A New Method for Determining the Size Distribution of the Working Particles in Colloidal Suspensions

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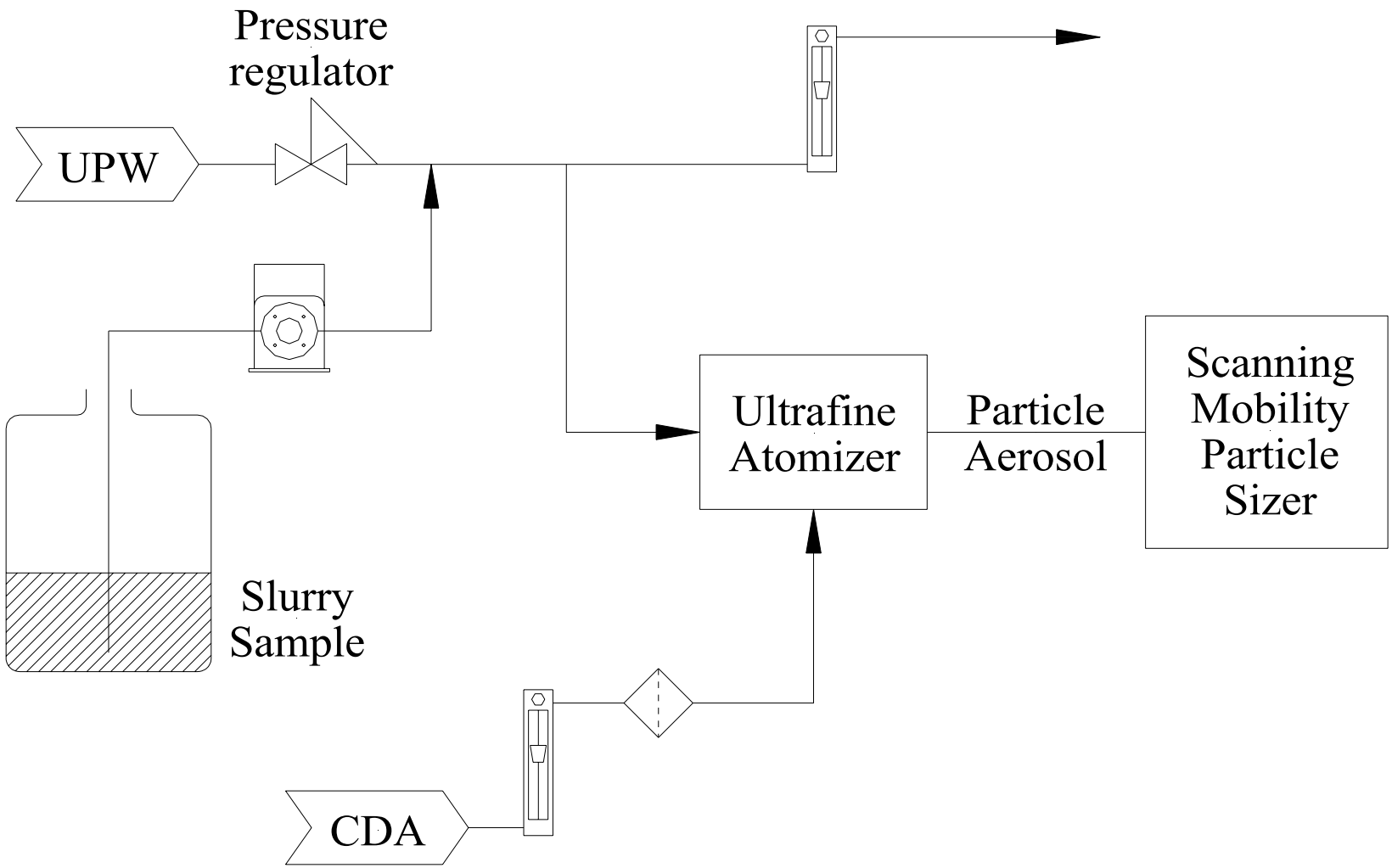
Introduction

- There are numerous processes where the size distribution of particles in colloidal suspensions influences the efficacy of the process.
- One example is chemical-mechanical planarization (CMP) slurries used in the semiconductor industry.
- The techniques presently used to determine the PSD typically only measure relative particle concentrations and often presume the shape of the distribution.
- This presentation describes a new technique that allows measurement of both size and concentration of the working particle size distribution.
- The presentation focuses on CMP slurries, but is applicable to numerous types of colloidal suspensions.

Outline

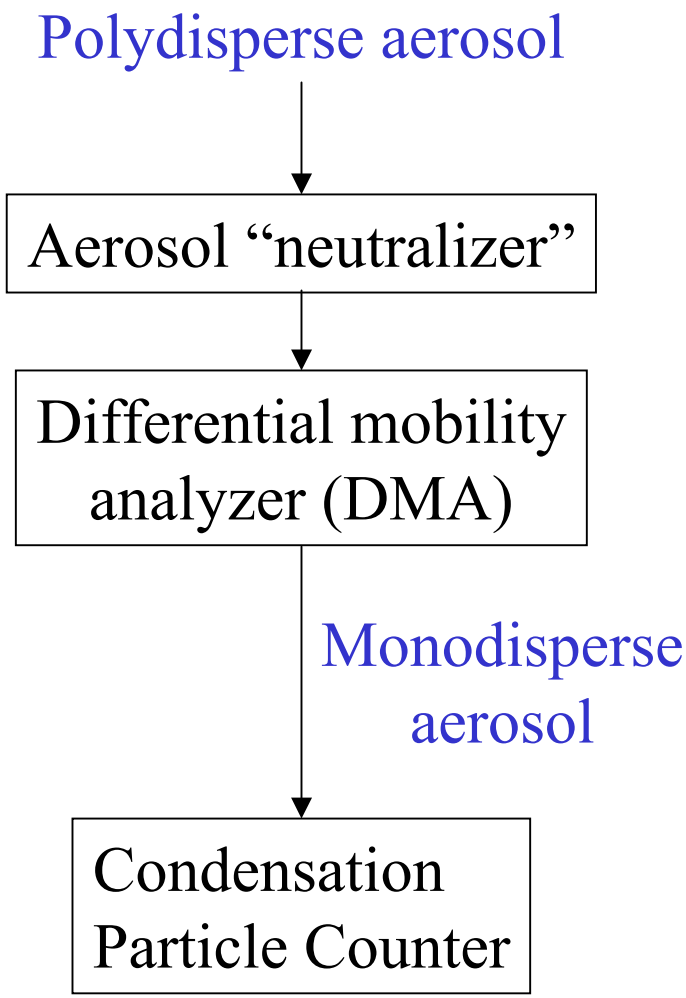
- Method description
- Measurement of “monodisperse” particles
  - Comparison to dynamic light scattering
  - Comparison of measured and claimed particle size uniformity
  - Comparison of measured concentrations
- Measurement of slurry particle size distributions
  - Comparison to dynamic light scattering
- Example of tracking slurry properties during handling
  - Comparison to dynamic light scattering
  - Comparison to large particle tail measurement
- Example of measuring filter particle retention efficiency
- Summary

Measurement method – Ultrafine atomization (UFA)

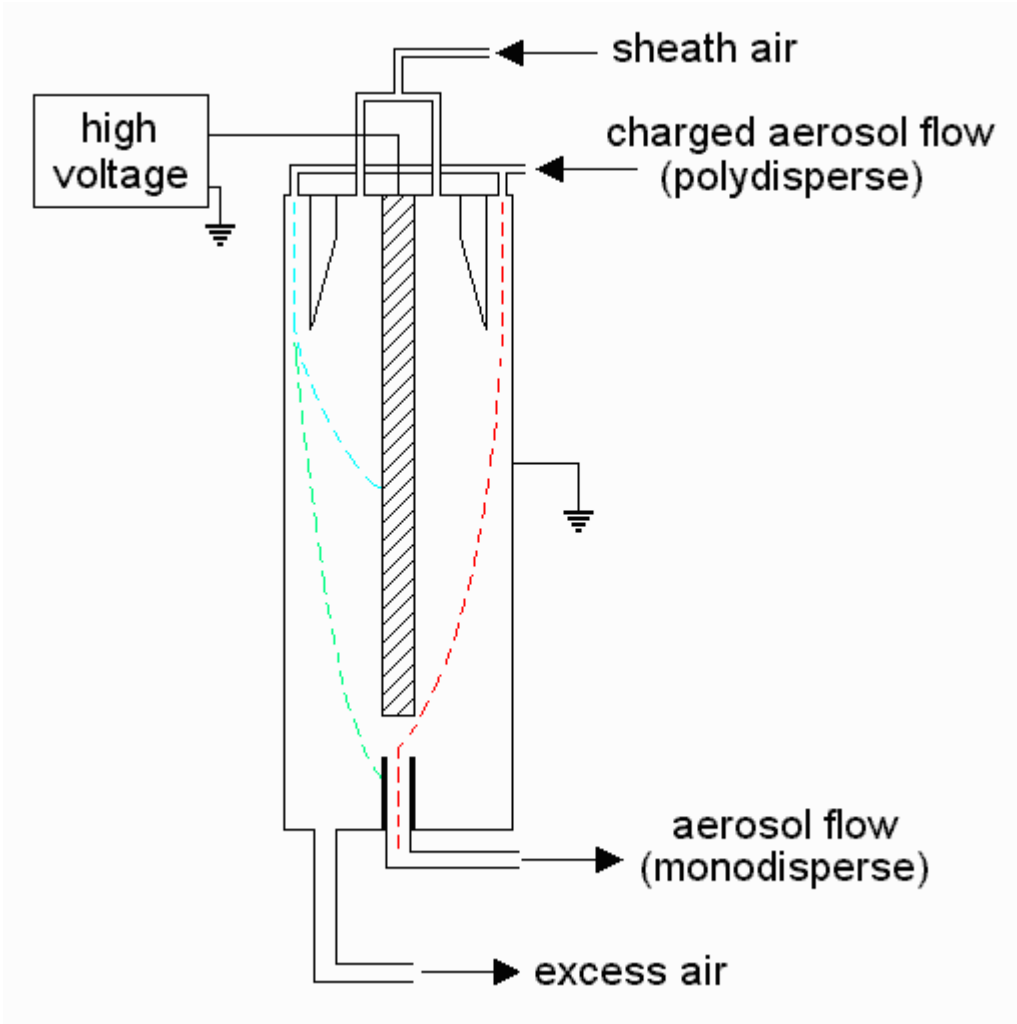


Patent pending.

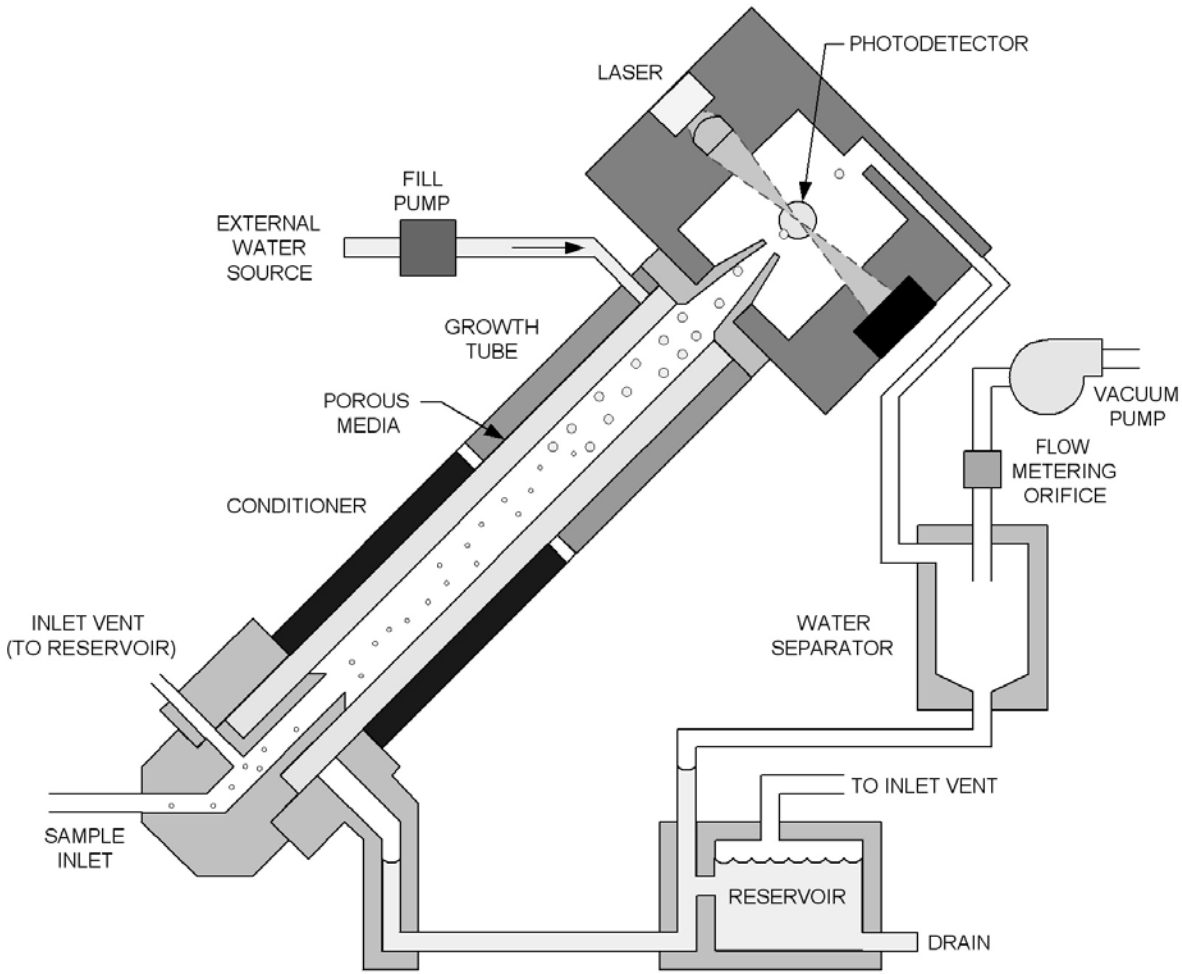
Scanning mobility particle sizer (SMPS)



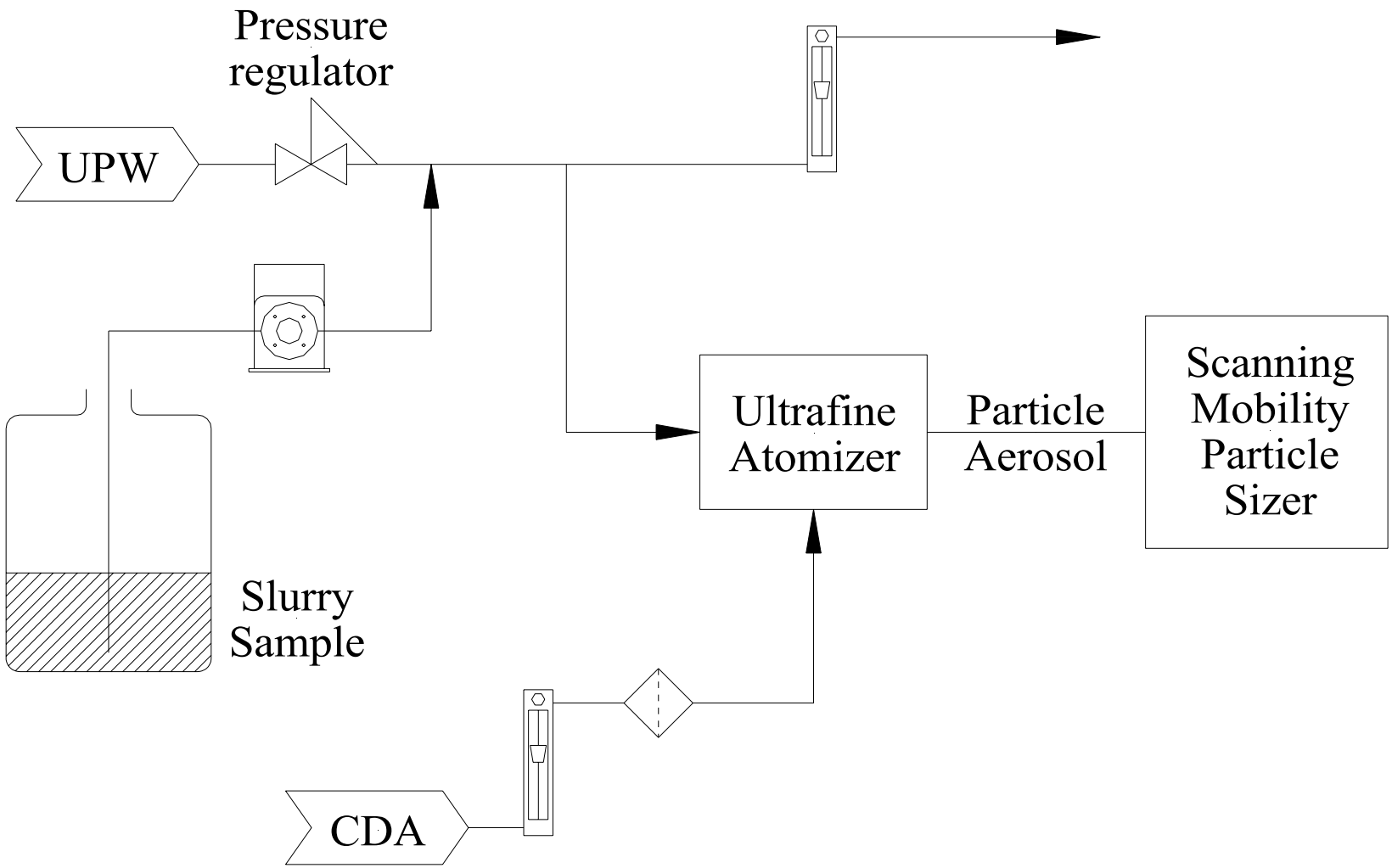
Differential mobility analyzer (DMA)



Condensation particle counter (CPC)



Measurement method – Ultrafine atomization (UFA)

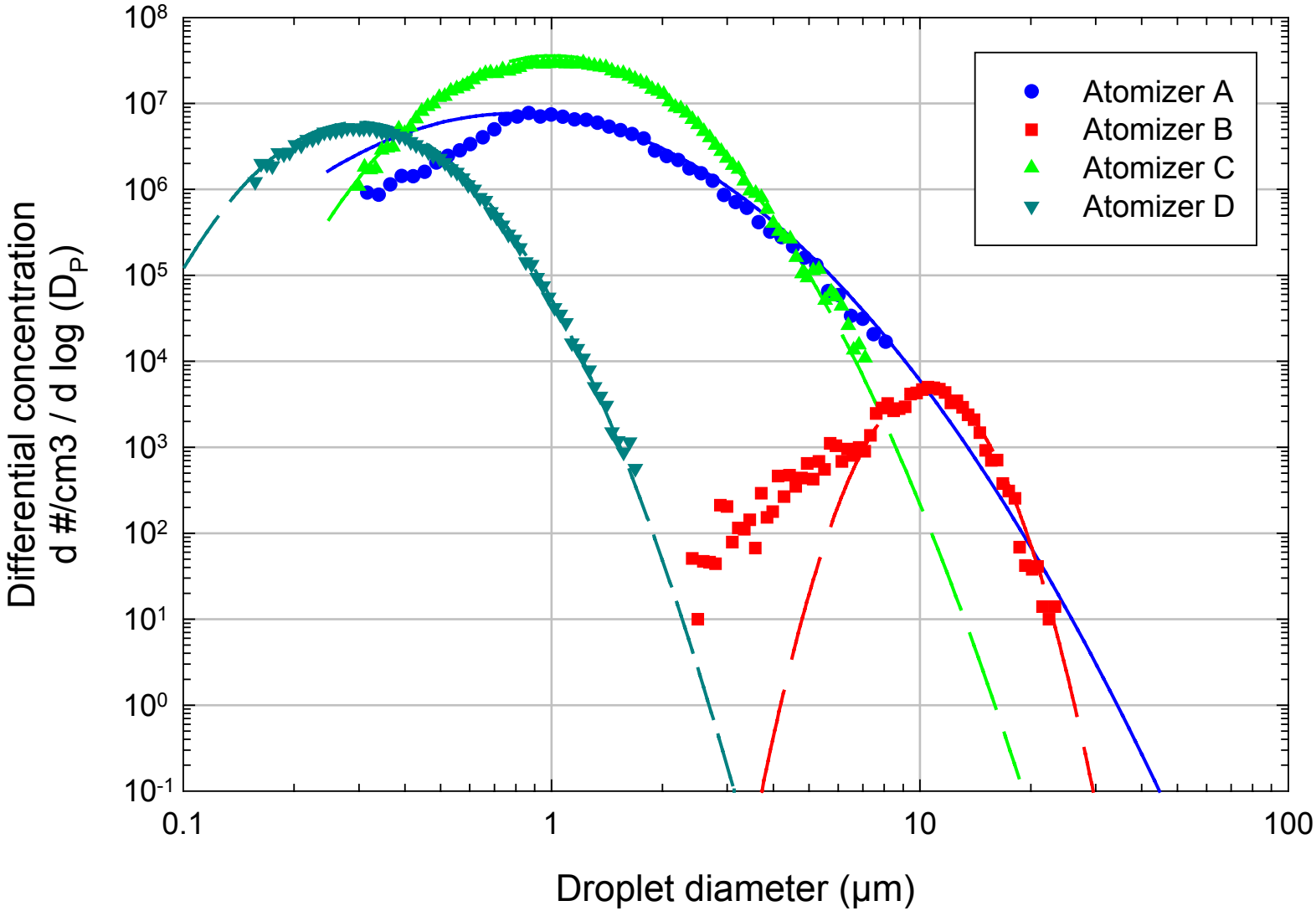


Patent pending.

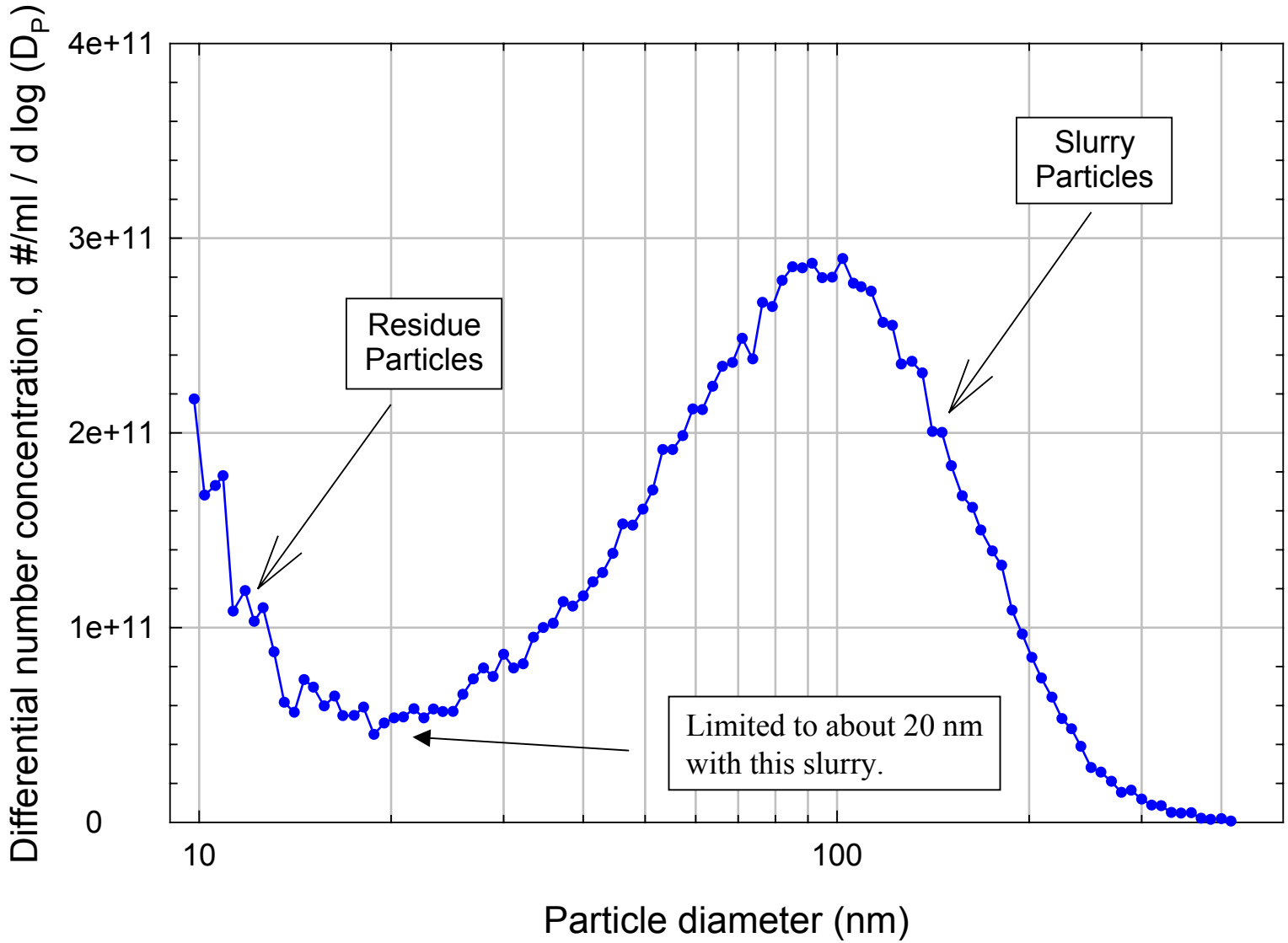
Key technical challenge

- Want to have no more than 1 particle in each droplet.
- Non-volatile dissolved residue in the UPW and slurry will form particles when the droplets from the atomizer are dried. These residue particles can interfere with the suspended particle analysis.
- The atomizer must produce small, uniformly-sized droplets to prevent interference with the particle analysis.

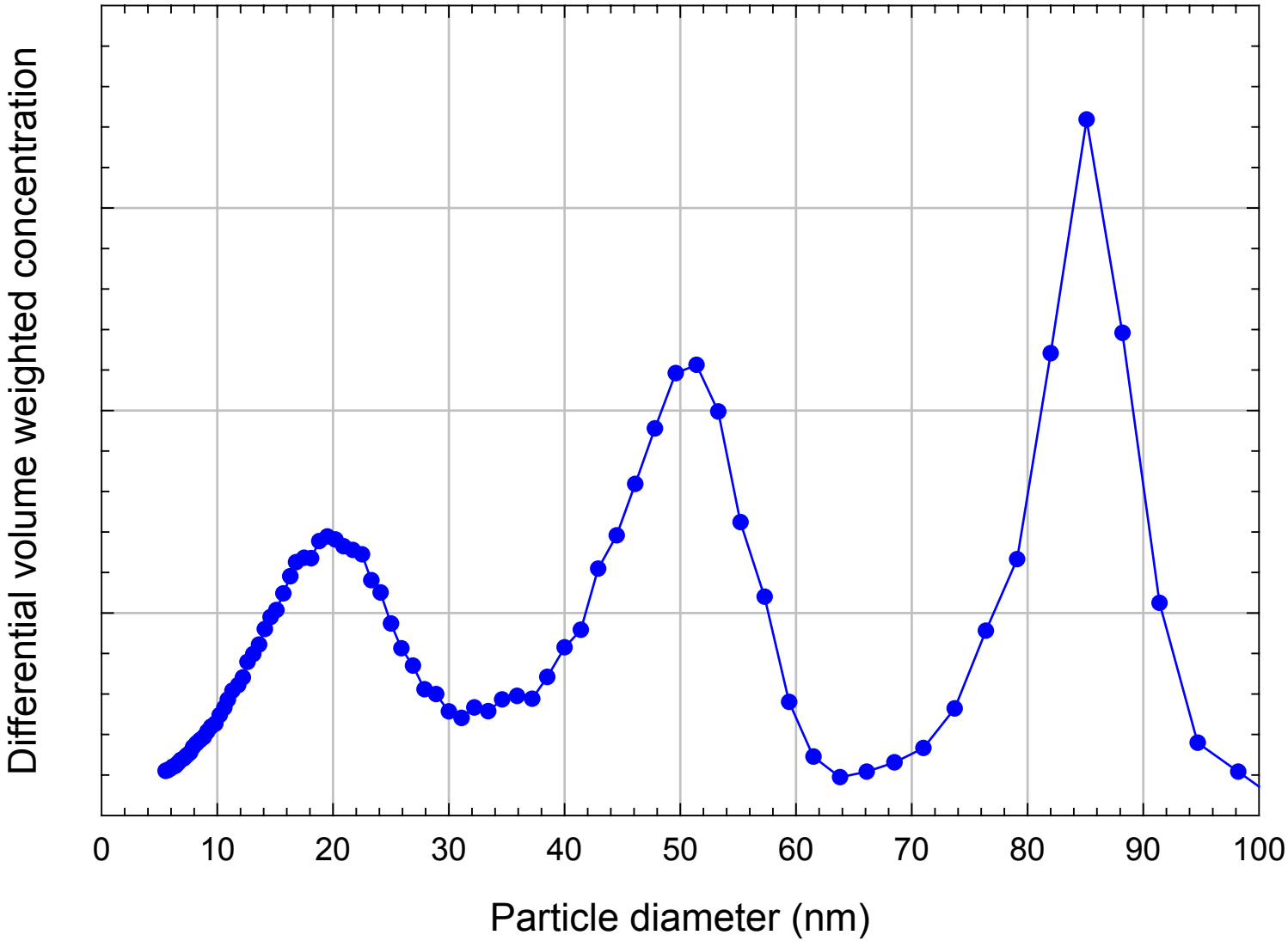
Droplet size distributions produced by different atomizers

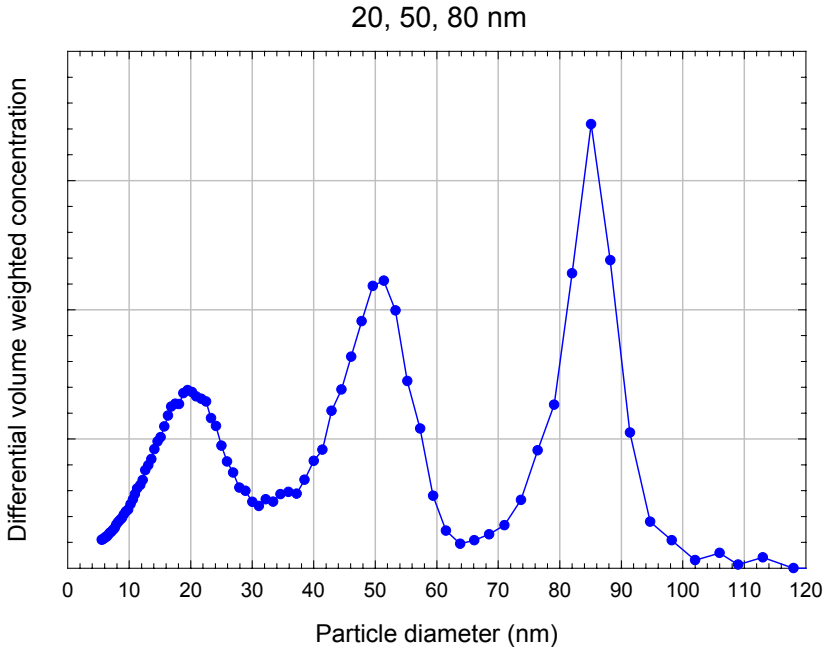


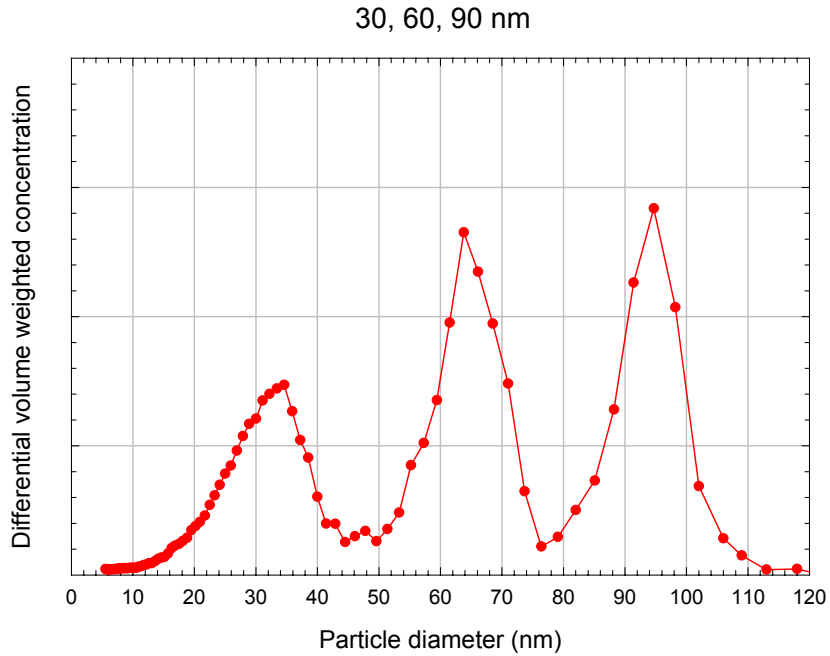
Residue interference with Atomizer D

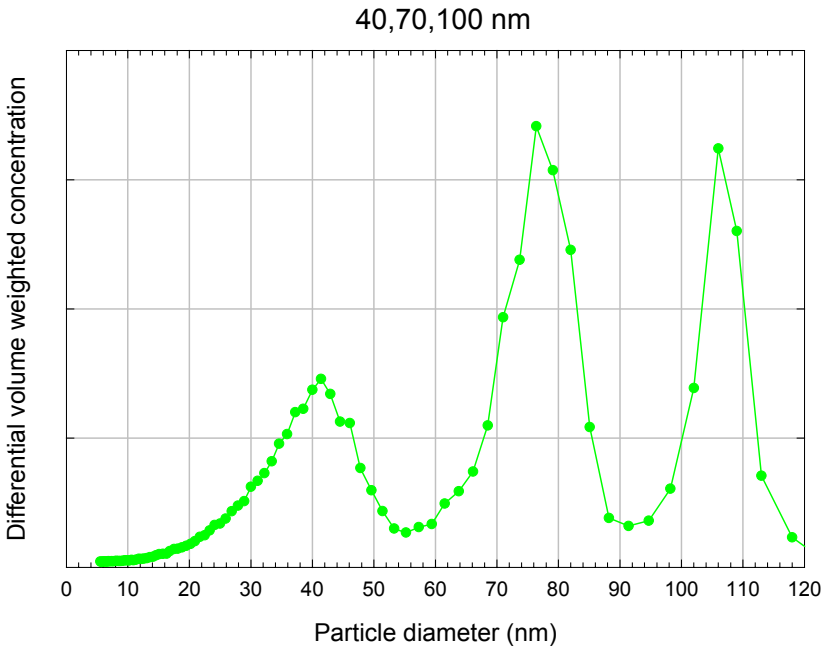


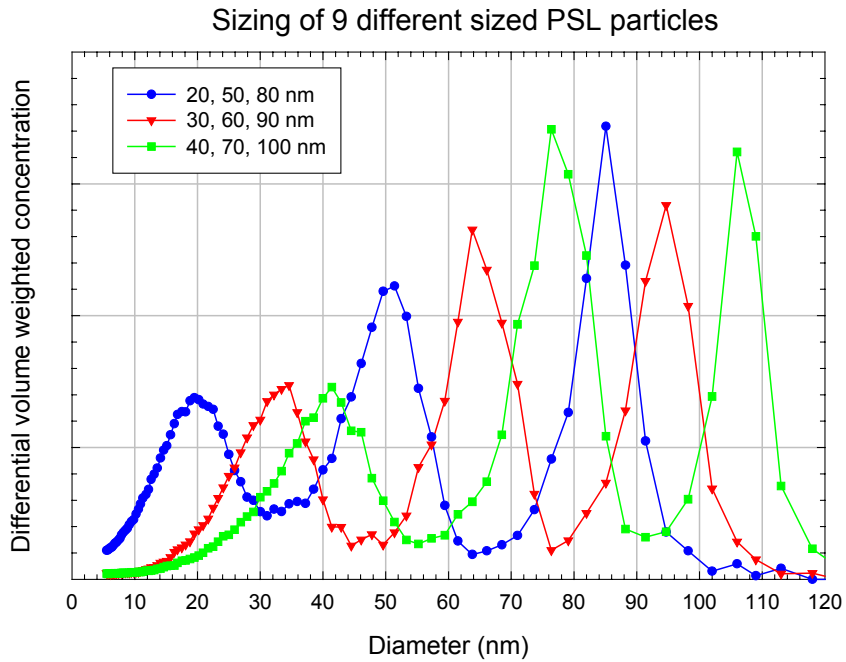
Sizing of 20, 50, and 80 nm PSL particles



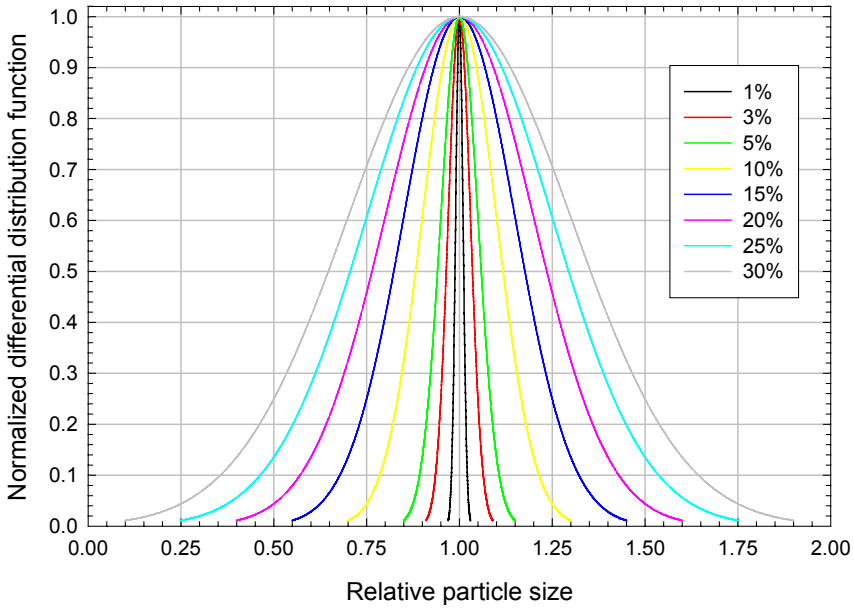

20, 50, 80 nm
Differential volume weighted concentration
0 10 20 30 40 50 60 70 80 90 100 110 120
Particle diameter (nm)


30, 60, 90 nm
Differential volume weighted concentration
0 10 20 30 40 50 60 70 80 90 100 110 120
Particle diameter (nm)

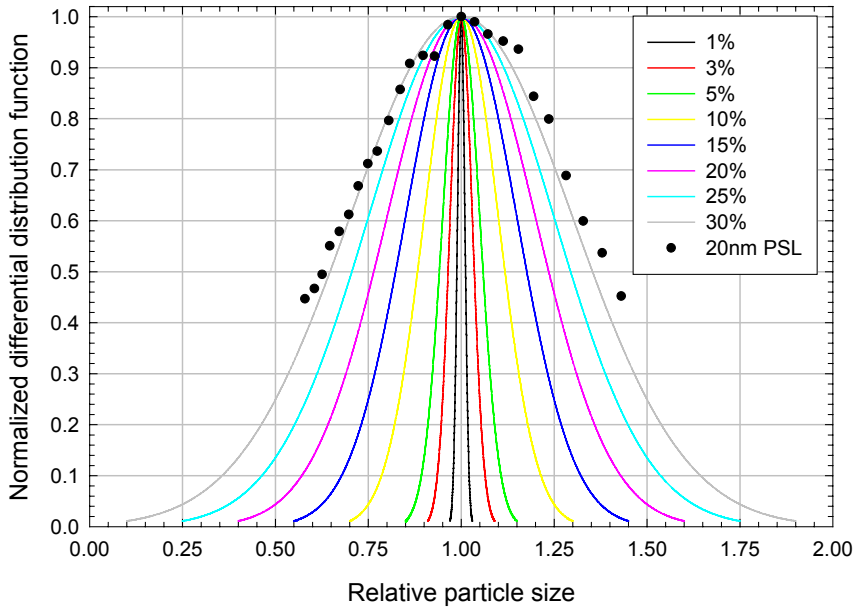

40,70,100 nm
Differential volume weighted concentration
0 10 20 30 40 50 60 70 80 90 100 110 120
Particle diameter (nm)


Sizing of 9 different sized PSL particles
20, 50, 80 nm
30, 60, 90 nm
40, 70, 100 nm
Differential volume weighted concentration
0 10 20 30 40 50 60 70 80 90 100 110 120
Diameter (nm)

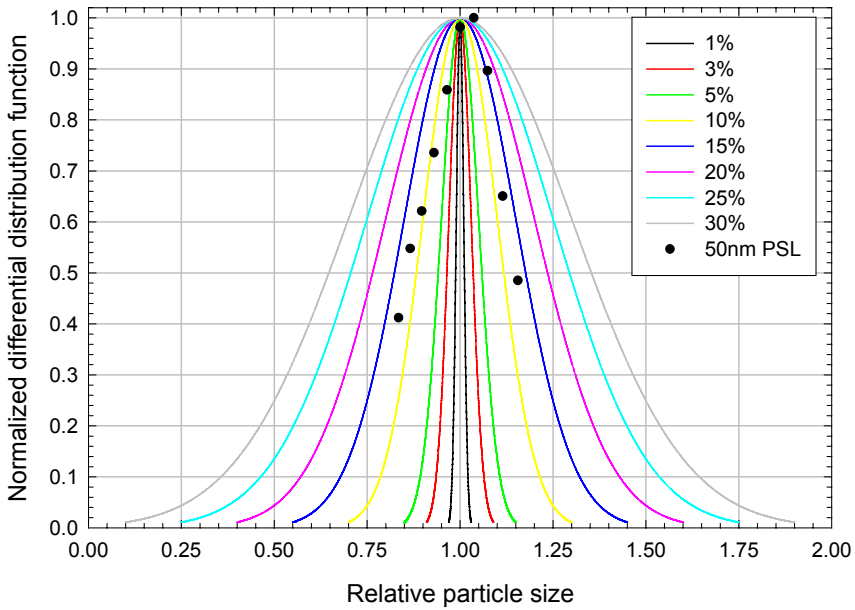
Normalized size distributions at different coellicients of variation (CVs)



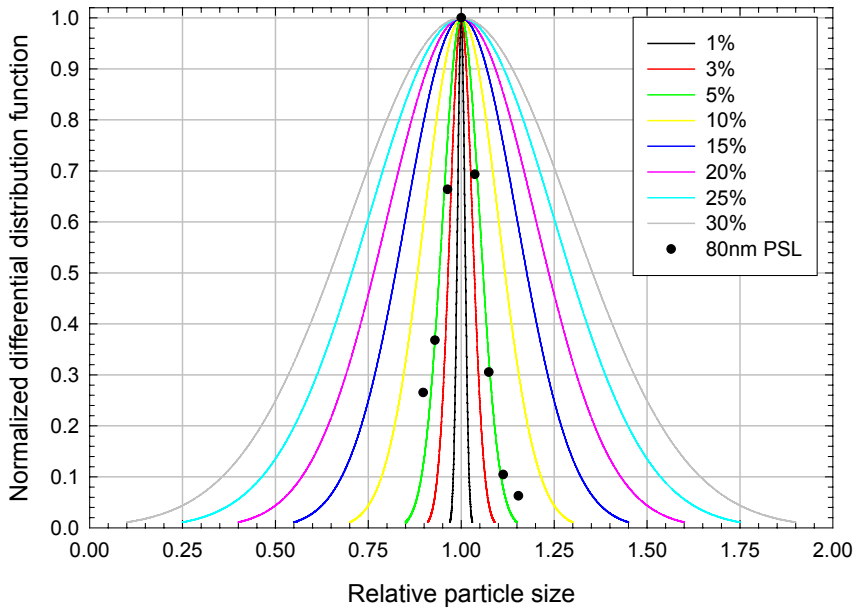
Measured CV of 20nm PSL



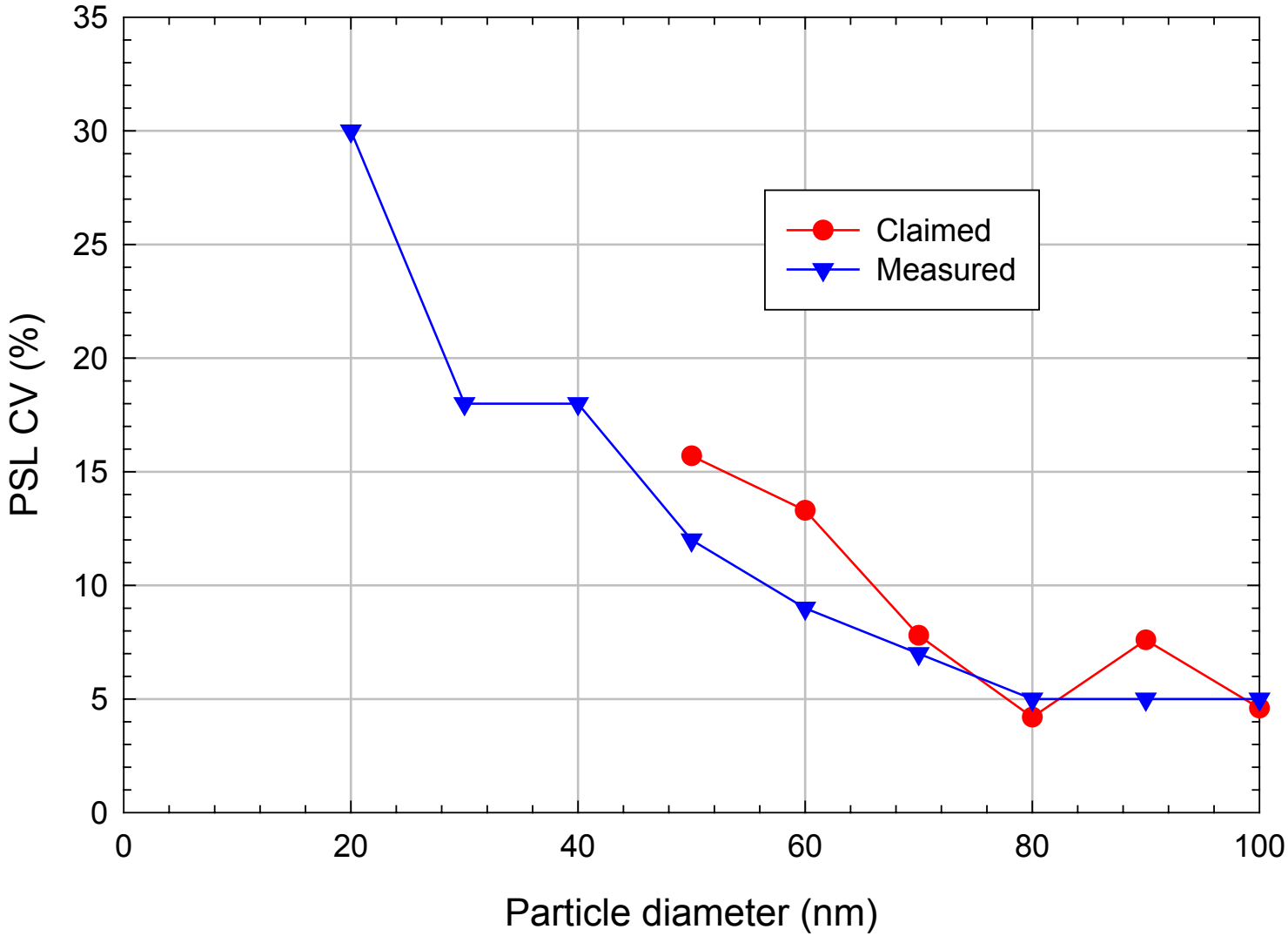
Measured CV of 50nm PSL



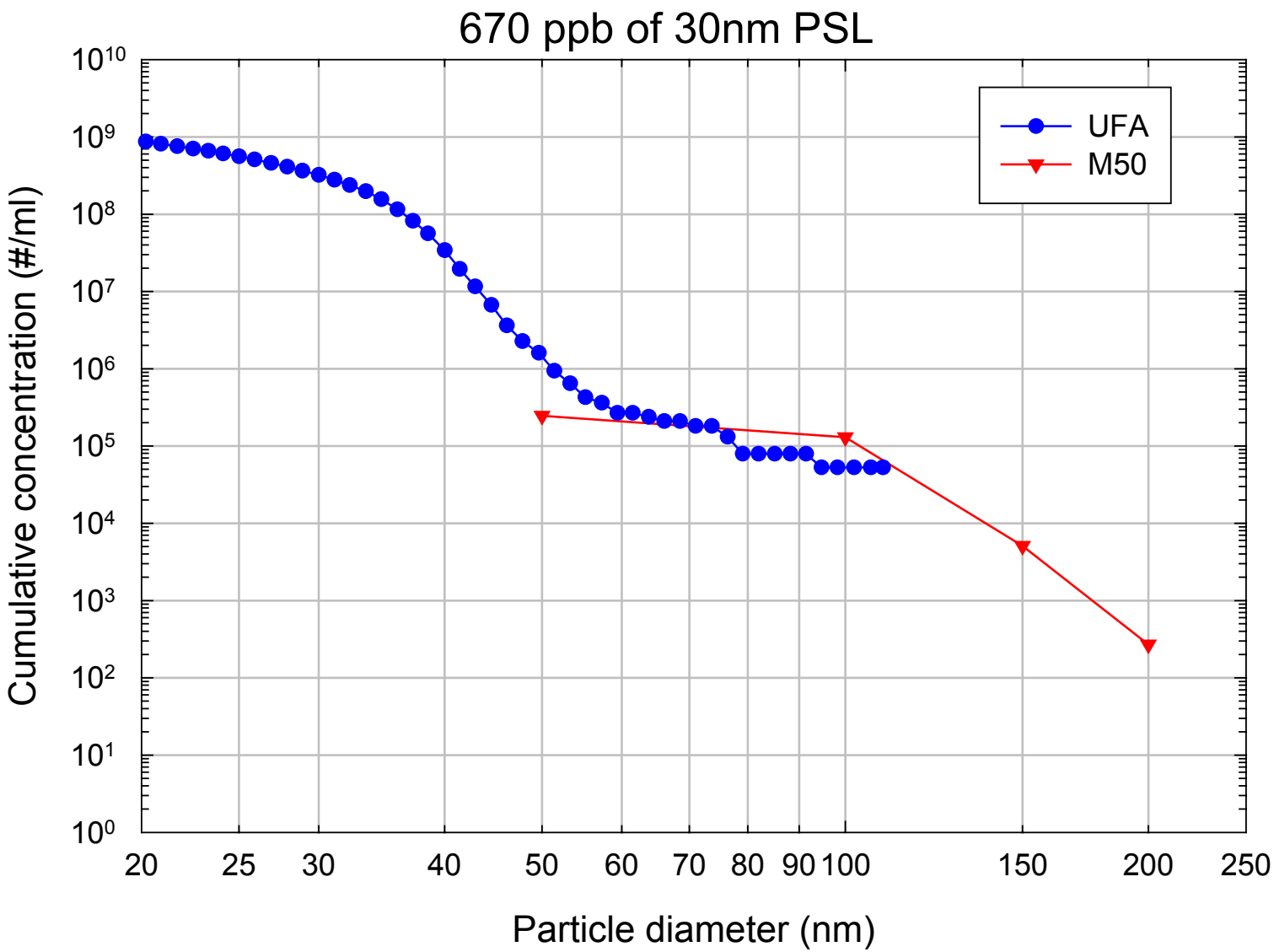
Measured CV of 80nm PSL

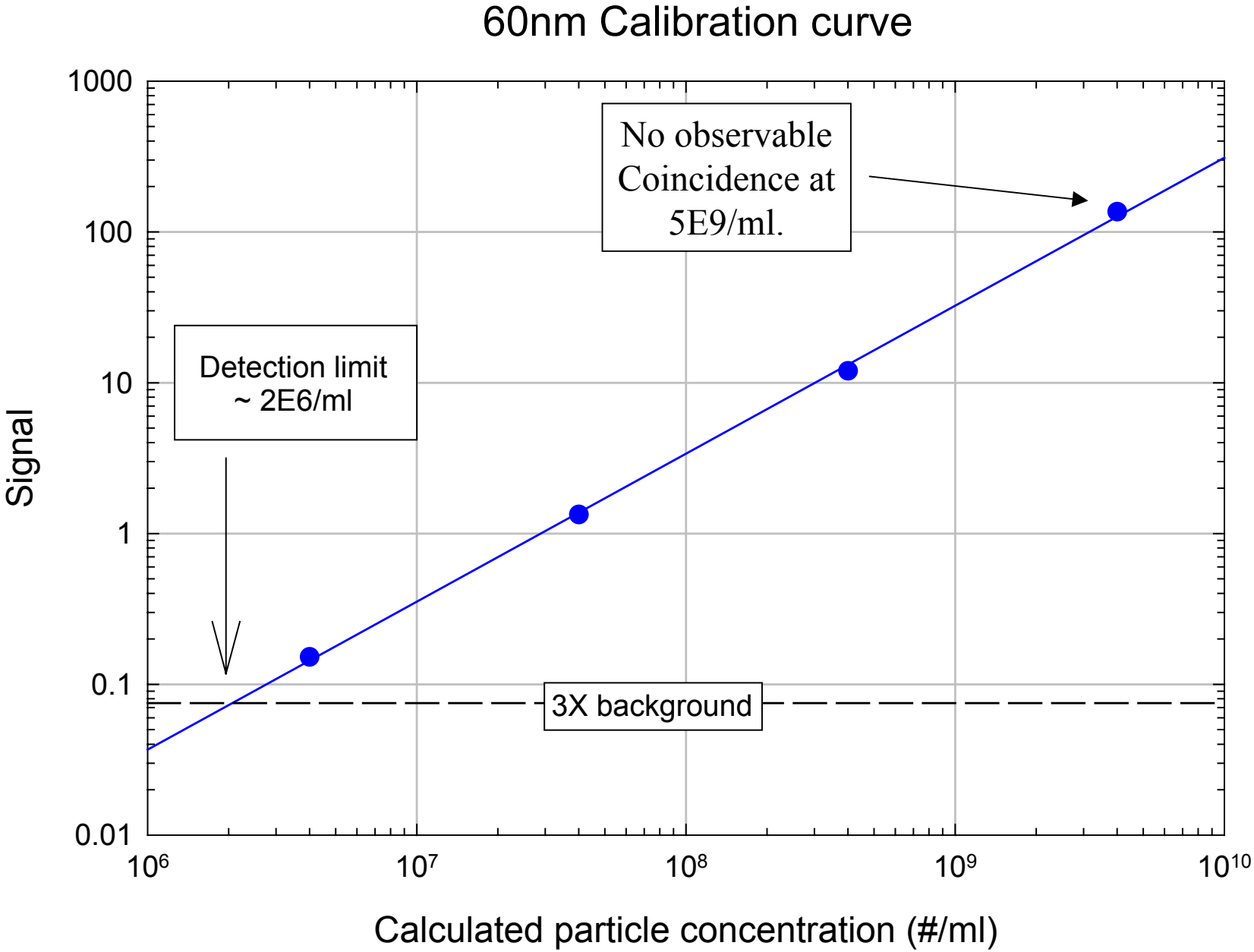


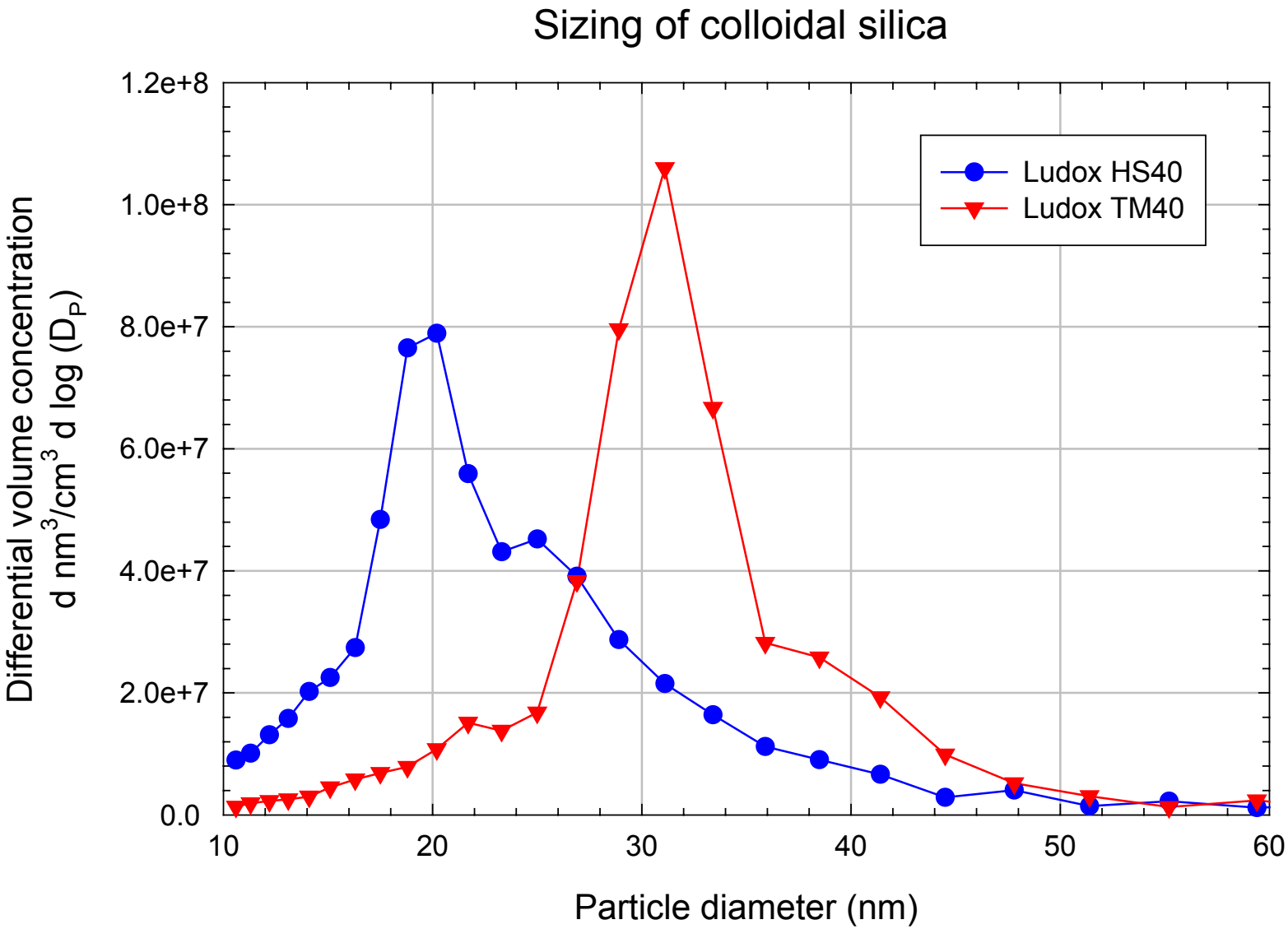
Comparison between claimed and measured PSL size uniformity



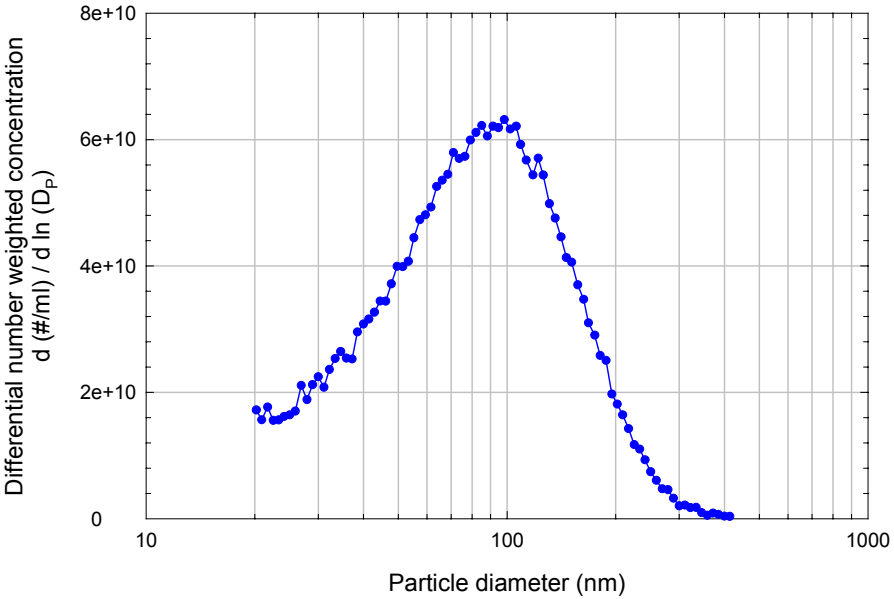
Comparison to 50nm Optical Particle Counter

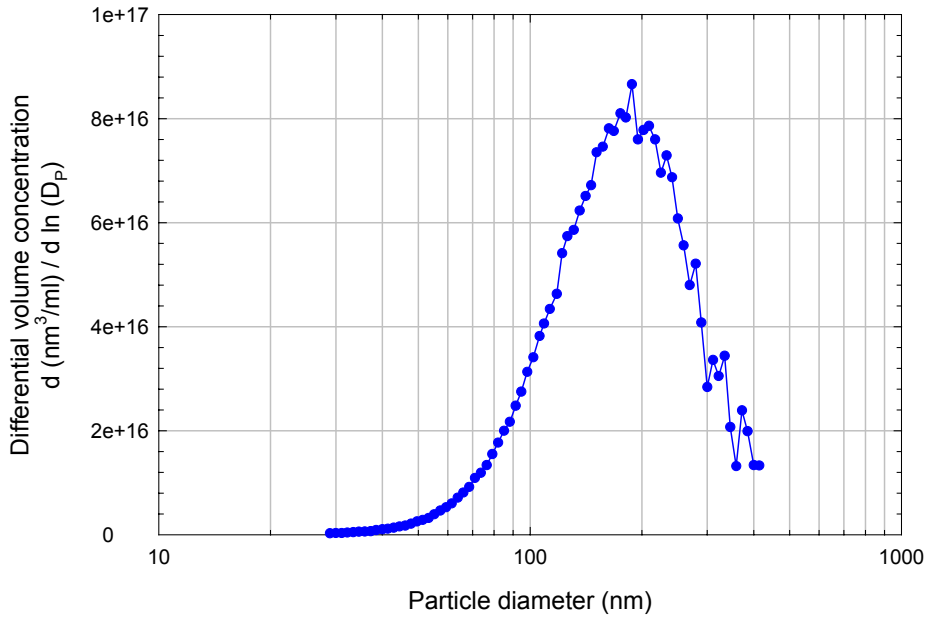



60nm Calibration curve
1000
100
10
1
0.1
0.01
Signal
No observable
Coincidence at
5E9/ml.
Detection limit
~ 2E6/ml
3X background
10^6
10^7
10^8
10^9
10^10
Calculated particle concentration (#/ml)

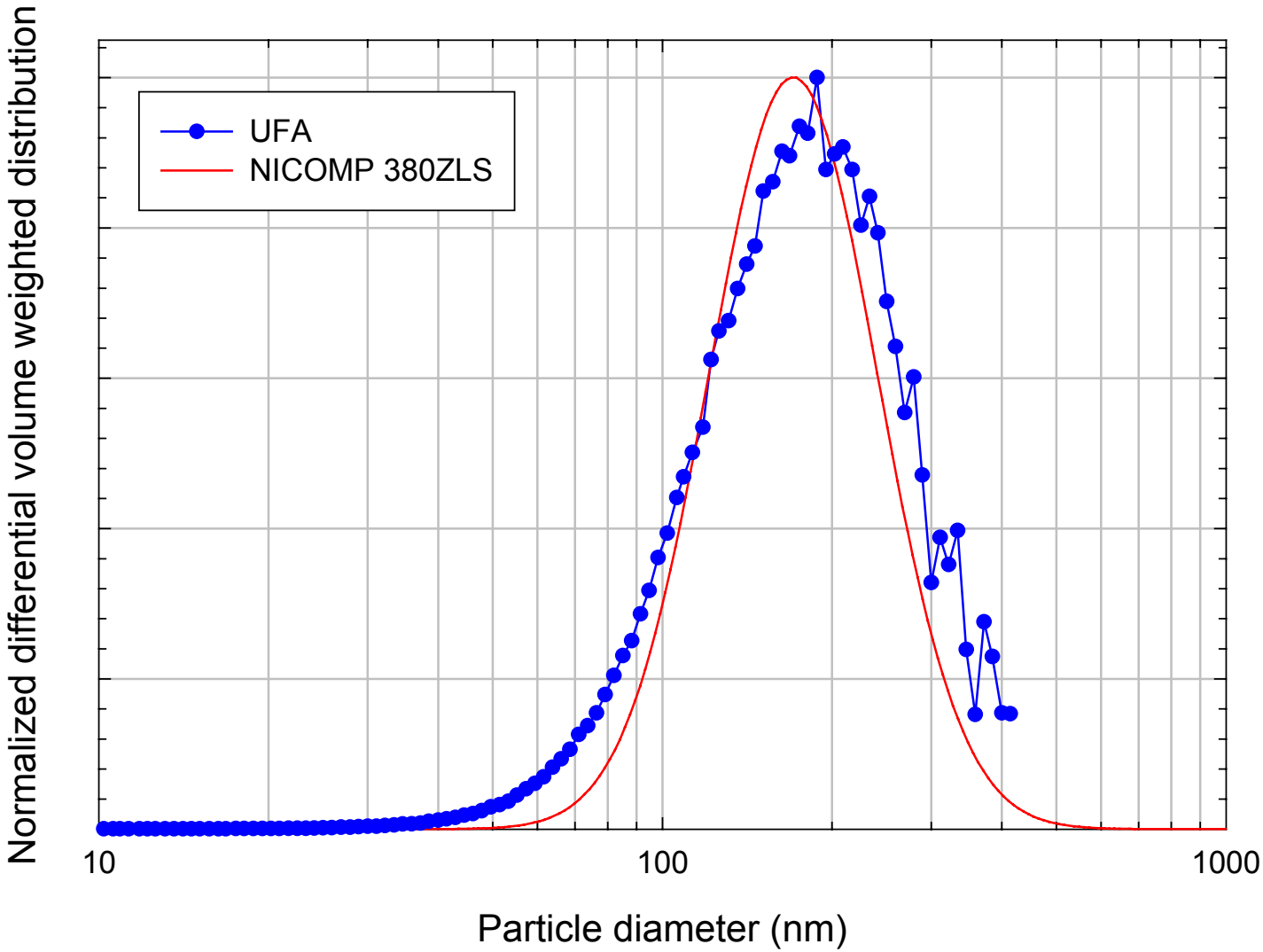

Sizing of colloidal silica
Differential volume concentration
d nm3/cm3 d log (DP)
1.2e+8
1.0e+8
8.0e+7
6.0e+7
4.0e+7
2.0e+7
0.0
10
20
30
40
50
60
Particle diameter (nm)
Ludox HS40
Ludox TM40

PSD in CMP slurry A – Silica particles

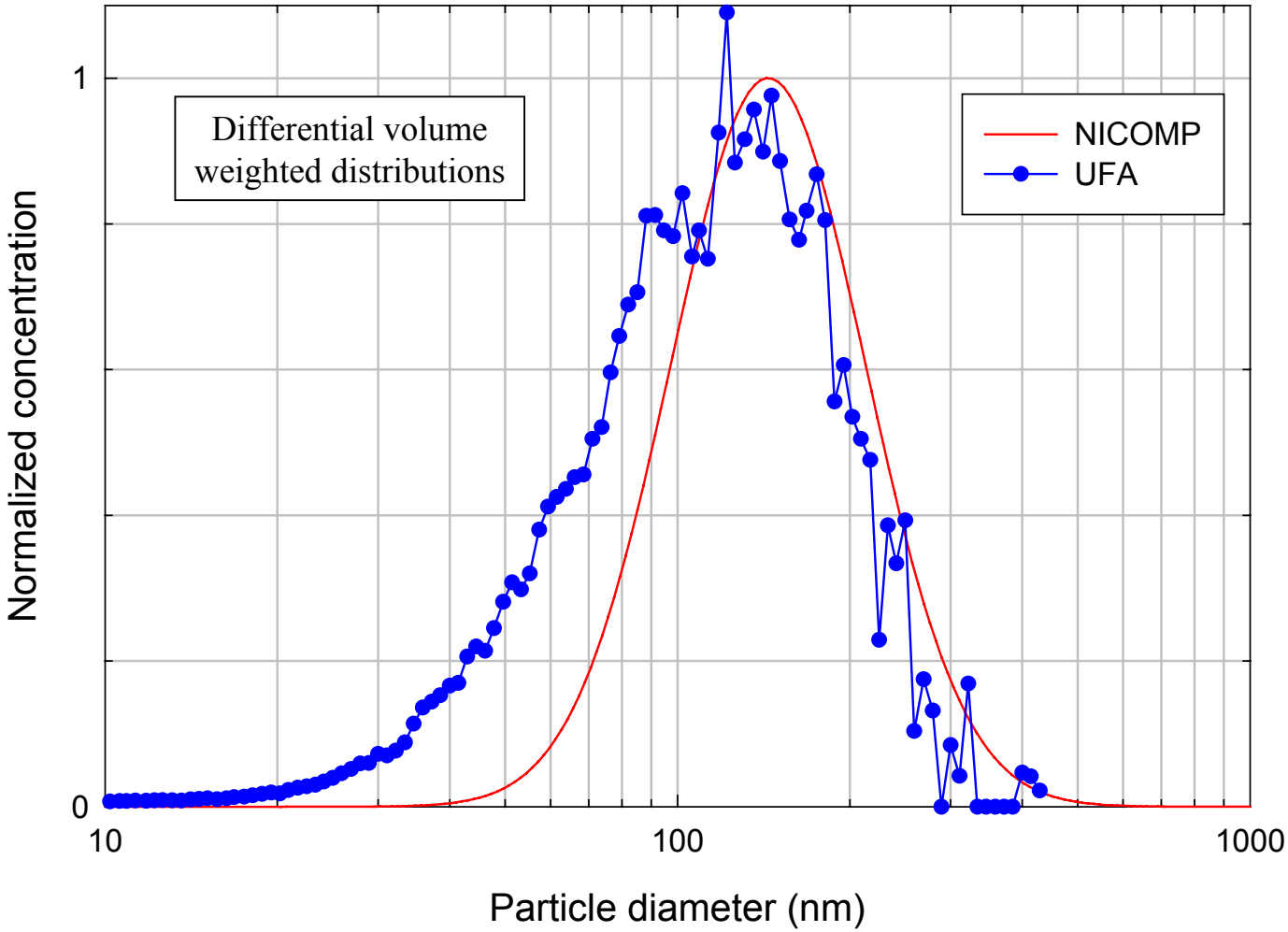




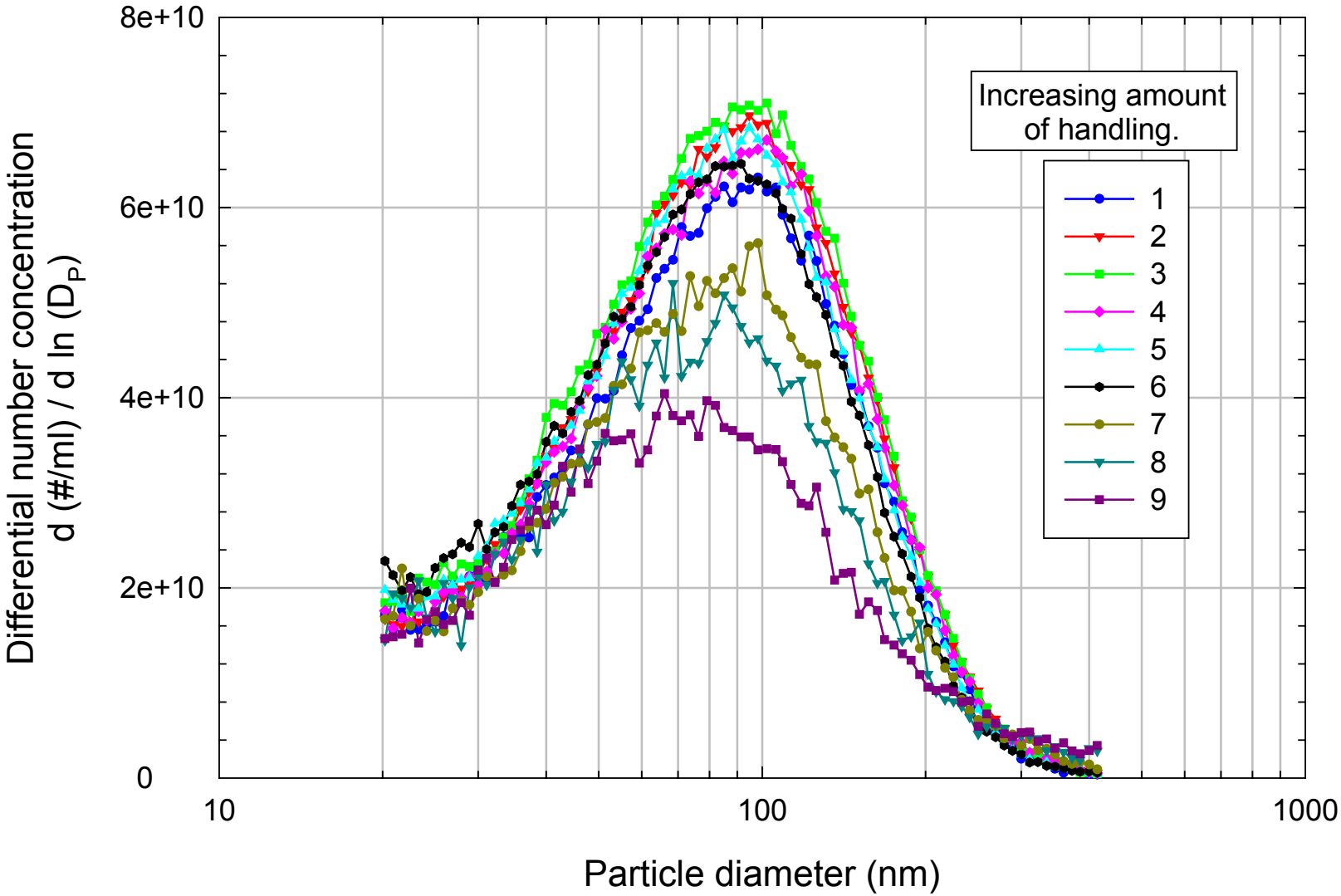
UFA – Dynamic Light Scattering (DLS) Comparison
Silica particle slurry A



PSD in silica particle slurry B

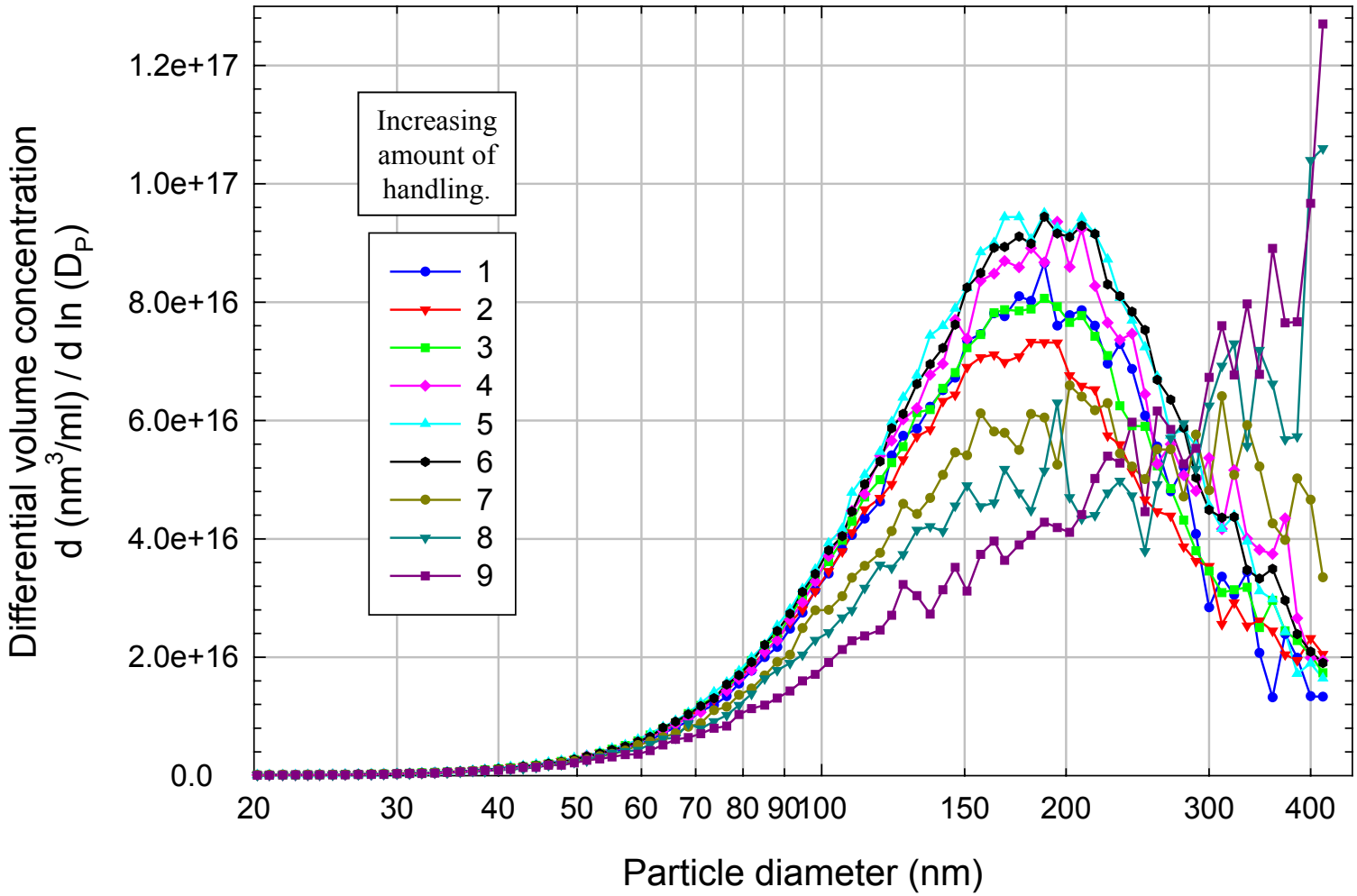


Measuring the effect of handling on Slurry A PSD



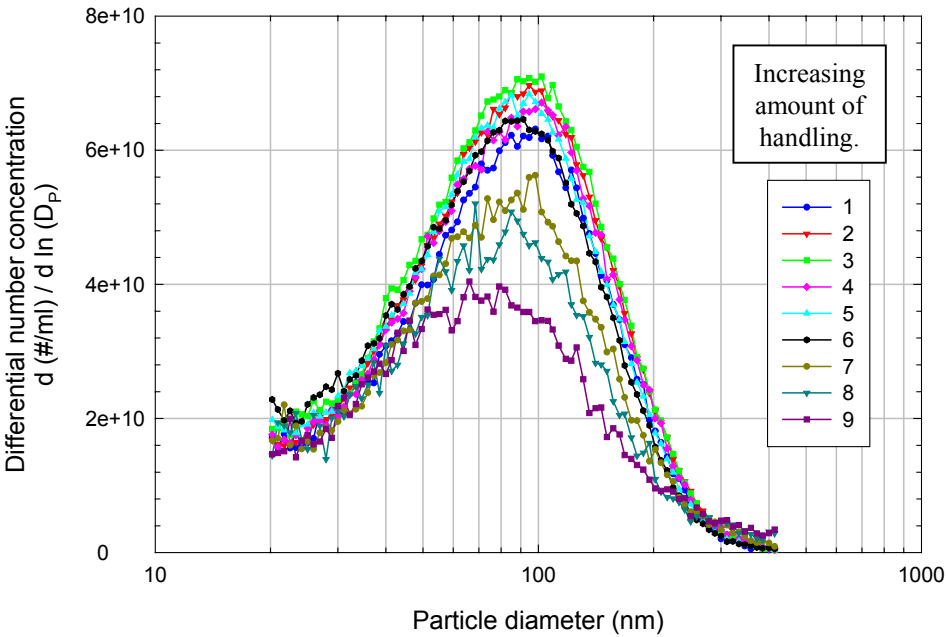
Measuring the effect of handling on slurry PSD

Volume weighted concentrations

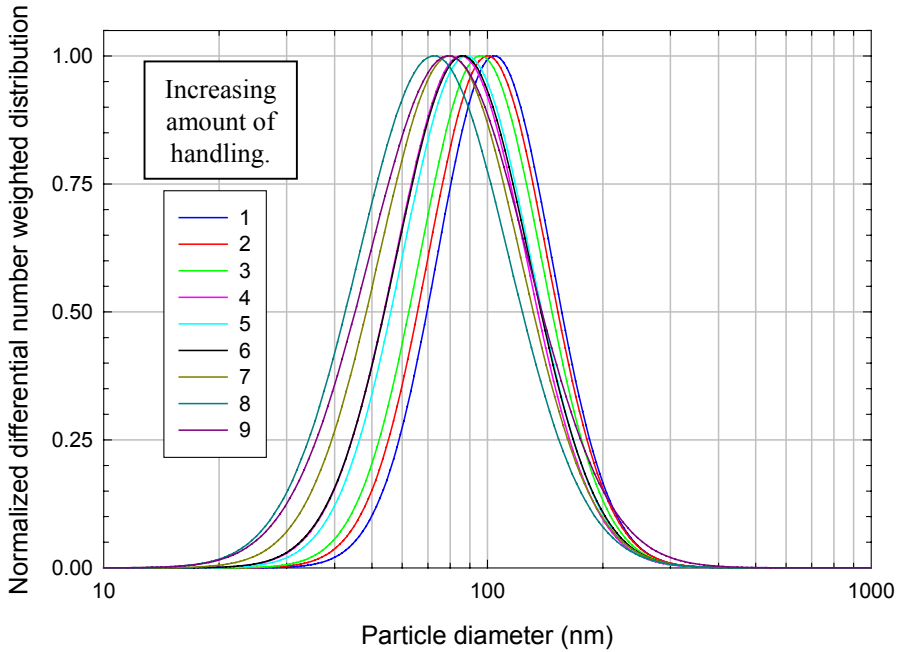


Effect of handling – comparison to dynamic light scattering (NICOMP 380ZLS)*

UFA



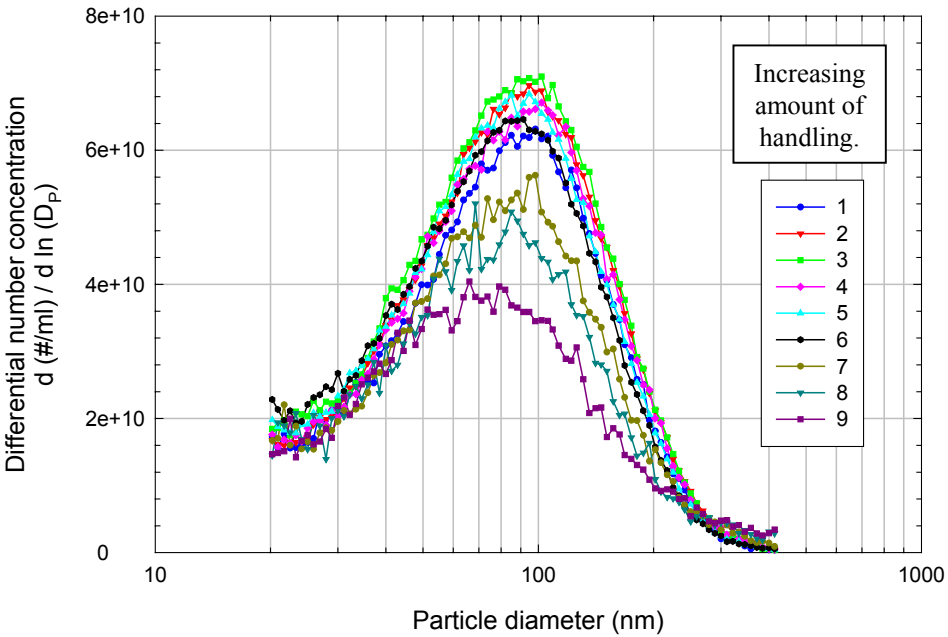
NICOMP



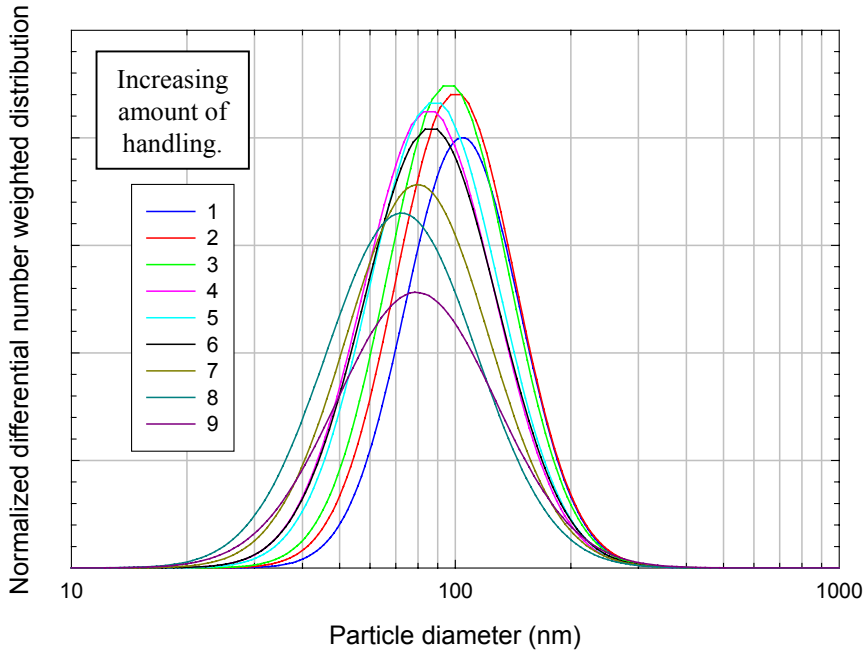
* - Particle Sizing Systems, Santa Barbara, CA.

Effect of handling – comparison to dynamic light scattering (NICOMP 380ZLS) – NICOMP normalized to UFA

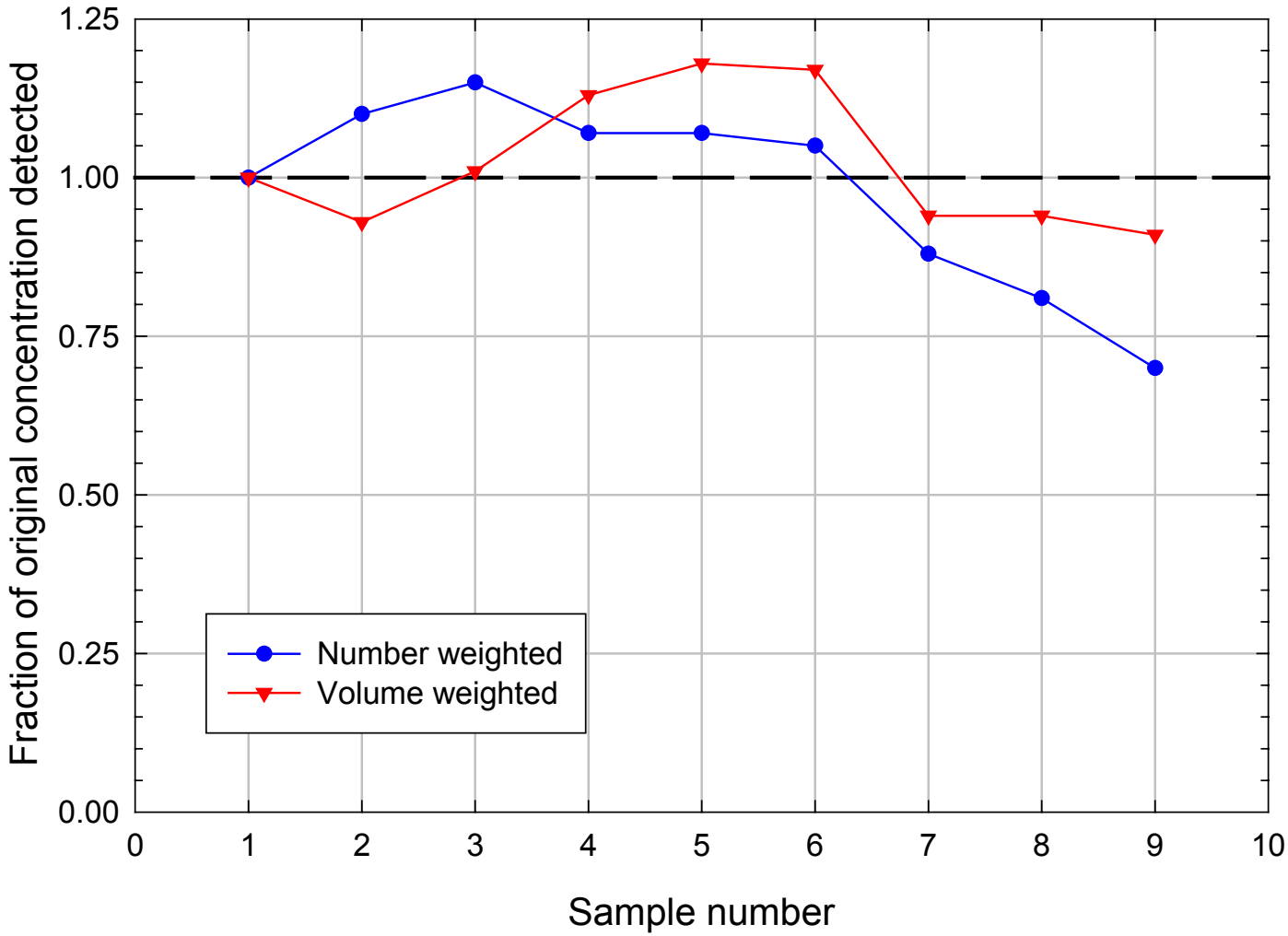
UFA



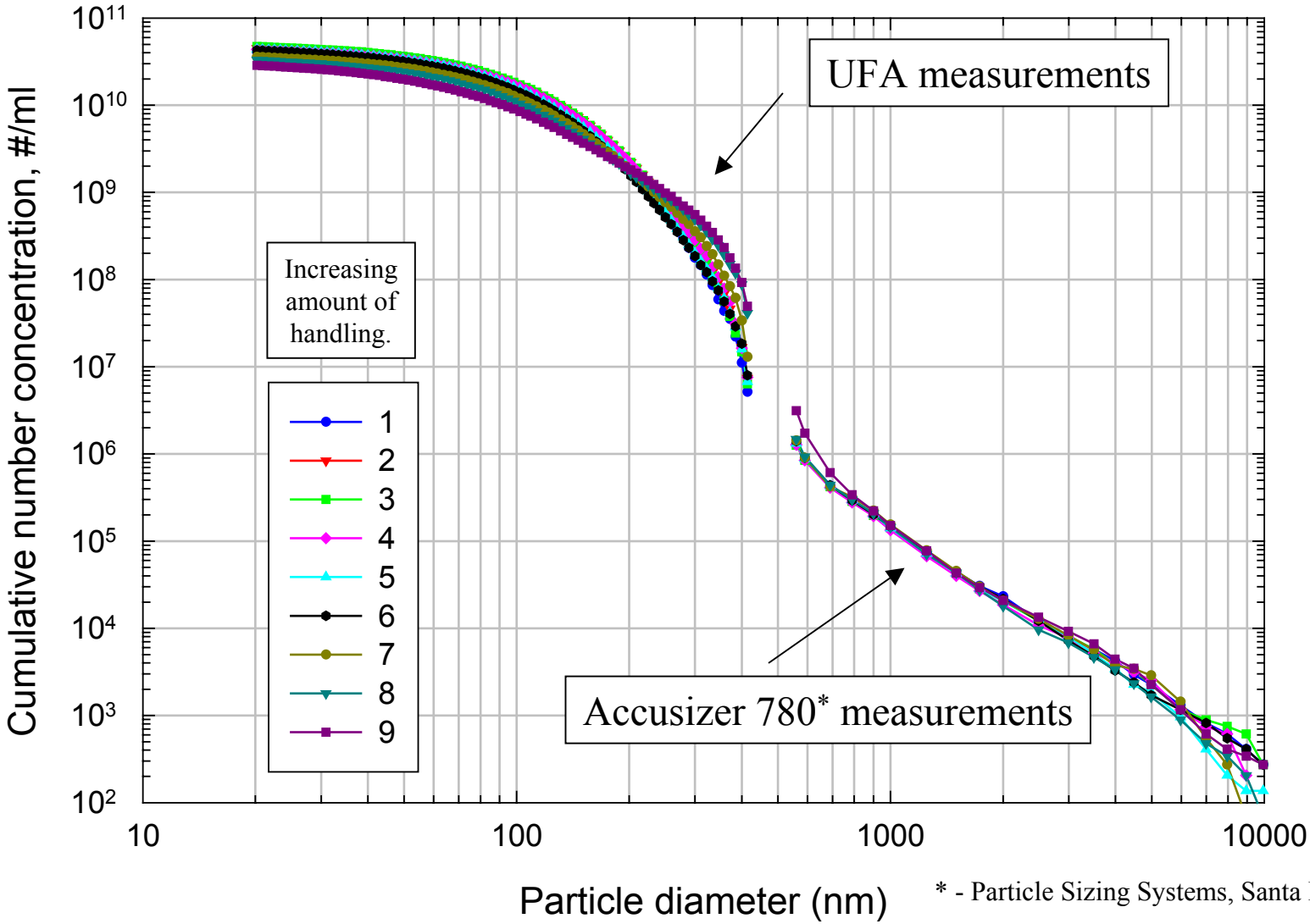
NICOMP



Change in cumulative concentrations over time during handling

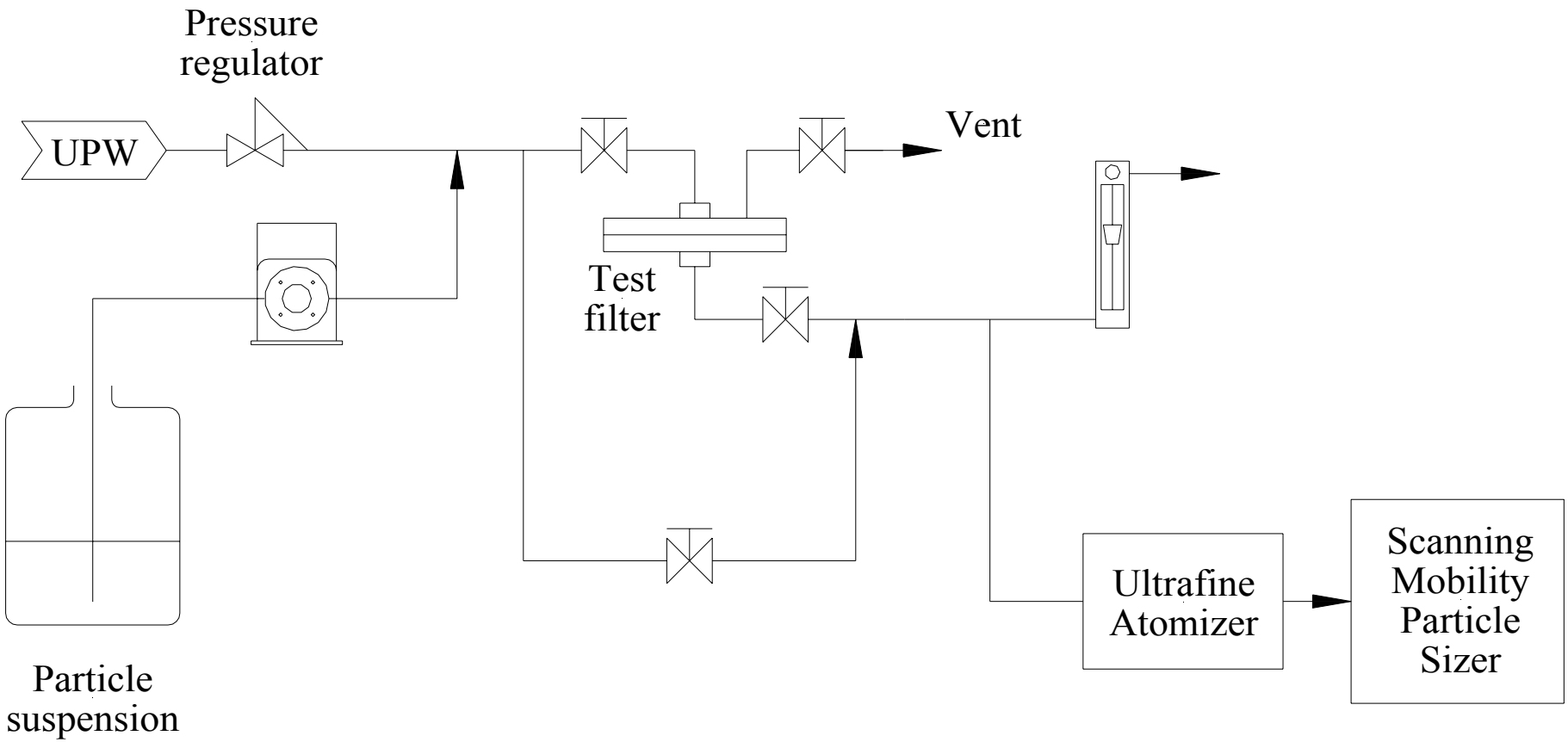


Comparison between UFA and large particle tail measurements during slurry handling

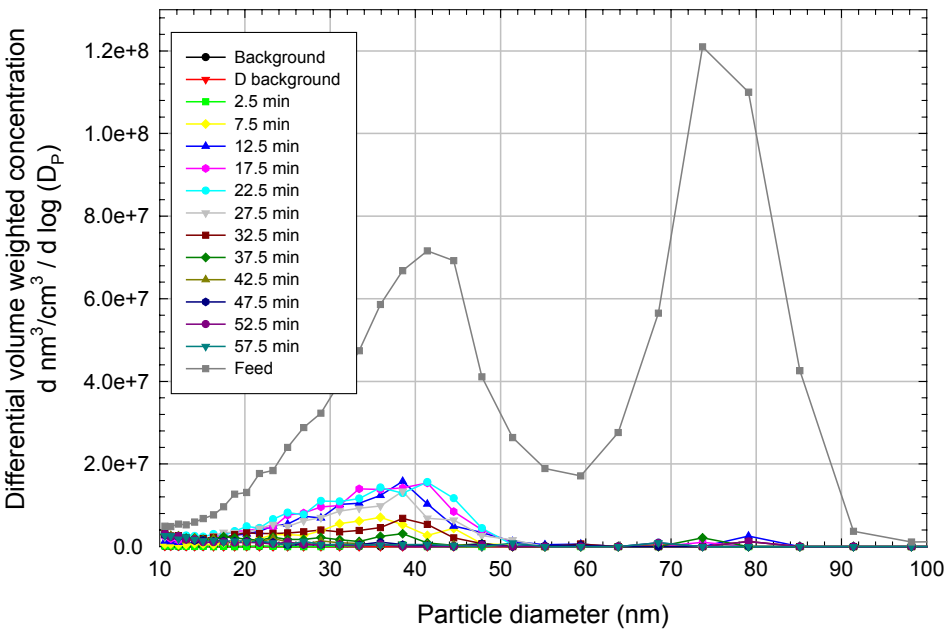


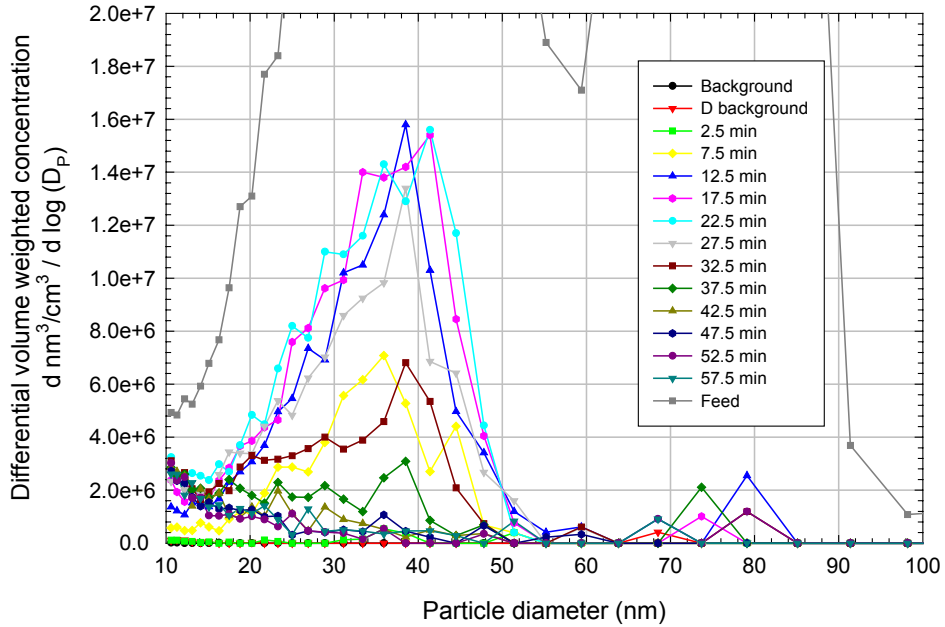
* - Particle Sizing Systems, Santa Barbara, CA.

Filter retention test stand schematic

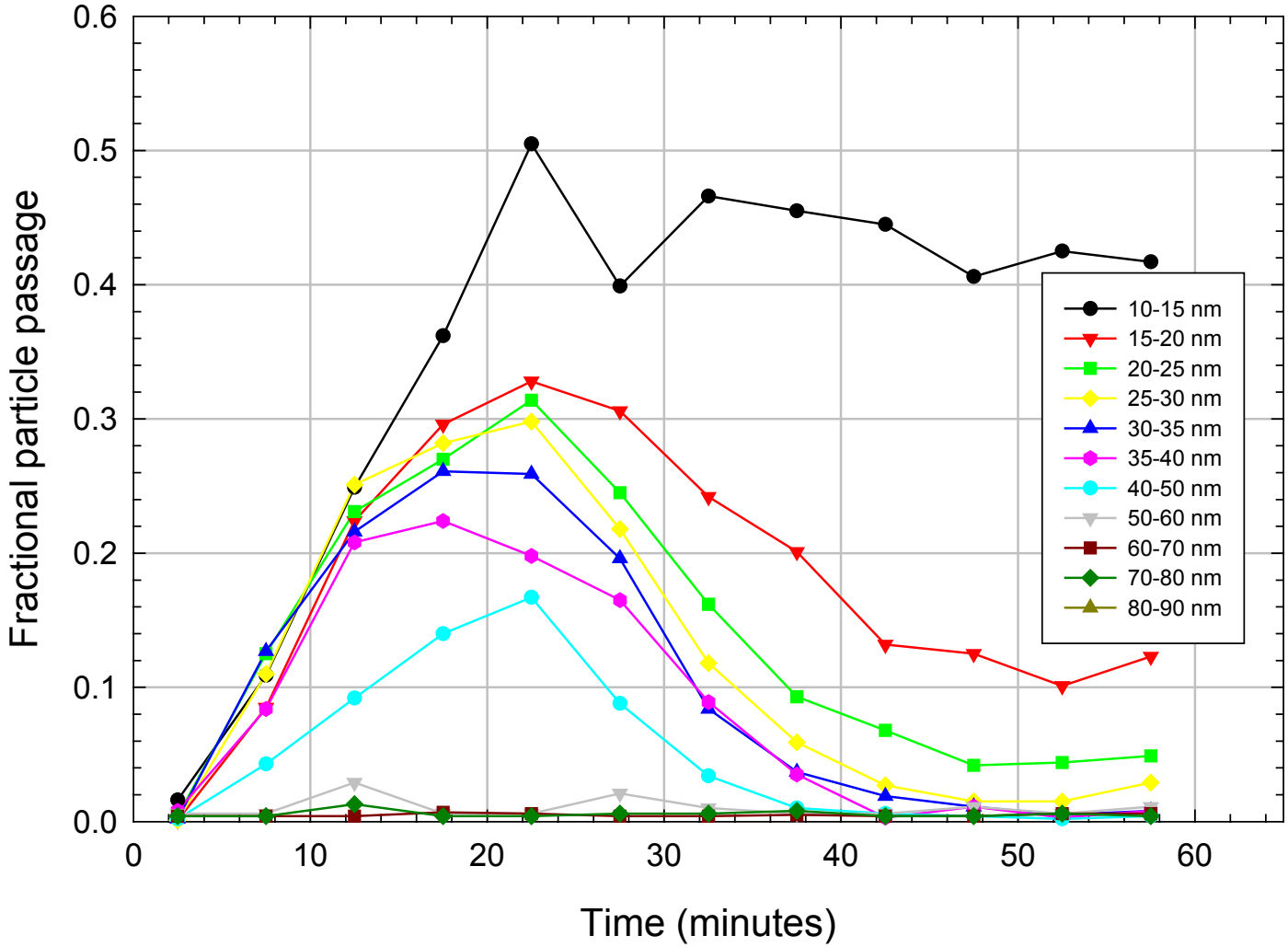


Filtrate concentrations over time





Example of filter retention over time



Summary

- A new method for the measurement of the working particle size distribution in colloidal suspensions has been described.
- The method allows measurement of particle concentrations as well as size.
- The method was shown to:
  - Accurately size and count PSL particles of known size
  - Allow measurement of the working particles in CMP slurries
  - Agree qualitatively with dynamic light scattering measurements of slurry working particle size distributions
  - Discern changes in slurry working particle size distributions induced by handling
  - When combined with single optical particle counting this technique allows measurement of particle concentrations from ~15 to > 10,000 nm
  - Allow measurement of particle retention by filters down to ~ 15 nm.