Simultaneous measurement of particulate and dissolved residue concentrations in colloidal dispersions

Mark Litchy[1], Donald Grant[1], Gary Schooneveld[1], Jim Farnsworth[2], Jacob Scheckman[2], Eric Willis[2] and Rob Caldow[2]

[1]CT Associates, Eden Prairie, MN, USA
[2]TSI Incorporated, Shoreview, MN, USA

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Introduction

- A new measurement technique has been developed that allows for measurement of particles in suspensions as small as 5 nm.
- Ability to quantify both the sizes and actual (not relative) concentrations of particles.
- Ability to measure both the dissolved non-volatile residue concentration and insoluble particle size distributions often simultaneously.
- The technique uniquely combines proven methods of counting and sizing aerosol particles with nebulizing technology to allow for measuring the particle size distribution of colloidal suspensions.

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Liquidborne Particle Sizing System

Nebulizer → Dryer

Liquid Particle Technology
Nanoparticle Nebulizer

Charge Neutralizer → DMA → CPC

Aerosol Technology
SMPS

How does it work?

- A colloidal suspension is dispersed into air as small, uniformly-sized droplets.
- The liquid is evaporated from the droplets and the size distribution of the resulting particles are measured.
- The suspension must be sufficiently dilute such that droplets formed contain either one or no particles prior to evaporation.
- Thus, the droplets dry to either the particle that was originally in the droplet **OR** to a “dissolved residue particle” whose size is determined by the concentration of dissolved material initially in the droplet.

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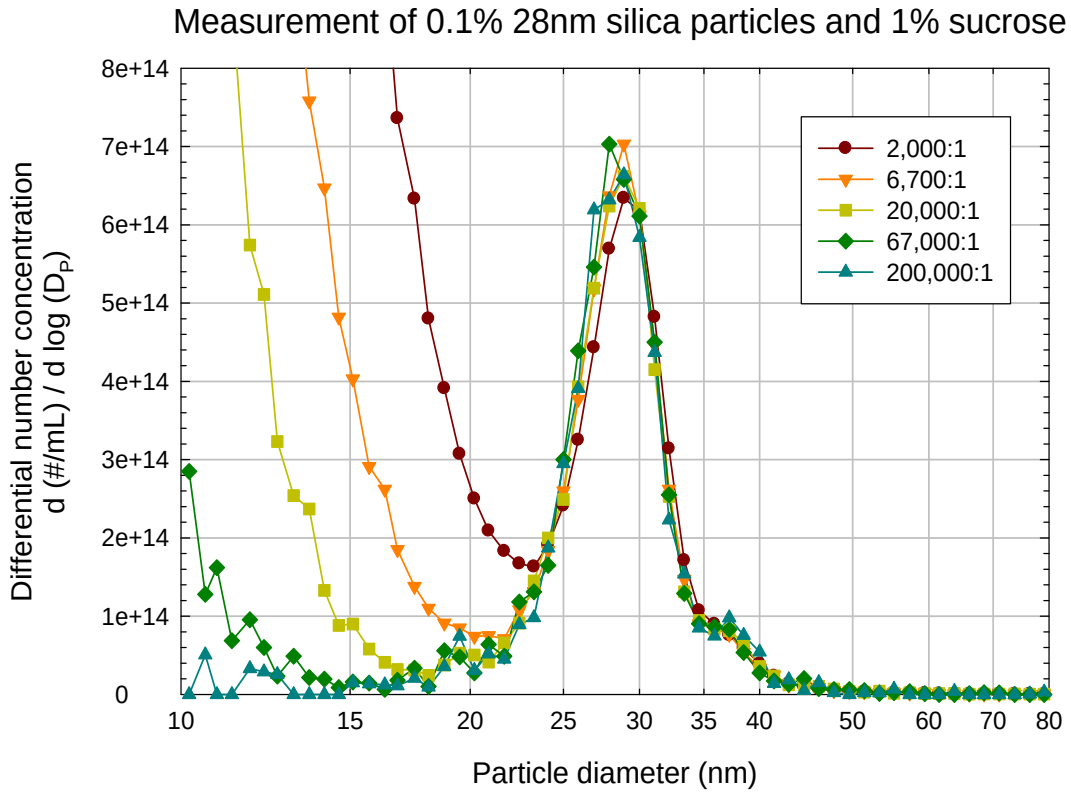
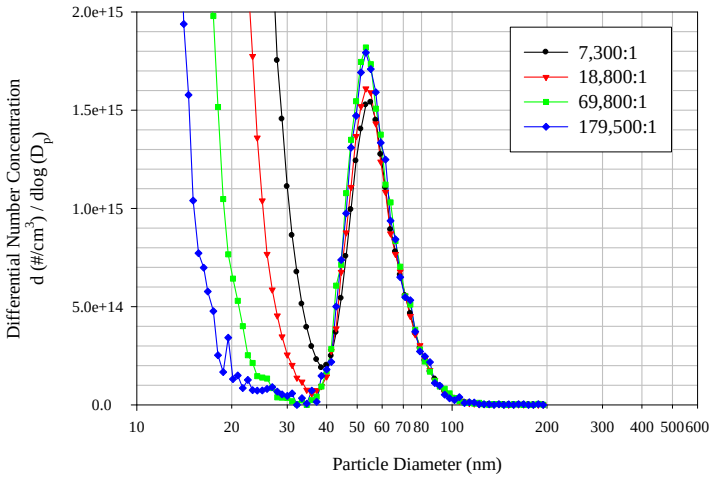
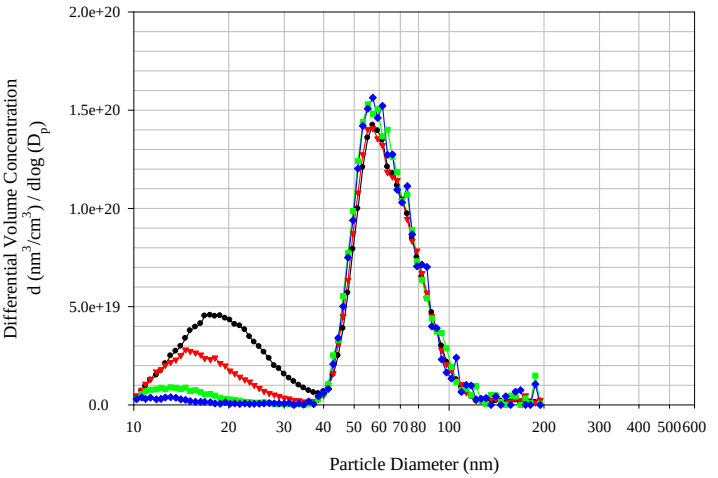
Distinguishing insoluble particles from “dissolved residue” particles



Measurement of a colloidal silica slurry with dissolved non-volatile residue





By increasing the dilution ratio, the dissolved non-volatile residue signature is shifted to smaller sizes, while the insoluble particle peak remains . In the volume distribution plot (right), the dissolved non-volatile peak was eliminated at the highest dilution ratio.

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Key technical challenge

1. Need to ensure that no more than 1 particle is present in each droplet
2. **AND** the amount of non-volatile dissolved residue in in each droplet is insufficient to produce a residue particle large enough to interfere with the insoluble particle analysis once the liquid in the droplet is evaporated

- Therefore, the nebulizer must produce small, uniformly-sized droplets.

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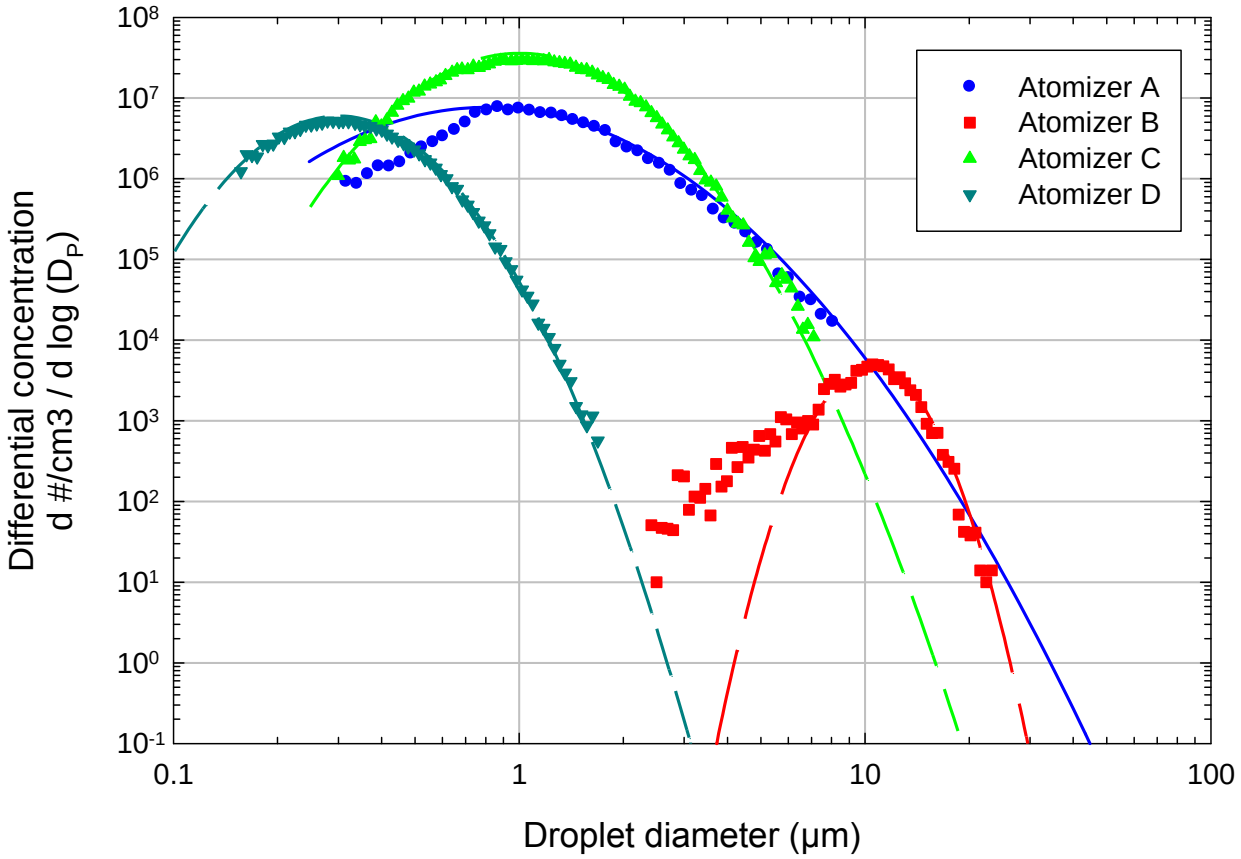
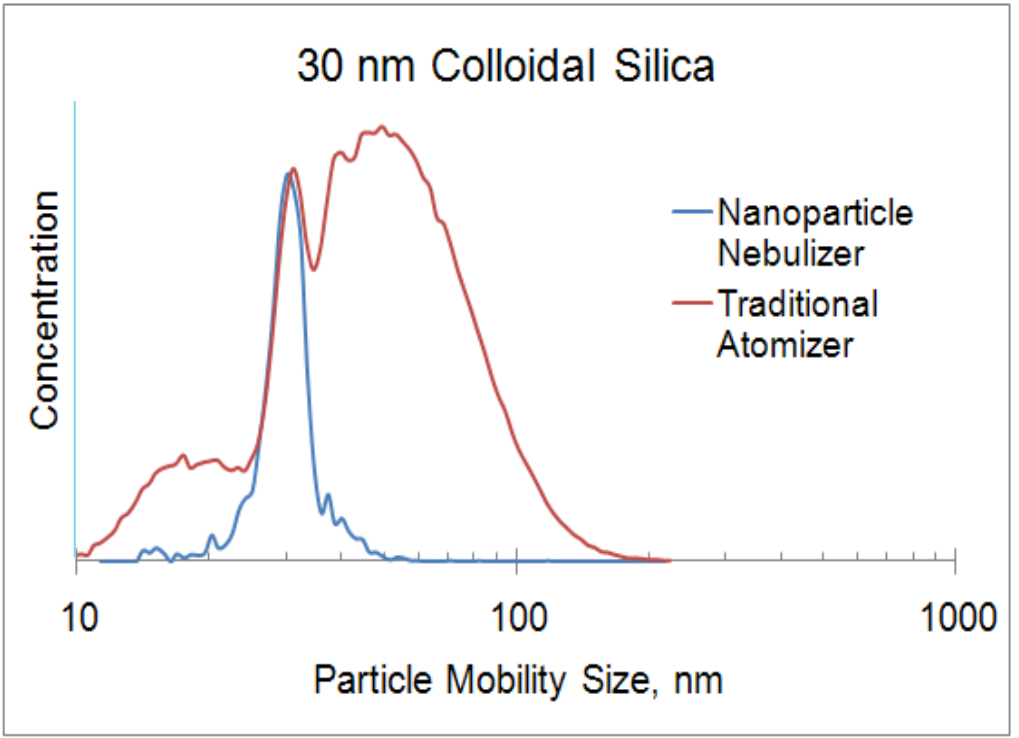
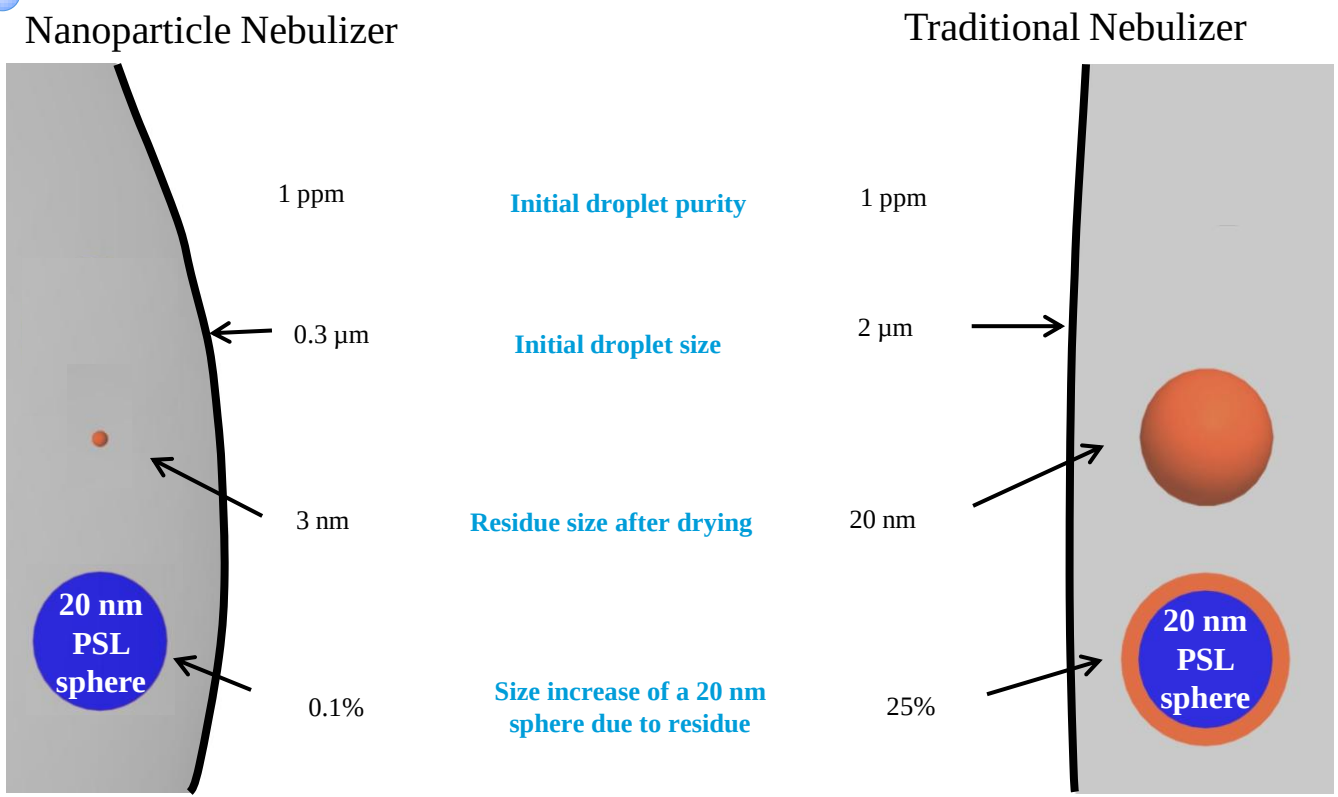
Droplet size distributions produced by different atomizers



Traditional vs. Nanoparticle Nebulizer



Dissolved Residue Interference



Liquidborne Particle Sizing System

Nebulizer → Dryer

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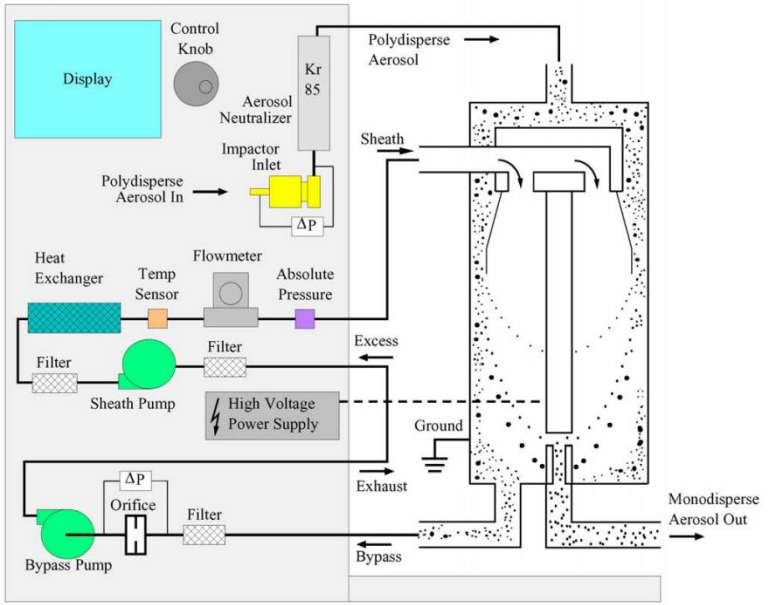
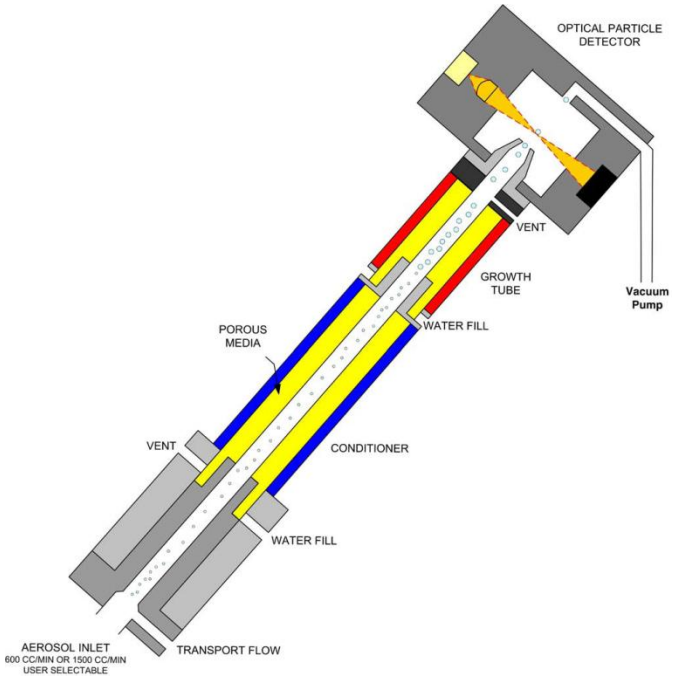
SMPS

SMPS measurement system

Differential mobility analyzer (DMA)



Water condensation particle counter (WCPC)



Advantages of this measurement technique

- Highly sensitive since individual particles are counted.
- Actual particle concentrations, not relative concentrations, are measured directly.
- Liquid number concentrations are measured directly.
- Shape of the particle size distribution is not assumed.
- Technique is independent of optical properties of the particles.
- Suitable for on-line or off-line measurements.
- On-line Dilution capability: 20:1 – 20,000:1.
- Lower detection limit ~5 nm assuming little soluble non-volatile residue in sample
- Instrument has broad operating range (10^8 to 10^{15} particles/mL)
- Based on proven SMPS technology used in the aerosol measurement community.

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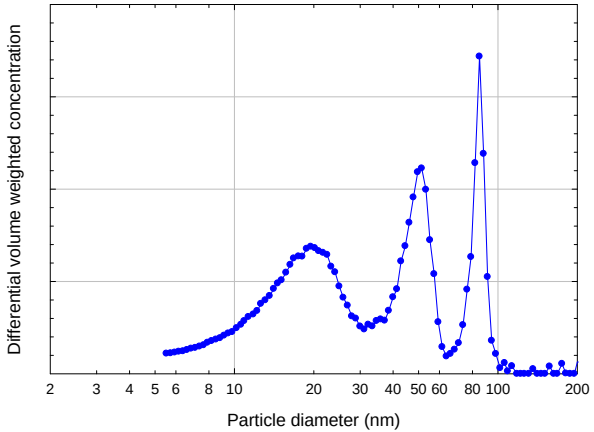
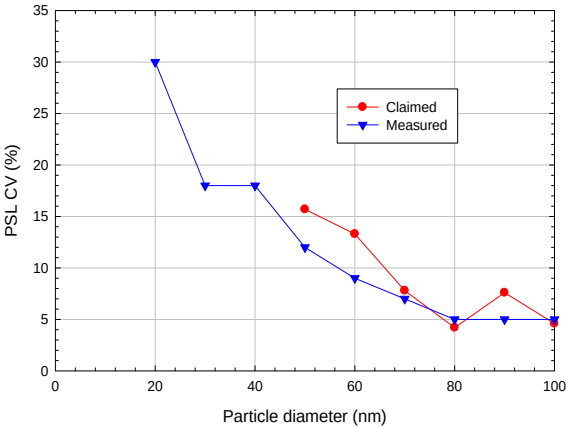
PSL Size Resolution and Analysis

Volume weighted size distribution



- Simultaneous measurement of 20, 50, and 83 nm PSL
- Instrument resolves each PSL size

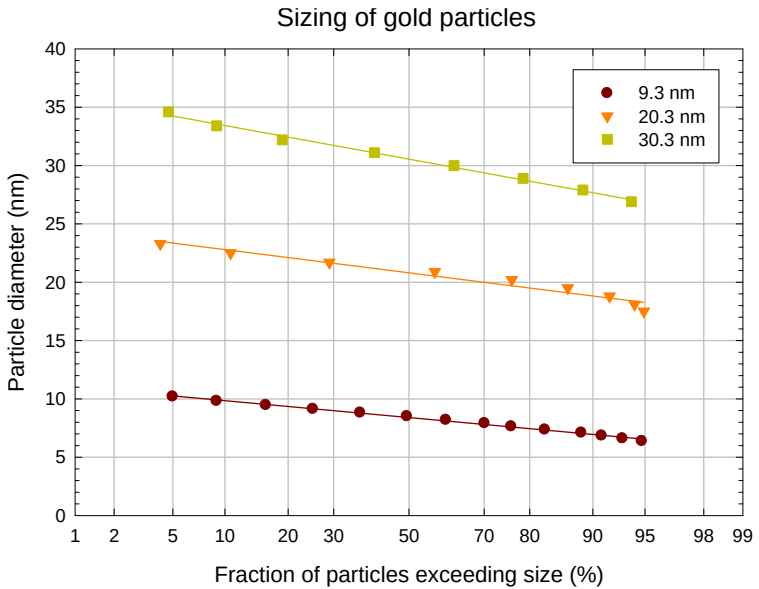
Coefficient of Variation (CV%) as claimed by Duke Scientific and as measured

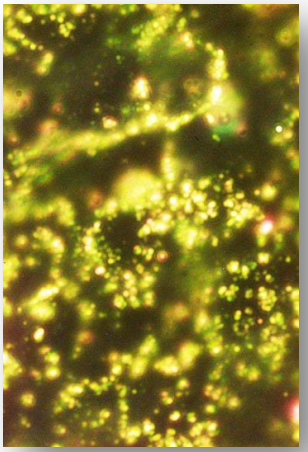


- Measured and claimed CV of individual sizes are similar indicating no variation due to instrument

Sizing of Gold Nanoparticles

Independent measurement of gold nanoparticles showing correlation to TEM data

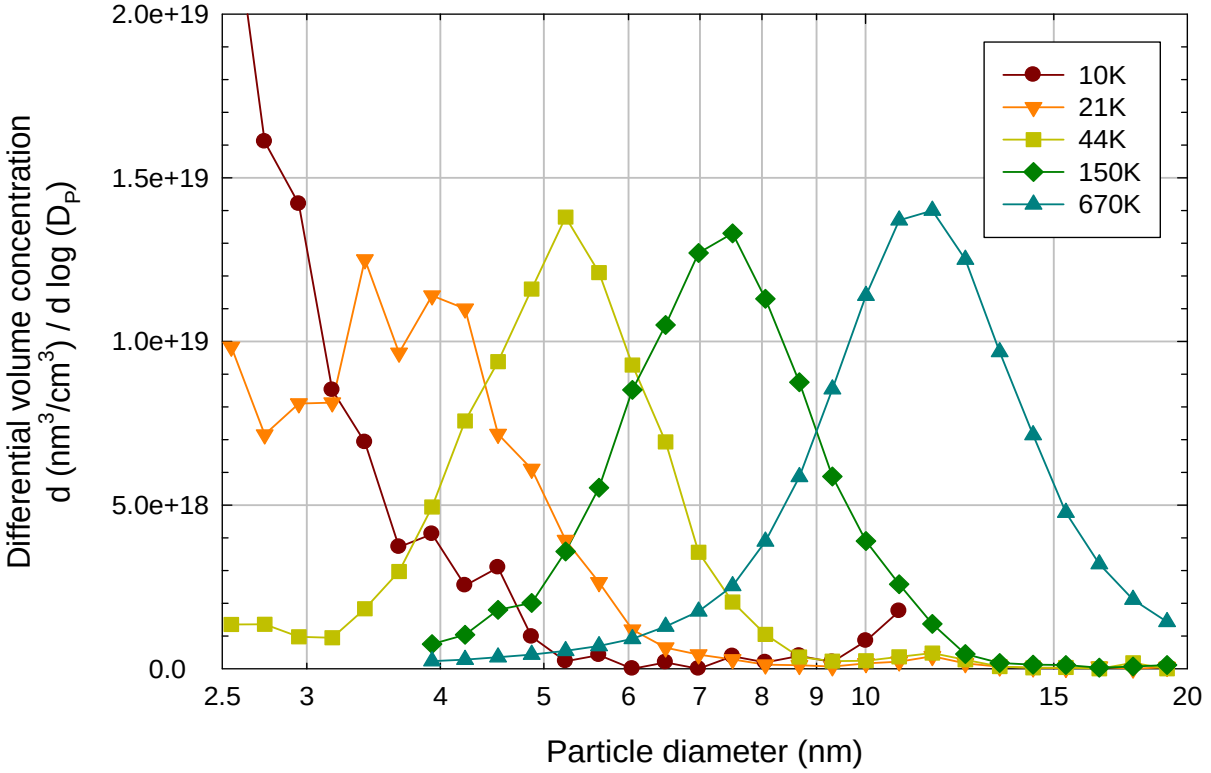




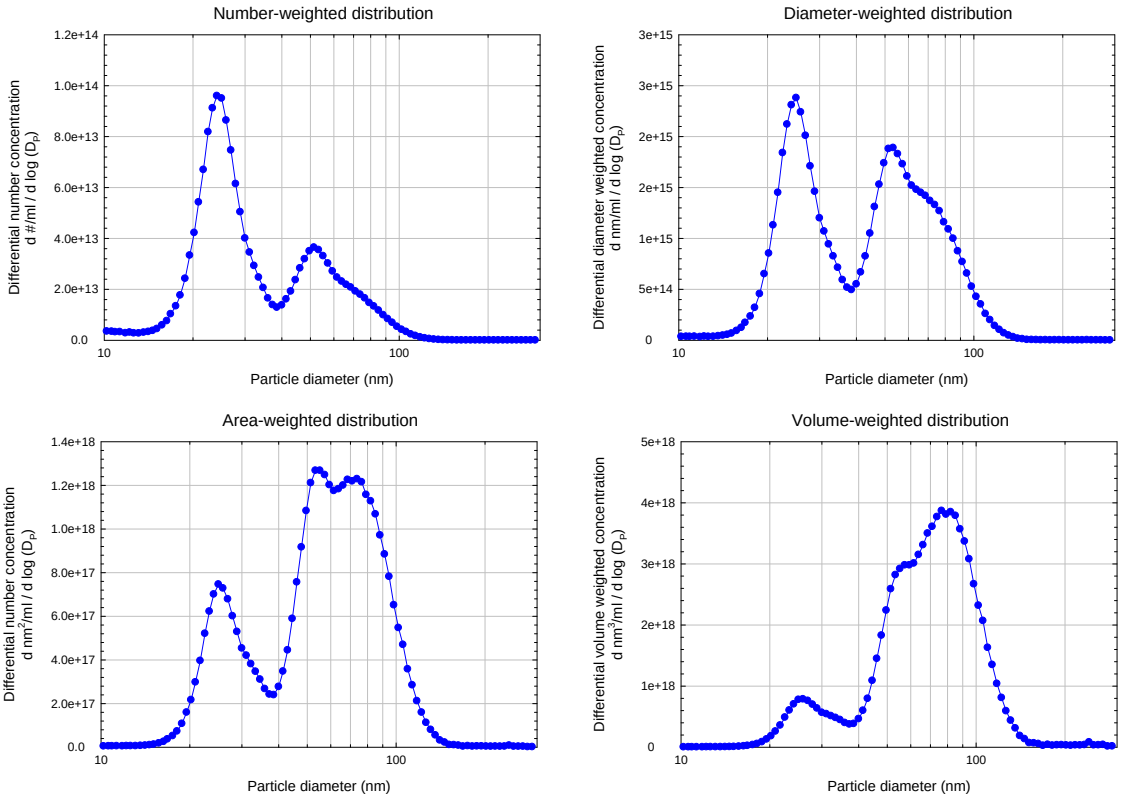
Gold nanoparticles

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

Sizing of Macromolecules

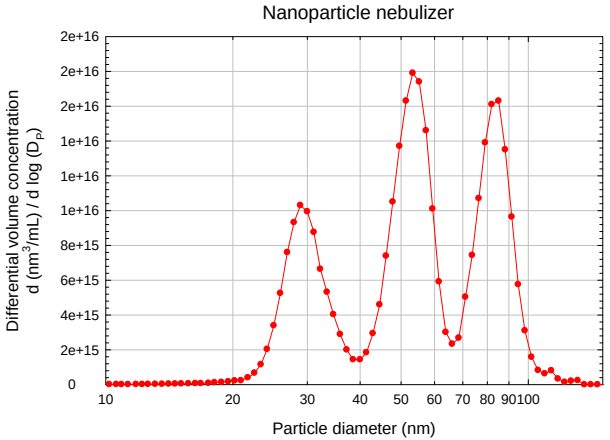


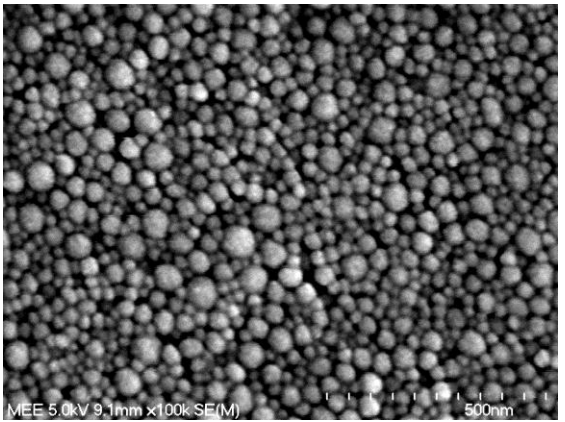
Example of a tri-modal colloidal silica slurry

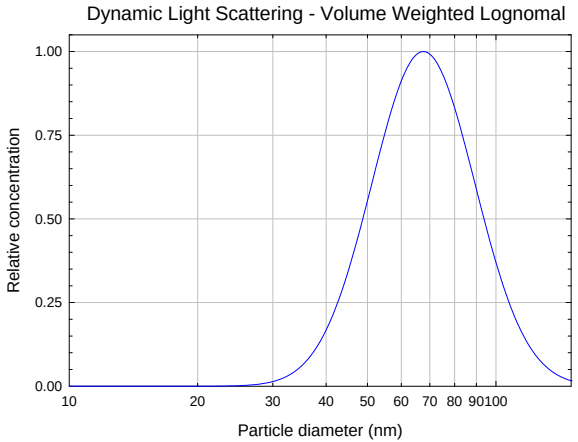


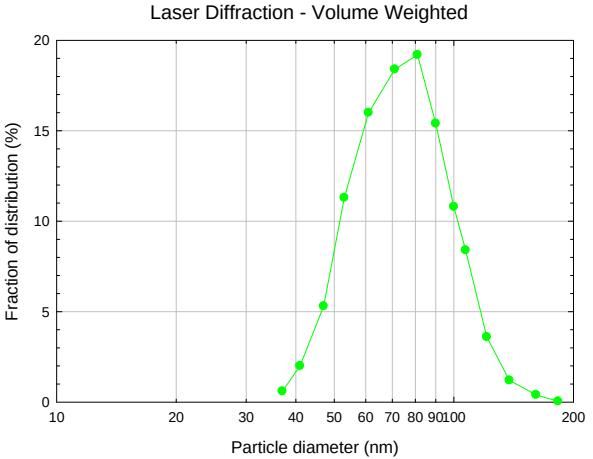
Alternative weightings such as surface area, volume, or diameter may be easily calculated from number-weighted distribution.

Comparison of Measurement Methods



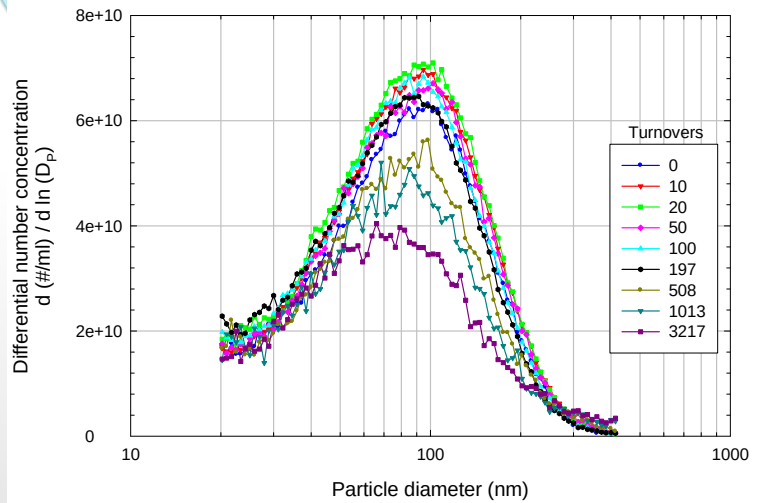




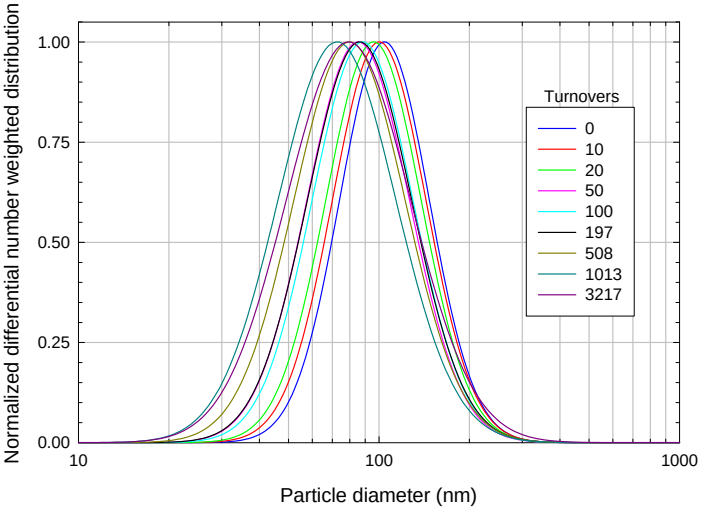


Actual particle concentration measurement vs. relative concentration measurement

UFA/SMPS

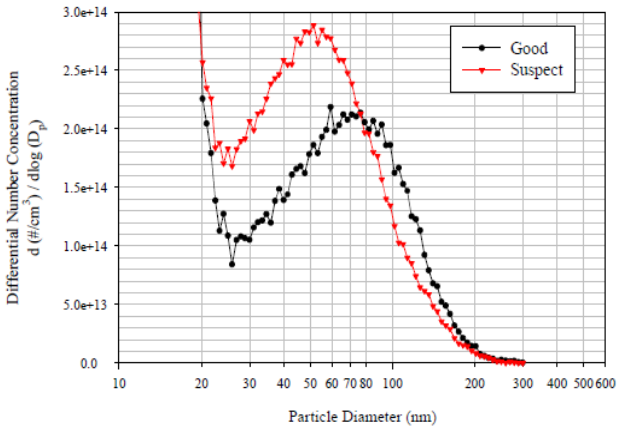


DLS

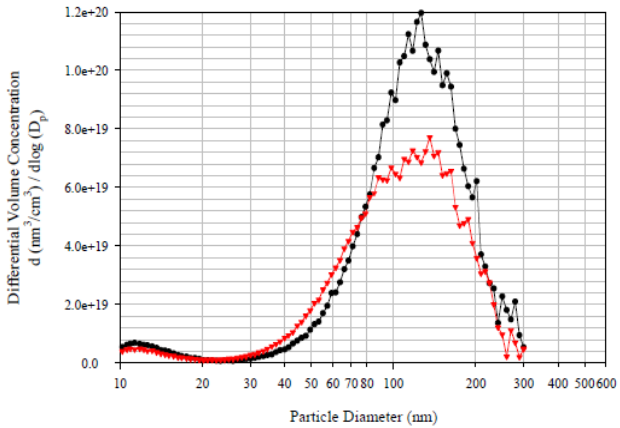


Identified batch of CMP slurry with a different polish rate

Number weighted size distribution



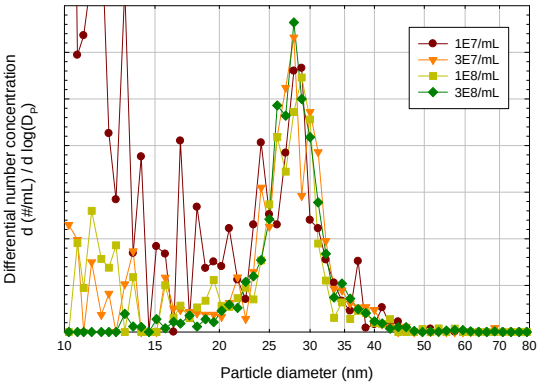
Volume weighted size distribution



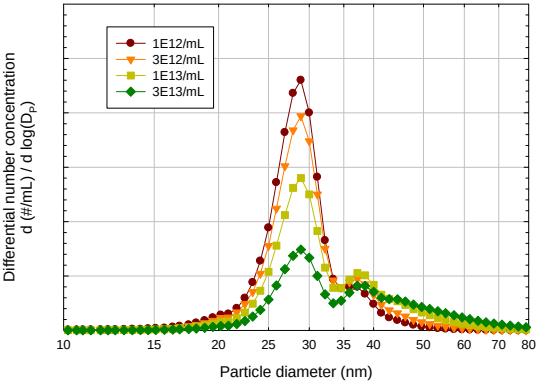
- Polishing rate of suspect slurry was 30% lower than good slurry.
- This method revealed approximately 30% less volume and a significant shift in the number distribution compared to a known good.

Calibration standard measured at low, “optimum”, and high concentrations

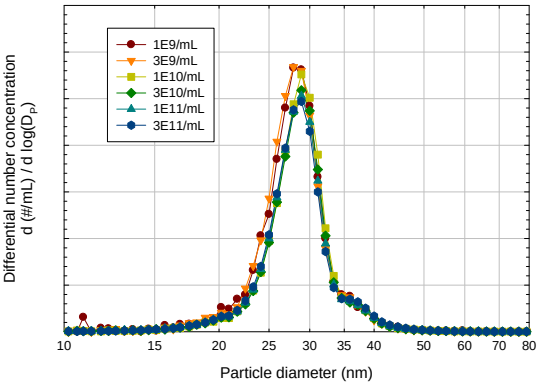
A. PSDs measured at lower concentrations



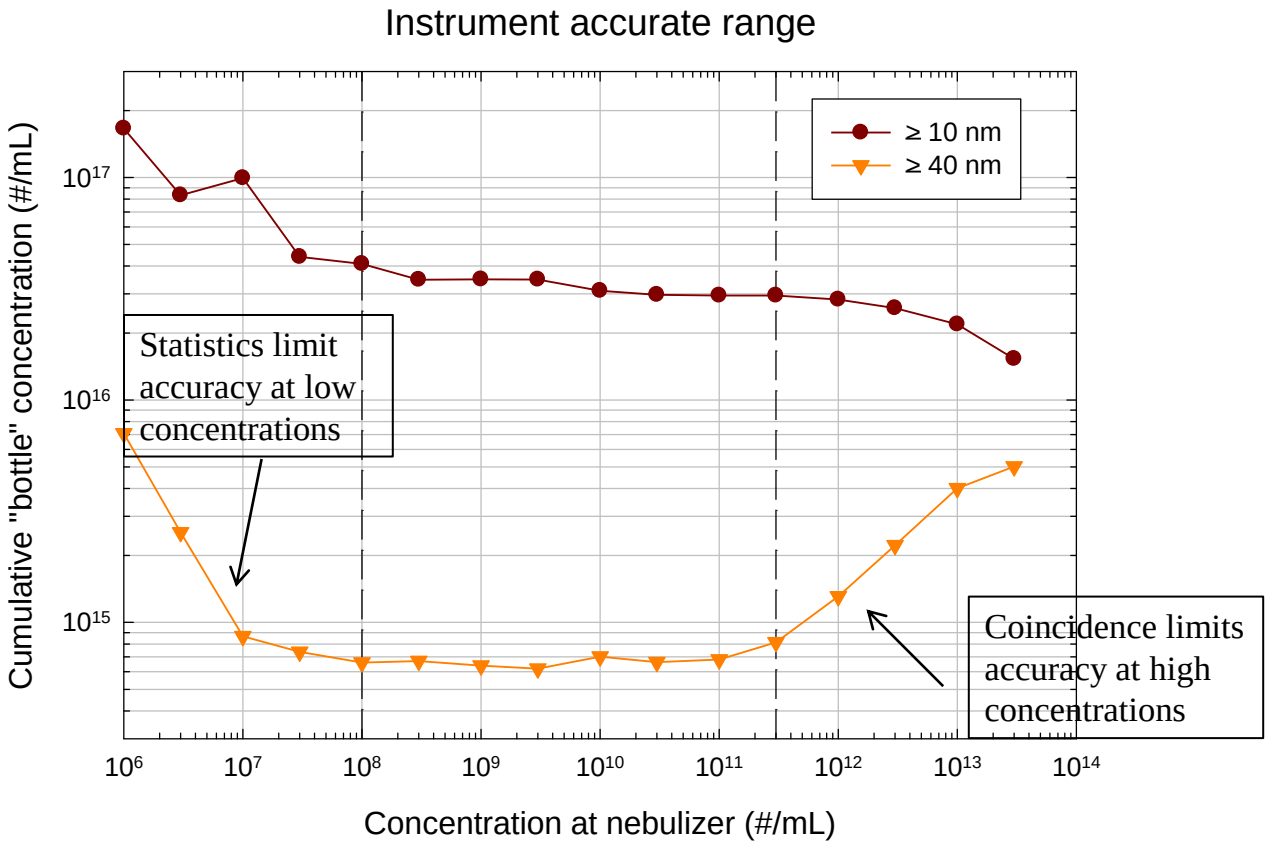
C. PSDs measured at high concentrations



B. PSDs measured at "optimum" concentrations



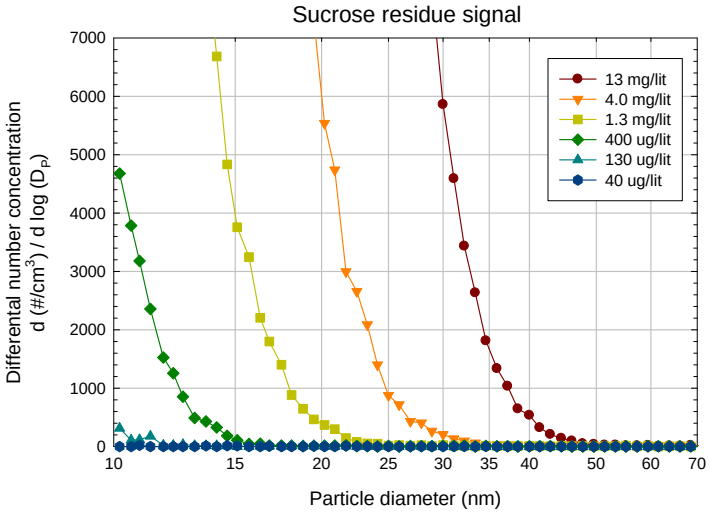
Broad optimum measurement range

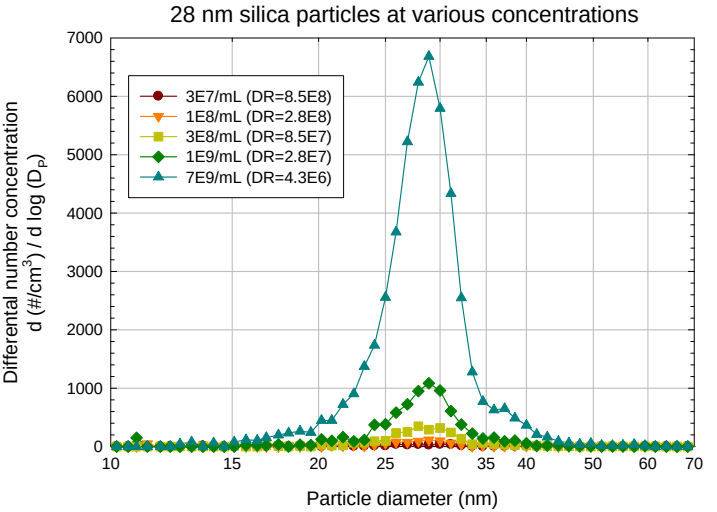


Measuring both insoluble particles and soluble residue

- Instrument is capable of separating insoluble particles and dissolved non-volatile residue.
- Ability to measure both the dissolved non-volatile residue concentration and insoluble particle size distributions often simultaneously.

Effect of varying dissolved residue and silica particle concentrations





- As dissolved residue concentration is decreased, the size of the resulting particles decreases

- As particle concentration is decreased, the size distribution remains unchanged, only the concentration decreases

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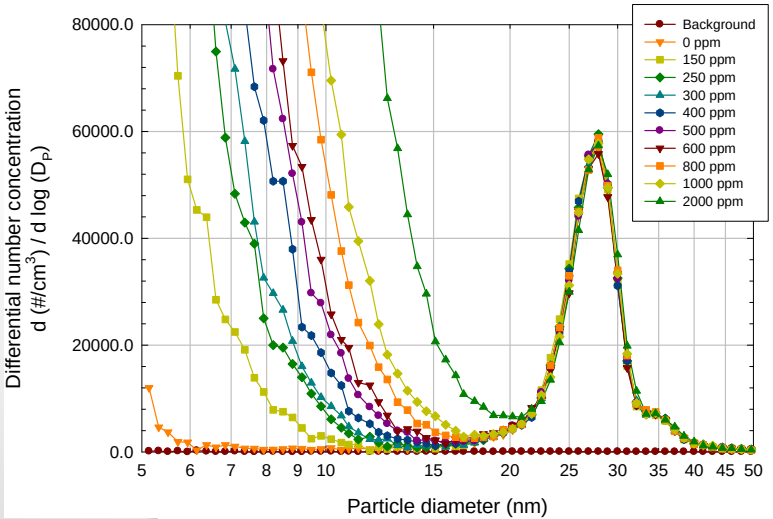
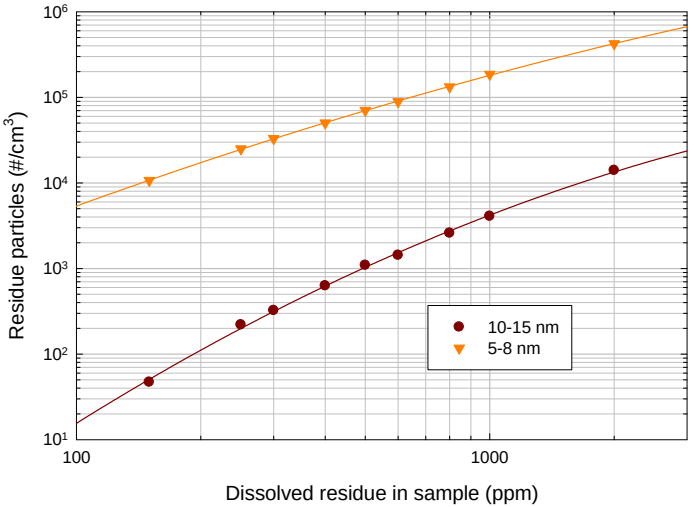
28 nm silica particles with varying amounts of dissolved non-volatile residue





- These data can be used to generate a calibration curve relating the concentration of particles formed from the soluble residue to the mass concentration of soluble residue.

Summary

- Instrument is capable of separating insoluble particles and dissolved non-volatile residue.
- Ability to measure both the dissolved non-volatile residue concentration and insoluble particle size distributions (size and concentration ~5 to 500 nm) often simultaneously.
- Highly sensitive since individual particles are counted.
- Actual liquid number concentrations, not relative concentrations, are measured directly.
- Shape of the particle size distribution is not assumed.
- Technique is independent of optical properties of the particles.
- Suitable for on-line or off-line measurements.
- On-line Dilution capability: 20:1 – 20,000:1.
- Size range ~5-500 nm
- Based on proven SMPS technology used in the aerosol measurement community.

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