Method Development for Dynamic Light Scattering

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Outline

- Introduction
- Suspension
- Filtration/clarification
- Sample cell choice
- Concentration
- Duration
- Number of Repeats

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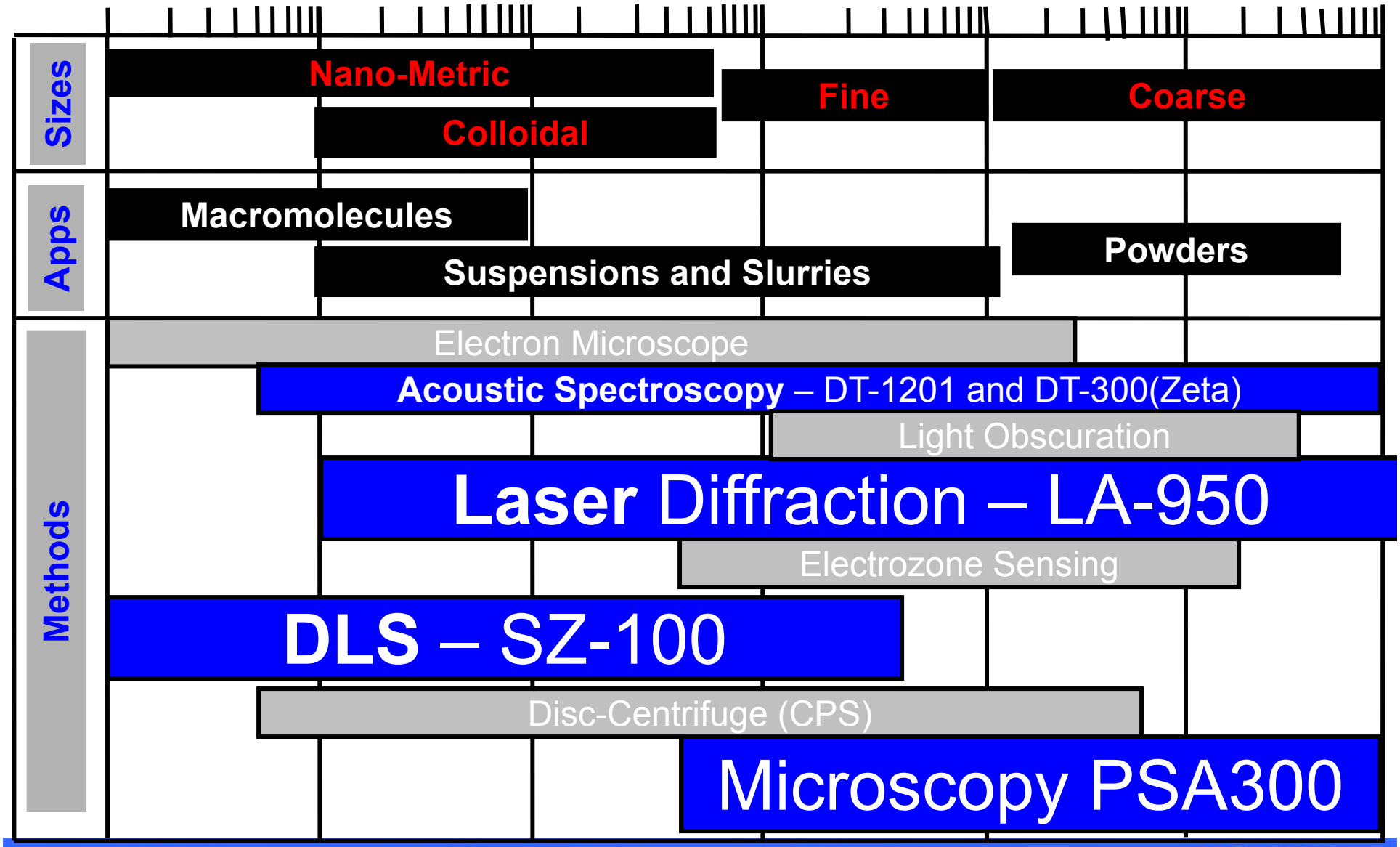
Particle Diameter (μm)



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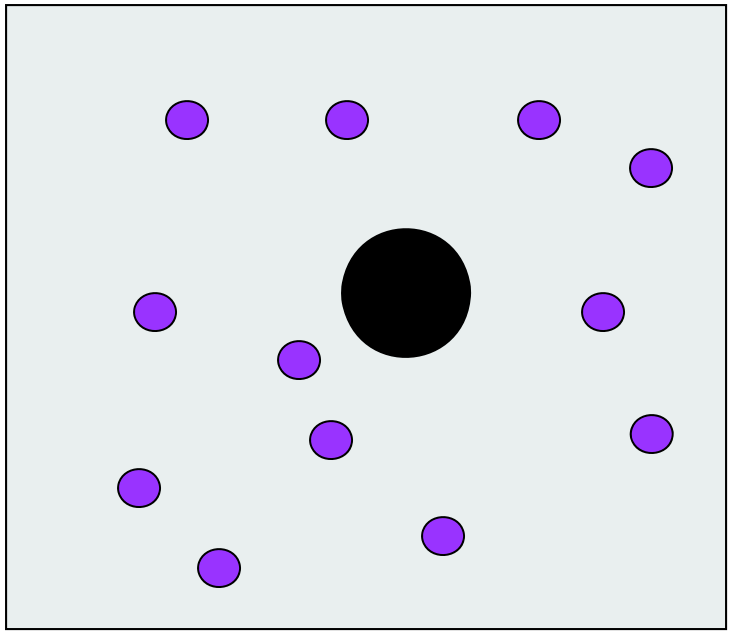
Brownian Motion

Particles in suspension undergo Brownian motion due to solvent molecule bombardment in random thermal motion.



- Brownian Motion
  - Random
  - Related to Size
  - Related to viscosity
  - Related to temperature

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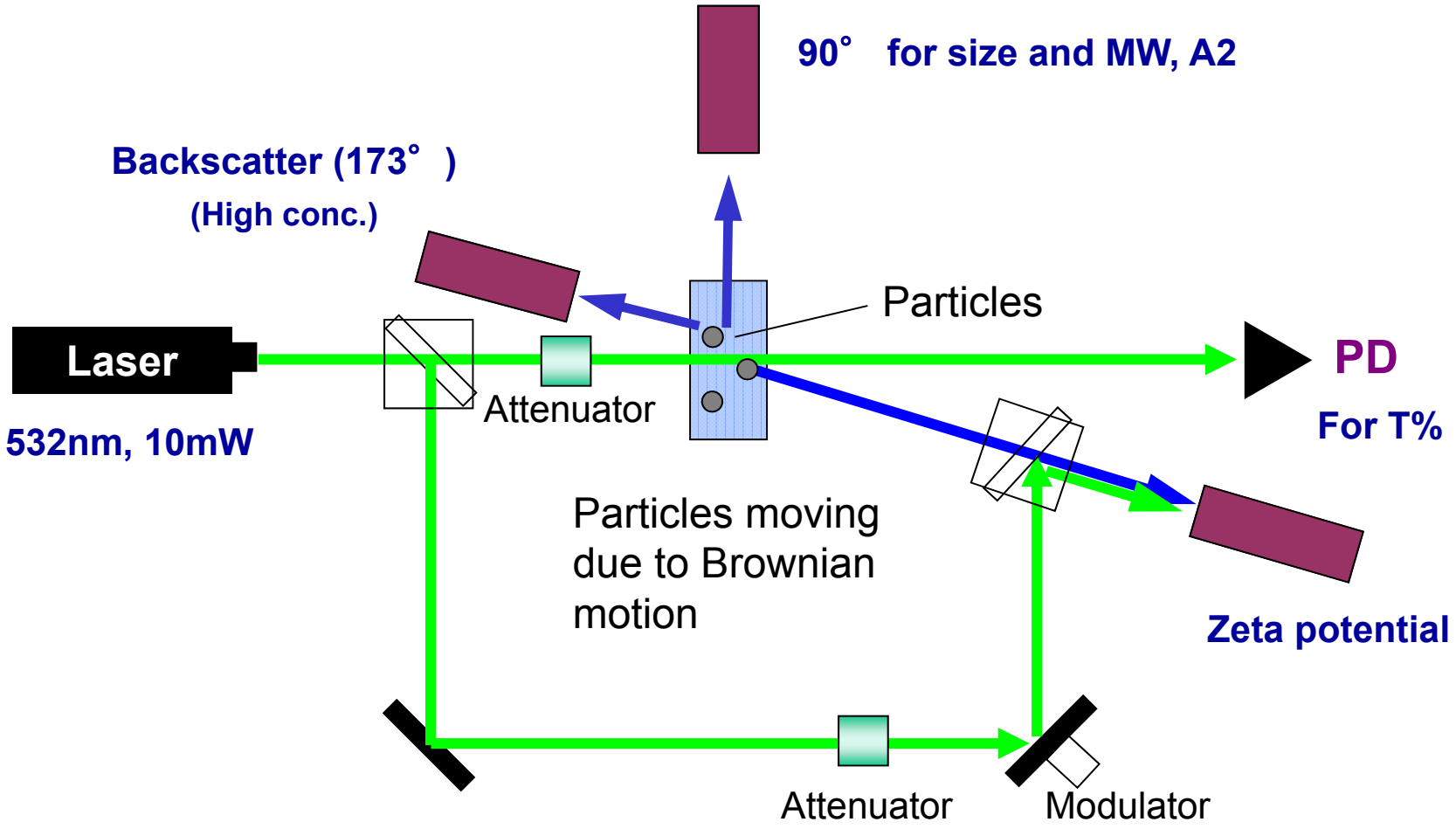
DLS Optics



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Why DLS?

- Non-invasive measurement
- Requires only small quantities of sample
- Good for detecting trace amounts of aggregate
- Good technique for macro-molecular sizing

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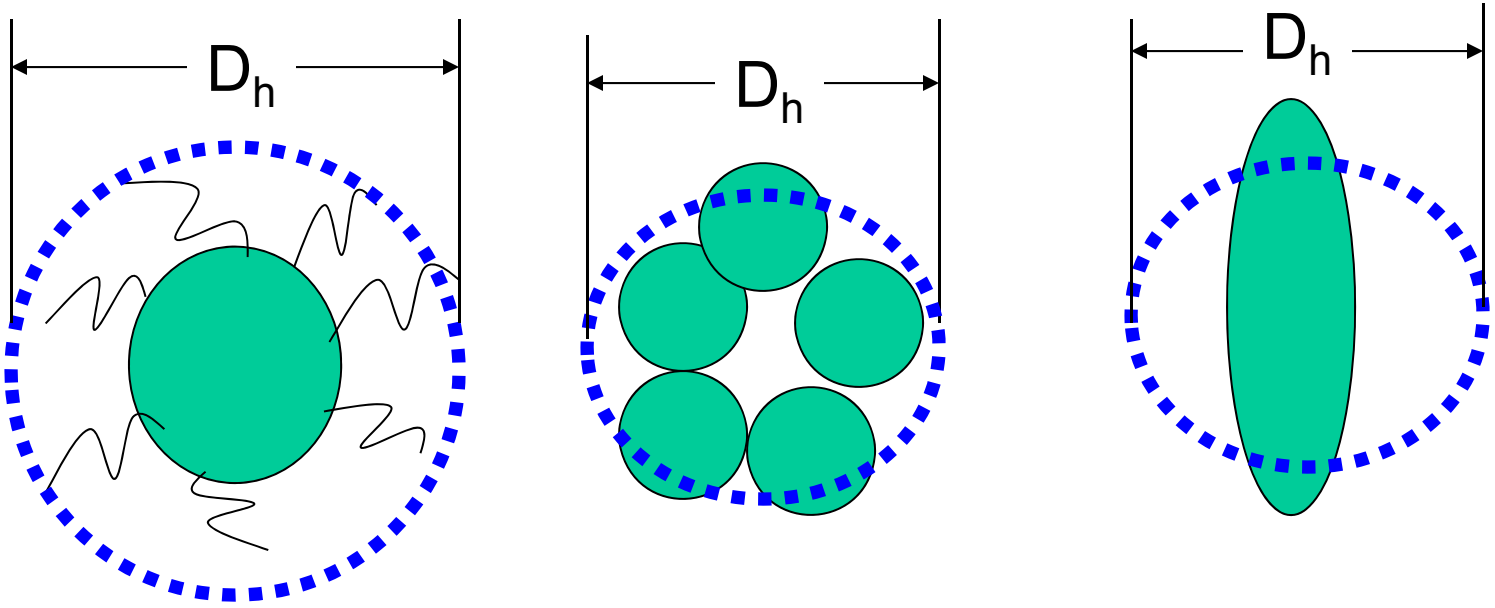
What is Hydrodynamic Size?

- DLS gives the diameter of a sphere that moves (diffuses) the same way as your sample.



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The SZ-100

- Single compact unit that performs size, zeta potential, and molecular weight measurements.

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Suspension

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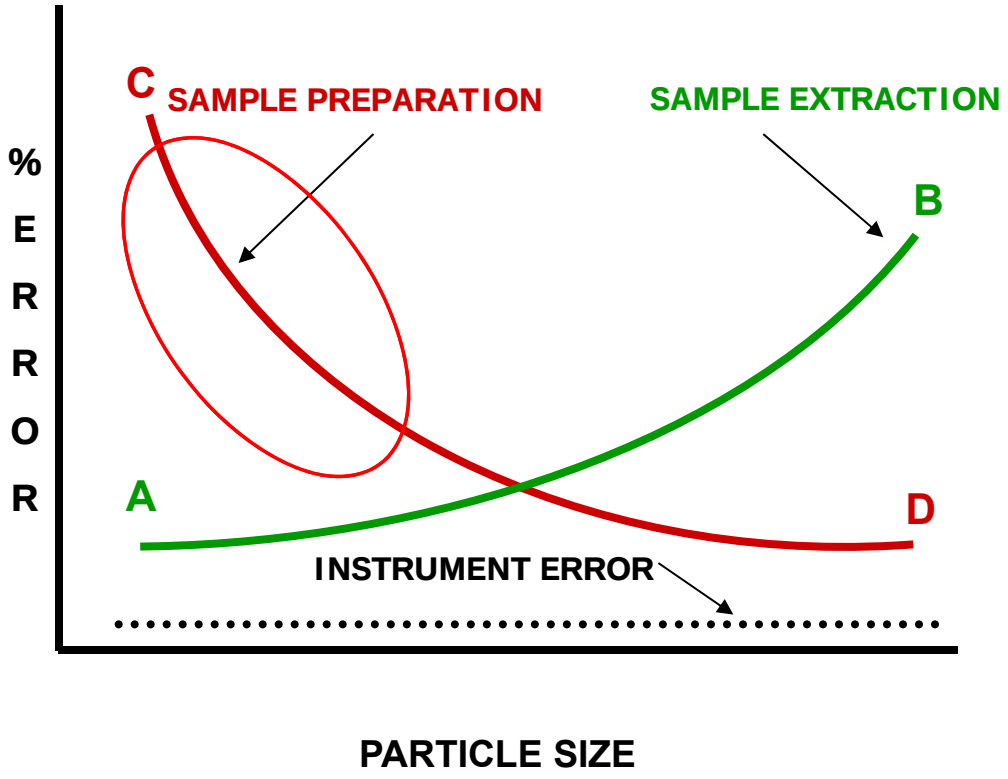
Measurement Error Sources

SMALL PARTICLES

- POTENTIALLY SMALL EXTRACTION ERRORS (A)
- POTENTIALLY LARGE SAMPLE PREP ERRORS (C)

LARGE PARTICLES

- POTENTIALLY LARGE EXTRACTION ERRORS (B)
- POTENTIALLY SMALL SAMPLE PREP ERRORS (D)



INSTRUMENT ERROR IS SMALL AND RELATIVELY CONSTANT

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Dispersion Strategies

- Powders
  - Choose liquid (avoid dissolution)
  - Wet powder (surfactant)
  - Dispersing aid to avoid re-agglomeration
  - Energy to break agglomerates into primary particles - ultrasound
- Suspensions
  - Choose diluent
  - Energy to break agglomerates into primary particles - ultrasound

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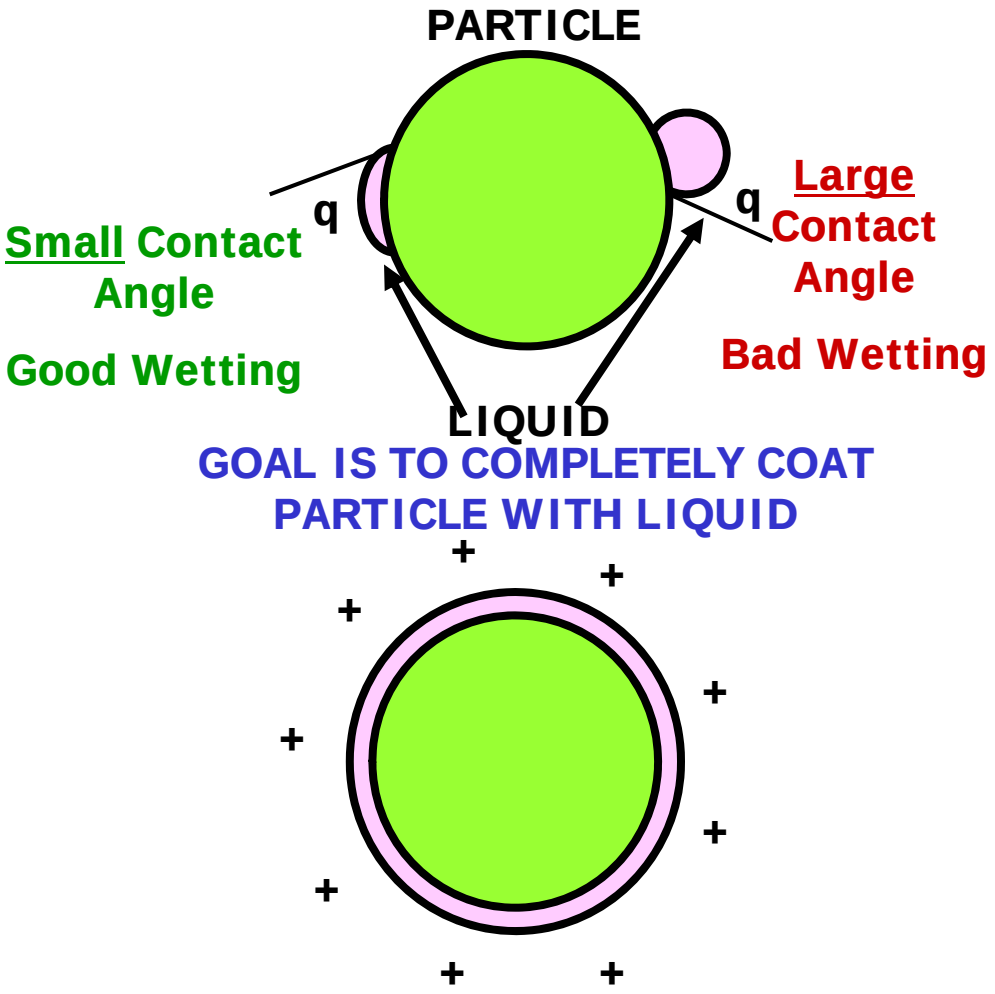
Particle Wetting

Surface Tension must be lowered so liquid will adhere to particles.



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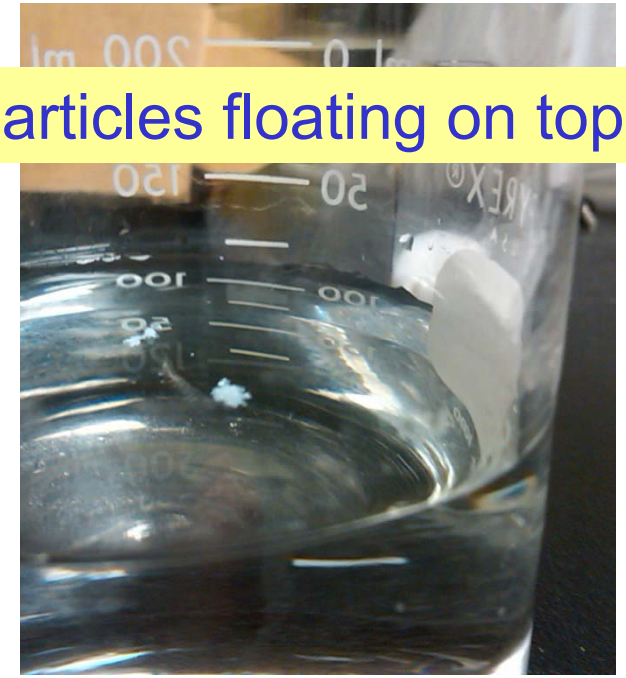
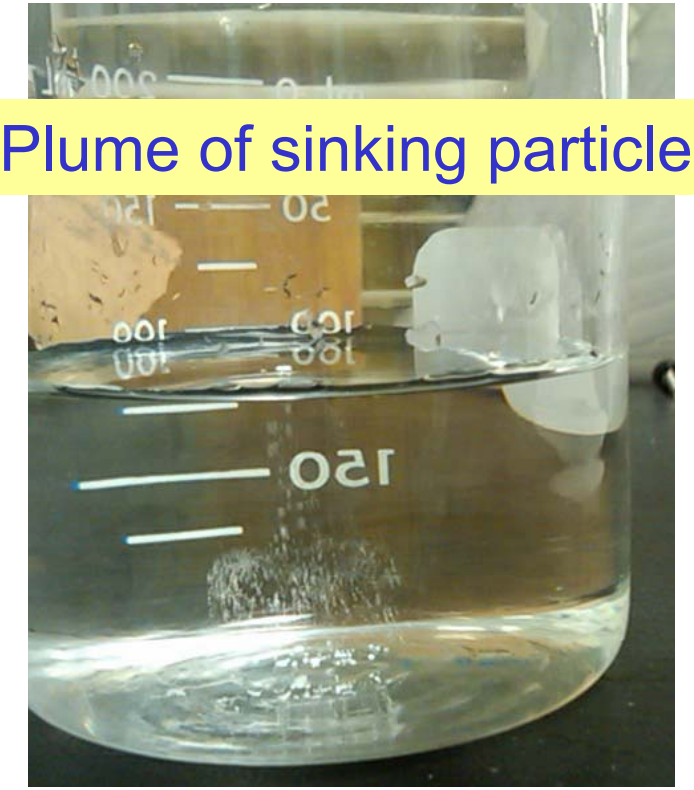
How to check for wetting

- Sprinkle particles on top of target dispersant. If the particles float on top and do not penetrate the water surface, they are not wetted. This is usually a bad sign.
- If the particles break through surface and sink, they are a) wetted or b) so big that gravity is more important than surface tension. If it is case (a), you are in luck.



Particles floating on top



Plume of sinking particles

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Changing solvents

- Working with aqueous systems is usually easier for many reasons.
- But don’t forget to try a less polar solvent such as isopropyl alcohol.
- And, don’t forget that organic solvents are more difficult to handle due to fire and health hazards.

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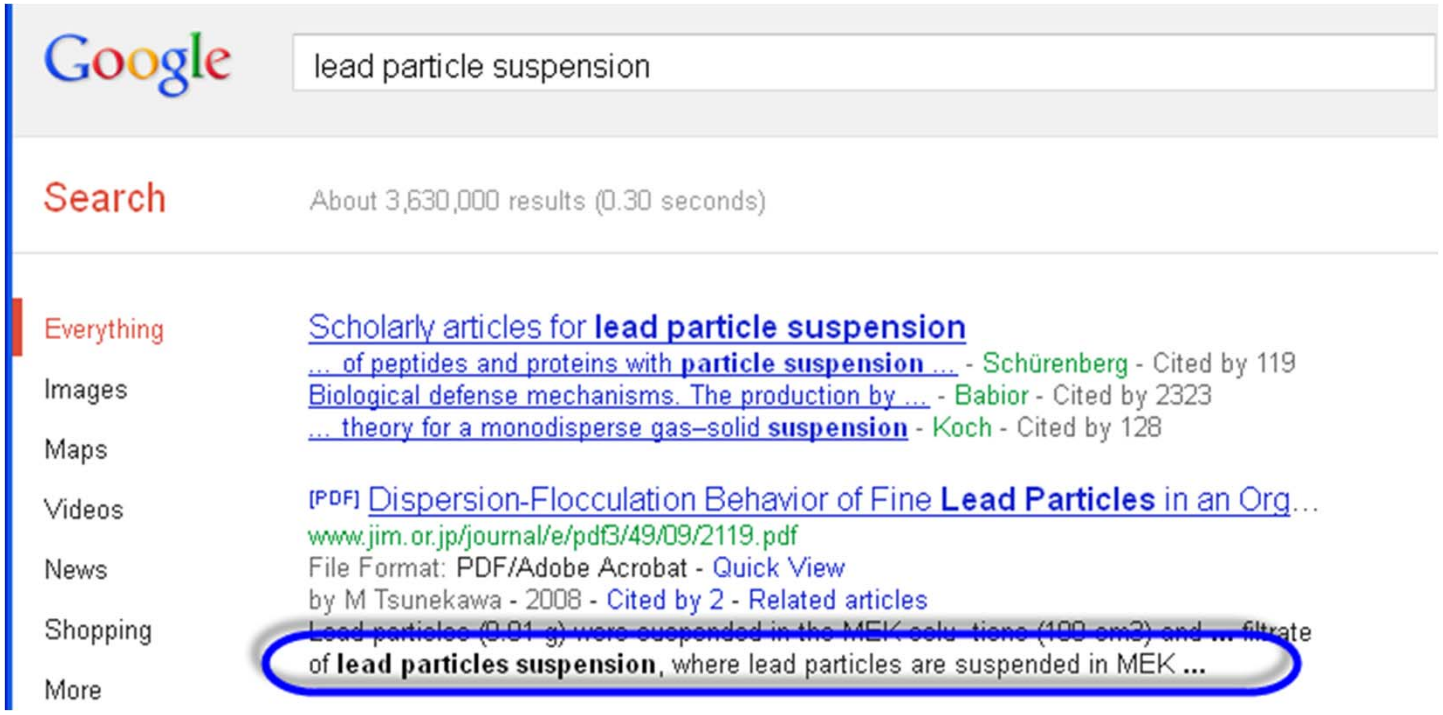
If the going gets tough…

- Check the literature and the web and see what other people use.
- Here I use Google to get the idea to use MEK with lead.



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If the going gets tough…

- Try a series of options.
- Here I make a series of suspensions and check them by eye, then measure.

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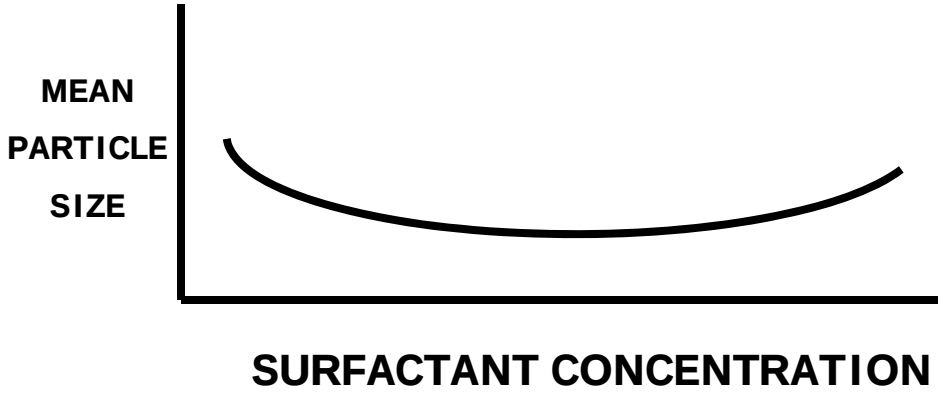
Effect of Surfactant Addition

Addition of surfactant to a sample will disperse the particles so a proper measurement may be made. However, addition of too much surfactant will cause agglomeration.



The graph illustrates that there is an optimum amount of surfactant to effect optimum dispersion. The Particle Size Analyzer can determine when the amount of surfactant exceeds the proper concentration.

As initial surfactant is added, the mean particle size will decrease. It will reach a minimum as the proper surfactant concentration is reached.

As additional surfactant is added, the apparent mean particle size will increase, indicating agglomeration of particles.

Common concentration: 0.01-0.1%

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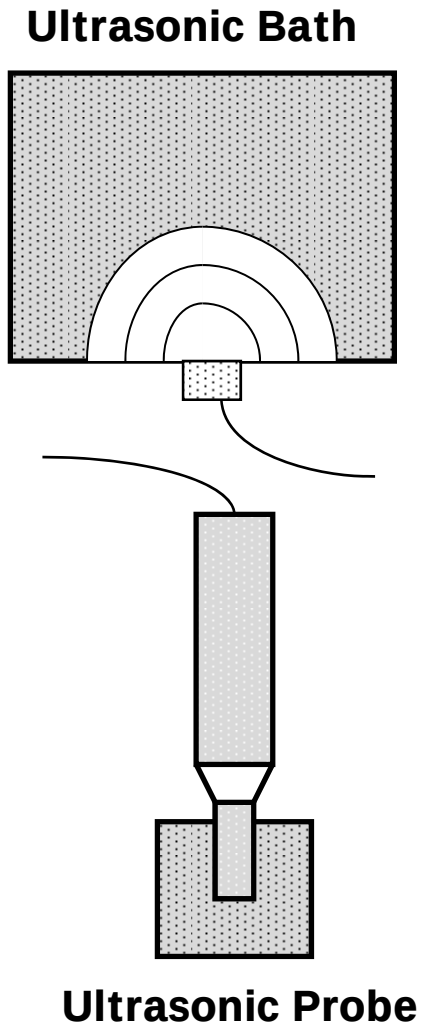
Dispersion: Ultrasonic Energy

- Ultrasonic waves generate microscopic bubbles or cavities (cavitation) which produce shearing action causing the liquid and suspended particles to become intensely agitated.

- Agglomerates are broken apart.
- In some cases fragile particles are shattered.
- The selection of appropriate type and level of ultrasonic energy must be made carefully.



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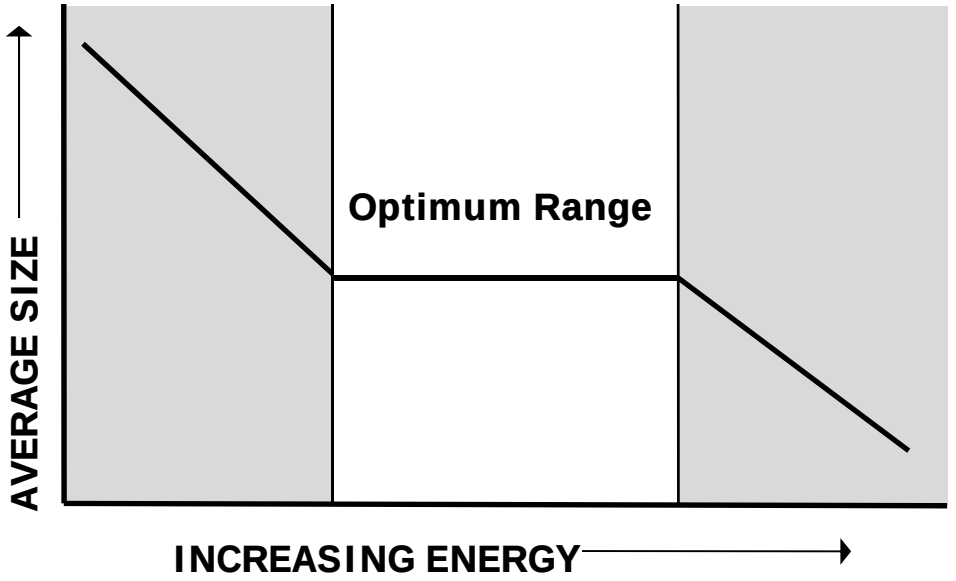
Effect of Applied Energy

- The effect of applied energy is to break up agglomerates into individual particles for size measurement. However, if too much energy is applied, particles may by broken into fragments. The desired result is to apply just enough energy to disperse material into basic particles for measurement without damaging friable materials.



- The graph illustrates how this can be accomplished. Effects of applied energy on particulate samples can be tested by using results from measurements made on the instrument. By treating the sample with varying levels of ultrasonic power, performing analyses, and noting the average particle size (mean, median) as a function of power level, one can choose a range of applied energy that is optimum for that material.

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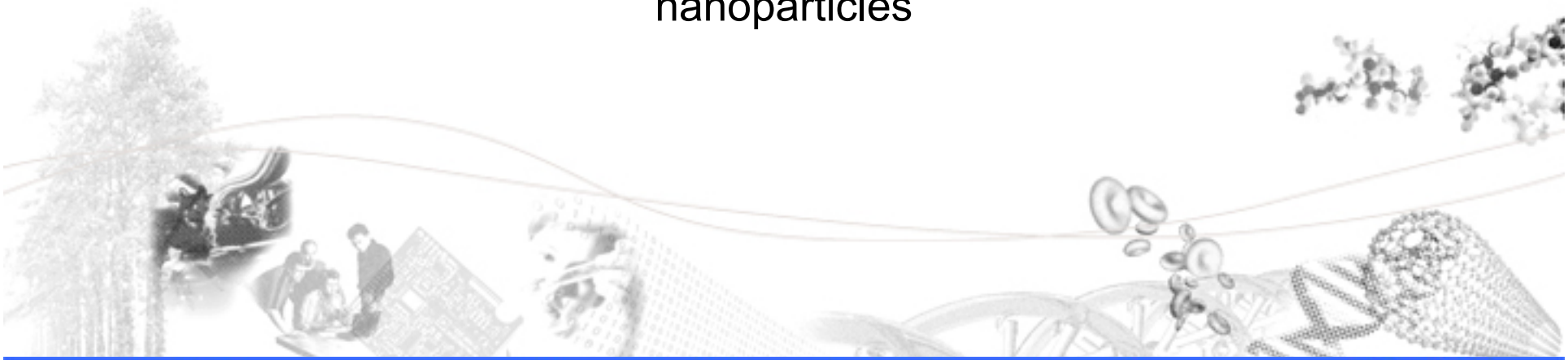
Filtration/Clarification

Because large dust particles scatter more than nanoparticles



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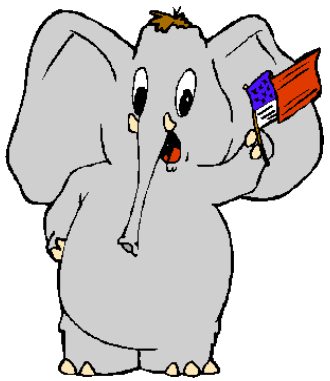
Dust

Dust: large, rare particles in the sample
Generally not really part of the sample



The elephant in the room…..(to twist an expression slightly)

- African elephants weigh on average 3000kg
- A praying mantis weighs about 3 g

There is a 1 million times difference in volume (assuming equal density)

The same difference between 10 μm dust particle and a 10 nm nanoparticle

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What happens?

- If you see elephants (dust), it is hard to notice the praying mantis' (nanoparticles).

- Use a fence (filter) to keep out the elephants….

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Filtering Sample

- If sample has large particle contamination and particle is small enough to pass through a filter, then filter entire suspension.
- If filtering sample, be careful! Filtering can remove large particle contamination that is important.
- Choose filter with pore size twice the size of the largest particle of interest.
- I generally use 0.1 or 0.2 micron filters

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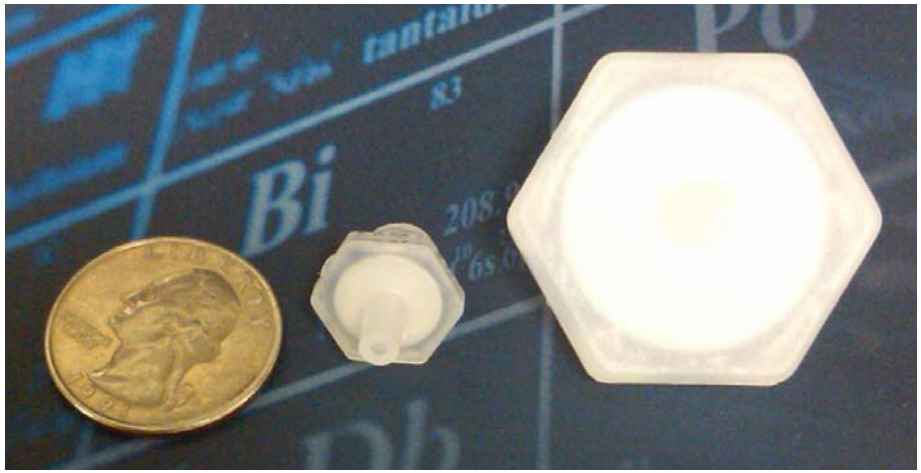
Choosing Filters

- Syringe type filters stay sealed (less introduction of dust from outside)
- Diameter
  - 10 mm diameter – cheaper, good for small volumes, less holdup
  - 25 mm diameter – a little more expensive, more holdup, but last for larger volumes (e.g., diluent)



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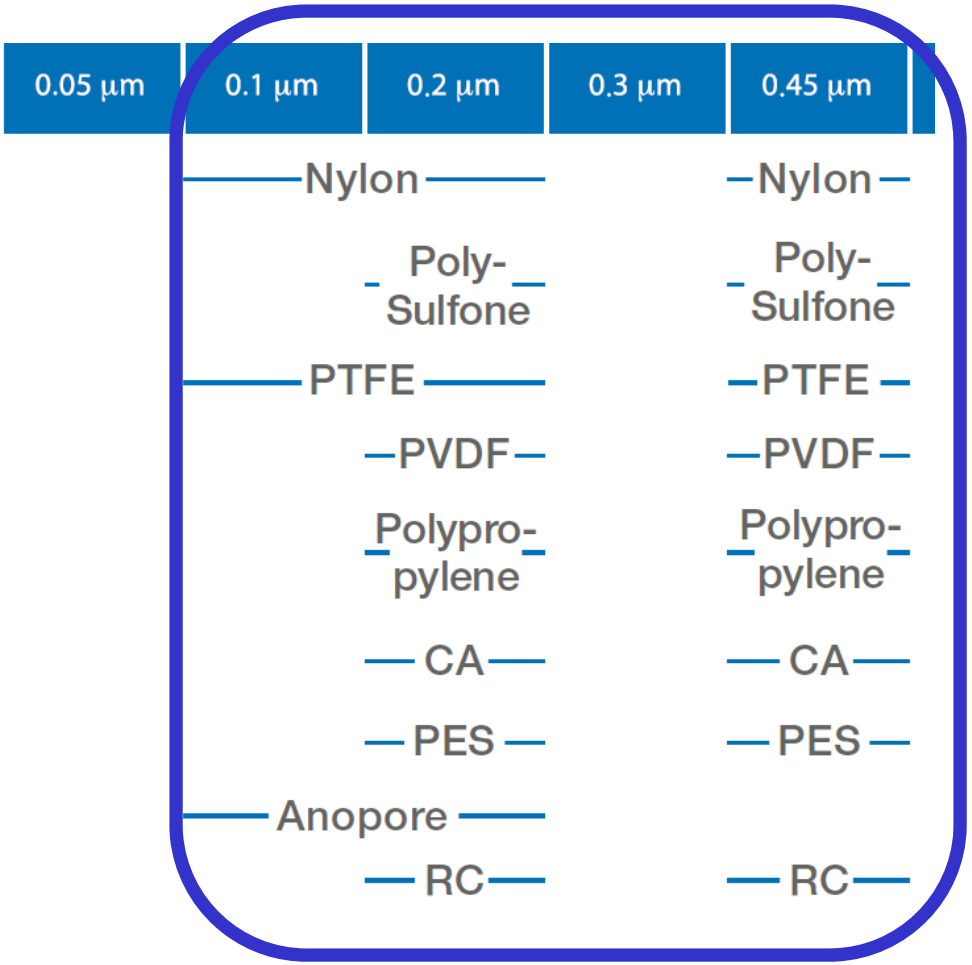
Choosing Filters

- Material: Many materials are available
- Choose material based on compatibility with your sample and liquid.
- Pay attention to price

Whatman filter materials:



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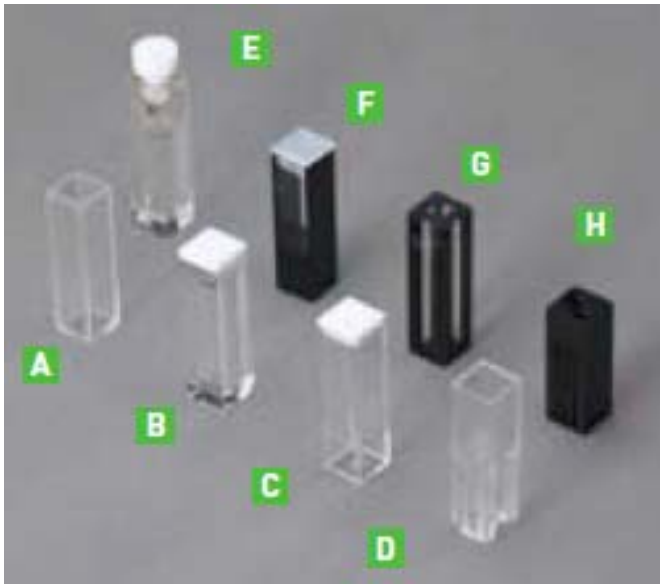
Sample Cell Choice

- Material
  - Plastic
    - Much less expensive (disposable)
    - Not very chemically resistant
  - Glass
    - More expensive
    - Good chemical resistance.
- As cell volume decreases:
  - More expensive
  - More difficult to clean
  - Less sample required



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Concentration

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Sample Concentration

- Too low
  - Noisy data
  - Too few particles for Siegert relationship (usually not an issue)
  - Theory assumes limit of near- zero concentration (and zero particle-particle interactions.
- Too high
  - Particle – Particle Interactions
  - Multiple Scattering

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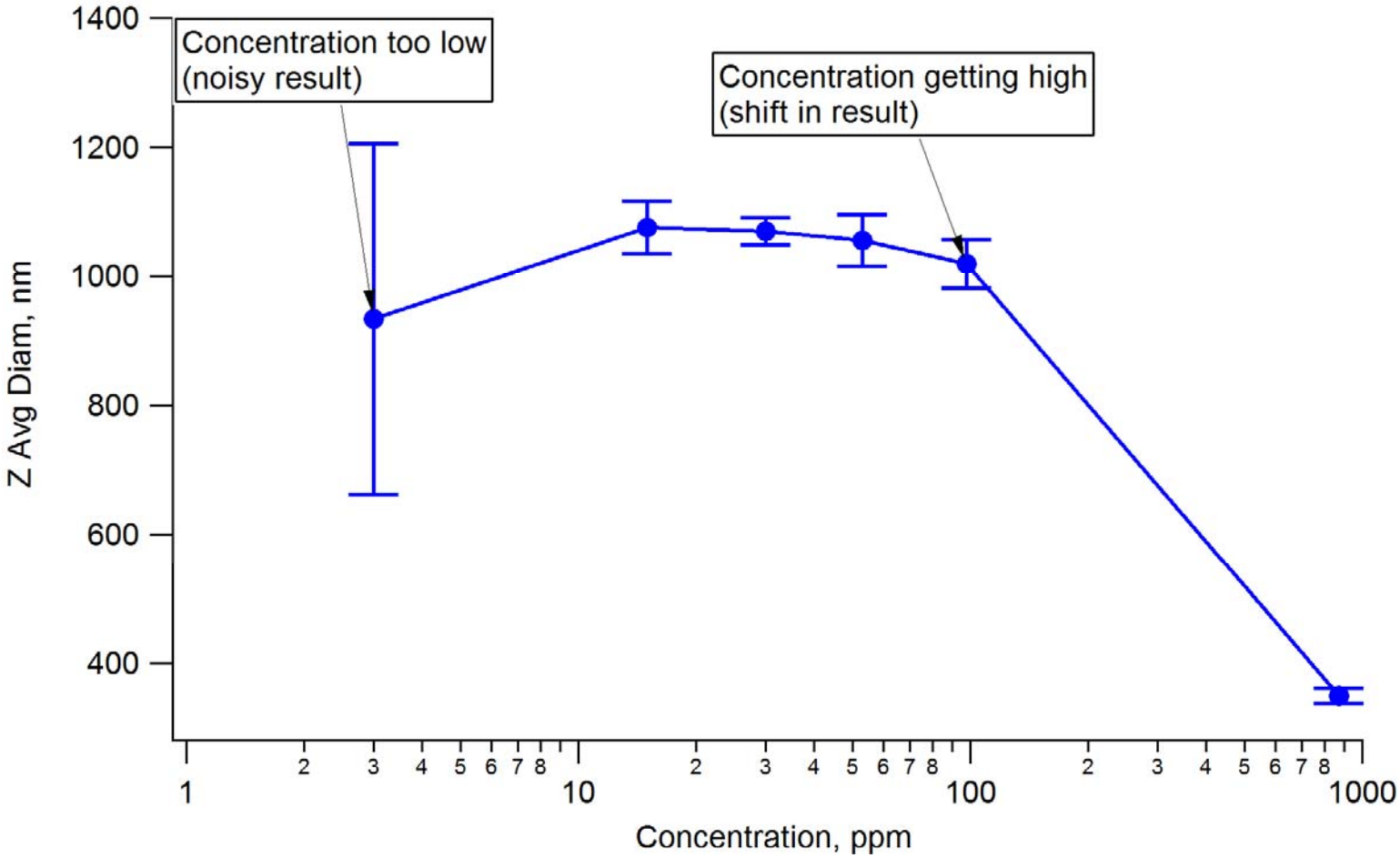
Measurement

- Make a plot like this to learn range of concentrations for your sample.
- Tails of distribution have an effect..



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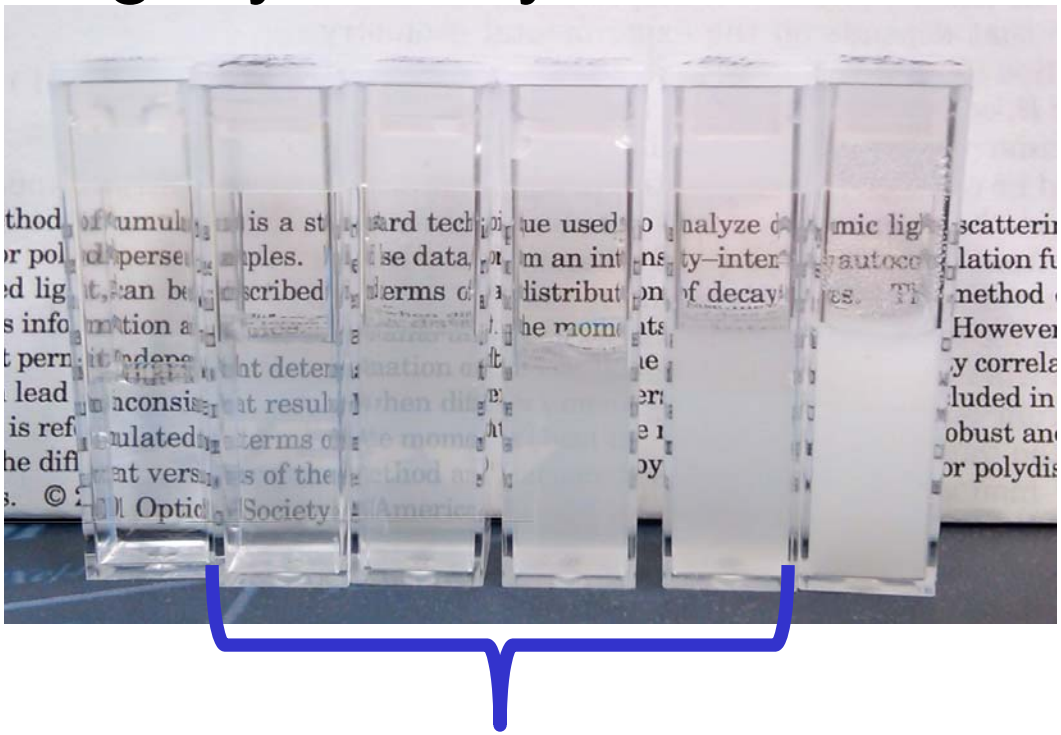
Eyeballing it

- Samples up to little bit cloudy are OK.
- I tend to pick samples that are clear or just slightly cloudy.



Best range for this material

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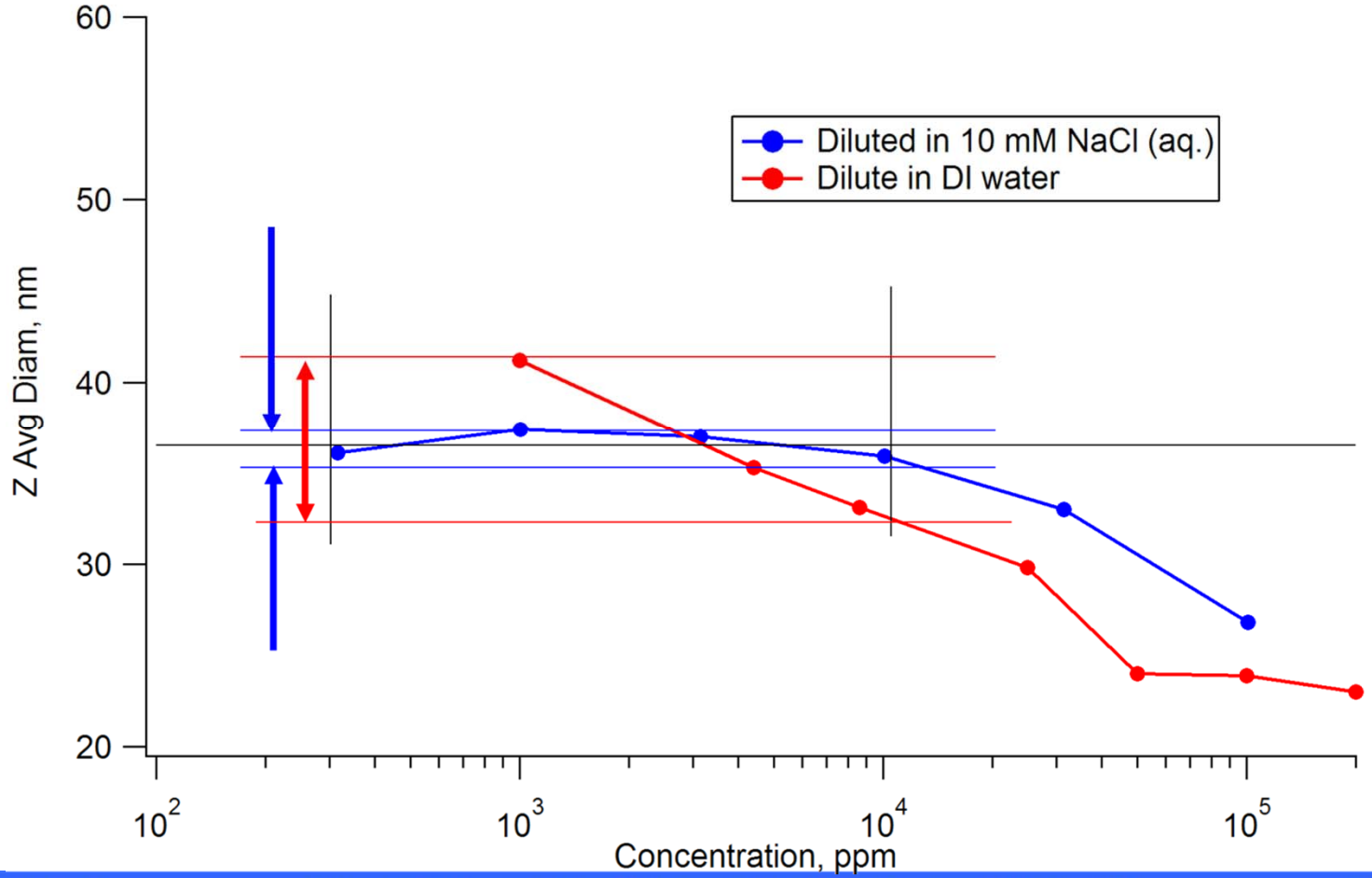
Diluent and Concentration

Note that when we suppress effect of charges by adding salt, the effect of concentration is suppressed.



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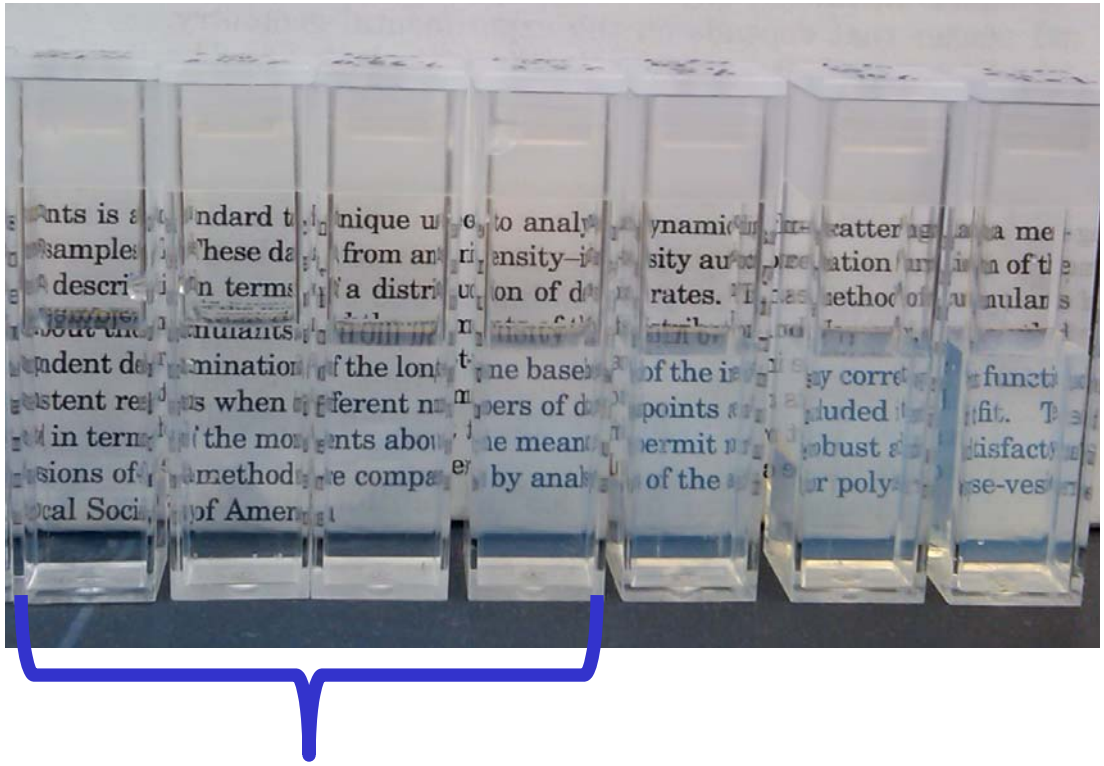
Eyeballing it

- Clear samples are better (smaller particle size)



Best range for this material

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Measurement Duration

- Time to reach thermal equilibrium after inserting cell into instrument.

- How long to measure?
  - 1 to 2 minutes per repeat is typical
- Number of repeats?
  - 3 to 6 is typical

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How Many Repeats?

- Confidence interval, C, on mean (assume normal distribution)

$$C_I = \frac{t_{\alpha/2,n-1} S}{\sqrt{n}} \qquad \frac{C_I}{M} = \frac{t_{\alpha/2,n-1} S}{M\sqrt{n}} = COV * \frac{t_{\alpha/2,n-1}}{\sqrt{n}}$$

n (num repeats)	t(0.10,n-1)	t/sqrt(n)	0.05*t/sqrt(n)
2	6.31	4.46	22%
3	2.92	1.68	8.4%
4	2.35	1.18	5.9%
5	2.13	0.95	4.8%
6	2.01	0.82	4.1%

typical

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Q&A

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Thank-you

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Thank you

Thank you

ありがとうございました

Cảm ơn

Dziękuję

ขอบคุณครับ

谢谢

Gracias

Grazie

اشْكُر

Σας ευχαριστούμε

धन्यवाद

நன்றி

Tacka

Danke

Merci

Obrigado

감사합니다

Большое спасибо

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