentration vs. size = -3 (log/log)
  - ~ 45,000 particles/mL ≥ 0.05 μm
- Test duration – 16 hours (concentration and duration simulate one year of typical filter loading).
- Measurement instrument is an OPC with a minimum channel size of 0.05 μm.

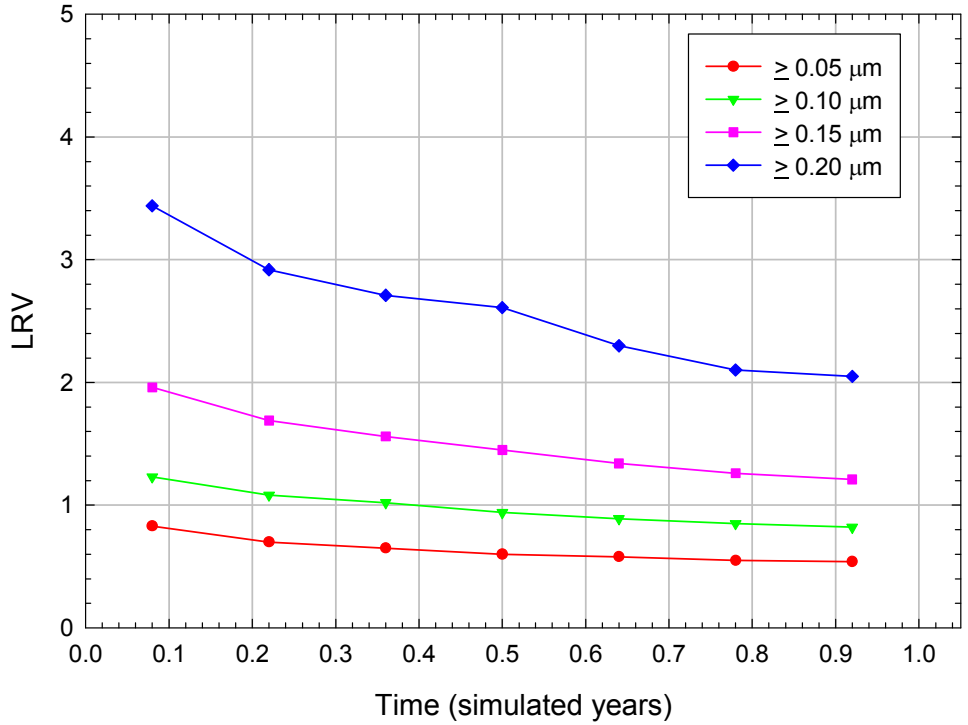
* Test Method for Determining Particle Contribution and Retention by UPW Distribution System Components (1992). Technology Transfer Number 92010949B-STD.

Method #1 Schematic



Method #1 Sample Data





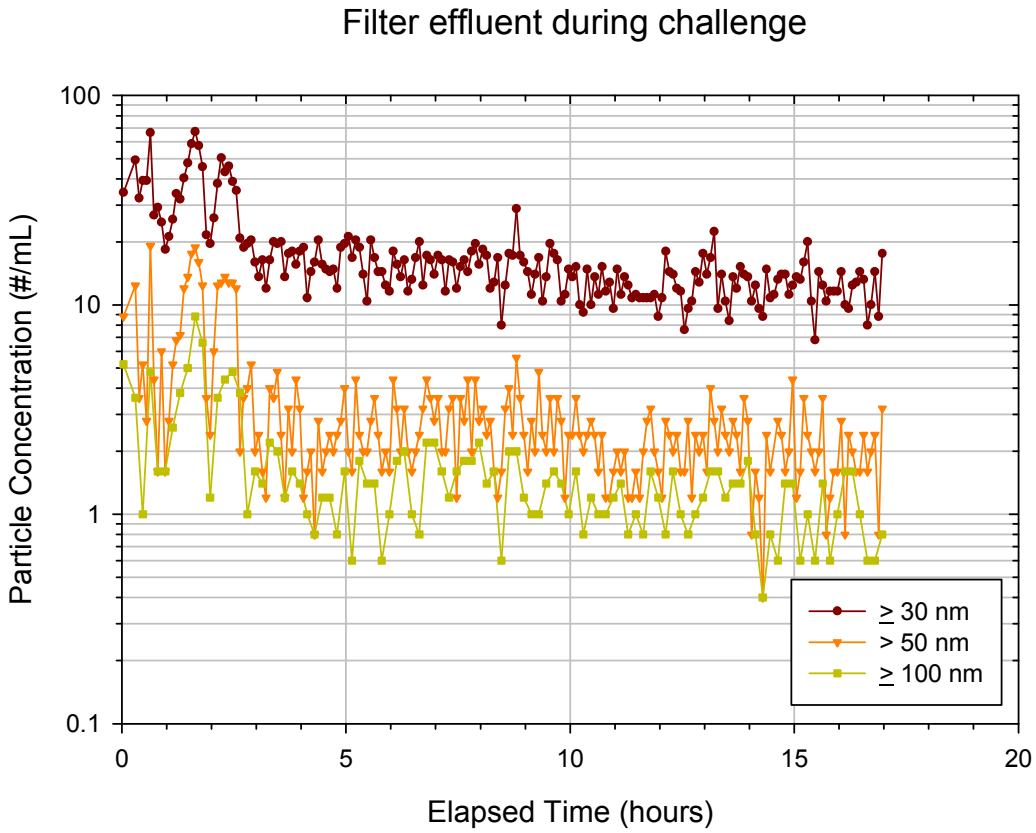
Method #1 Benefits and Limitations

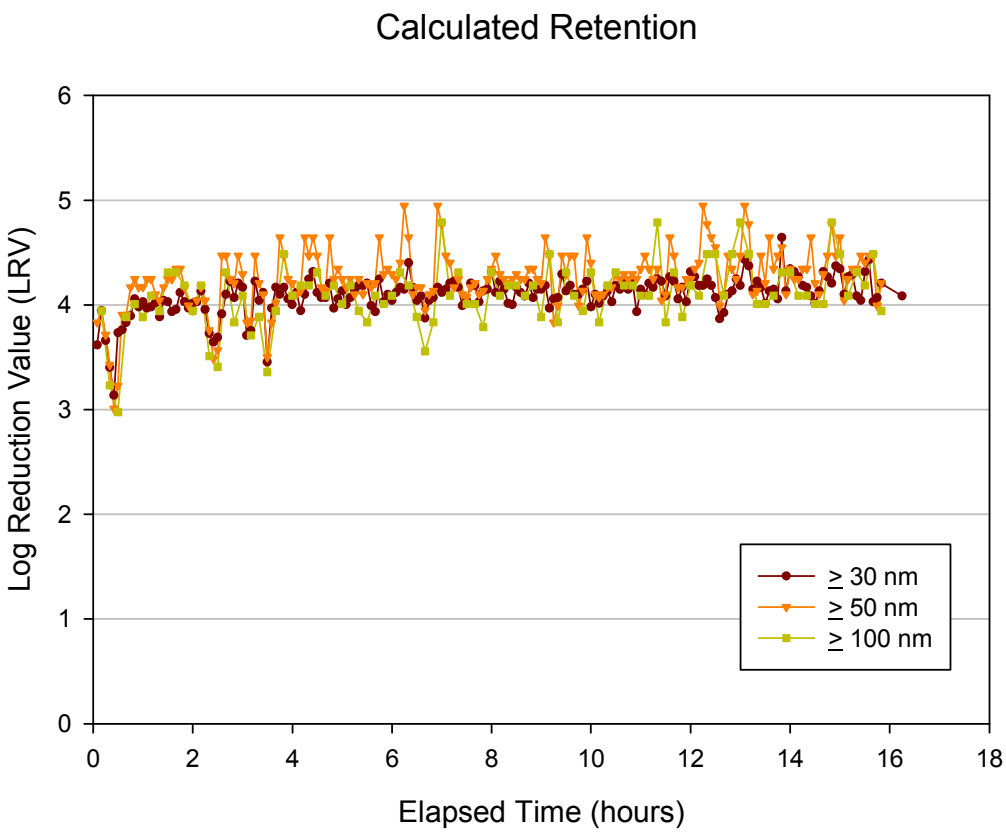
- Benefits:
  - Particle challenge mimics a “real-world” particle size distribution.
  - Large historical database.
  - Data available for retention as a function of size
- Limitations:
  - PSL is not a real-world particle found in water or chemical delivery systems.
  - Potential interaction between PSL and membrane surface.
  - Requires the use of optical particle counters (size limitation).

Method #1 Potential Improvements

- Improved OPC's
  - PMS UltraChem 40
  - Lighthouse NC30+ and NC25+
  - Rion KS-18FX
- Challenge solutions with smaller PSL
  - 30 nm to 150 nm
  - 30 nm to 200 nm
  - 30 nm to 300 nm
- Addition of ligand or surfactant to reduce interaction between PSL and membrane (such as Triton X-100)

Sample data from 30 – 300 nm PSL retention test





Particle Counter: Lighthouse NC30+
Filter: 20 nm rated hydrophobic

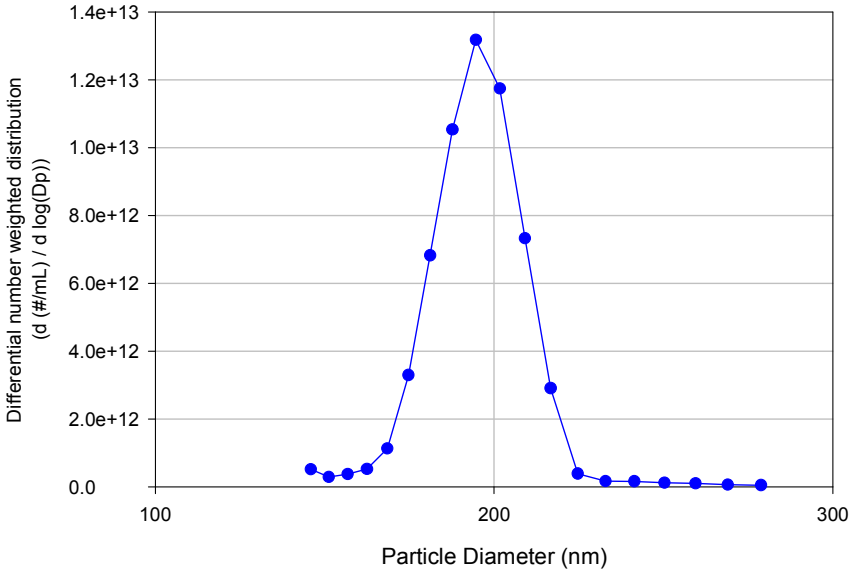
Method #2. SEMI F110-0712*

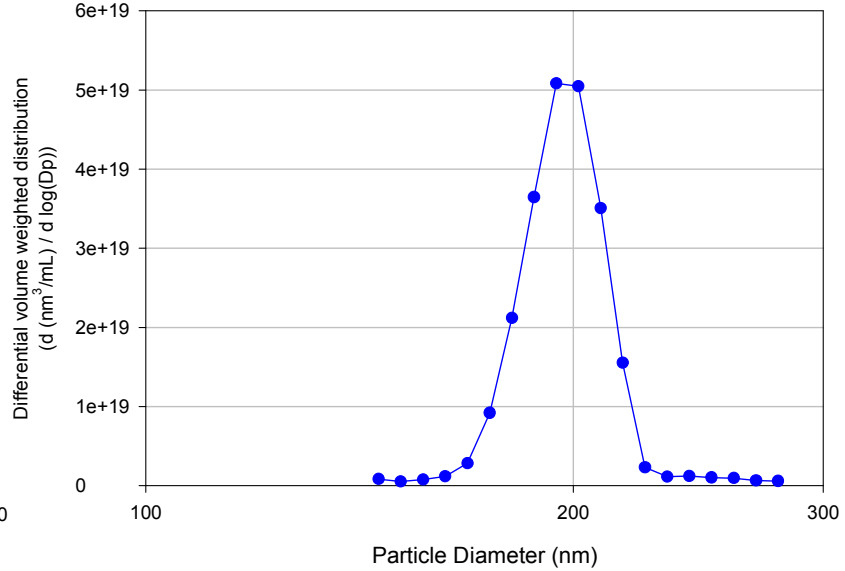
- Similar to test method #1 except:
  - Single size PSL is used.
  - Filter is pretreated with a surfactant prior to testing.
  - Challenge concentration target is 1,000,000 particles per mL.
  - Test is run for 2 hours.
- Benefits:
  - Relatively short test duration.
  - Useful as a screening test.
  - PSL test standards are readily available.
- Drawbacks:
  - Unrealistic filter loading that could effect retention.
  - Low retention filter could result in OPC coincidence (inaccurate measurements).
  - PSL uniformity deteriorates as the PLS size gets smaller. ▻

* SEMI F110-0712 Test Method for Mono-Dispersed Polystyrene Latex (PSL) Challenge of Liquid Filters

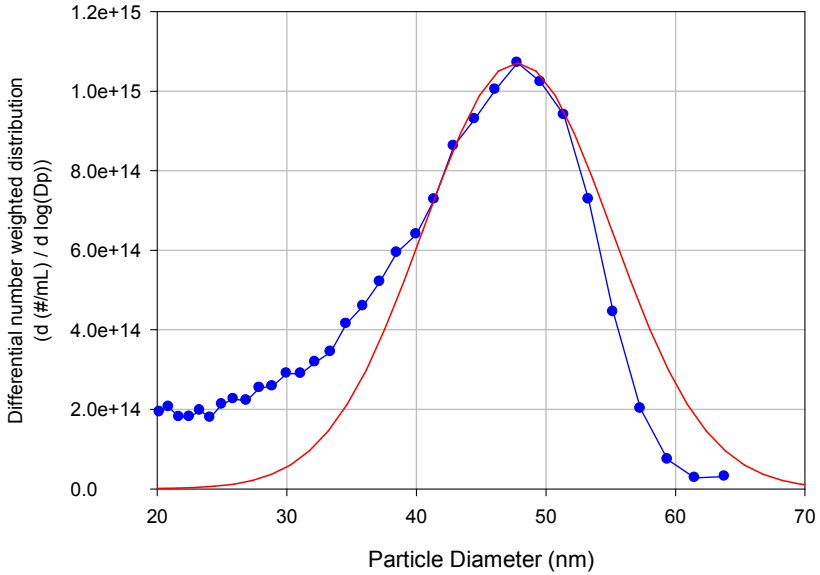
Particle size distribution of polystyrene latex

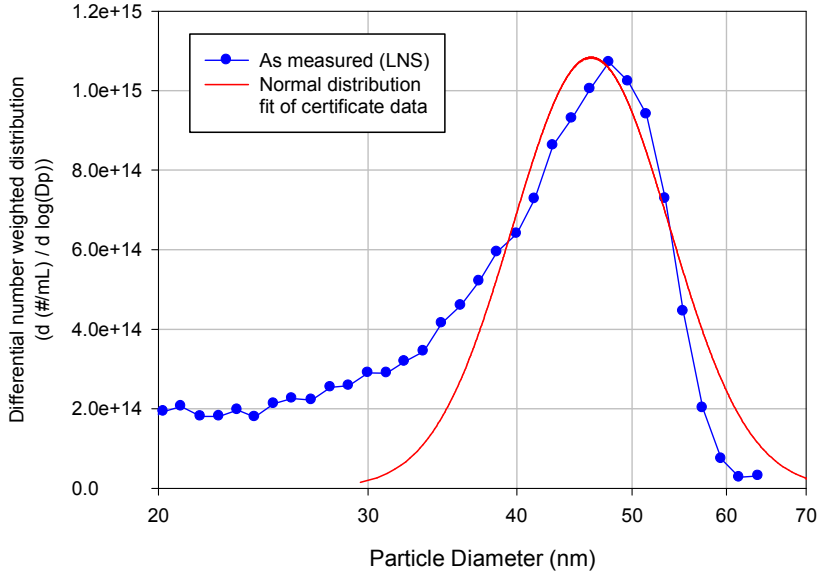
NIST Traceable 200 nm PSL
(203 ± 5 nm)





NIST Taceable 50 nm PSL
(Reported Size - 46±2nm)

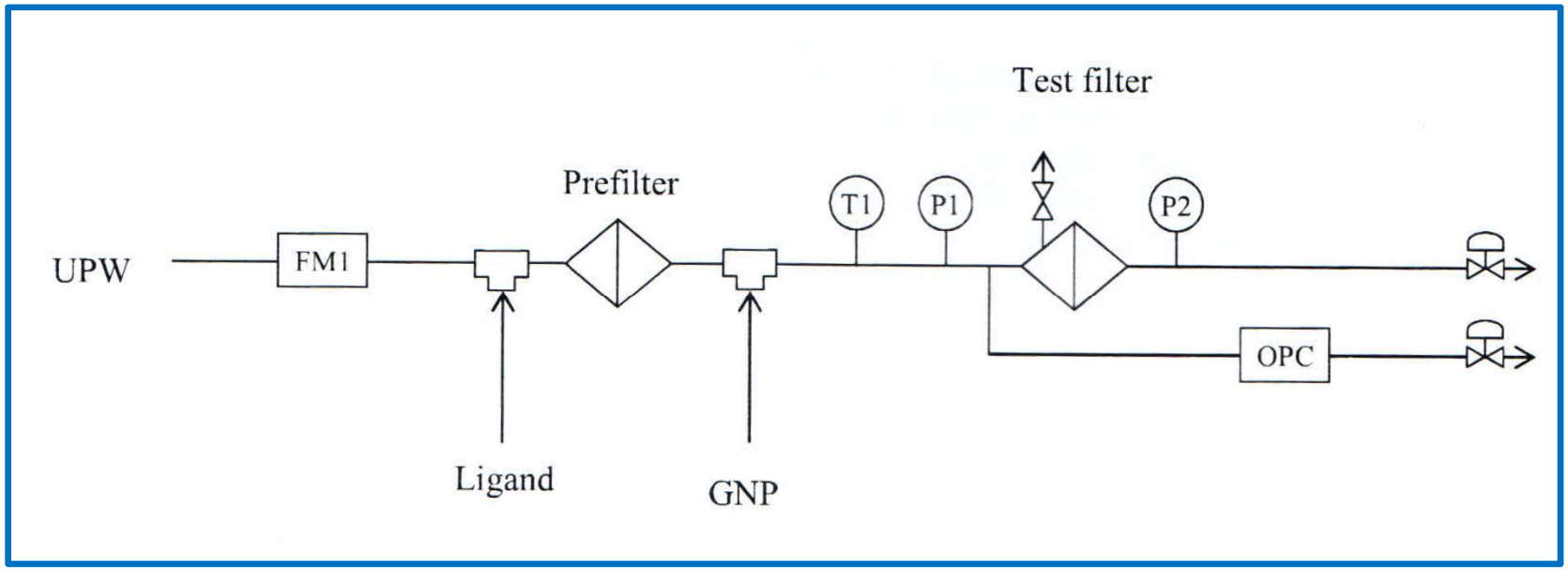




Method #3 – SEMI C82-0713[3]

- Similar method to SEMI F110 except gold nanoparticles (GNP) are used instead of PSL.
  - Applicable for filters rated from 20 to 50 nm.
  - A ligand is used during the test to treat the filter and GNPs.
  - Particle concentration at the filter is specified to be from 1E+06 to 1E+08 per mL.
  - Test runs for one hour.

Test Schematic

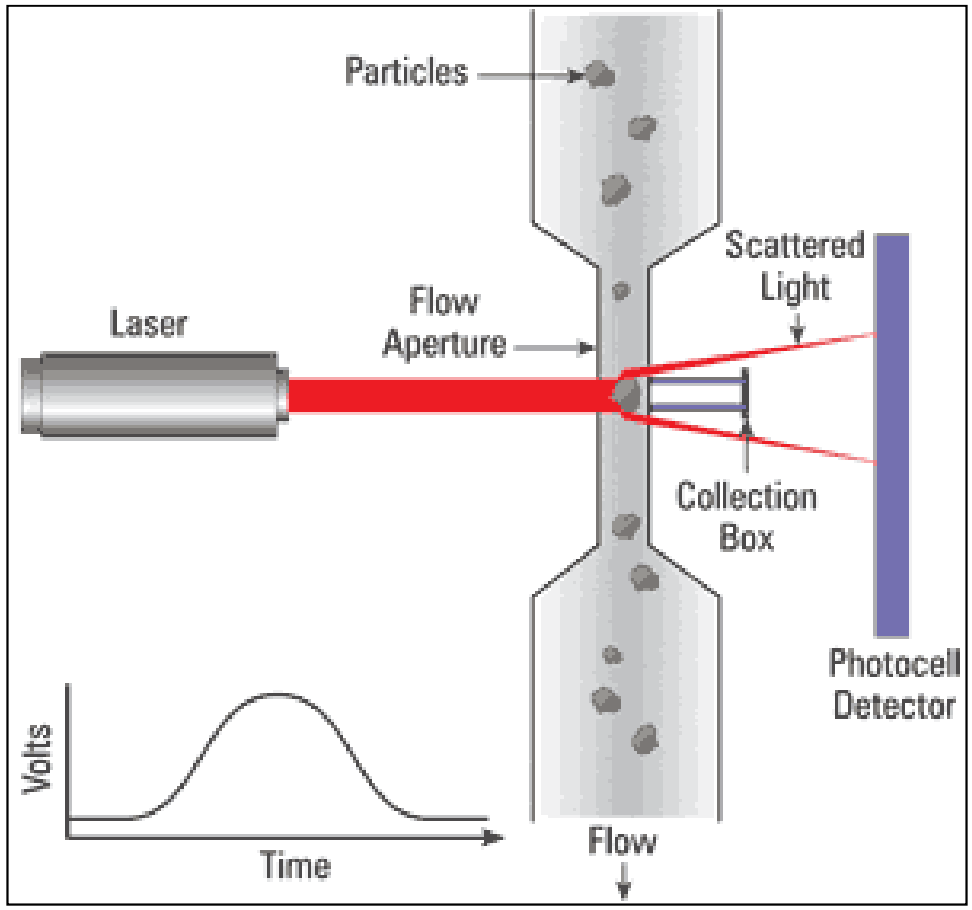


3. SEMI C82-0713. Test Method for Particle Removal Performance of Liquid Filter Rated 20 – 50 nm with Liquid-Borne Particle Counter

Method #3 Benefits and Drawbacks

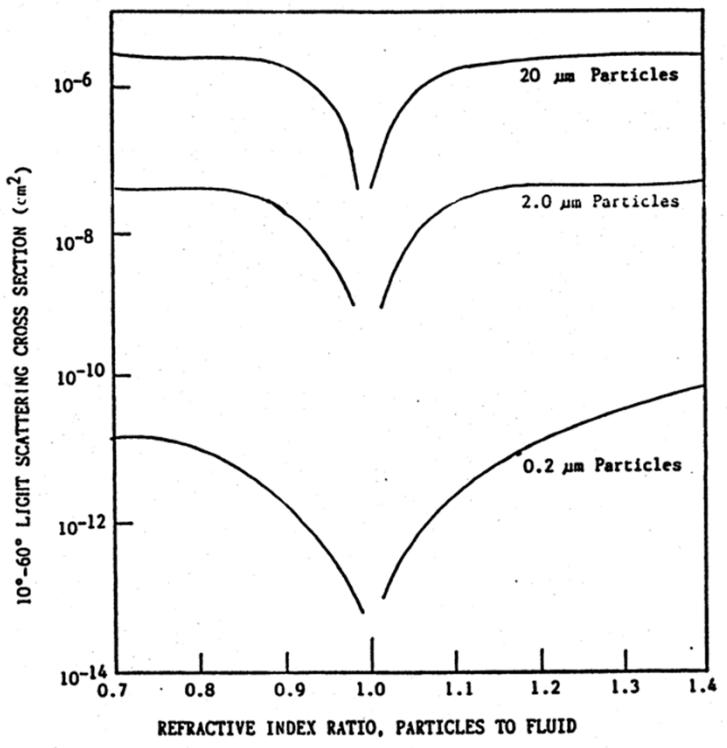
- Benefits:
  - Takes advantage of the optical properties of gold nanoparticles to allow detection of the particles using currently available OPC's. ⊳
  - Uses particles that can be NIST traceable.
  - Particle size distribution of gold nanoparticles is well defined.
  - Short test duration
- Drawbacks:
  - Gold is not a real-world particle found in UPW or chemical delivery systems.
  - Gold typically interacts with the membrane surface and requires the use of a ligand to minimize this interaction.
  - Selection and concentration of the ligand is not specified and is left up to the discretion of the user.
  - Gold nanoparticles are expensive, 10 – 20 times > than PSL.

Optical Particle Counter Operation



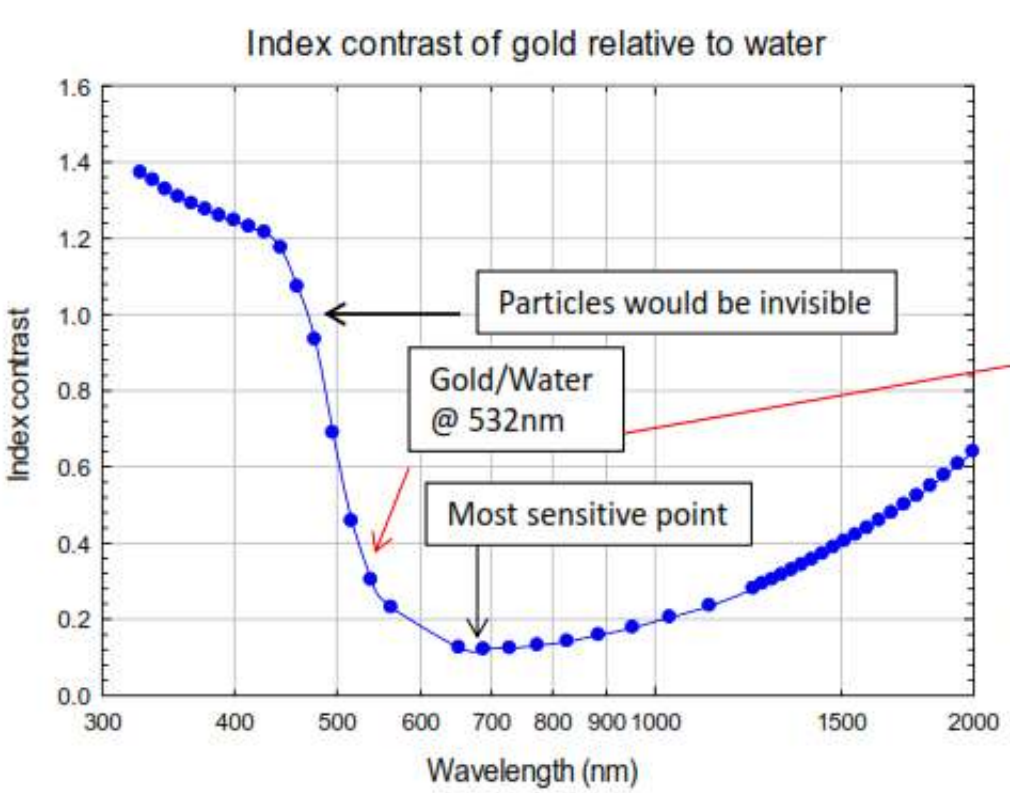
Courtesy of Noria Communications

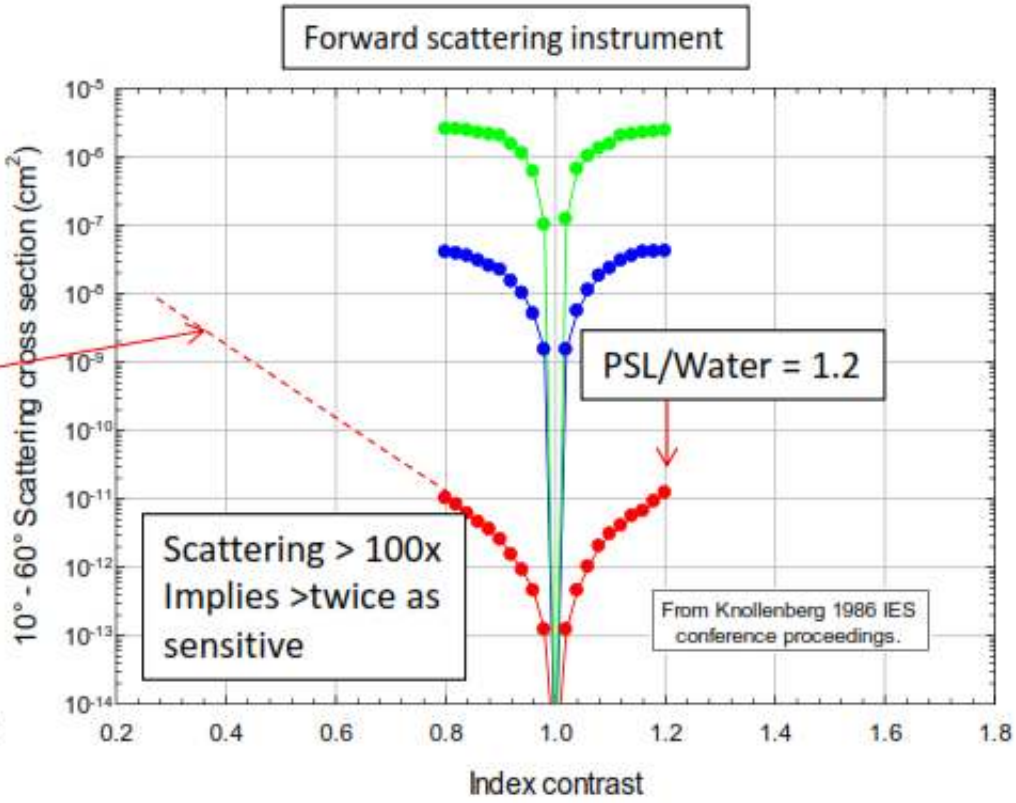
$$\text{Index contrast} = \frac{\text{Particle refractive index}}{\text{Medium refractive index}}$$



Courtesy of R. Knollenberg, Particle Measuring Systems

Gold's effect on particle sizing using a light scattering OPC





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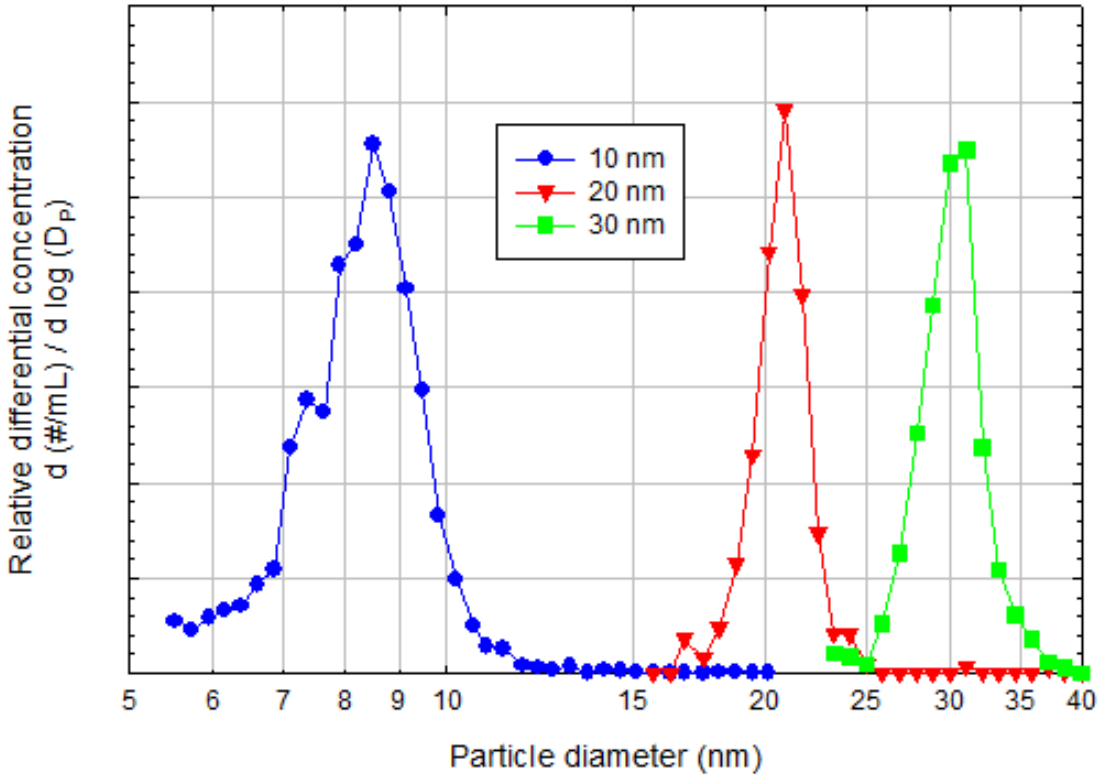
Size distributions of gold nanoparticles



Nominal Size (nm)	Claimed size (TEM)		Measured size (LNS)	
	Mean (nm)	CV (%)	Mean (nm)	CV (%)
10	9.3	< 15	8.4	13.0
20	20.3	< 8	20.8	7.4
30	30.3	< 8	30.5	7.3

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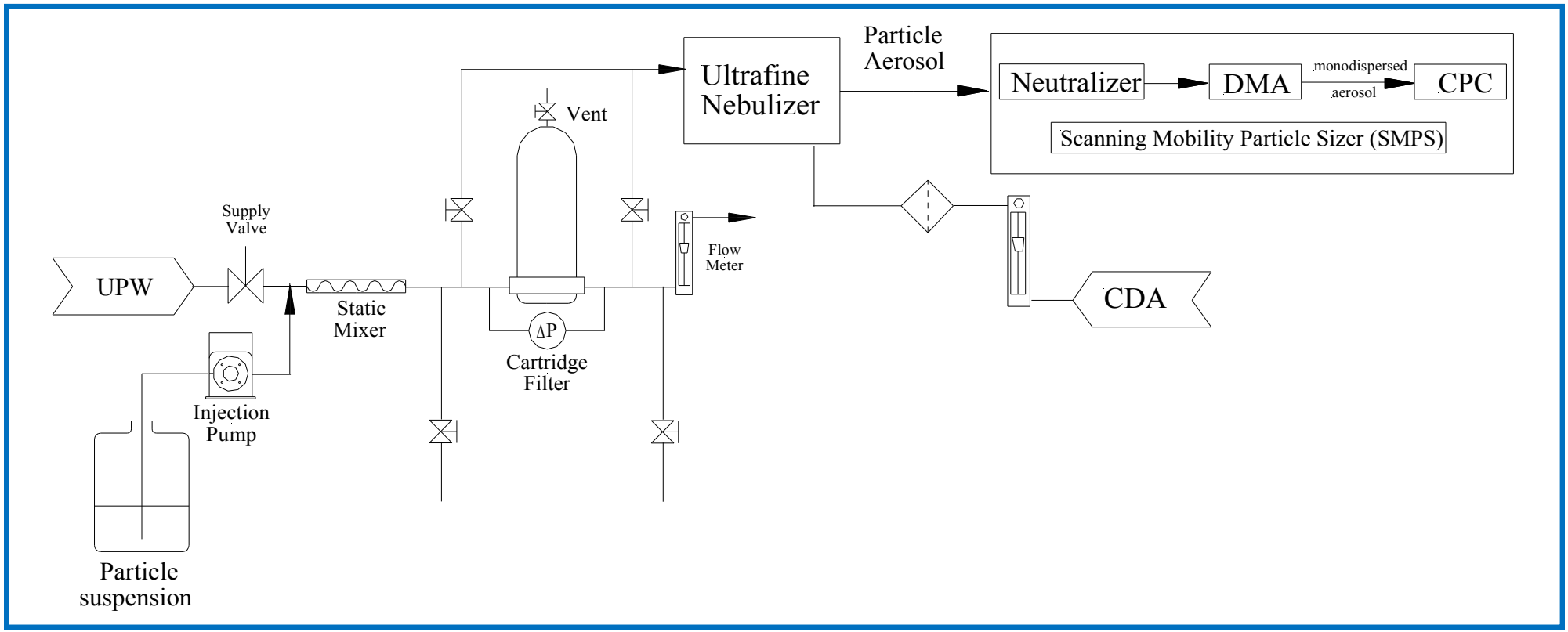
Method #4. SEMI C79-0113*

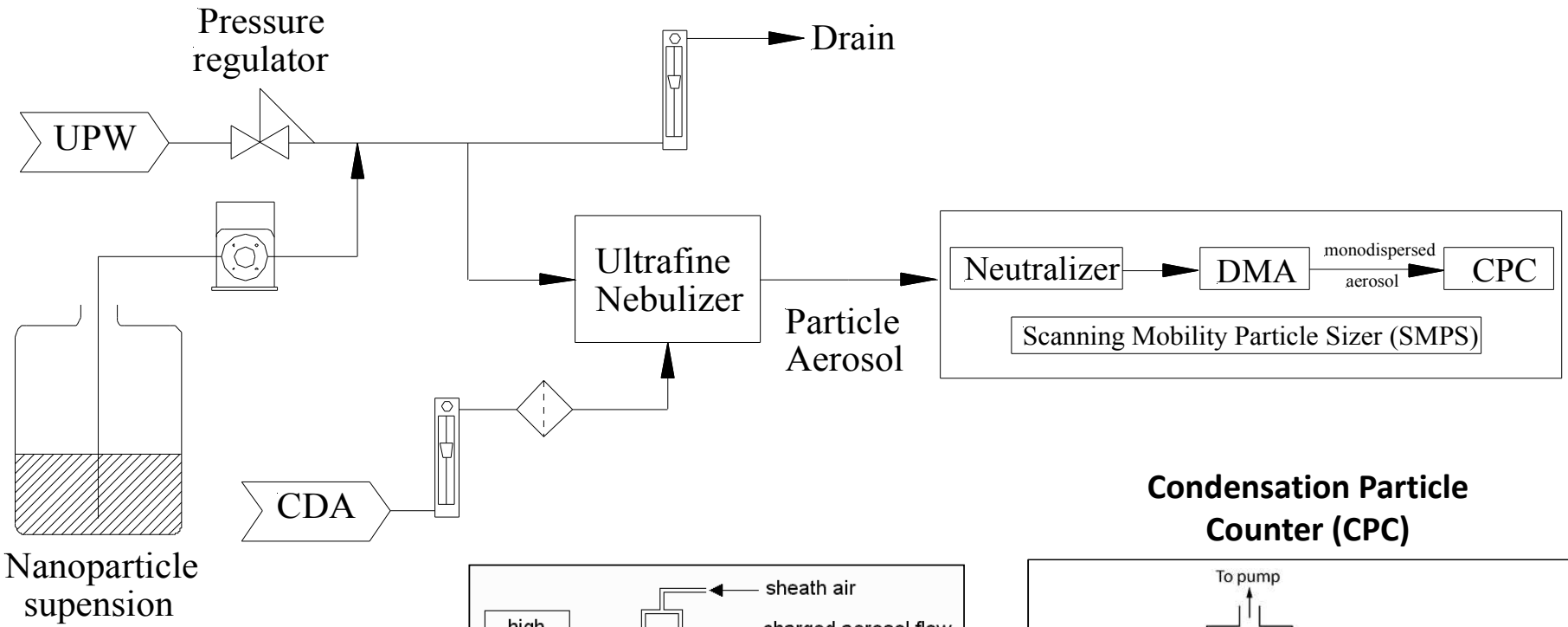
- Generally used for testing cartridge filters but is also applicable to UF modules.
- Flow rate is established as a function of filter surface area (face velocity of 0.8 cm/min.)
- The challenge solution is a colloidal silica with an mean particle size between 5 and 15 nanometers.
- Suggested colloidal concentration is 5E+09 particles per mL.
- Test is run until the filter is challenged to a minimum of one monolayer equivalent (typically 4 - 6 hours).
- Grab samples are taken for off-line concentration analysis via inductively-coupled plasma mass spectrometry (ICP/MS).
- Continuous measuring of particles by nebulization and dynamic mobility analysis (LNS).

- SEMI C79-0113 - Guide to Evaluate the Efficacy of Sub-15 nm Filters Used in Ultrapure Water (UPW) Distribution Systems

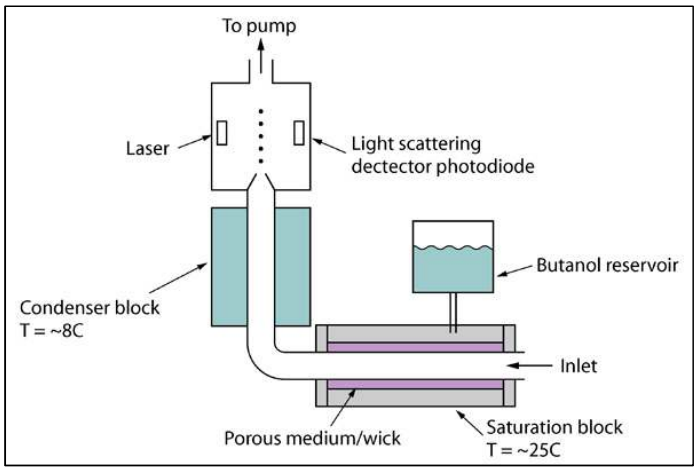
Method #4 Test Schematic



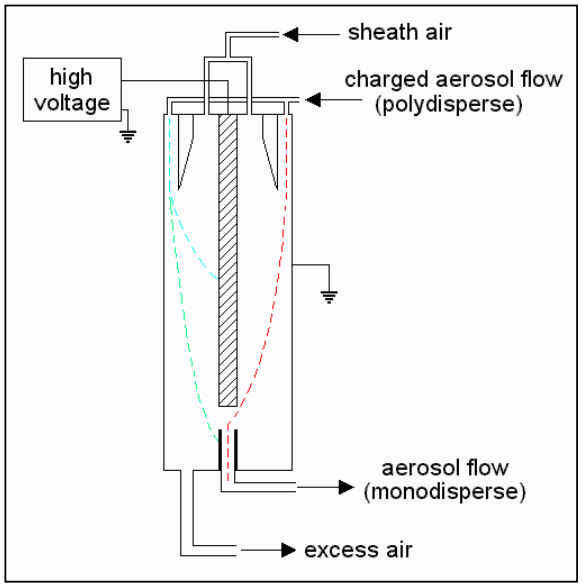
Schematic of the Liquid Nanoparticle Sizing (LNS) System



Condensation Particle Counter (CPC)



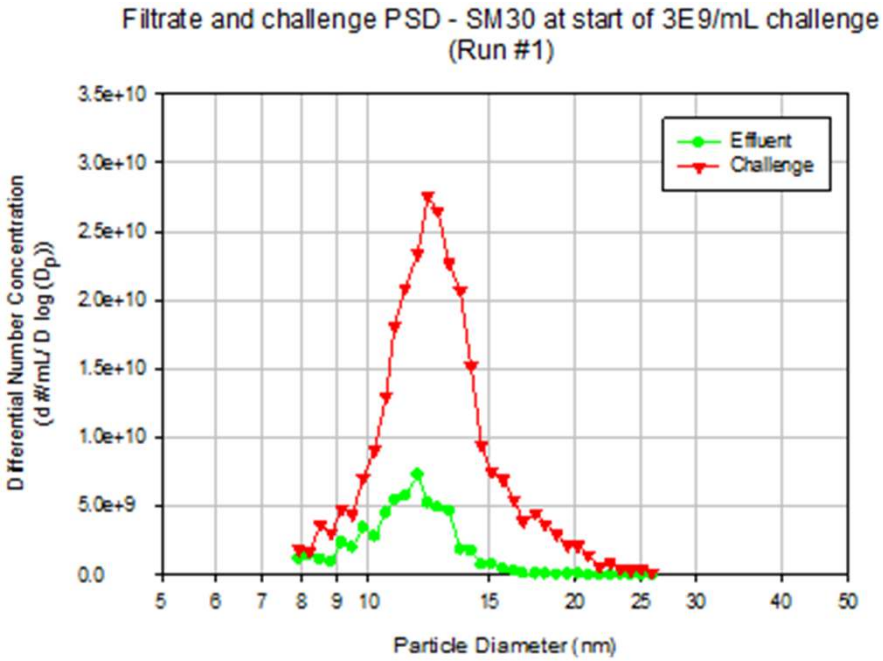
Dynamic Mobility Analyzer (DMA)

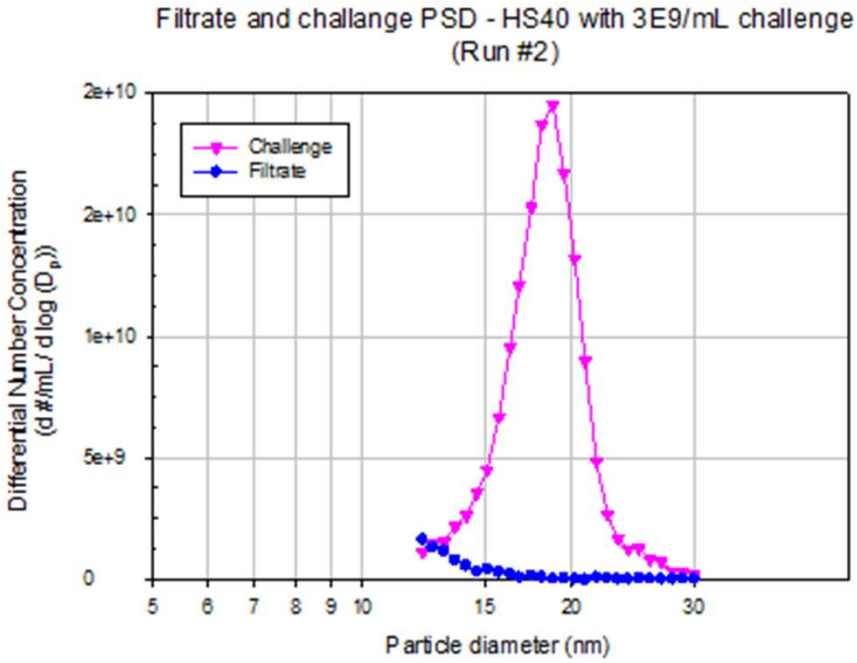


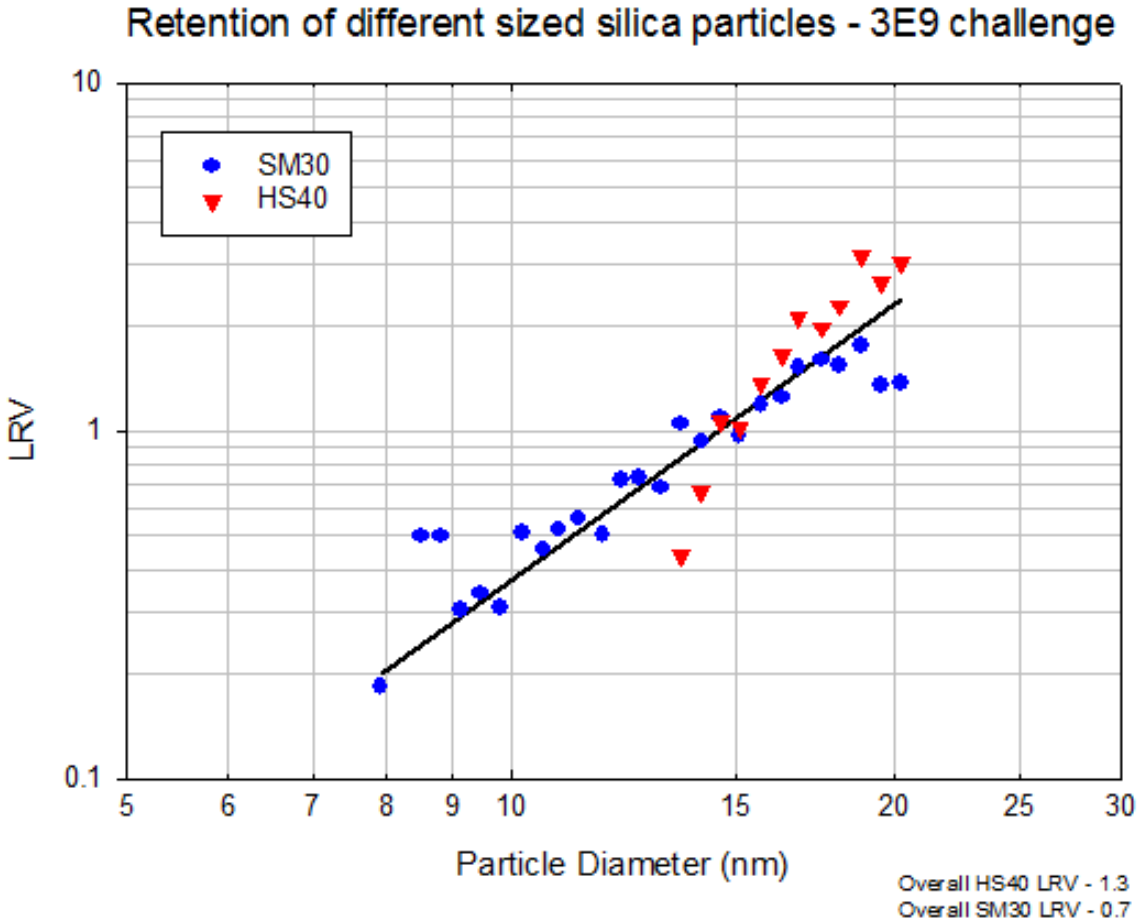
Method #4 Sample Data

- Two filters tested; same pore size rating and same manufacturer.
- One filter challenged with 12.6 nm mono-distributed silica particles, the other with 18.8 nm mono-distributed silica.
- Prior to the particle challenge, the filters were flushed with UPW to reduce particle shedding.
- 3×10^9/mL particle concentration was used.
- Particle concentrations measured upstream and downstream of the filter (scan mode).
- Filter particle retention was calculated as a function of particle size.

Filter retention as a function of particle diameter.





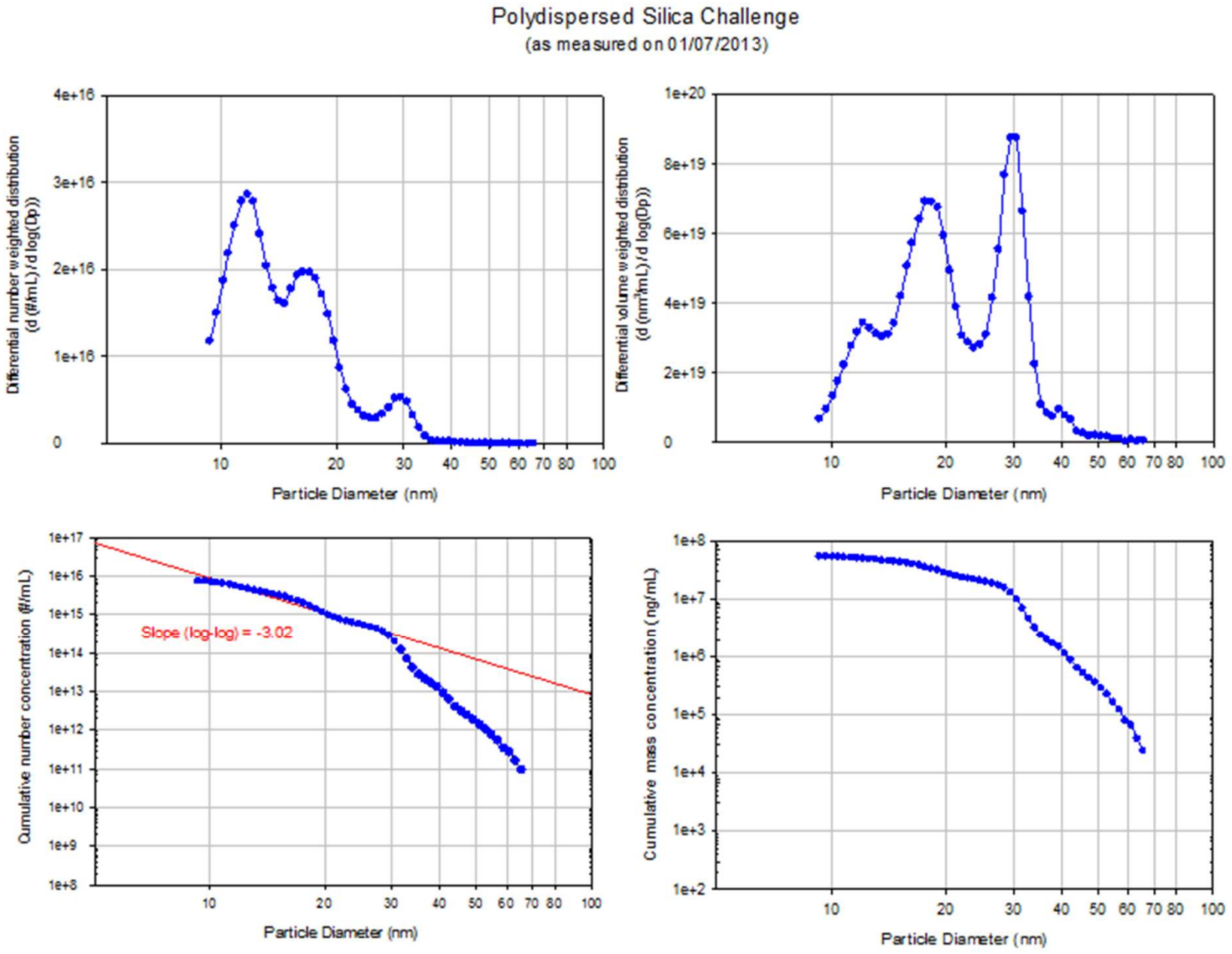


Test method work conducted in support of developing SEMI test guidelines for measuring retention of 5-15 nm filters used with UPW.

Method #4: Filter capture of poly-distributed colloidal silica particles

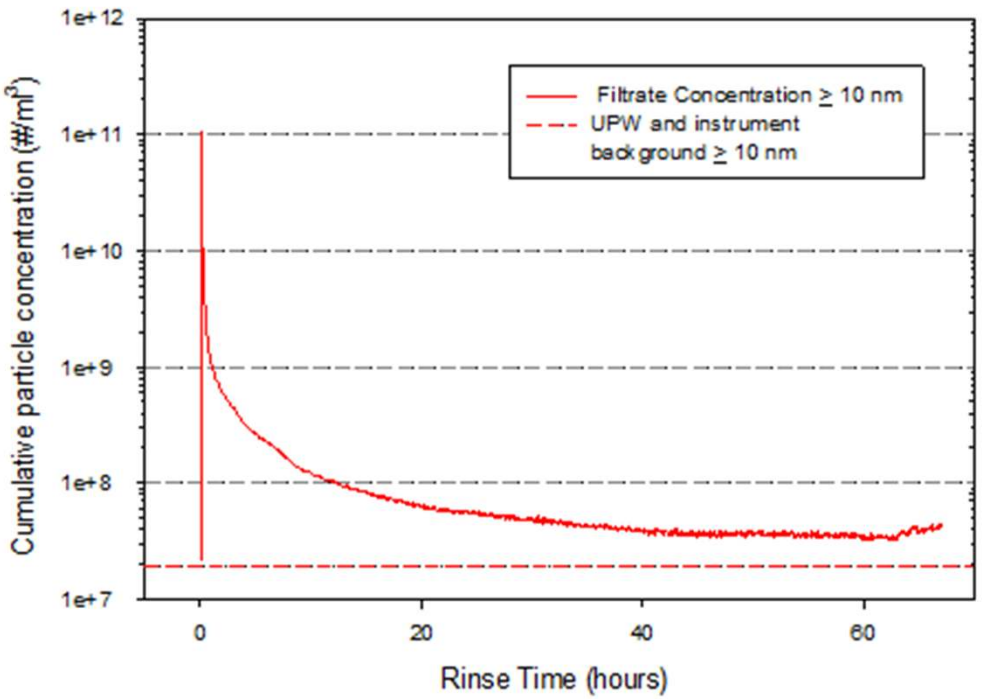
- Filter retention test using poly-distributed silica in UPW.
- Three silica size mixture: 12, 18, and 28 nm.
- Flush filter with UPW to reduce particle shedding. Measure particle concentration during rinse.
- $5x10^9$/mL ≥ 10 nm particle concentration was used.
- Measure particle concentrations upstream and downstream of the filter (scanning mode).
- Filter particle retention was calculated as a function of particle size and loading.

Silica challenge particle size distribution

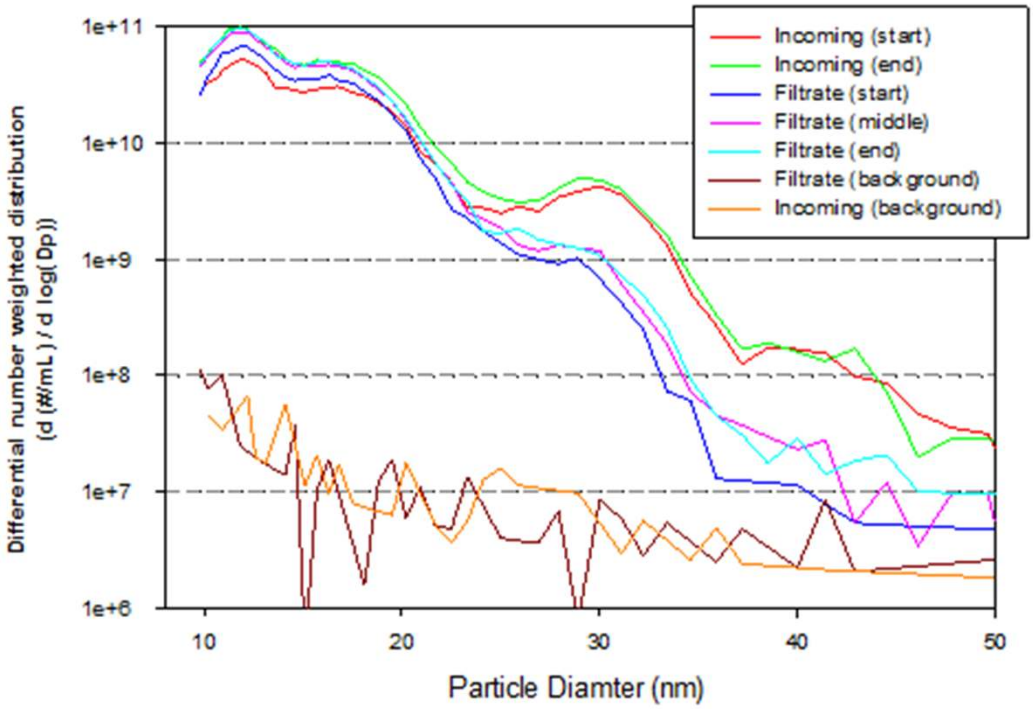


Method #4 Filter Test Results

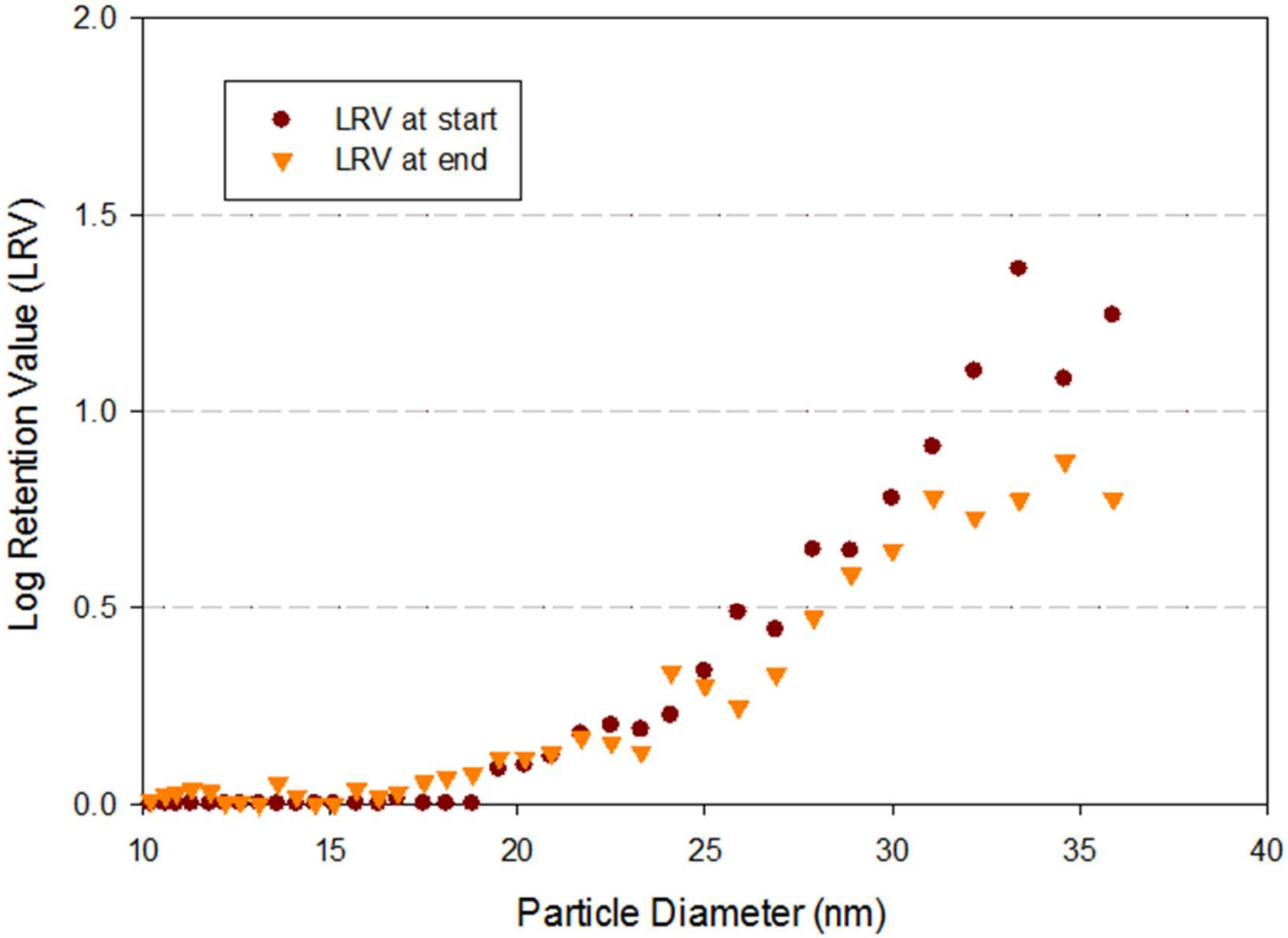
Filter rinse in UPW



Retention Data



Method #4 Filter Retention Analysis

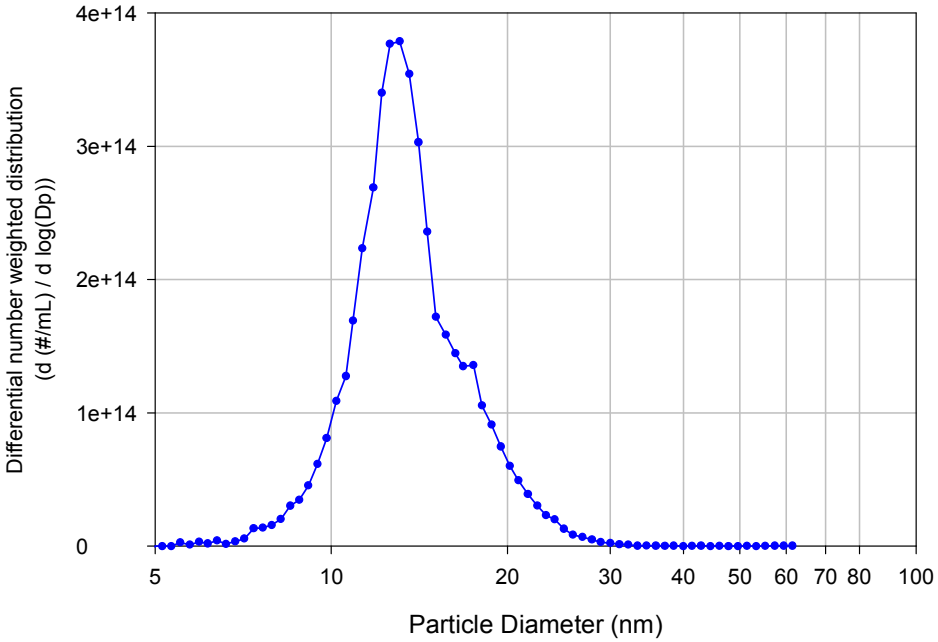


Method #4 Benefits and Drawbacks

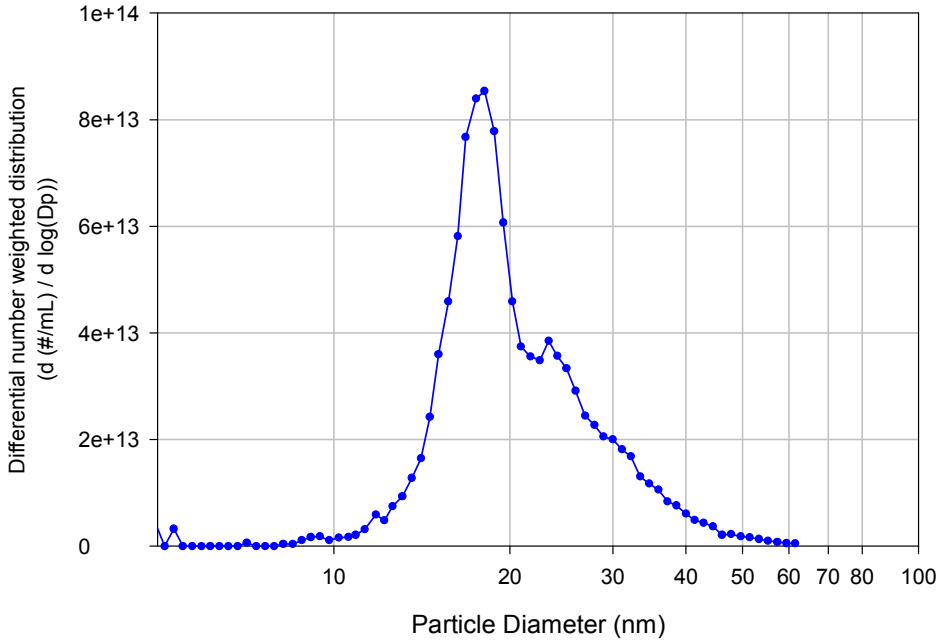
- Benefits:
  - Test particles (silica) are expected to be found in ultrapure water systems.
  - Test particles can be ERM traceable.
  - Silica nanoparticle PSD are more uniform than PSL at these sizes. ⊳
  - No ligand or surfactant addition are necessary.
  - Face velocities are consistent and reasonable for the expected applications.
  - Test particles are inexpensive.
- Drawbacks:
  - Test instrumentation (LNS) is not commercially available at this time.
  - Challenge concentrations are several orders of magnitude higher that would be expected in real applications (5E+09 vs. 1E+04 to 1E+05).
  - Test duration is long relative to Methods #2 and 3.

Size distributions of silica nanoparticles

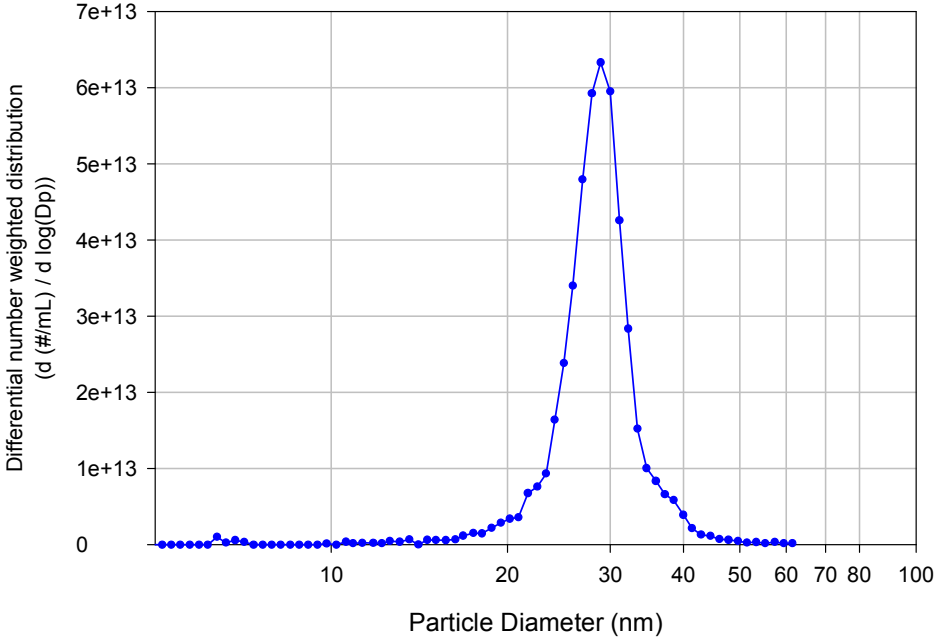
10 nm Silica



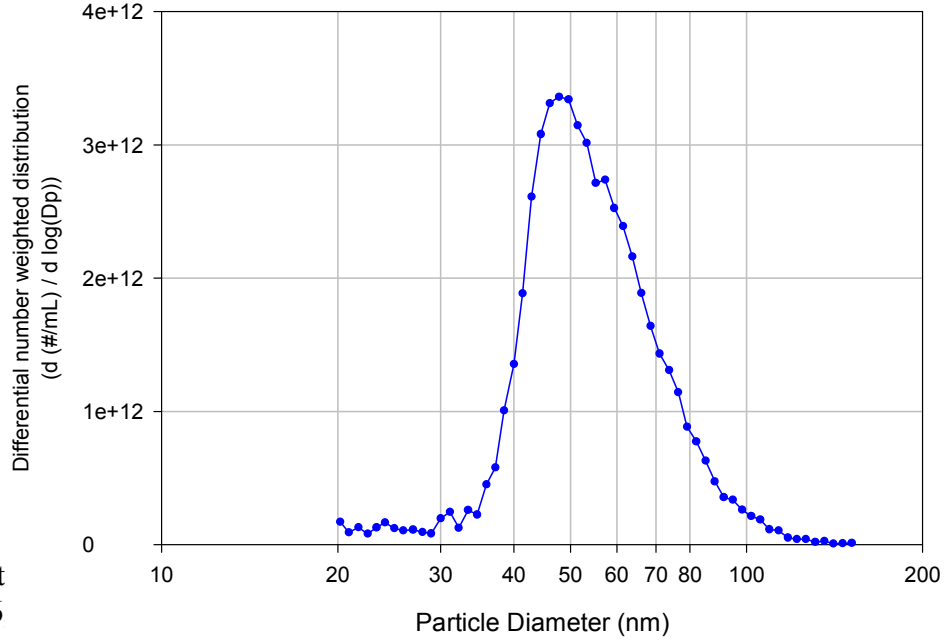
20 nm Silica



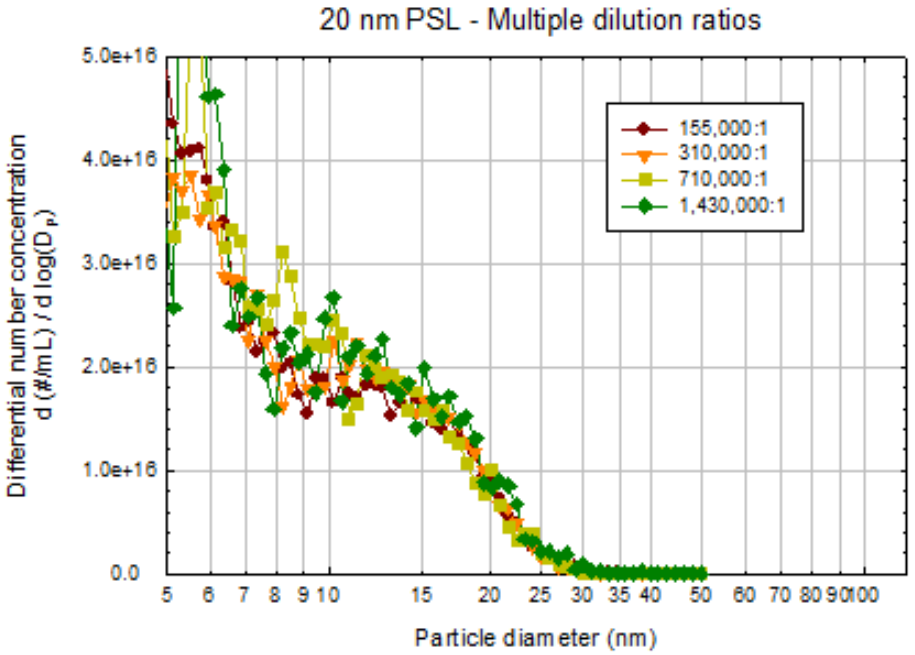
30 nm Silica

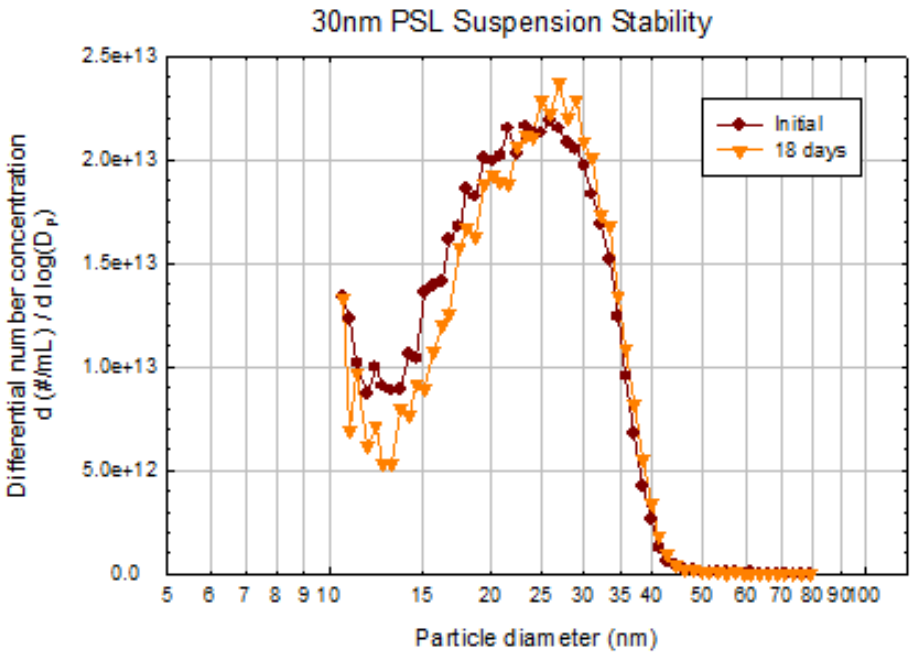


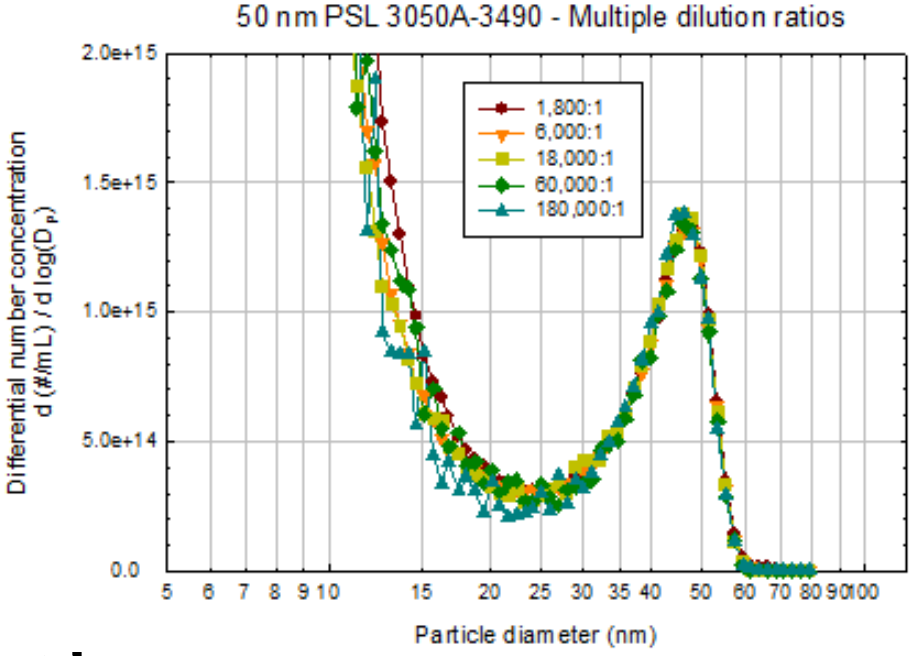
50 nm Silica

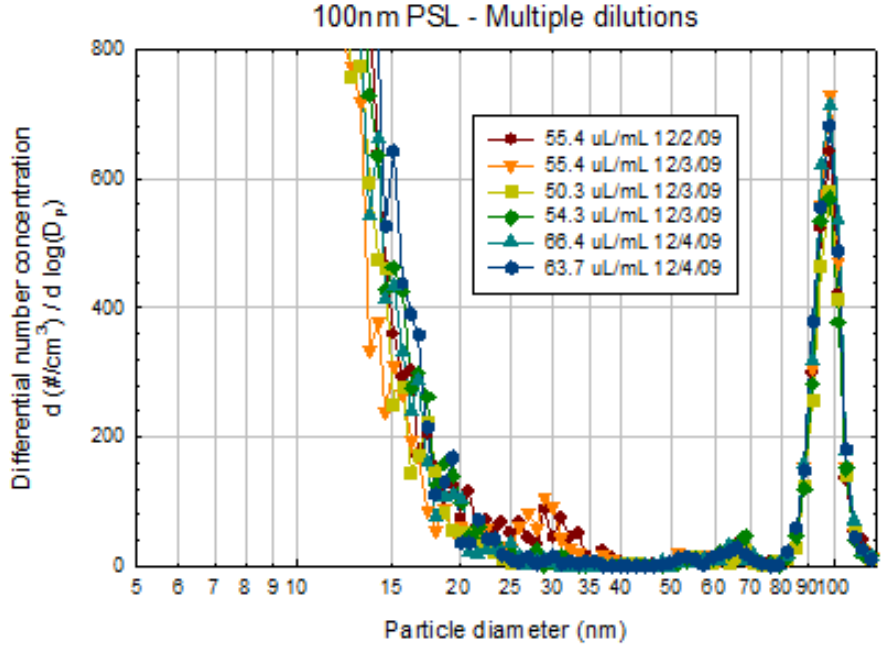


Examples of PSL particle size distributions









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Summary

- Multiple test methods are available to measure the retention efficacy of liquid filters below 100 nm.
- Each method has benefits and limitations.
- At this time, no single method has yet to be adopted as the preferred method.
- Only SEMI C79 (Method #4) has demonstrated the ability to measure retention down to 10 nm.