HORIBA Instruments

Particle Analysis

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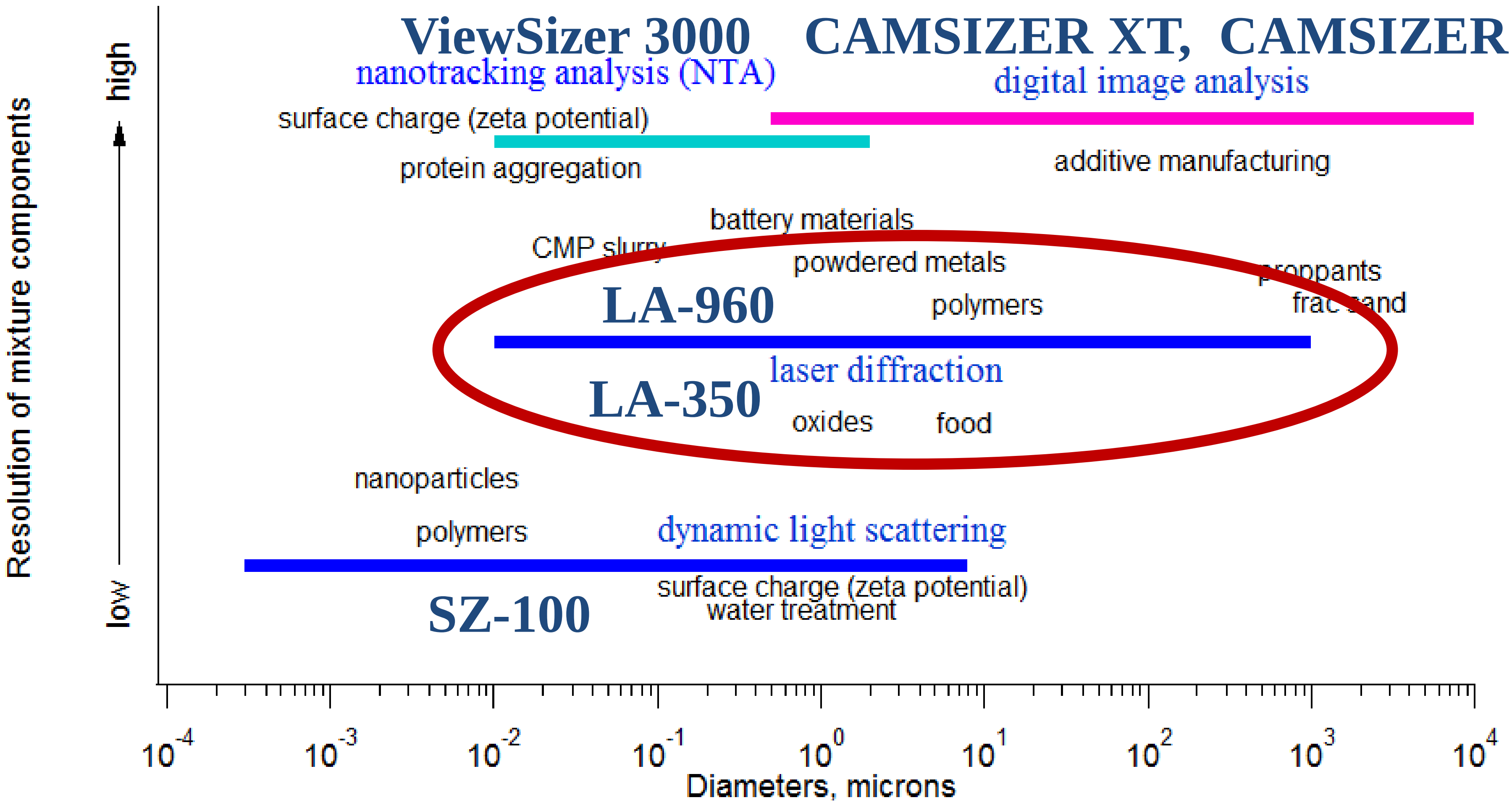
The Basics of Laser Diffraction

November 29, 2018

Perspective



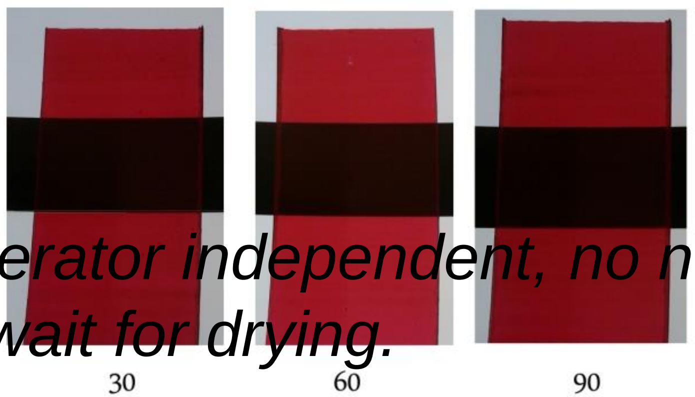
Why Particle Size?

Size affects material behavior and processing across a number of industries.

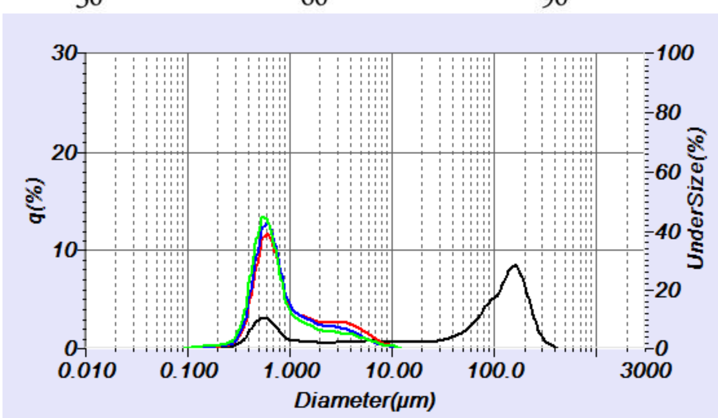
Industry		Industry	
Ceramic	 	**Construction**	
Oil/rubber	 	**Chemical**	
Battery		**Pharmaceutical**	
Electricity		**Food/Drink**	 
Automobile		**Paper/Pulp**	 
Mining		**Ink/Toner**	 

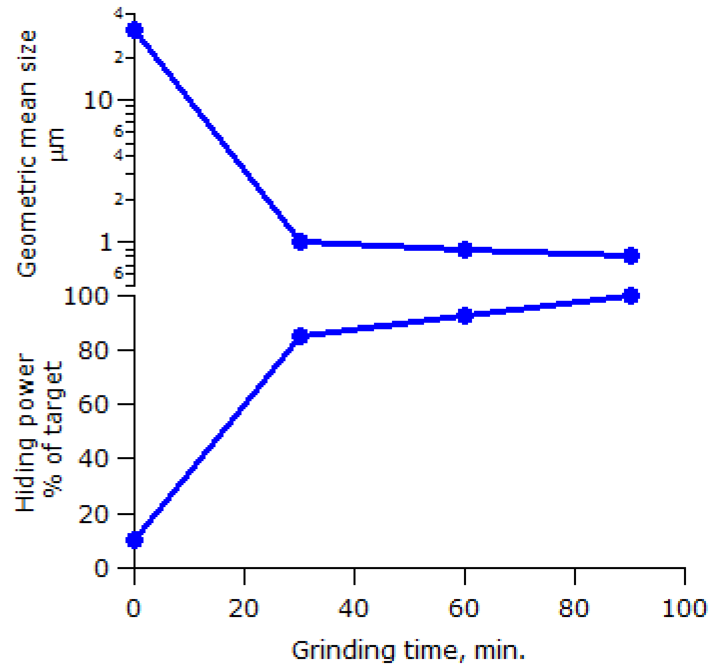
Application: Pigment Hiding Power

Operator dependent, need to wait for drying.



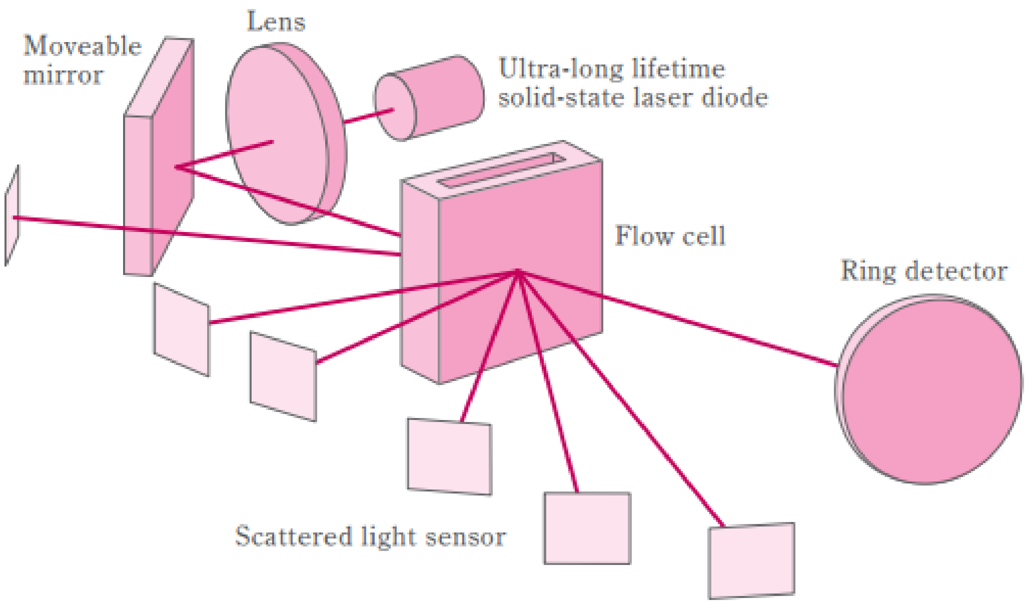
Operator independent, no need to wait for drying.

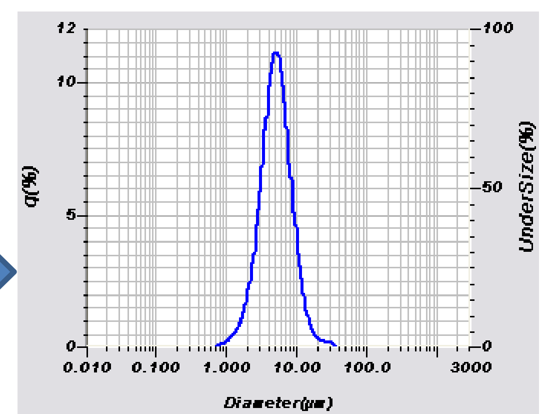




Core Principle

Investigate a particle with light and determine its size

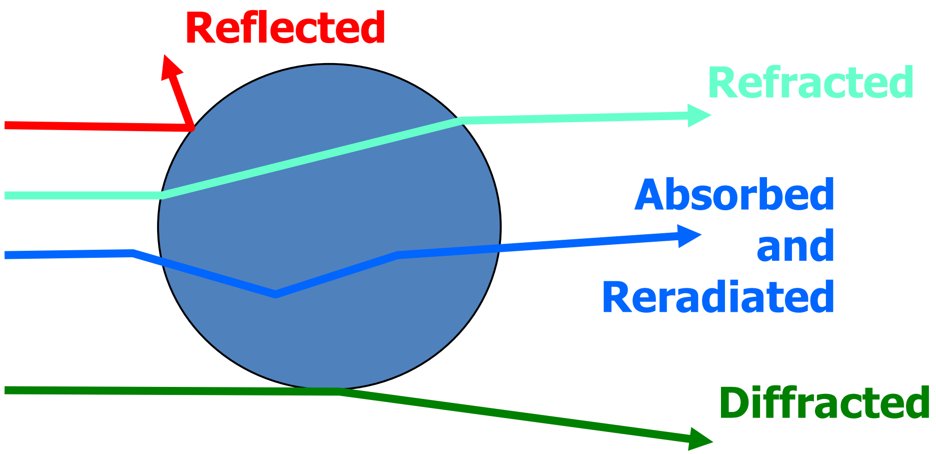




When a Light beam Strikes a Particle

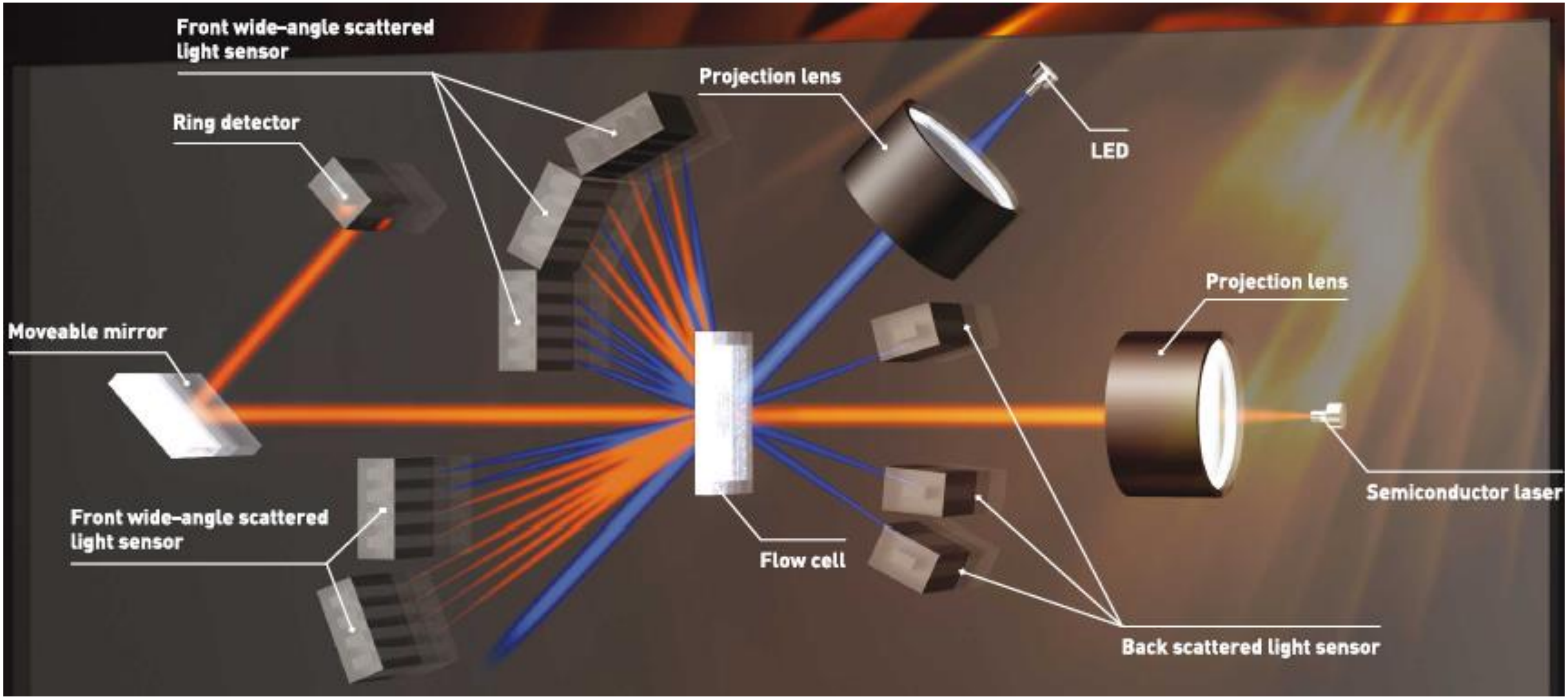
Some of the light is:

Diffracted
Reflected
Refracted
Absorbed and Reradiated

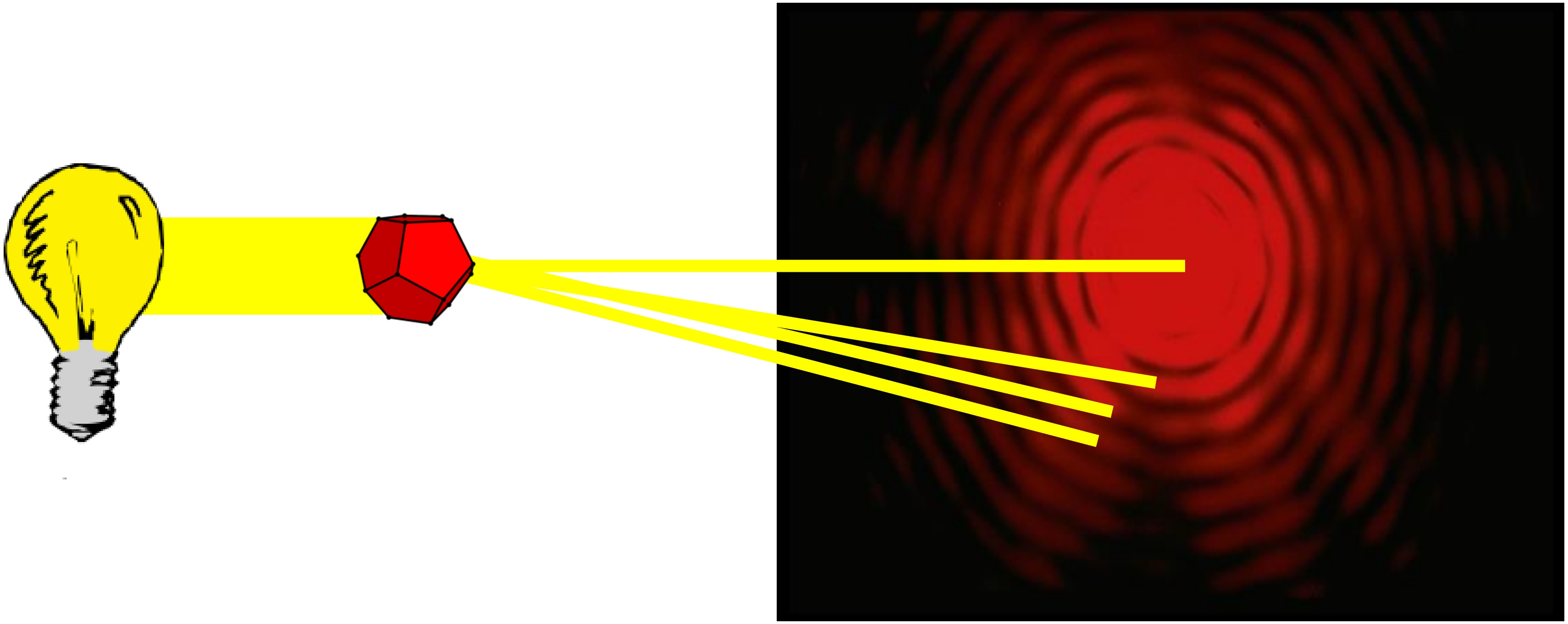


- **Small particles require knowledge of optical properties:**
  - **Real Refractive Index (bending of light, wavelength of light in particle)**
  - **Imaginary Refractive Index (absorption of light within particle)**
  - **Refractive index values less significant for large particles**
- **Light must be collected over large range of angles**

LA-960 Optics



Diffraction Pattern



Light

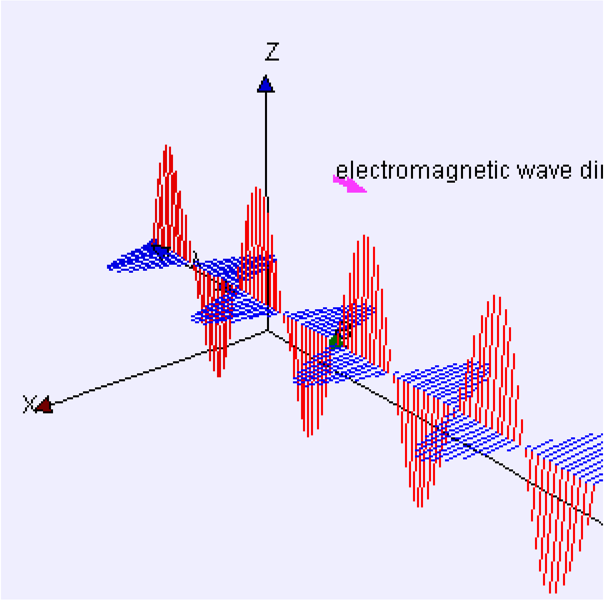
Expressed in just in y-direction

$$E = E_0 \sin(ky - \omega t)$$

Oscillating electric field

$$H = H_0 \sin(ky - \omega t)$$

Oscillating magnetic field (orthogonal to electric field)



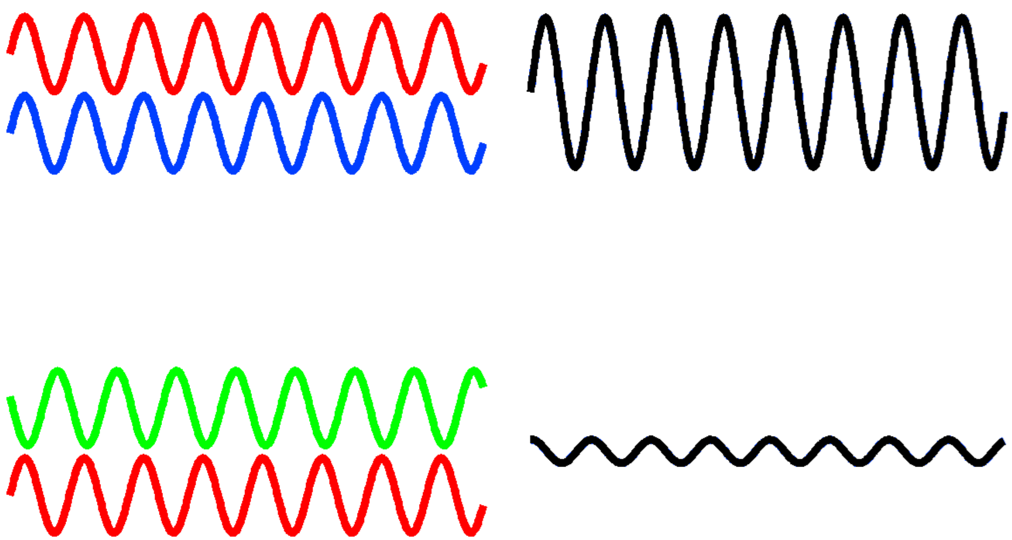
Complements of Lookang @ weelookang.blogspot.com

Light: Interference

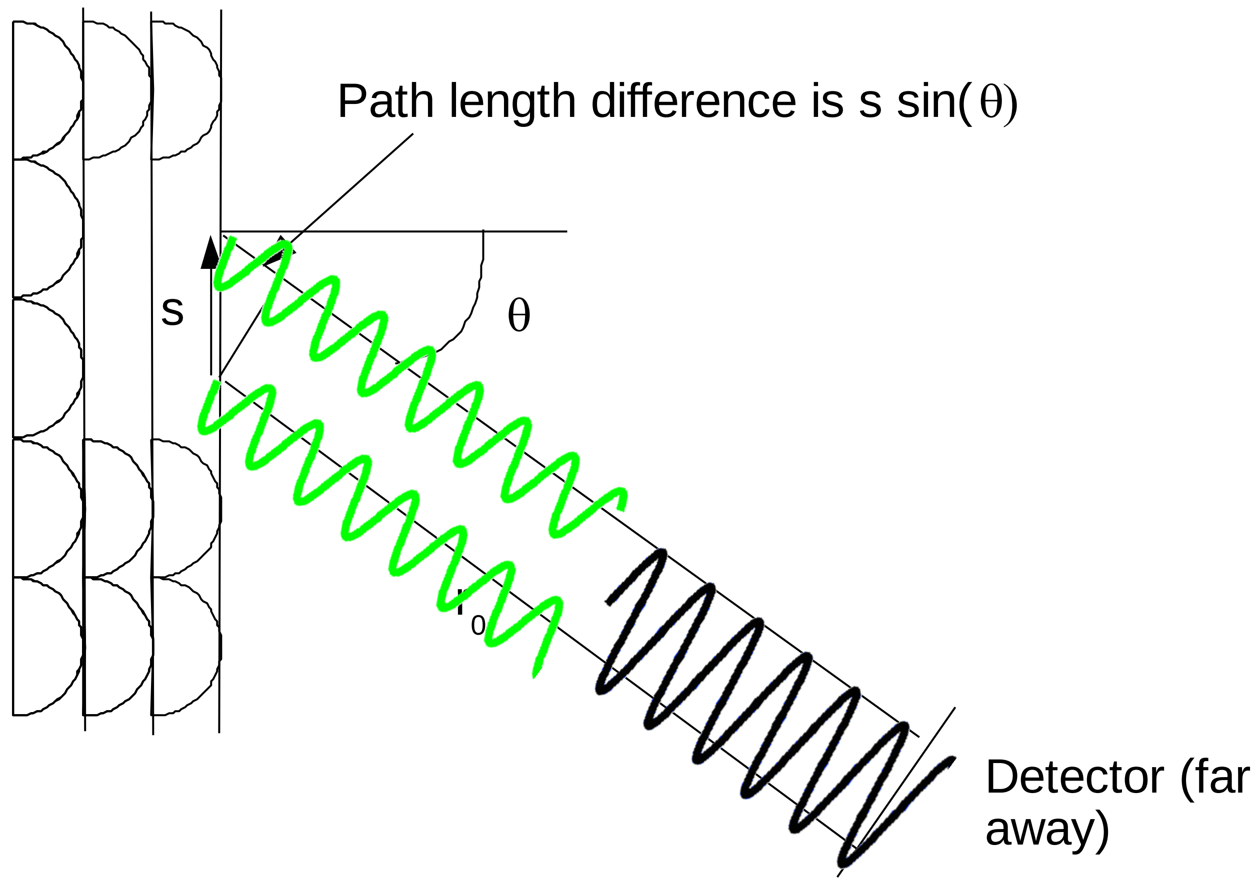
Look at just the electric field.

$$E = E_0 \sin(kx - \omega t + \phi)$$ Oscillating electric field

$$E = E_0 \sin(kx - \omega t)$$ Second electric field with phase shift



Path Length Difference



Use models to interpret data

- Scattering data typically cannot be inverted to find particle shape.

- We use optical models to interpret data and understand our experiments.

Laser Diffraction Models

- **Large particles -> Fraunhofer**
  - **More straightforward math**
  - **Large, opaque particles as 2-D disks**
  - **Use this to develop intuition**

- **All particle sizes -> Mie**
  - **Messy calculations**
  - **All particle sizes as 3-D spheres**

Fraunhofer Approximation

$$(S_1)^2 = (S_2)^2 = \alpha^4 \left[\frac{J_1(\alpha \sin \Theta)}{\alpha \sin \Theta} \right]^2$$

$$I(\Theta) = \frac{I_0}{k^2 a^2} \alpha^4 \left[\frac{J_1(\alpha \sin \Theta)}{\alpha \sin \Theta} \right]^2$$

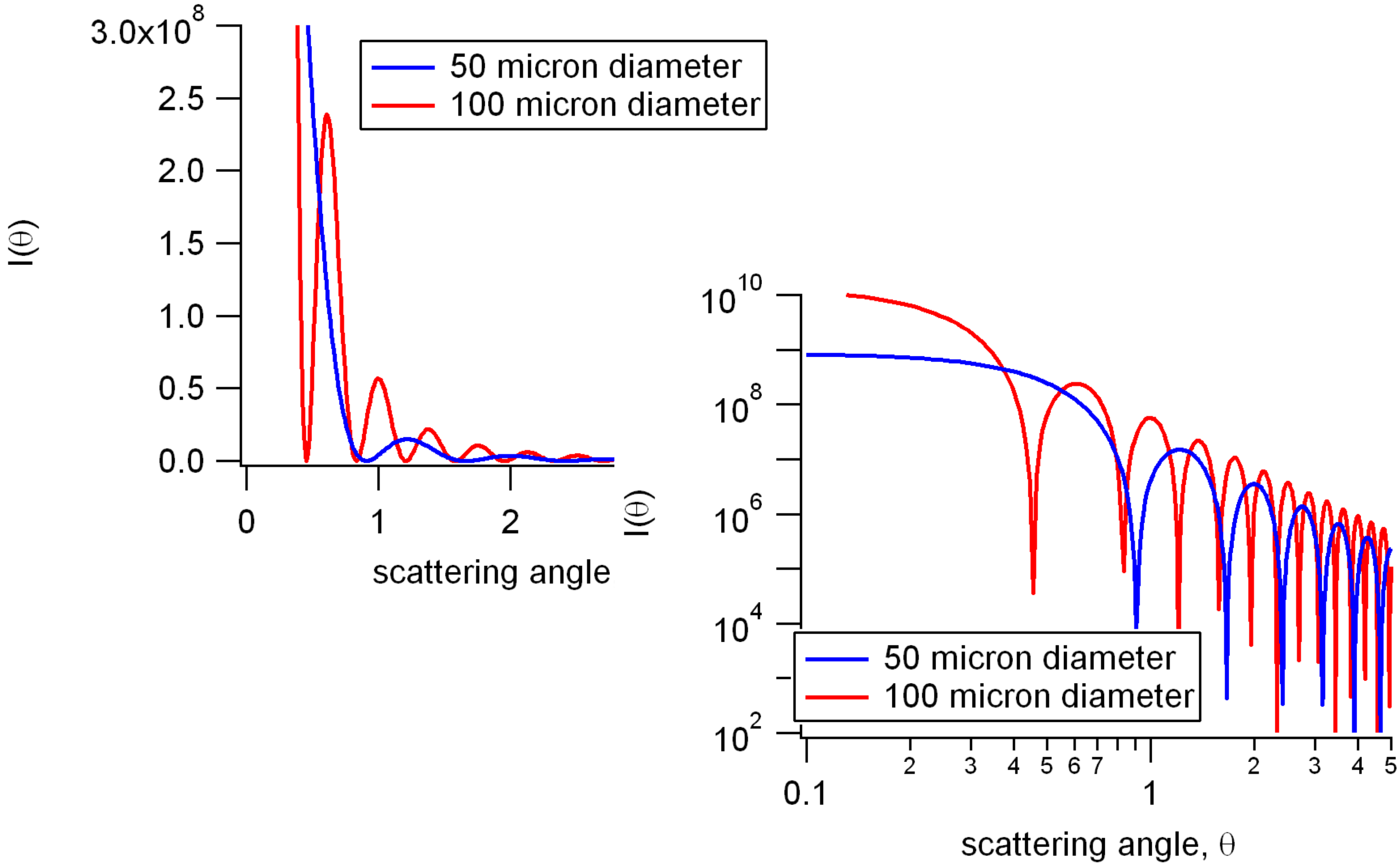
dimensionless size parameter $\alpha = \pi D / \lambda$;

J_1 is the Bessel function of the first kind of order unity.

Assumptions:
a) all particles are much larger than the light wavelength (only scattering at the contour of the particle is considered; this also means that the same scattering pattern is obtained as for thin two-dimensional circular disks)
b) only scattering in the near-forward direction is considered (*Q* is small).

Limitation: (diameter at least about 40 times the wavelength of the light, or α >>1)*
If λ=650nm (.65 µm), then 40 x .65 = 26 µm
If the particle size is larger than about **26 µm**, then the Fraunhofer approximation gives good results.

Fraunhofer: Effect of Particle Size

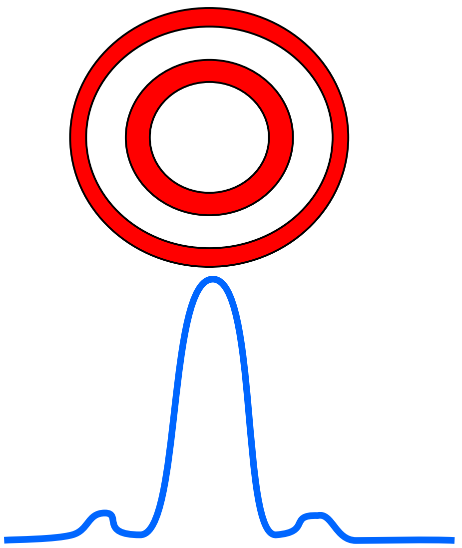


Diffraction: Large vs. Small

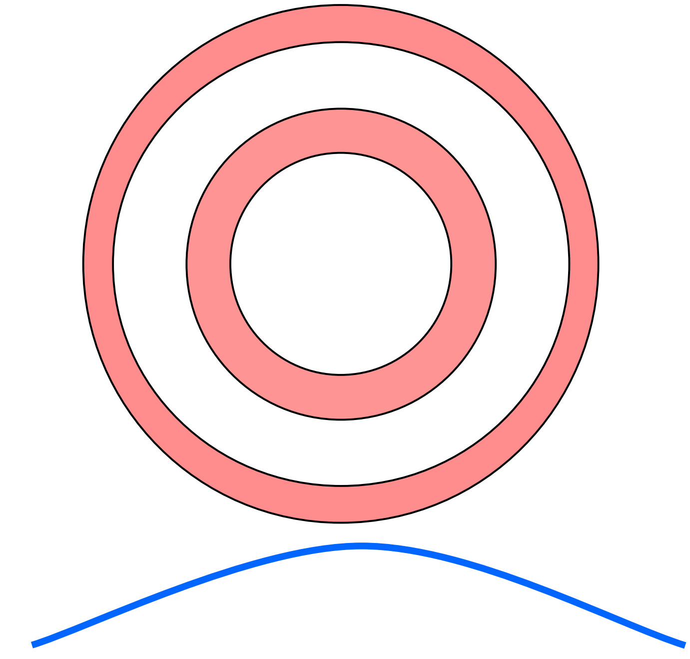
LARGE PARTICLE:

Peaks at low angles

Strong signal



Narrow Pattern - High intensity



Wide Pattern - Low intensity

- ## SMALL PARTICLE:
  - **Peaks at larger angles**
  - **Weak Signal**

Poll

How many of you work with particles with sizes over 1 mm?

How many of you work with particles with sizes over 25 microns?

How many of you work with particles with sizes less than 1 micron?

Mie Scattering

$$I_s(m,x,\theta) = \frac{I_0}{2k^2r^2}\left(|S_2|^2 + |S_1|^2\right)$$

Use computer for the calculations!

$$S_1(m,x,\theta) = \sum_1^{\infty} \frac{2n+1}{n(n+1)}\{a_n\pi_n + b_n\tau_n\}$$

$$S_2(m,x,\theta) = \sum_1^{\infty} \frac{2n+1}{n(n+1)}\{a_n\tau_n + b_n\pi_n\}$$

$$a_n = \frac{m\psi_n(mx)\psi_n'(x) - \psi_n(x)\psi_n'(mx)}{m\psi_n(mx)\xi_n'(x) - \xi_n(x)\psi_n'(mx)}$$

$$b_n = \frac{\psi_n(mx)\psi_n'(x) - m\psi_n(x)\psi_n'(mx)}{\psi_n(mx)\xi_n'(x) - m\xi_n(x)\psi_n'(mx)}$$

$$\pi_n = \frac{P_n^1(\cos\theta)}{\sin\theta}$$

$$\tau_n = \frac{d}{d\theta}\left(P_n^1(\cos\theta)\right)$$

ξ, ψ: Ricatti-Bessel functions

P_n^1: 1st order Legendre Functions

Critical Variables

The equations are messy, but require just three inputs which are shown below. The nature of the inputs is important.

$$x = \pi D / \lambda$$

Decreasing wavelength is the same as increasing size. So, if you want to measure small particles, decrease wavelength so they "appear" bigger. That is, get a blue light source for small particles.

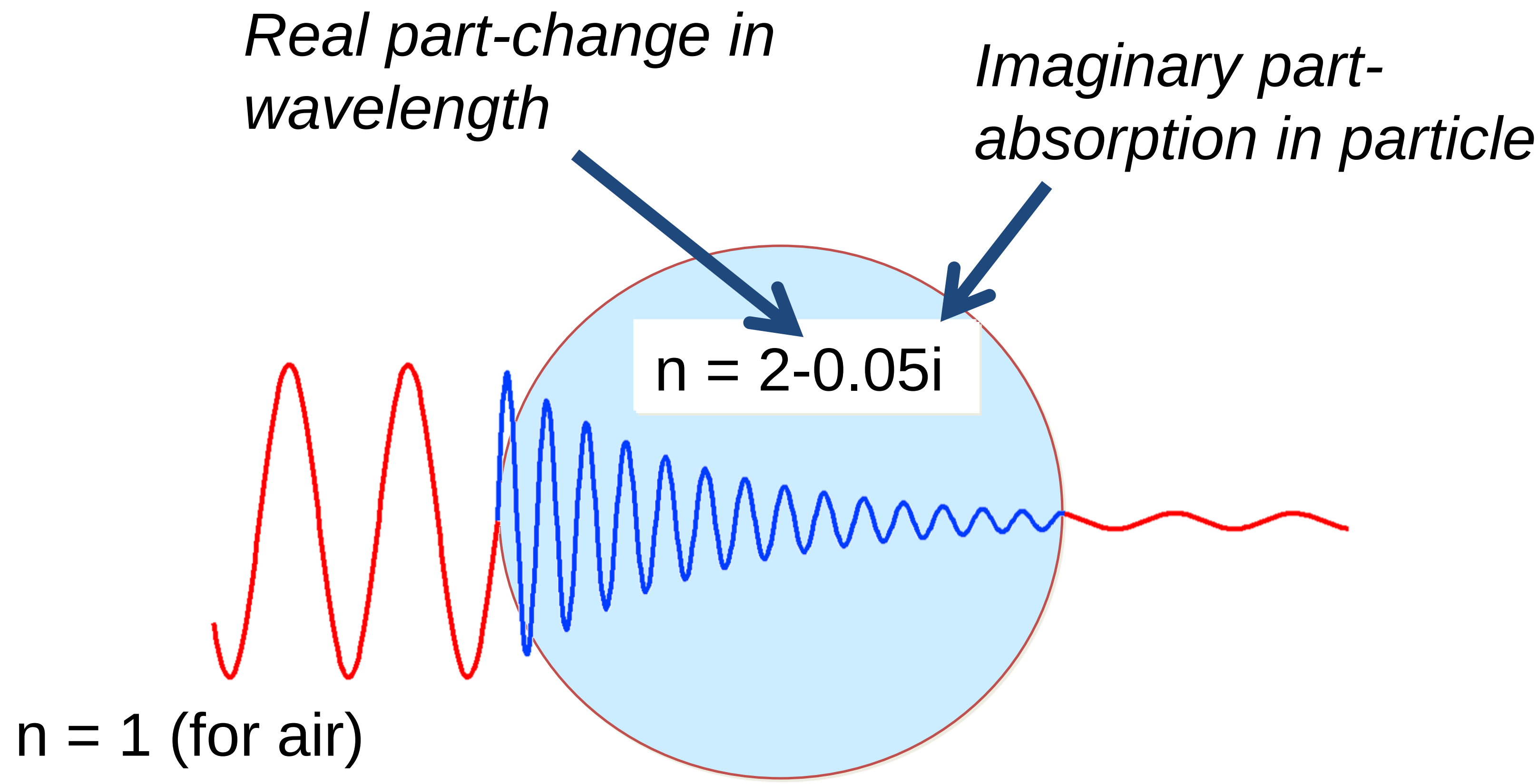
$$m = n_p / n_m$$

We need to know relative refractive index. As this goes to 1 there is no scattering.

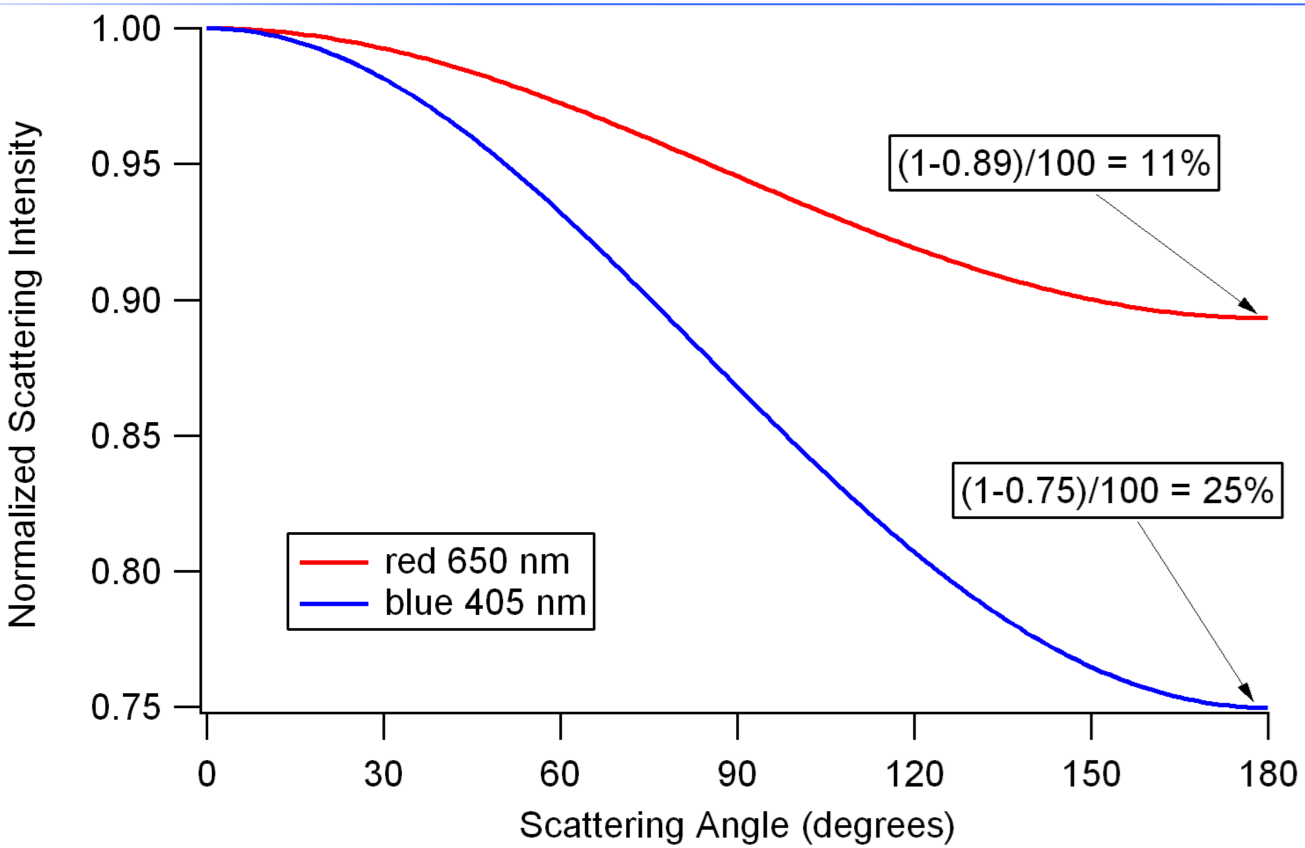
$$\theta$$

Scattering Angle

Refractive Index

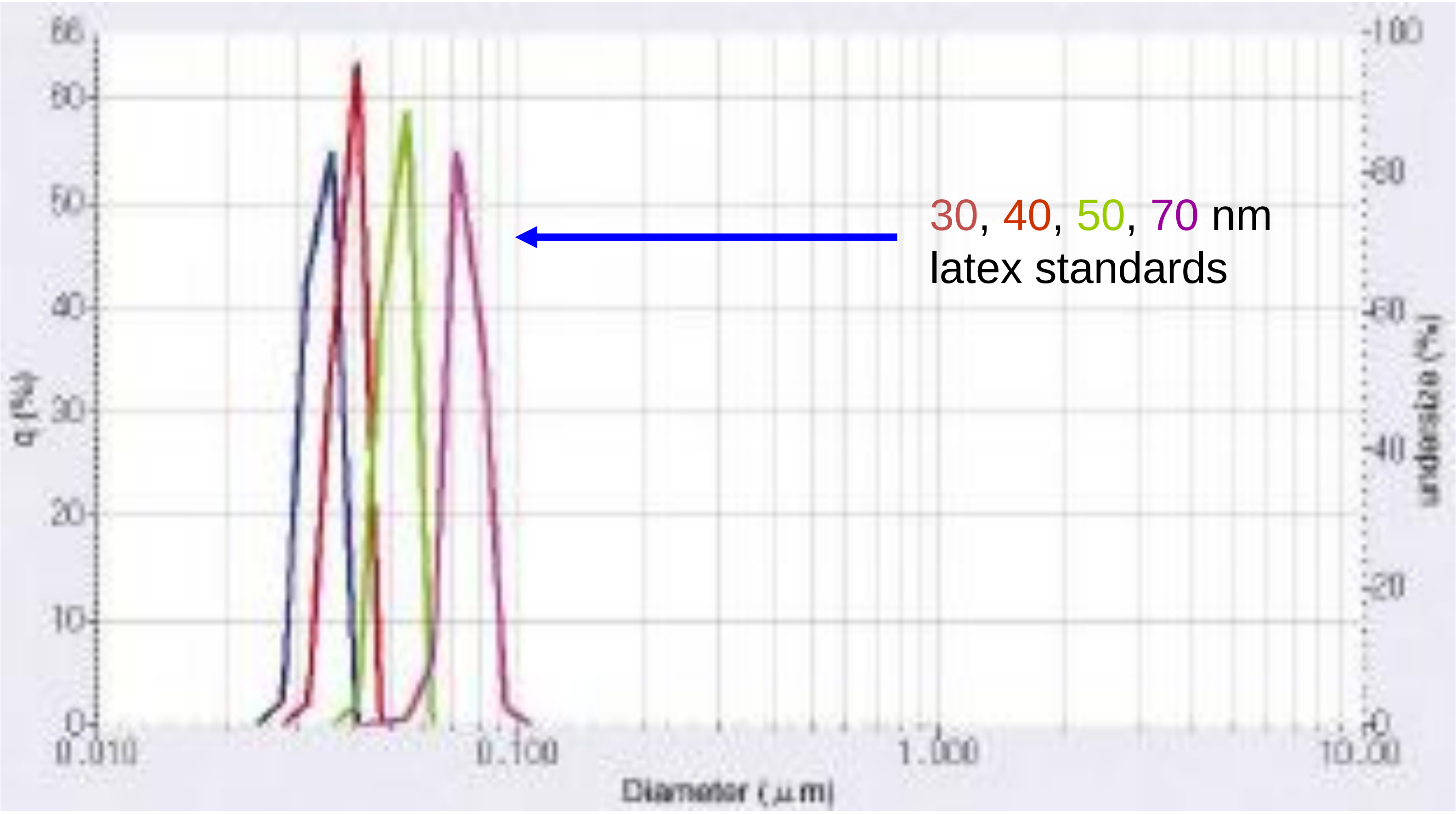


Small Particles -> Blue light



By using blue light source, we double the scattering effect of the particle. This leads to more sensitivity. This plot also tells you that you need to have the background stable to within 1% of the scattered signal to measure small particles accurately.

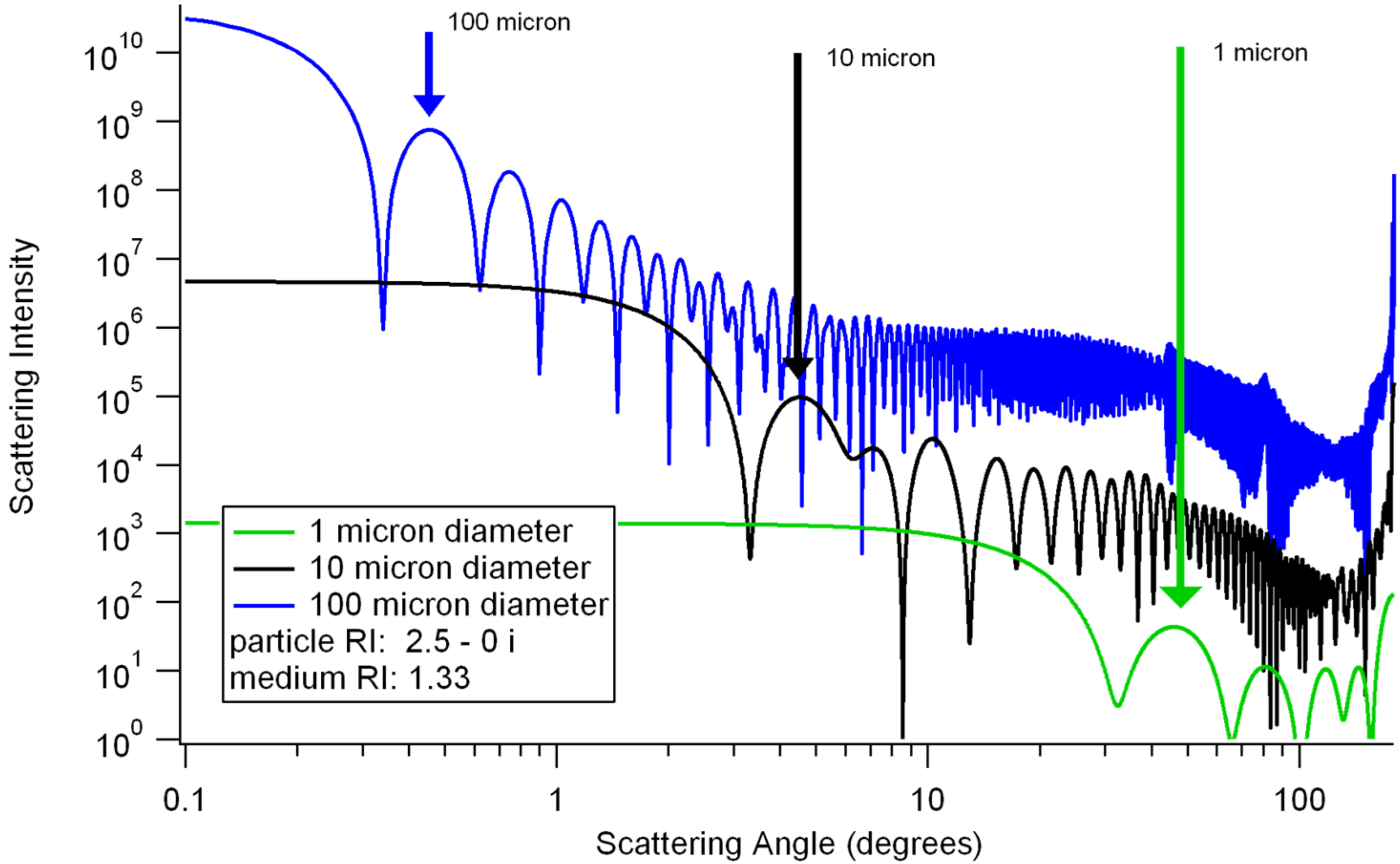
Example Results



30, 40, 50, 70 nm latex standards

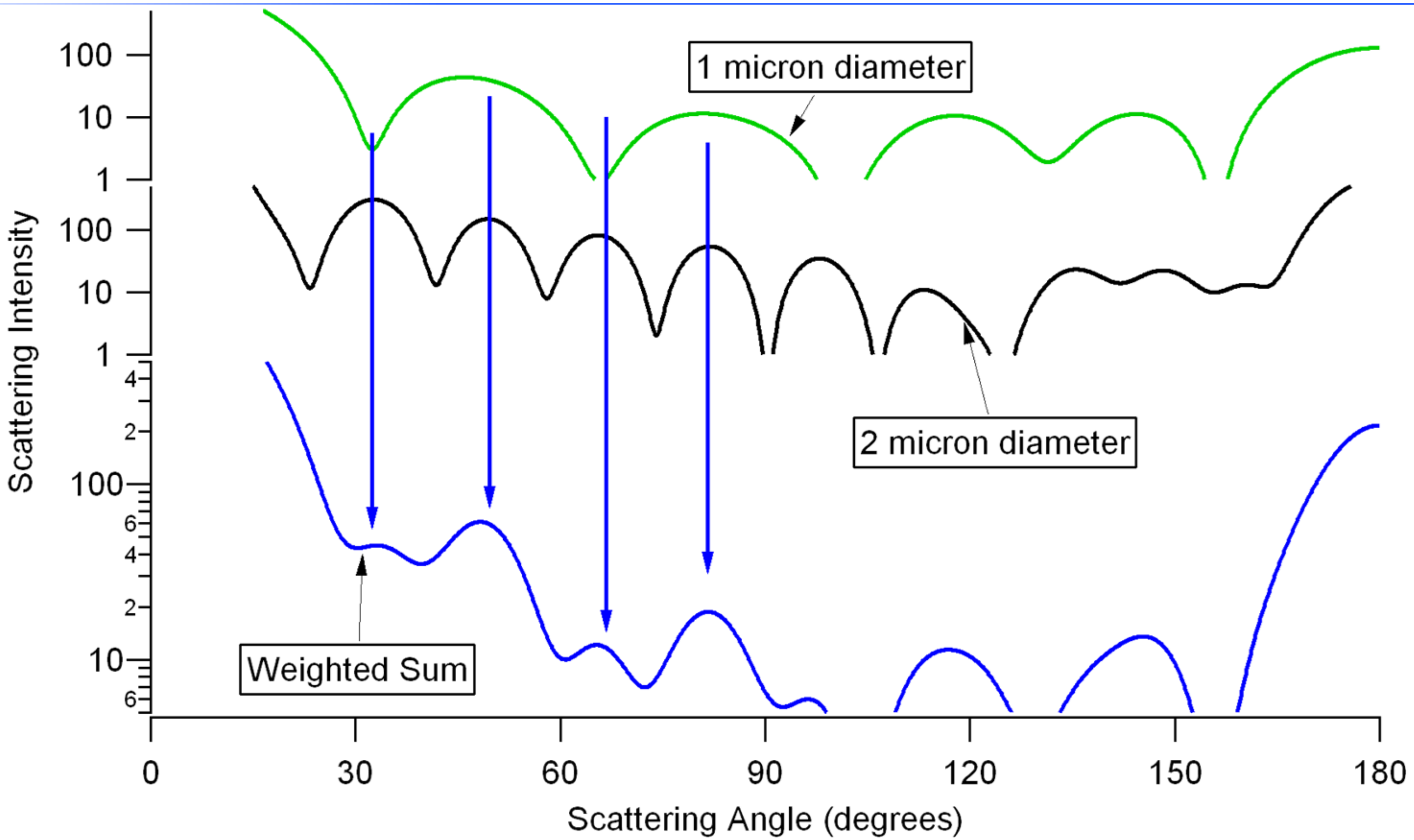
Data from very small particles.

Effect of Size



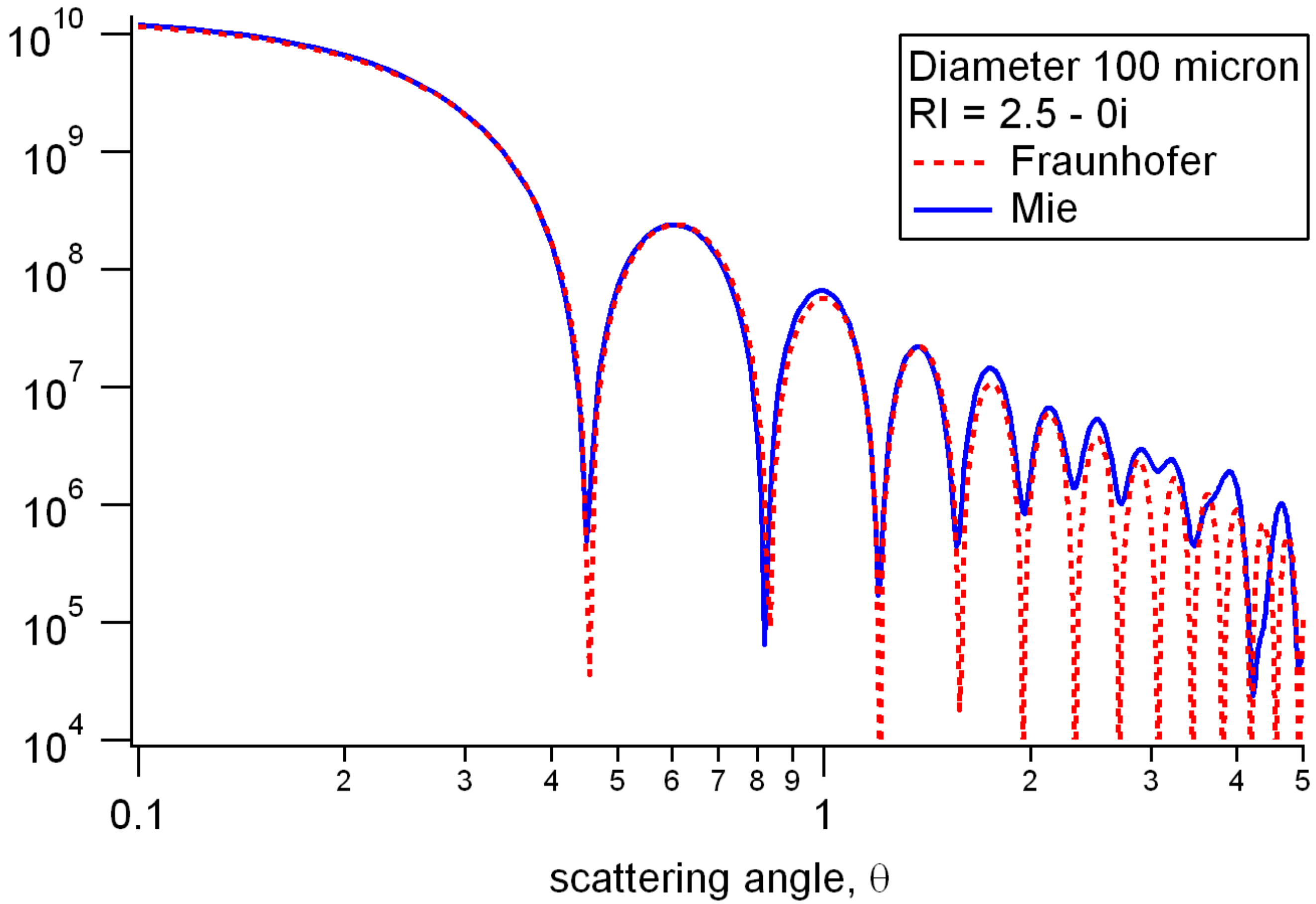
As diameter increases, intensity (per particle) increases and location of first peak shifts to smaller angle.

Mixing Particles? Just Add



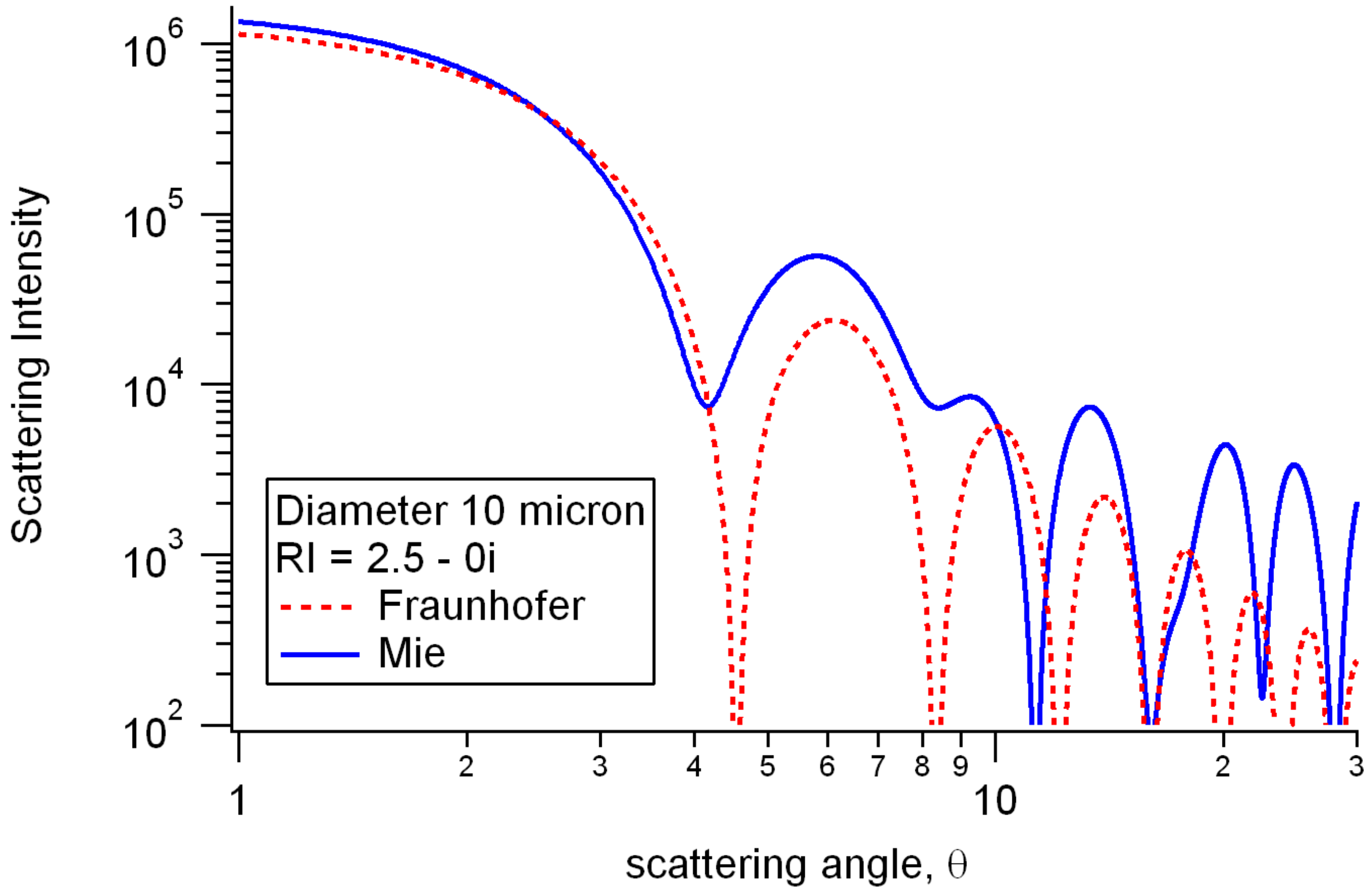
The result is the weighted sum of the scattering from each particle. Note how the first peak from the 2 micron particle is suppressed since it matches the valley in the 1 micron particle.

Comparison, Large Particles



For large particles, match is good out to through several peaks.

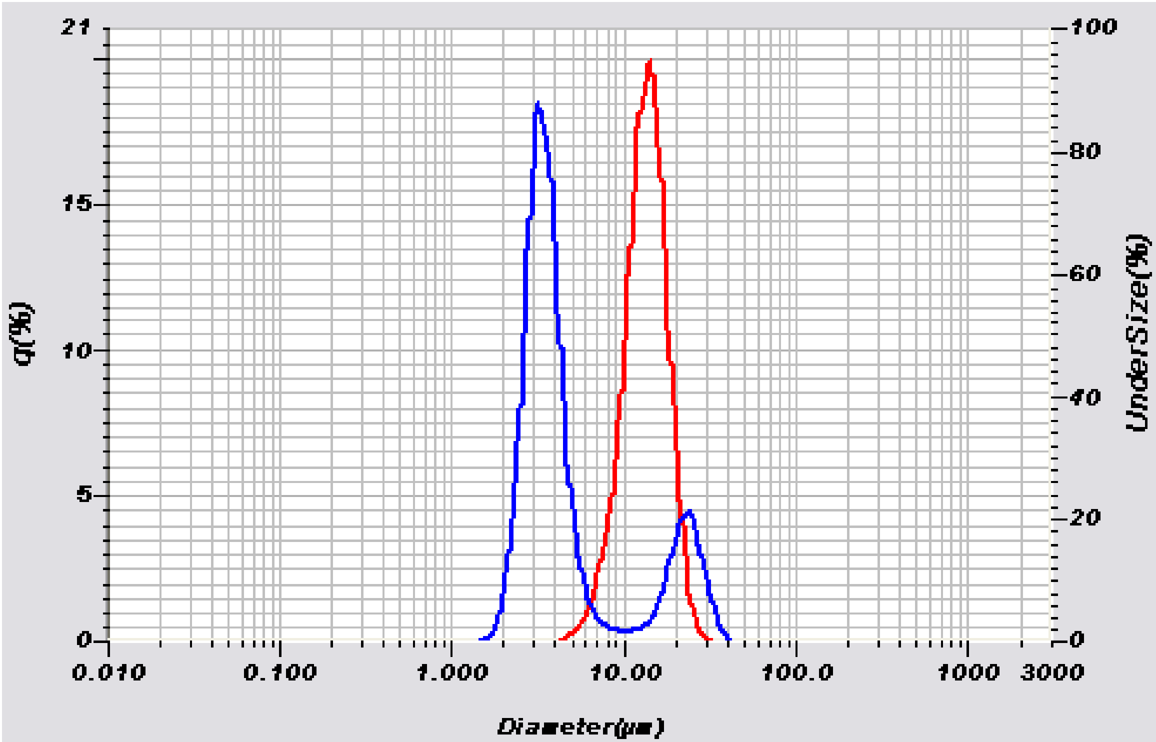
Comparison, Small Particles



For small particles, match is poor. Use Mie.

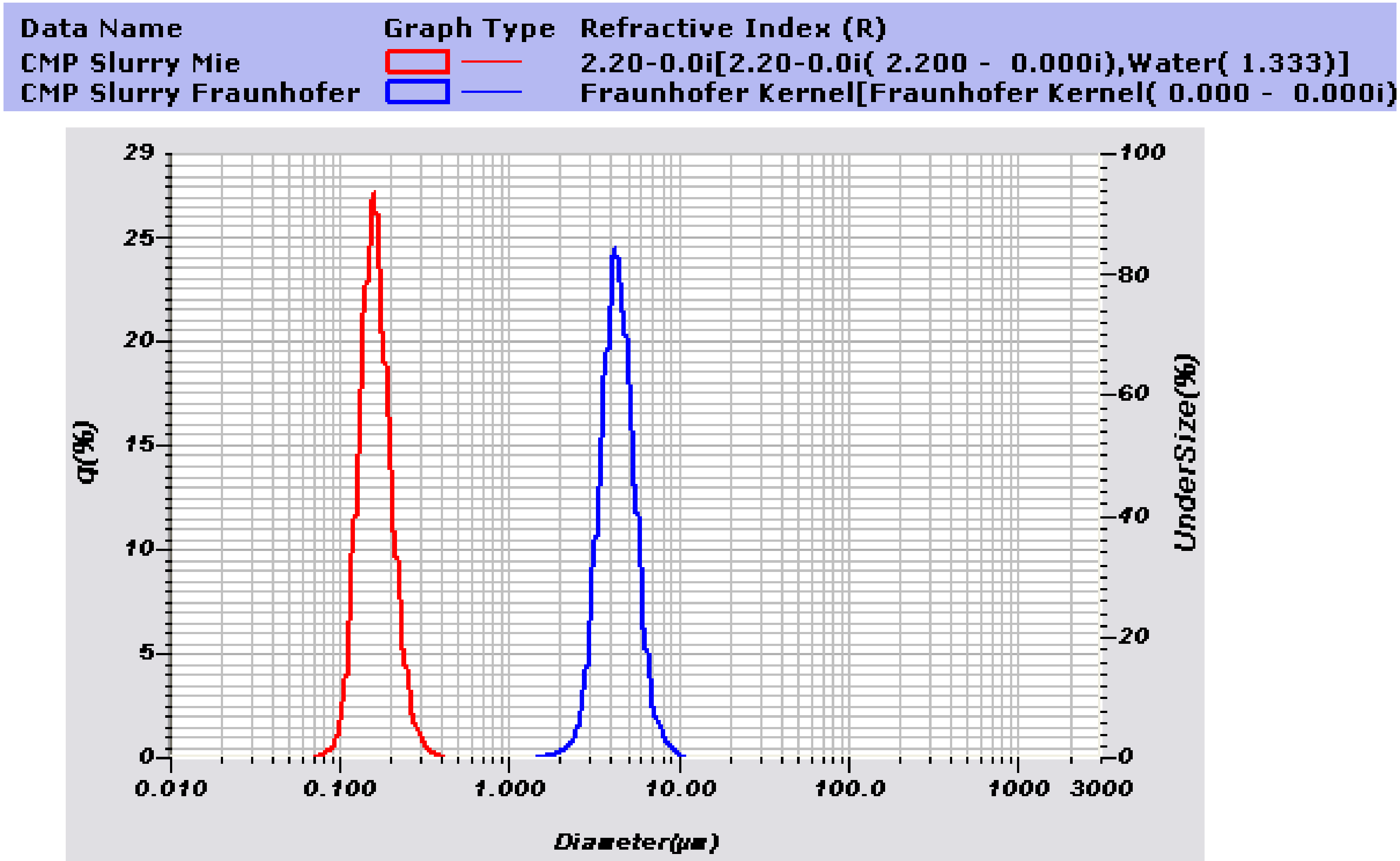
Glass Beads and Models

Data Name	Graph Type	Refractive Index (R)
Standard Glass Beads Mie		STD-GLASSBEADS[STD-GLASSBEADS(1.510 - 0.000i),'
Standard Glass Beads Fraunhofer		Fraunhofer Kernel[Fraunhofer Kernel(0.000 - 0.000i]



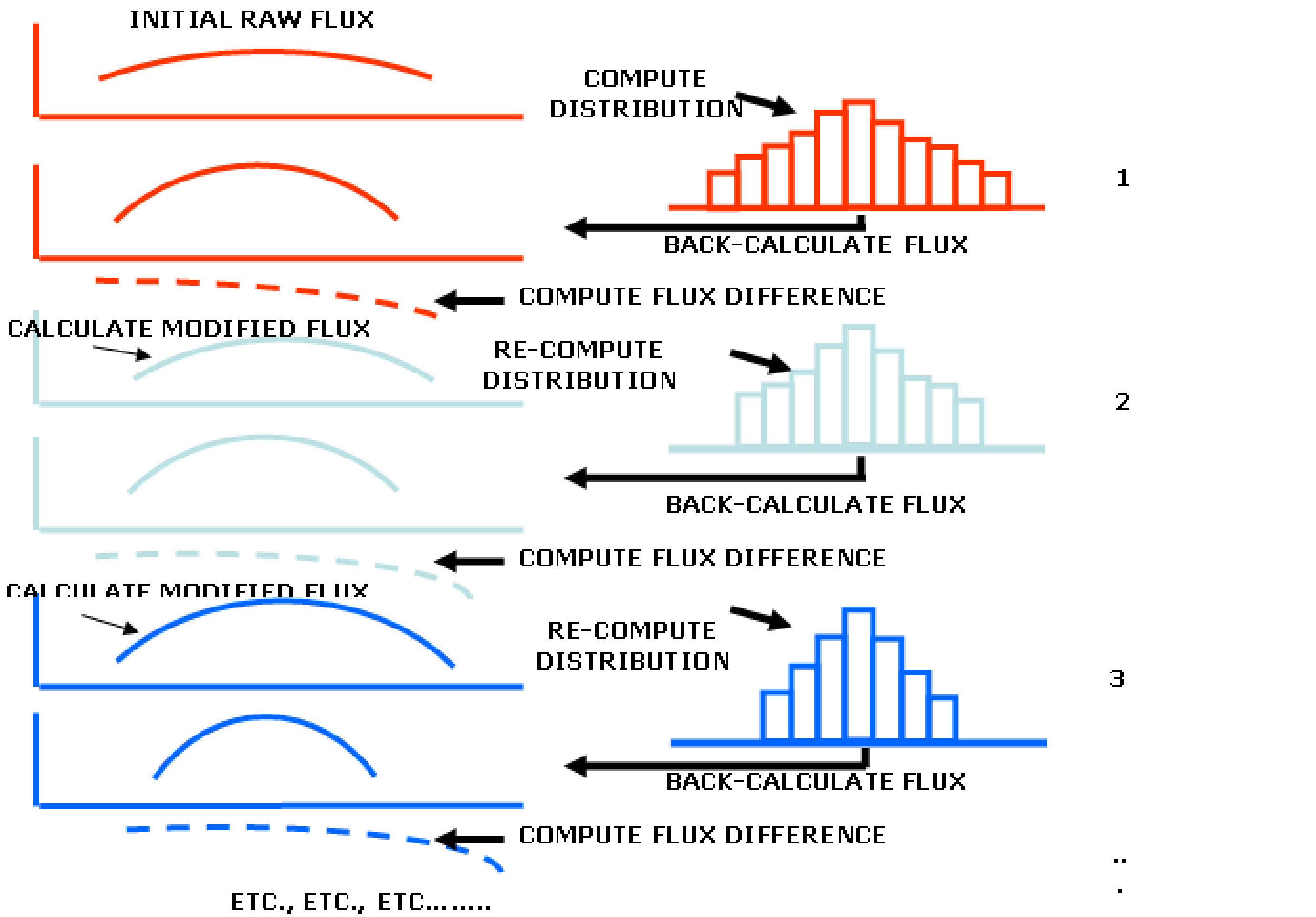
Graph Type	D(v,0.1)	D(v,0.5)	D(v,0.9)
	8.98783(µm)	13.47741(µm)	18.8536
	2.58072(µm)	3.62044(µm)	22.3174

CMP Slurry



Data Name
Graph Type
Refractive Index (R)
CMP Slurry Mie
2.20-0.0i[2.20-0.0i(2.200 - 0.000i),Water(1.333)]
CMP Slurry Fraunhofer
Fraunhofer Kernel[Fraunhofer Kernel(0.000 - 0.000i)
q(%)
29
25
20
15
10
5
0
100
80
60
40
20
0
UnderSize(%)
0.010
0.100
1.000
10.00
100.0
1000
3000
Diameter(µm)

Analyzing Data: Convergence



Other factors

- **Size, Shape, and Optical Properties also affect the angle and intensity of scattered light**
- **Extremely difficult to extract shape information without *a priori* knowledge**

Assume spherical model

Pop Quiz

What particle shape is used for laser diffraction calculations?

A. Hard sphere
B. Cube
C. Triangle
D. Easy sphere

Pop Quiz

What particle shape is used for laser diffraction calculations?

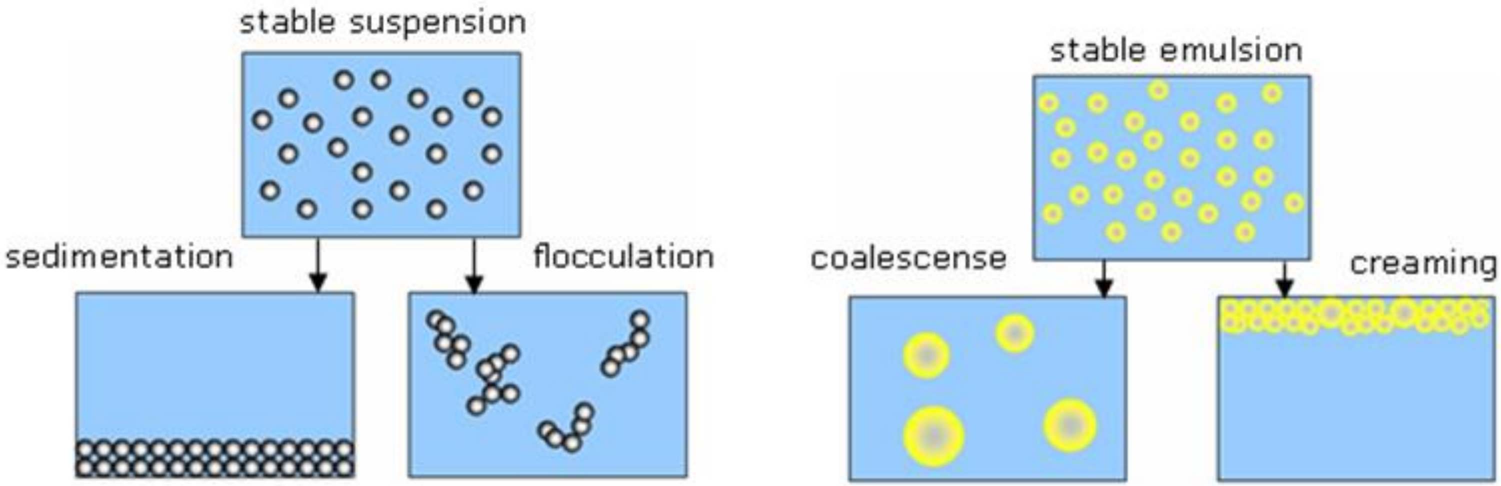
A. **Hard sphere**
B. **Cube**
C. **Triangle**
D. **Easy sphere**

Either gets full credit!

Measurement Workflow

Prepare the sample

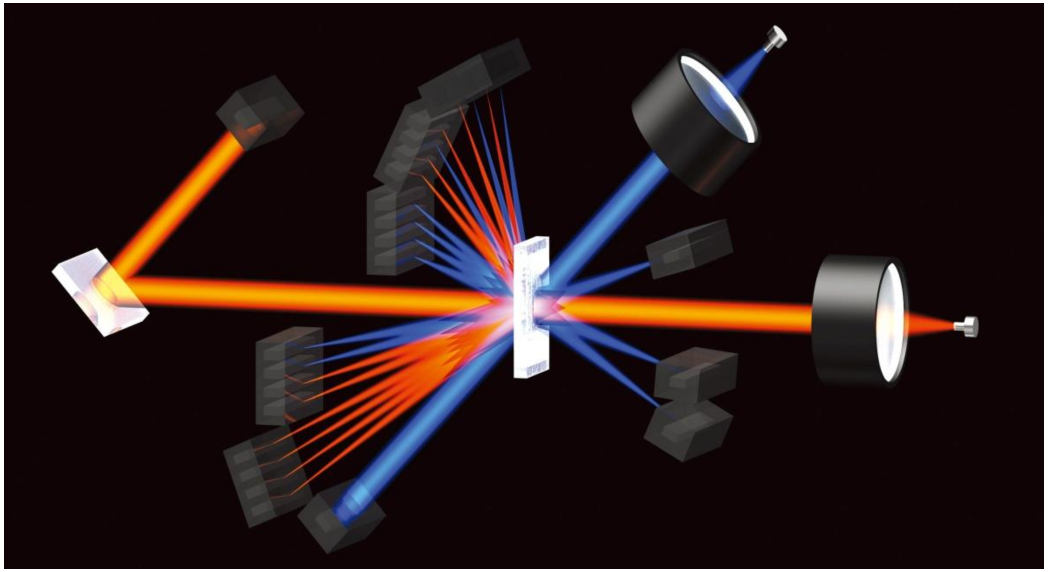
- Good sampling and dispersion a must!
- May need to use surfactant or admixture



Measurement Workflow

Prepare the system

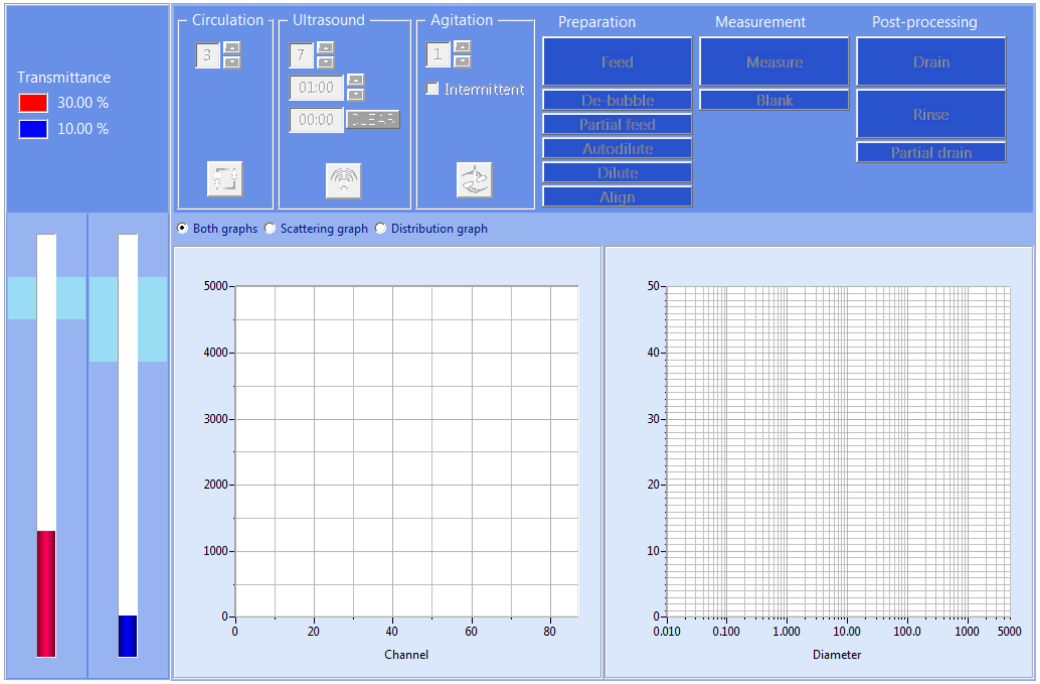
- Align laser to maximize signal-to-noise
- Acquire blank/background to reduce noise



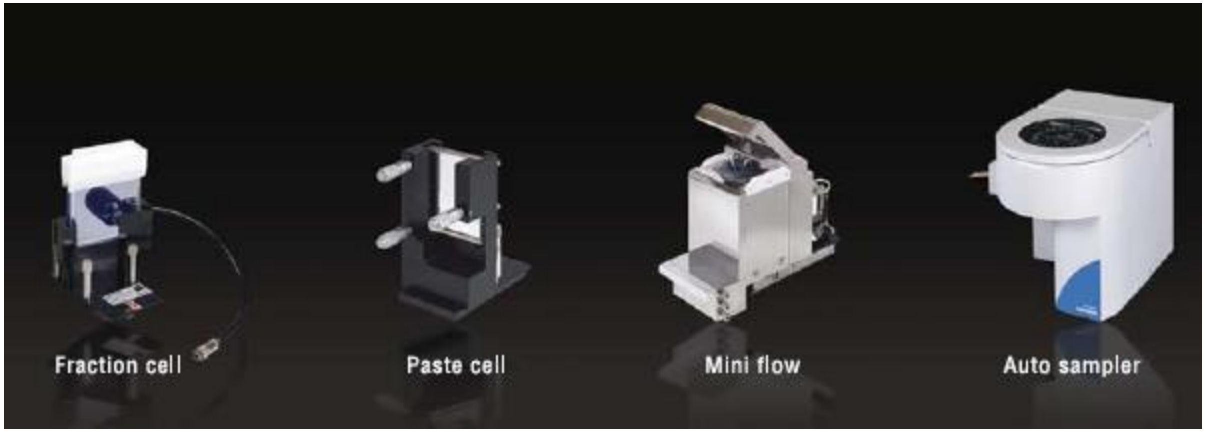
Measurement Workflow

Introduce sample

Add sample to specific concentration range
Pump sample through measurement zone
Final dispersion (ultrasonic)



Flexible Sample Handlers



10 ml *35 ml* *200 ml* *powders*

- *Wide range of sample cells depending on application*
- *High sensitivity keeps sample requirements at minimum*
- *Technology has advanced to remove trade-offs*

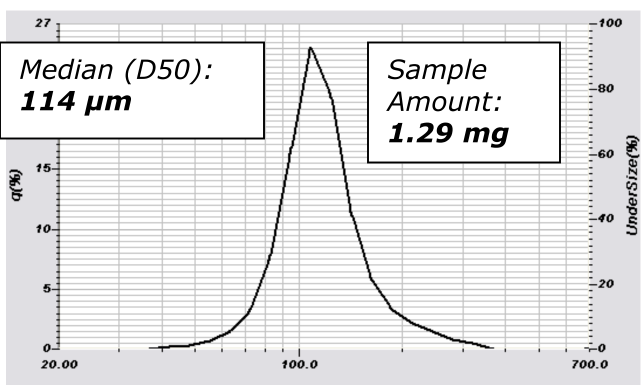
How much sample (wet)?

It depends on sample, but here are some examples.

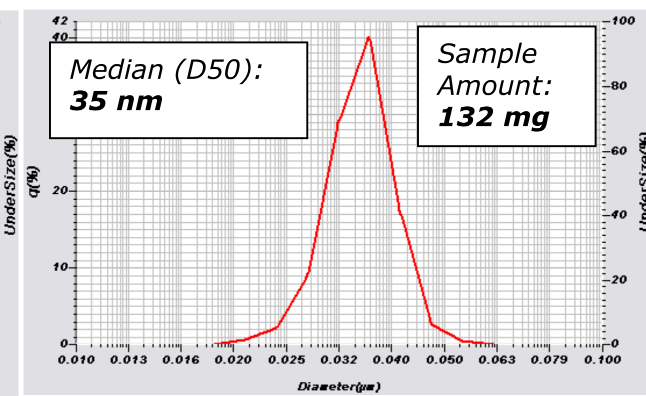
- **Larger, broad distributions require larger sample volume**
- **Lower volume samplers for precious materials or solvents**

Sample Handlers	Dispersing Volume (mL)
Aqua/Solvo Flow	**180 - 330**
MiniFlow	**35 - 50**
Fraction Cell	**15**
Small Volume Fraction Cell	**10**

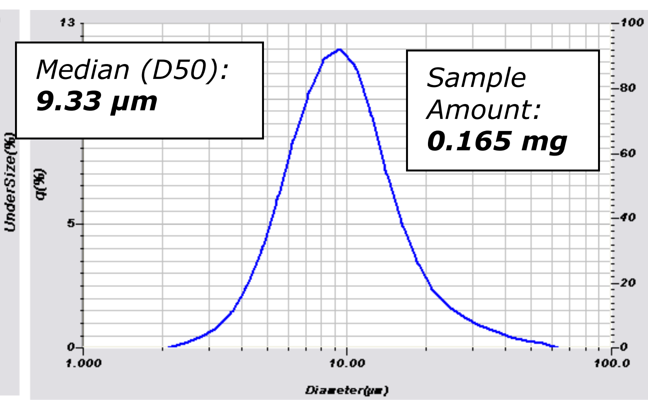
Note: Fraction cell has only magnetic stir bar, not for large or heavy particles



Bio polymer



Colloidal silica



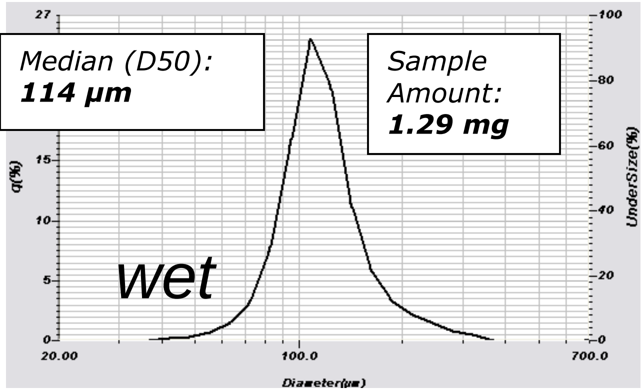
Magnesium stearate

How much sample (dry)?

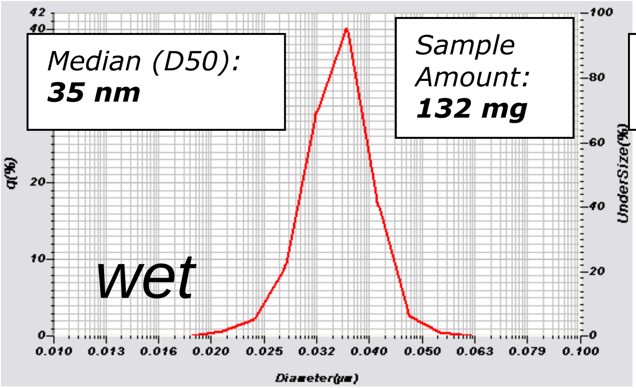
It depends on sample …..

Larger, broad distributions require larger sample quantity

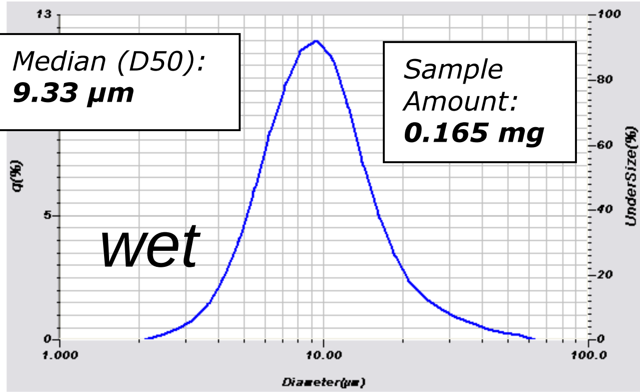
Can measure less than 5 mg (over a number of particle sizes).



Bio polymer



Colloidal silica



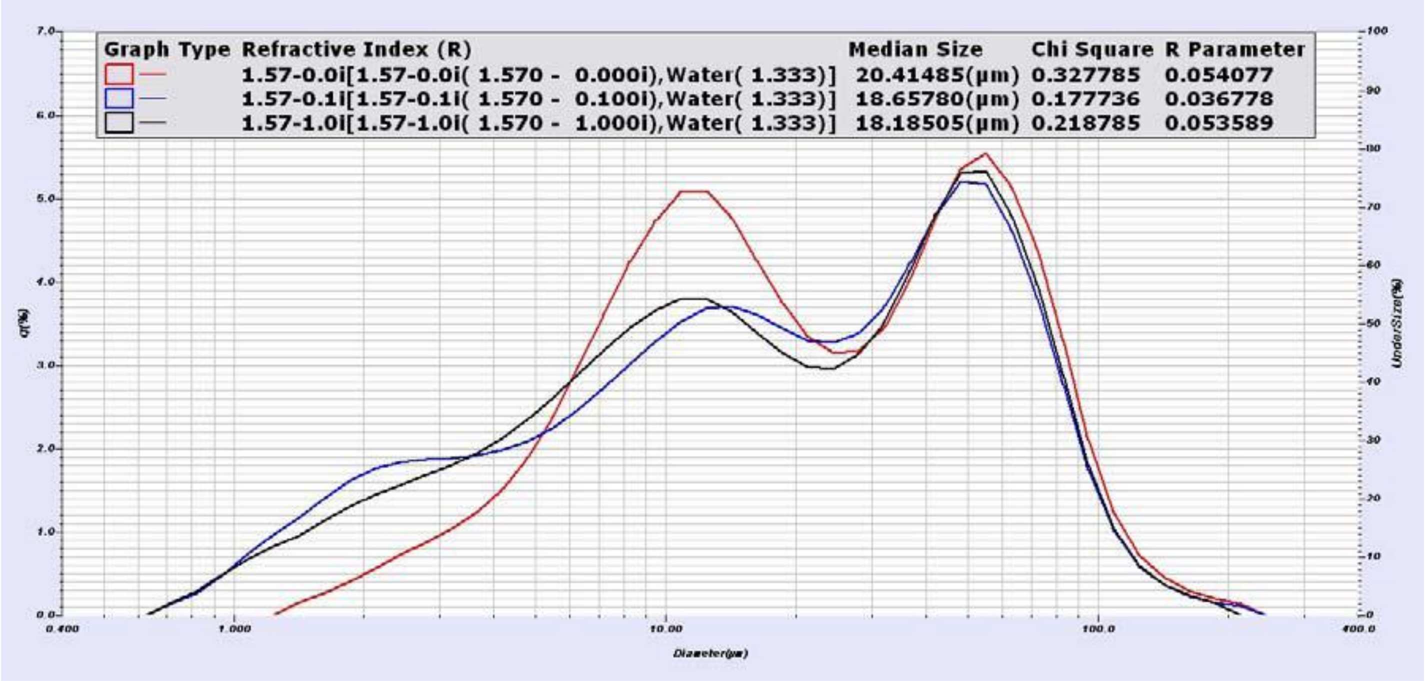
Magnesium stearate

Method Workflow

- Determine particle refractive index (RI)
- Choose diluent (water, surfactants, hexane, etc.)
- Sampler selection: sample volume
- Pump & stirrer settings
- Concentration
- Measurement duration
- Does the sample need ultrasound?
  - Document size-time plot
  - Disperse sample, but don’t break particles
  - Check for reproducibility

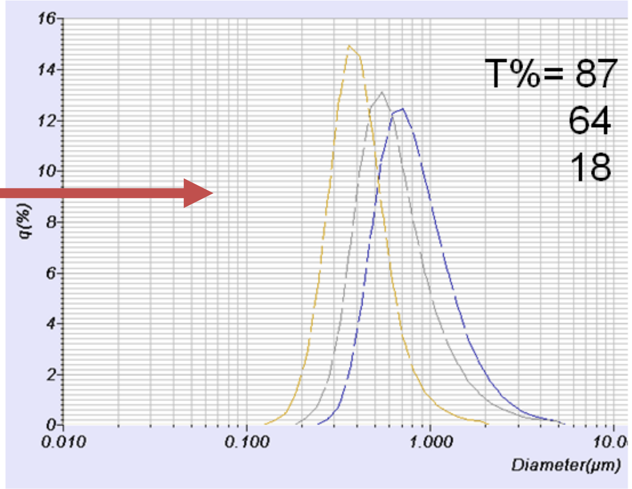
Determine Refractive Index

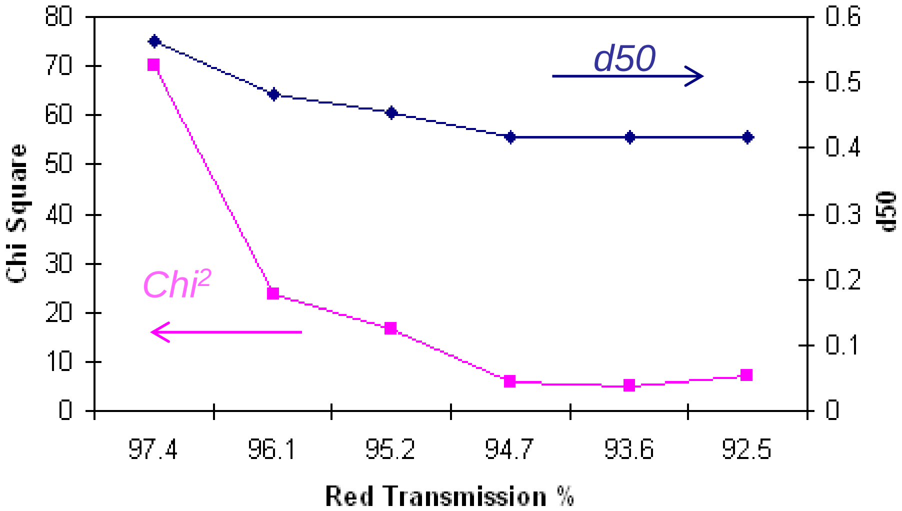
- Real component via literature or web search, Becke line, etc.
- Measure sample, vary imaginary component to see if/how results change
- Recalculate using different imaginary components, choose value that minimizes R parameter error calculation

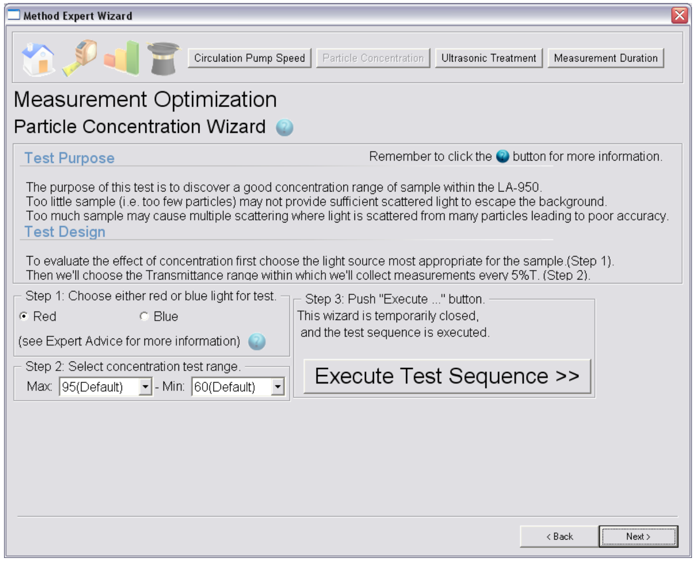


Concentration

- High enough for good S/N ratio
- Low enough to avoid multiple scattering
- Typically 95 – 80 %T
- Measure at different T%, look at d50 result, Chi Square calculation





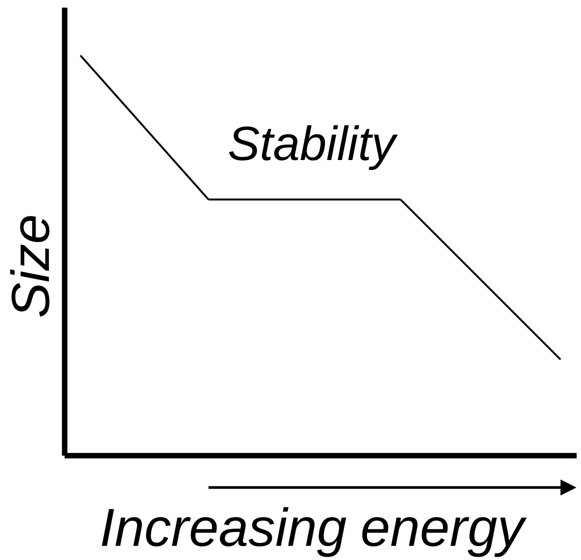


Ultrasonic Dispersion

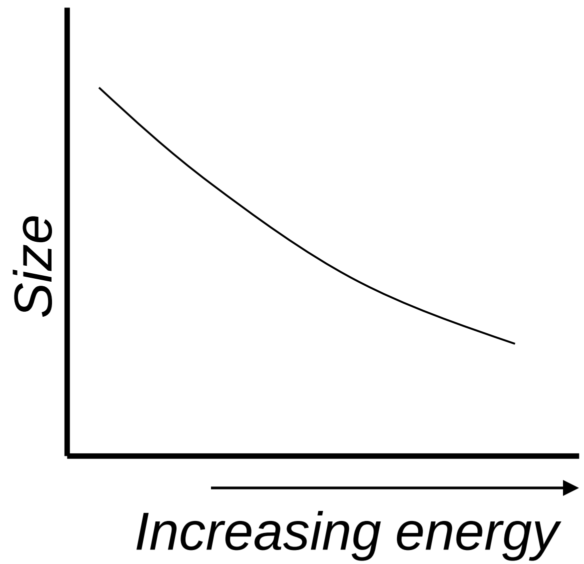
- Adding energy to break up agglomerates – disperse to primary particles, without breaking particles
- Similar to changing air pressure on dry powder feeder
- Typically set to 100% energy, vary time (sec) on
- Investigate tails of distribution
  - High end to see if agglomerates removed
  - Small end to see if new, smaller particles appear (breakage)
- Test reproducibility, consider robustness
- Note:
  - Do not use on emulsions
  - Can cause thermal mixing trouble w/solvents - wait
  - Use external probe if t> 2-5 minutes

Dispersion vs. Breakage

Theoretical



Actual

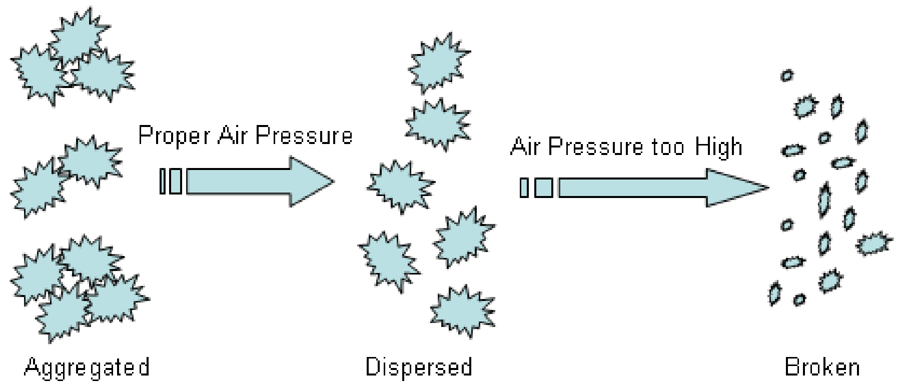


Higher air pressure or longer ultrasound duration

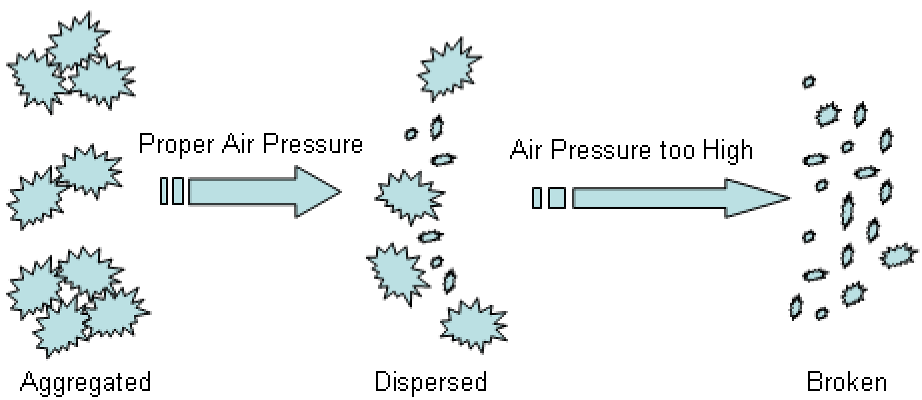
Dispersion vs. Breakage

Dispersion and milling can be parallel rather than sequential processes

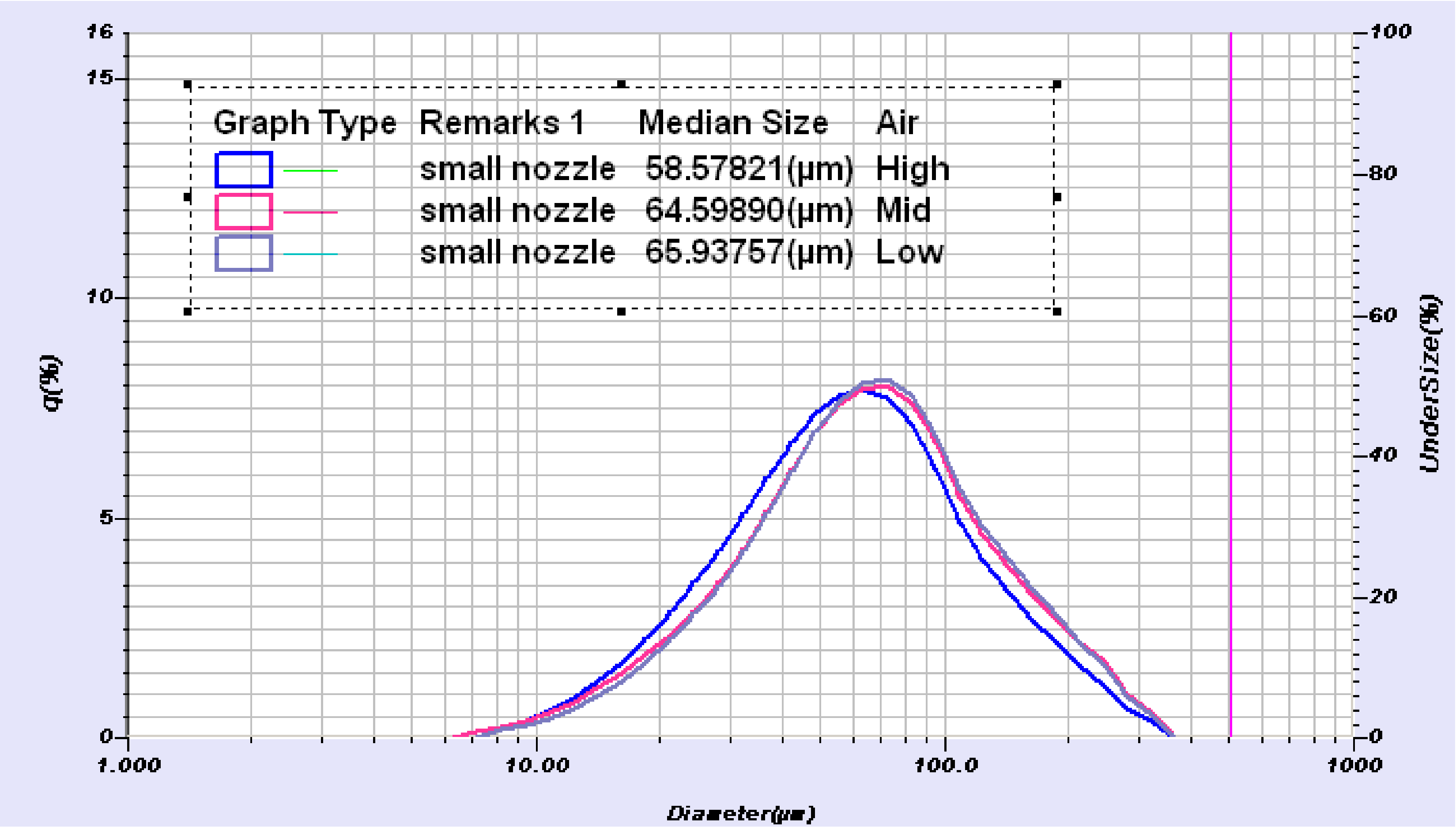
Theoretical



Actual



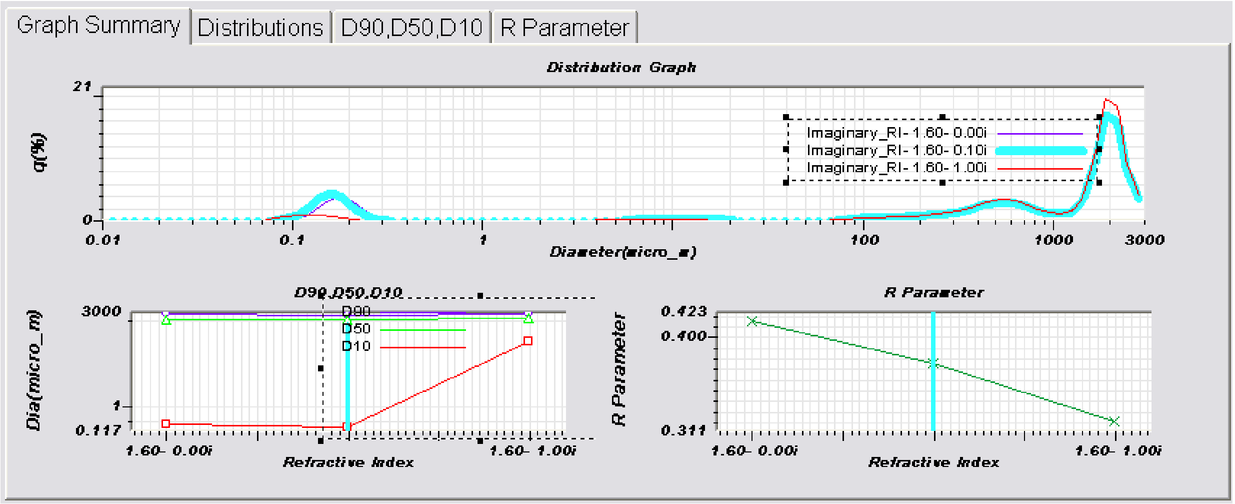
Effect of Air Pressure: MCC



LA-960 Method Expert

Method Expert guides user to prepare the LA-960 for each test

Results displayed in multiple formats: PSD, D50, R-parameter



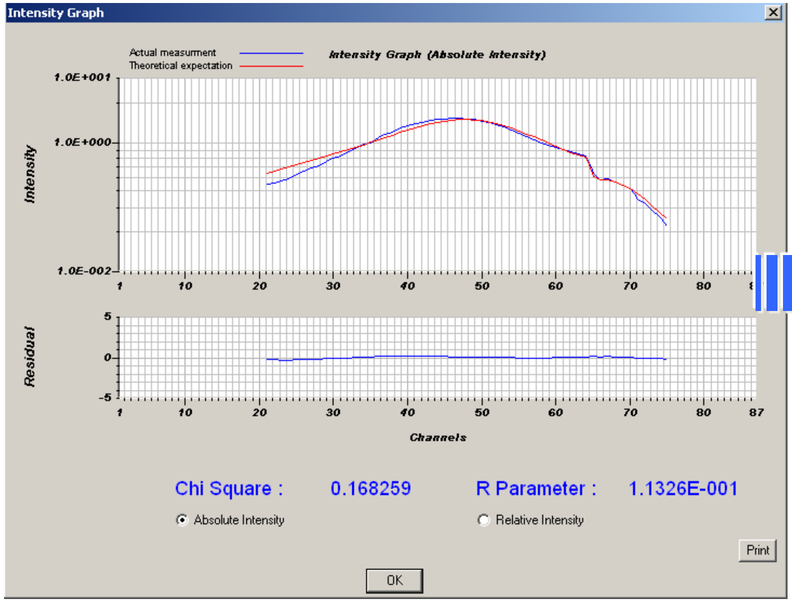
Measurement Workflow

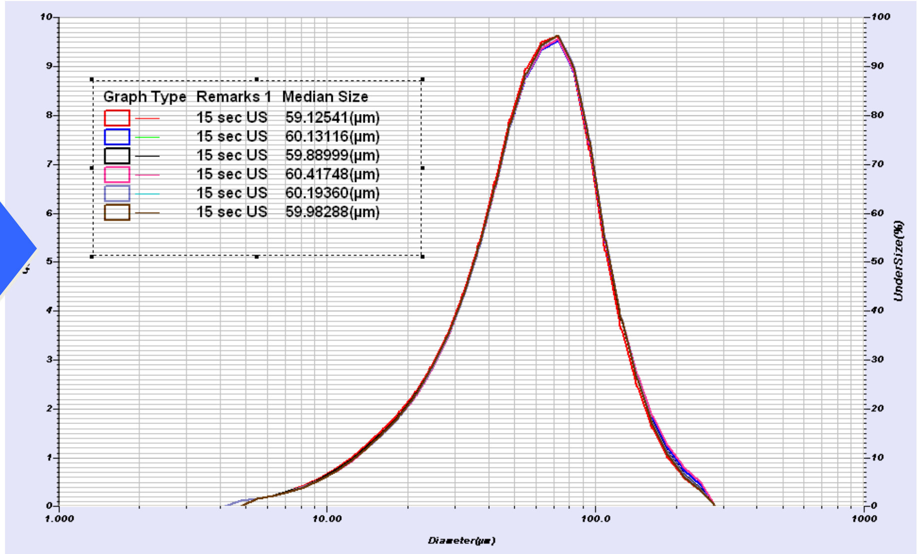
Measurement

Click “Measure” button

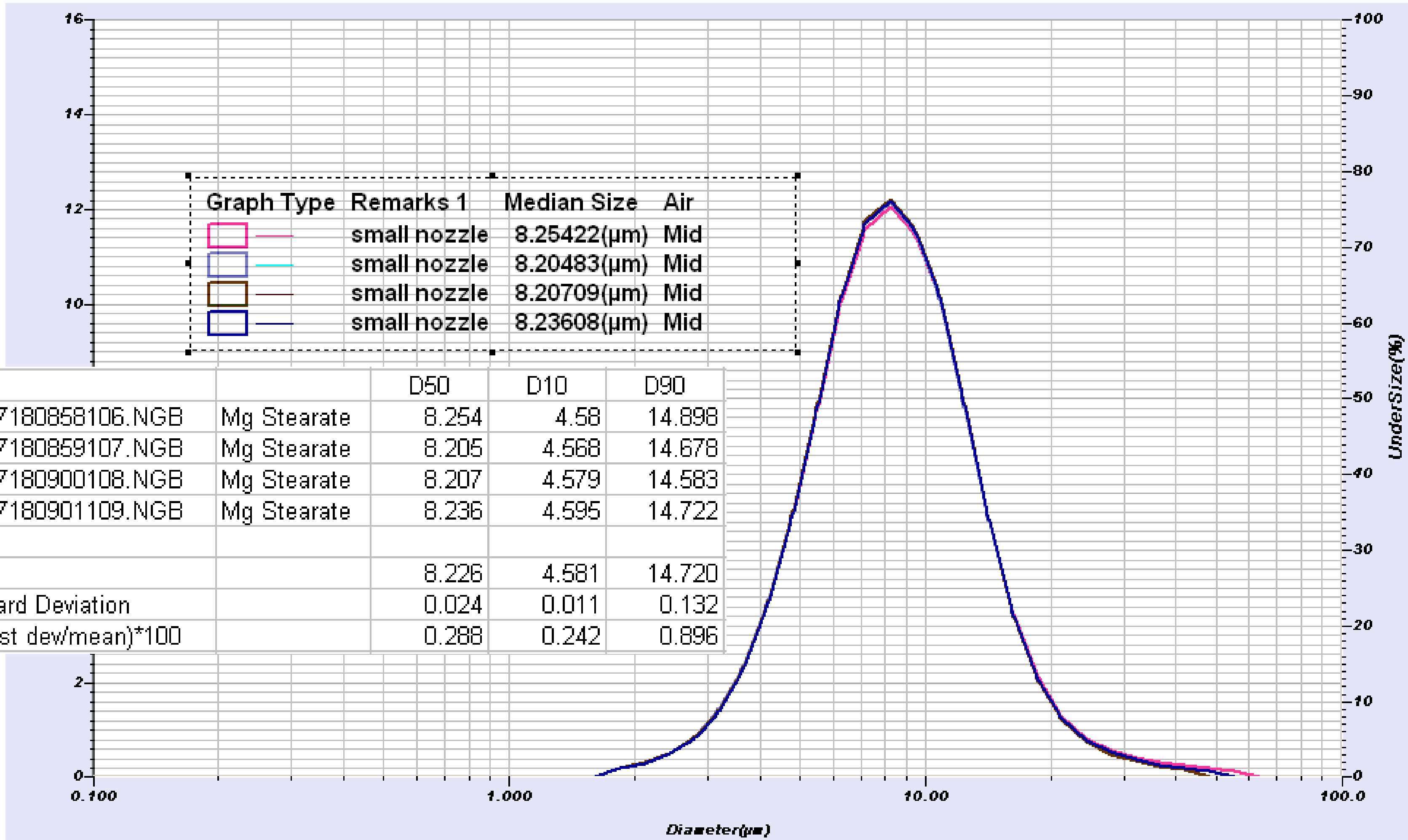
Hardware measures scattered light distribution

Software then calculates size distribution





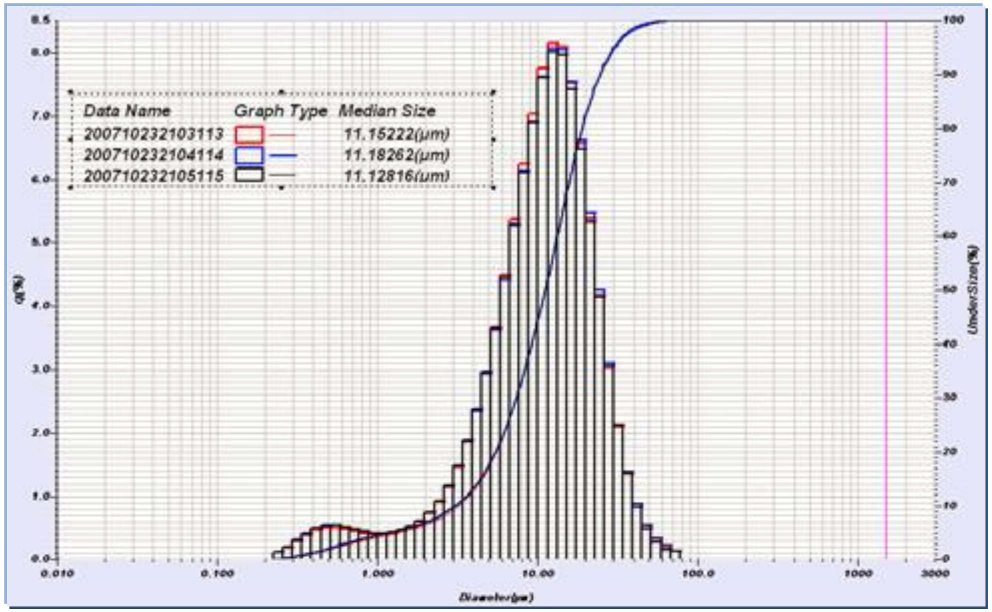
Reproducibility– Mg Stearate dry, 2 bar



		D50	D10	D90
200707180858106.NGB	Mg Stearate	8.254	4.58	14.898
200707180859107.NGB	Mg Stearate	8.205	4.568	14.678
200707180900108.NGB	Mg Stearate	8.207	4.579	14.583
200707180901109.NGB	Mg Stearate	8.236	4.595	14.722
Mean		8.226	4.581	14.720
Standard Deviation		0.024	0.011	0.132
COV (st dev/mean)*100		0.288	0.242	0.896

Cement Dry

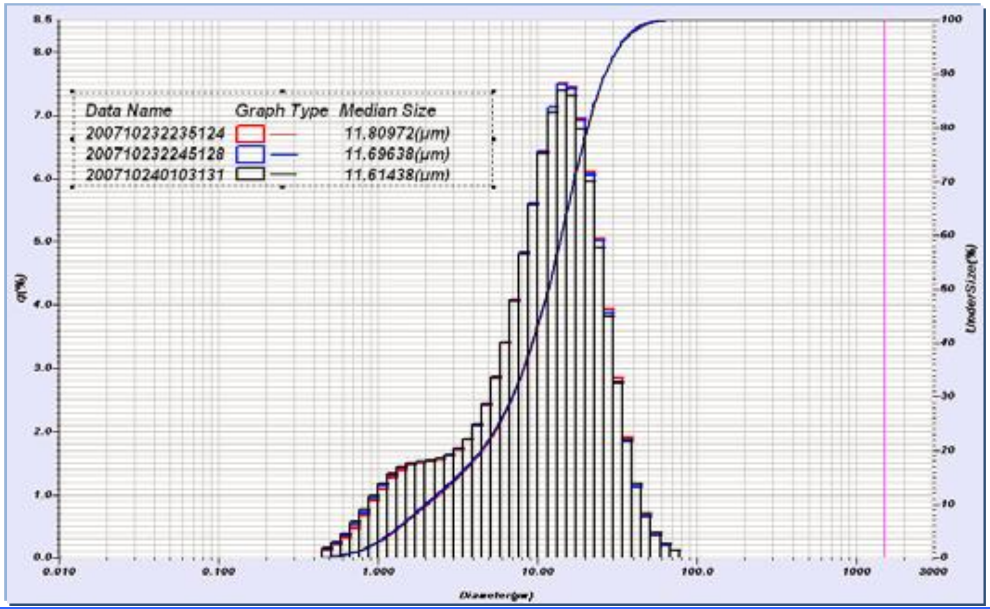
	D10	D50	d90
Portland Cement 1	3.255	11.152	24.586
Portland Cement 2	3.116	11.183	24.671
Portland Cement 3	3.112	11.128	24.92
Average	3.161	11.154	24.726
Std. Dev.	0.082	0.027	0.173
CV (%)	2.6	0.24	0.70



Cement Wet

Measure in isopropyl alcohol (IPA) (not water)

	D10	D50	d90
Portland Cement 1	2.122	11.81	27.047
Portland Cement 2	2.058	11.696	26.743
Portland Cement 3	1.999	11.614	27.001
Average	2.06	11.707	26.93
Std. Dev.	0.062	0.098	0.164
CV (%)	3.0	0.84	0.61



Instrument to instrument variation

20 instruments, 5 standards

Sample	CV D10	CV D50	CV D90
PS202 (3-30µm)	**2%**	**1%**	**2%**
PS213 (10-100µm)	**2%**	**2%**	**2%**
PS225 (50-350µm)	**1%**	**1%**	**1%**
PS235 (150-650µm)	**1%**	**1%**	**2%**
PS240 (500-2000µm)	**3%**	**2%**	**2%**
These are results from running polydisperse standards on 20 different instruments			

Instrument to instrument variation

Industrial Samples

[illegible]	Dmean	D5	D10	D50	D90	D95
Average (nm)	155	112	119	152	193	208
Std. Dev. (nm)	0.8	0.8	0.7	1.0	1.1	0.7
CV (%)	0.5	0.7	0.6	0.6	0.6	0.3

e 8: Instrument to instrument variation across four LA-950 systems for Formulation 1.

[illegible]	Dmean	D5	D10	D50	D90	D95
Average (nm)	193	136	147	187	247	264
Std. Dev (nm)	1.5	0.5	0.4	0.6	0.4	1.1
CV (%)	0.8	0.4	0.3	0.3	0.2	0.4

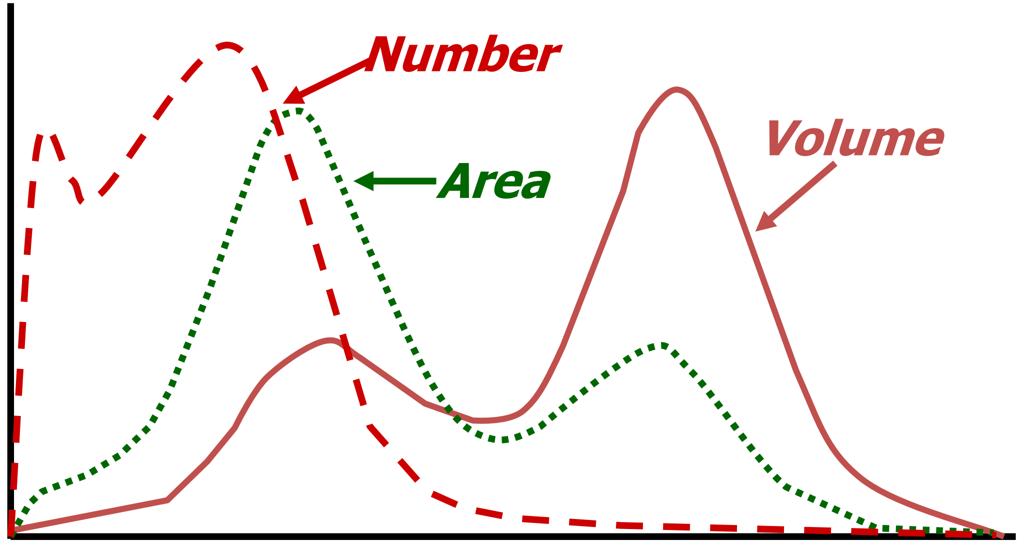
e 9: Instrument to instrument variation across four LA-950 systems for Formulation 2.

Diffraction Drawbacks

Volume basis by default

Although excellent for mass balancing, cannot calculate number basis without significant error

No shape information



Benefits

- **Wide size range**
  - **Most advanced analyzer measures from 10 *nano* to 5 *milli***
- **Flexible sample handlers**
  - **Powders, suspensions, emulsions, pastes, creams**
- **Very fast**
  - **Allows for high throughput, 100's of samples/day**
- **Easy to use**
  - **Many instruments are highly automated with self-guided software**
- **Good design = Excellent precision**
  - **Reduces unnecessary investigation/downtime**
- **First principle measurement**
  - **No calibration necessary**
- **Massive global install base/history**

Q&A

Ask a question at [labinfo@horiba.com]

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Thank-you