Introduction to Laser Diffraction

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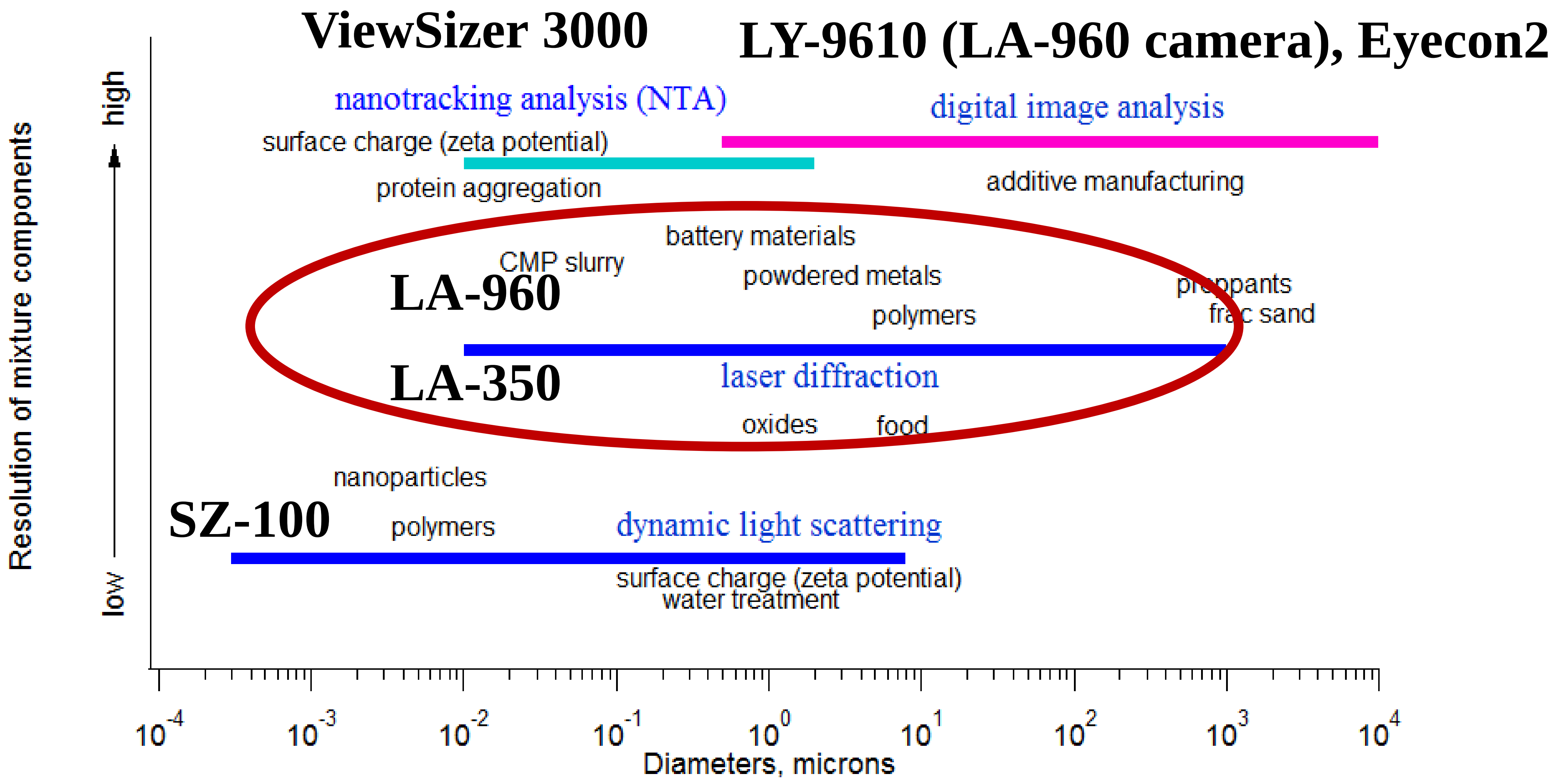
Perspective



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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**	 

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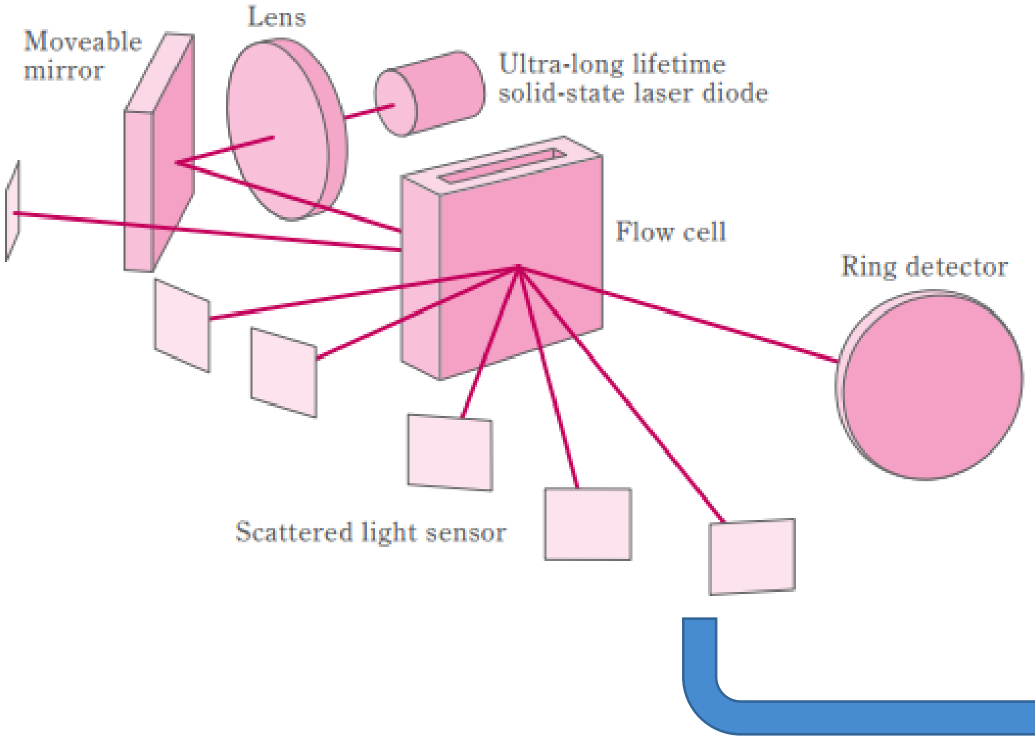
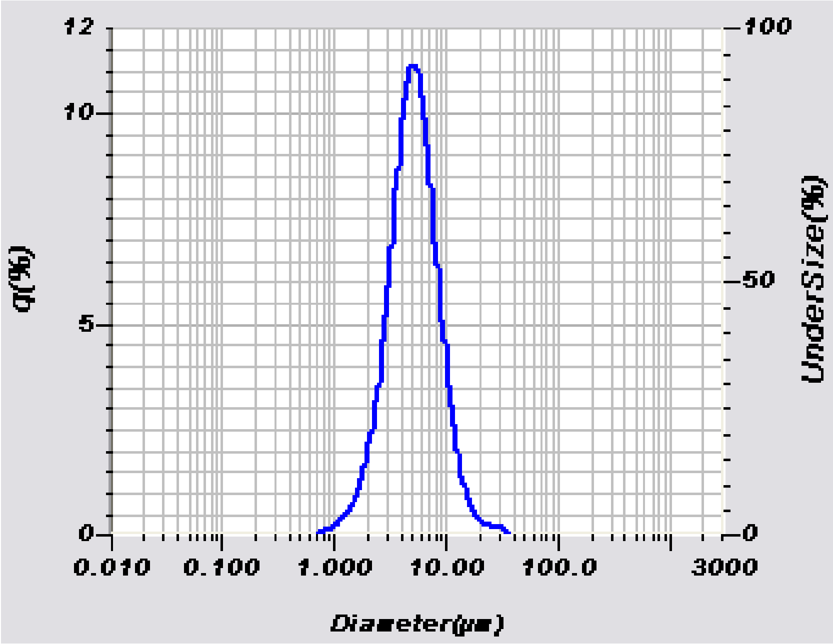
Core Principle

Investigate a particle sample with light and determine size distribution.





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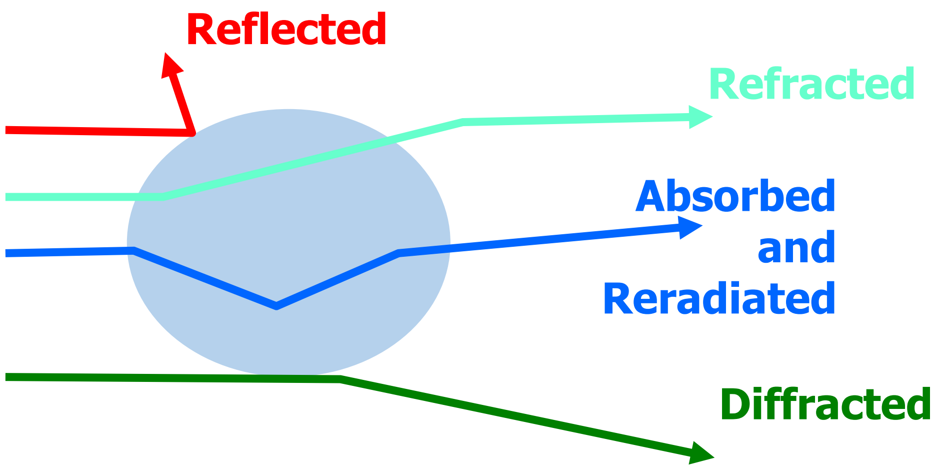
When light strikes a particle

Some of the light is:

Diffracted
Reflected
Refracted
Absorbed and Reradiated



Small particles require knowledge of optical properties to tell math what light does inside of particle:

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

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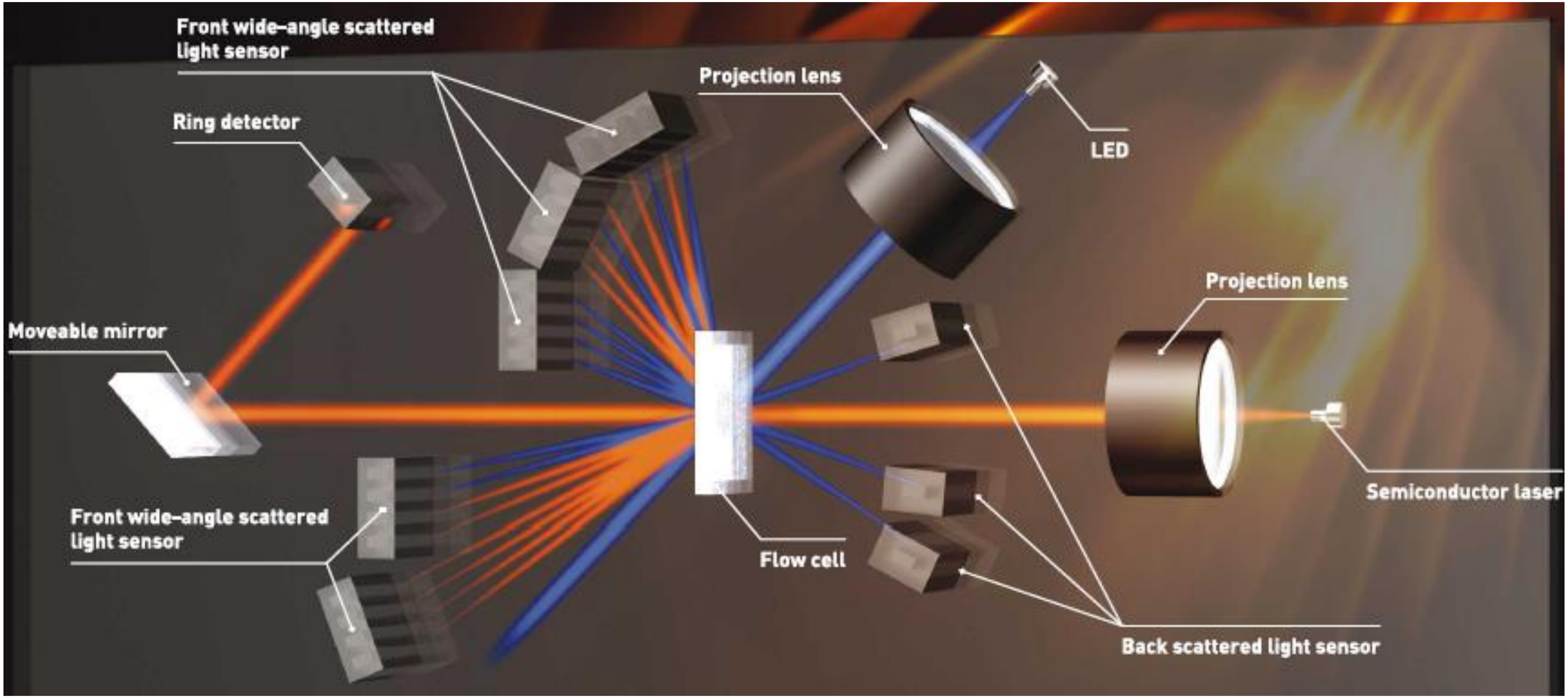
LA-960 optics



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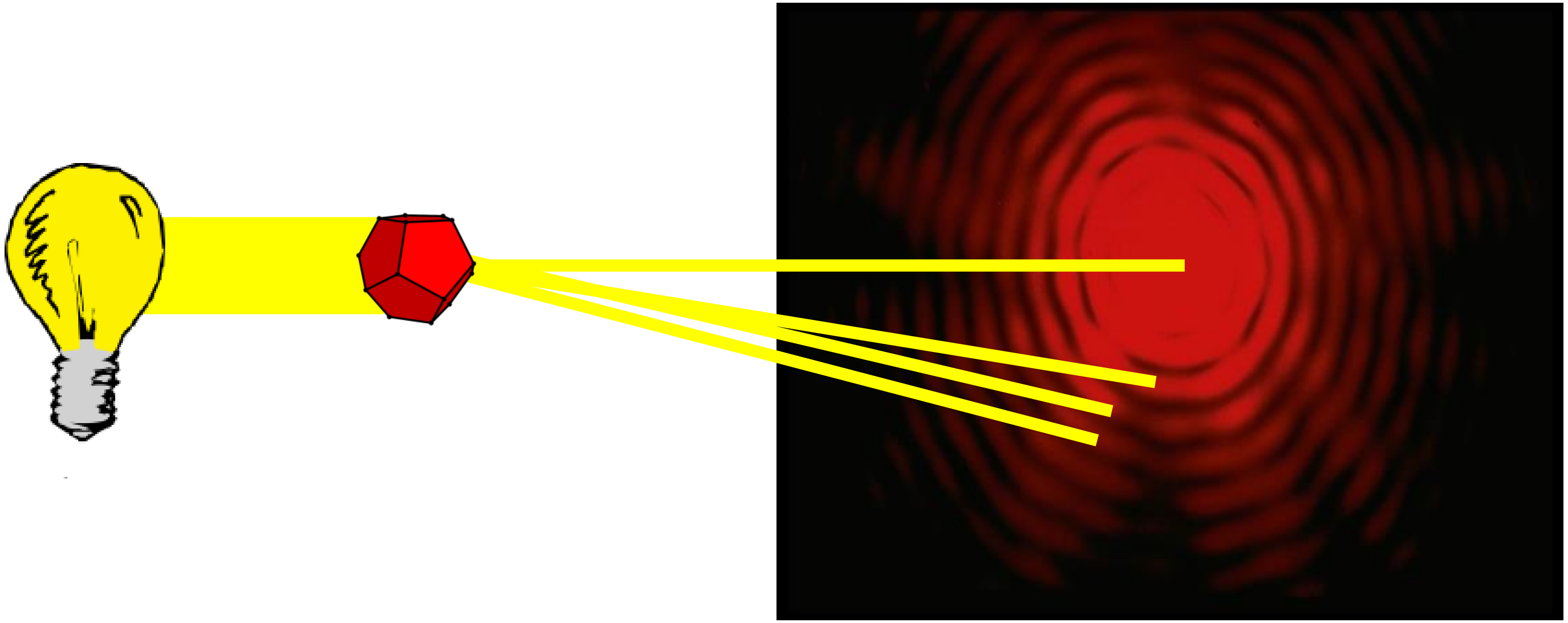
Diffraction pattern



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Light

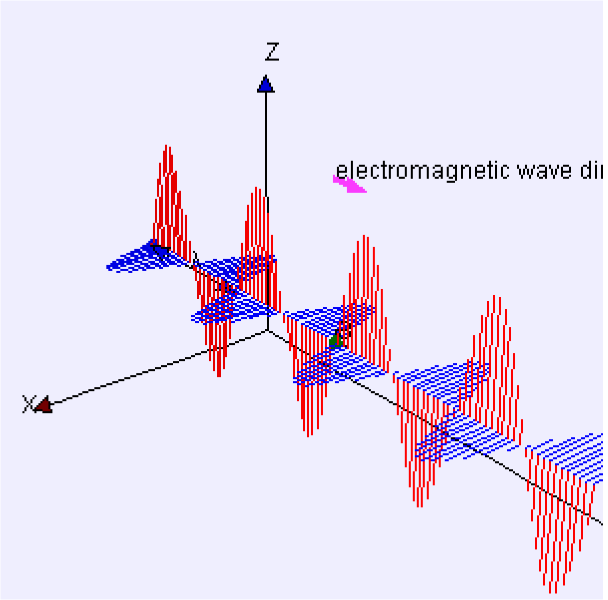
Expressed in just in y-direction

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

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

Oscillating electric field

Oscillating magnetic field (orthogonal to electric field)



Complements of Lookang @ weelookang.blogspot.com

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Light: Interference

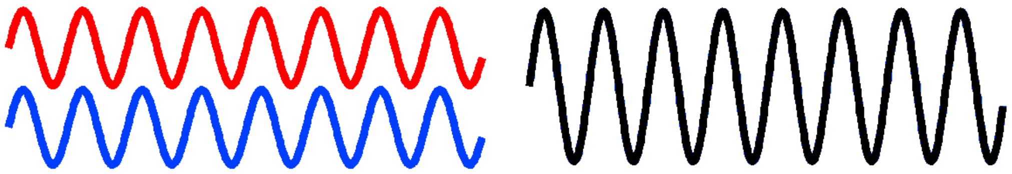
Look at just the electric field.

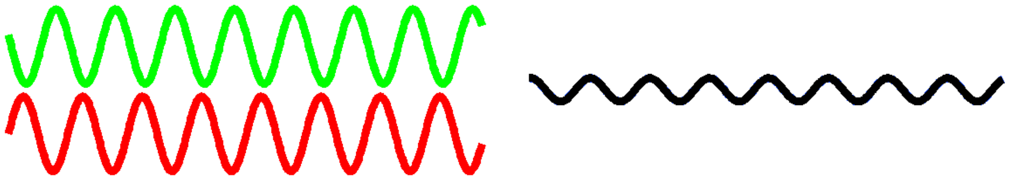
Oscillating electric field

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

Second electric field with phase shift

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





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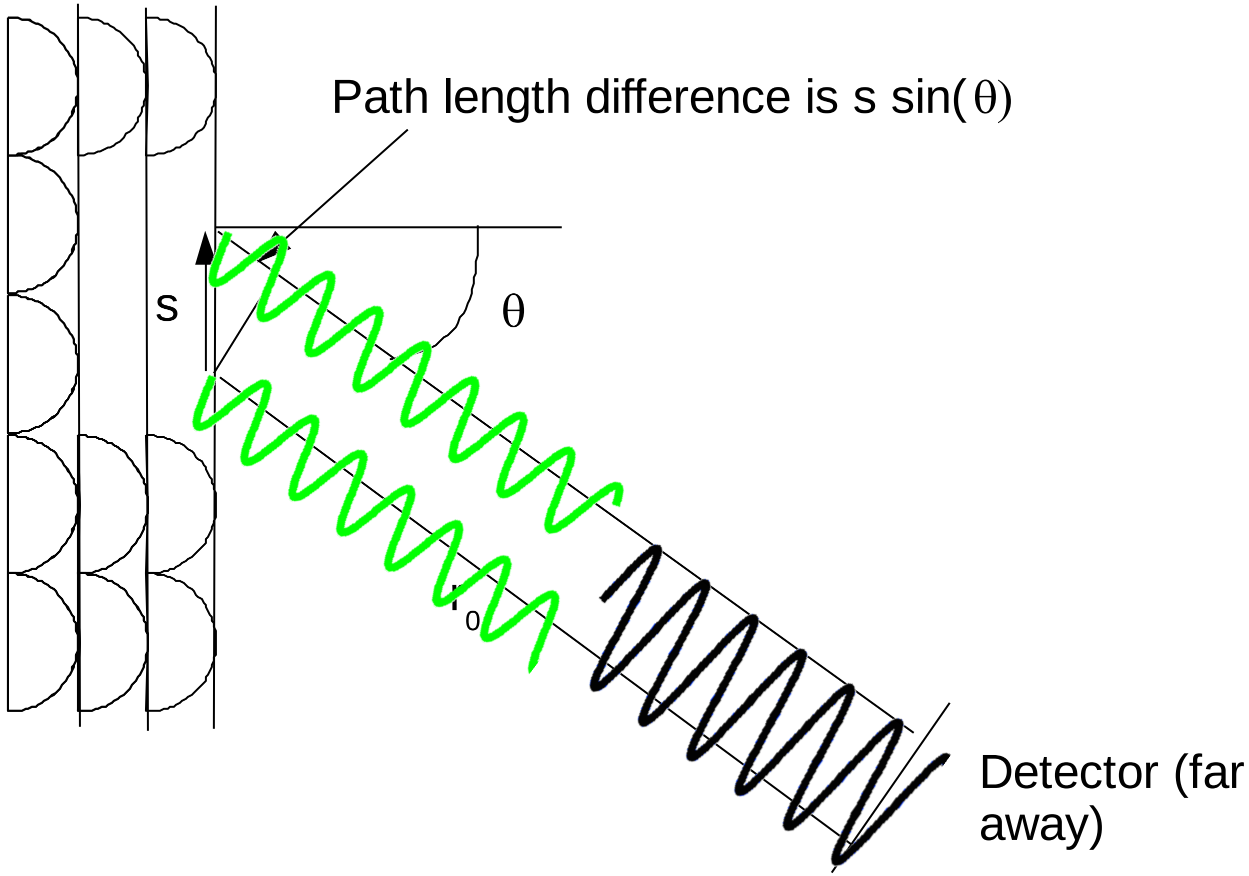
Path Length Difference



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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.

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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

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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 **50 µm**, then the Fraunhofer approximation gives good results.

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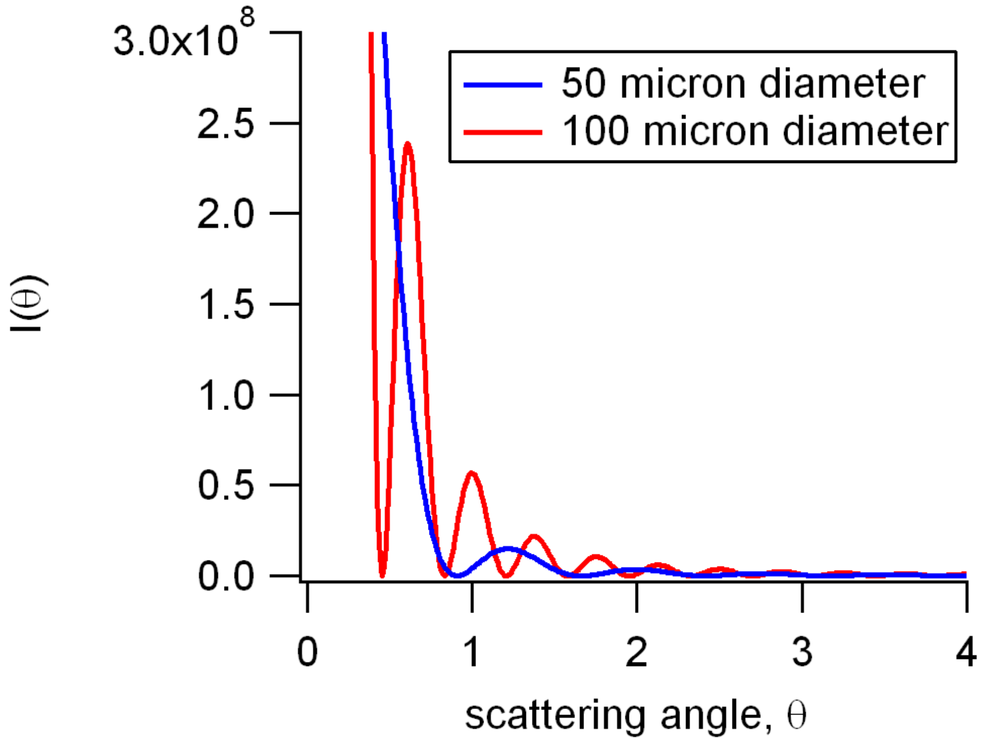
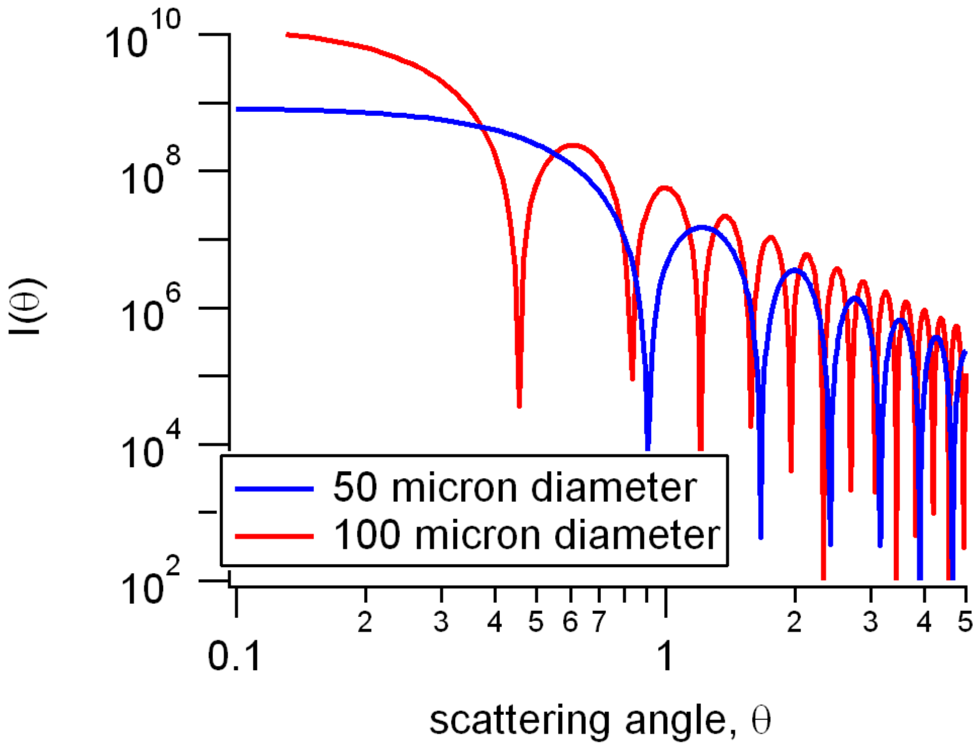
Fraunhofer: Effect of Particle Size





Smaller angles for larger particles
High intensity for larger particles

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Poll

Do you work with Particles

Over 1 mm?

Between 50 microns and 1 mm?

Between 2 microns and 50 microns?

Less than 2 microns?

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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!

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

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

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

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

ξ, ψ: Ricatti-Bessel functions

P_n^1:1st order Legendre Functions

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

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

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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

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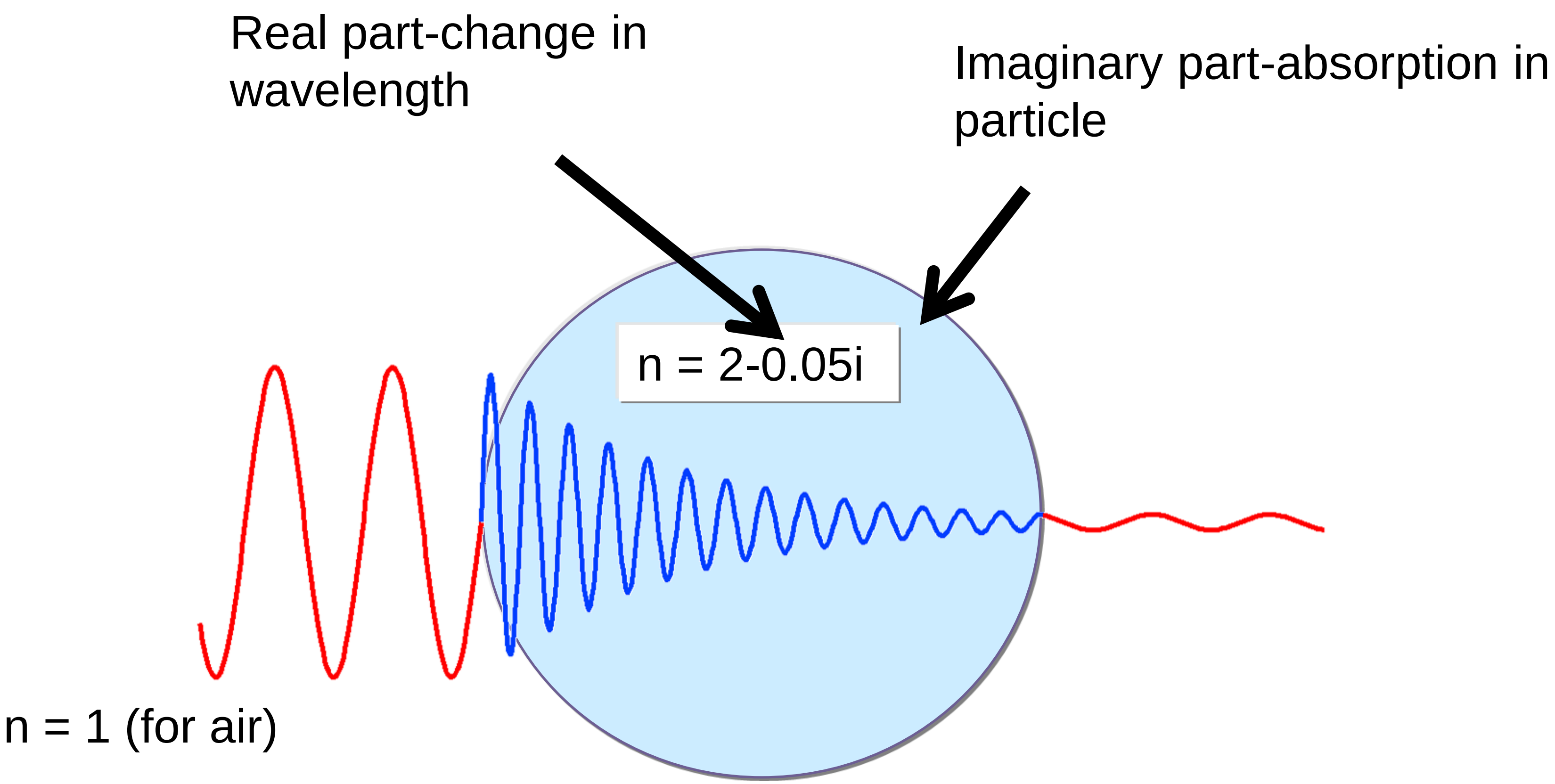
Refractive Index



ISO-13320:2020, 5.5.4: "To obtain traceable results it is essential that the refractive index values are used as reported."

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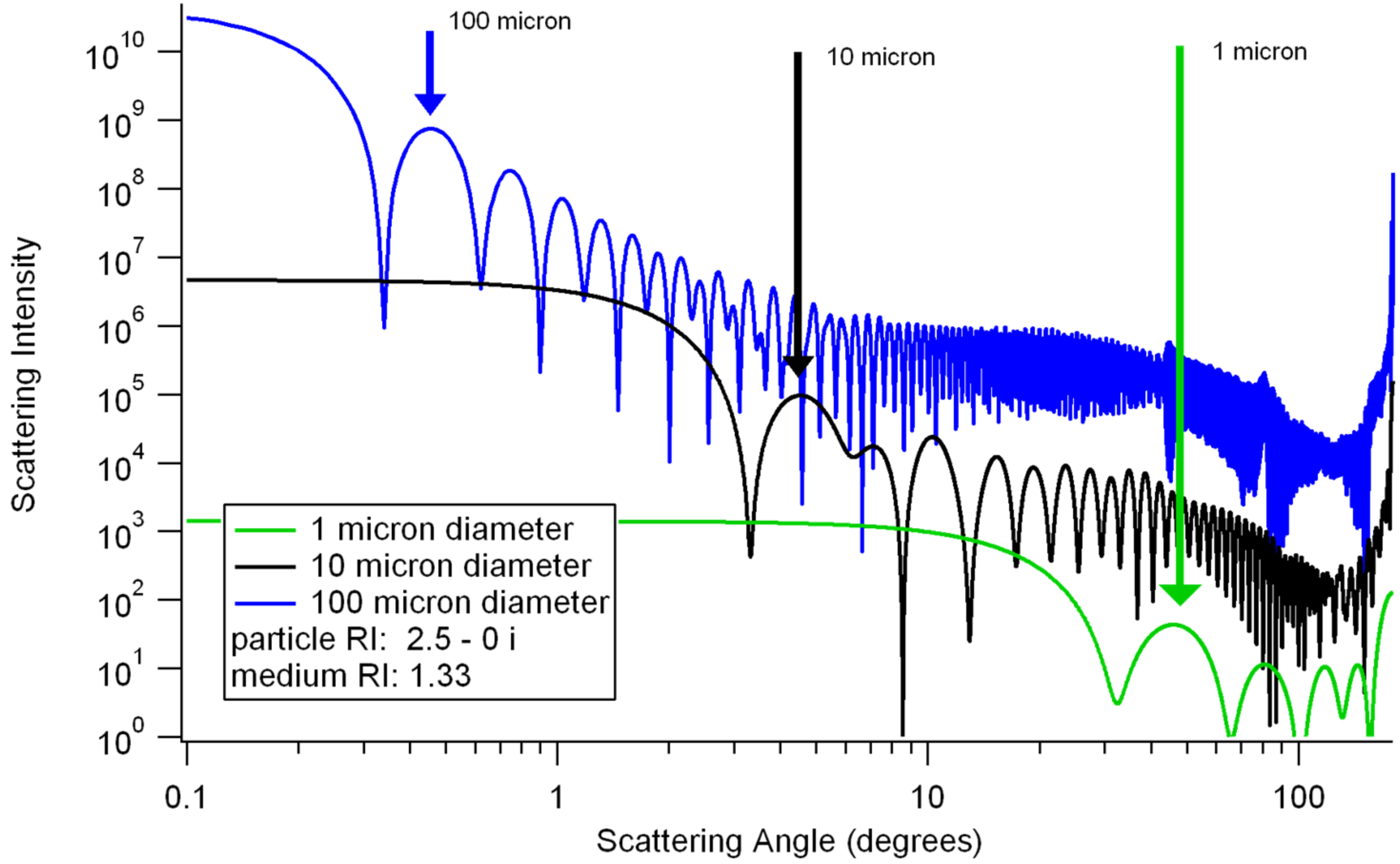
Effect of Size



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

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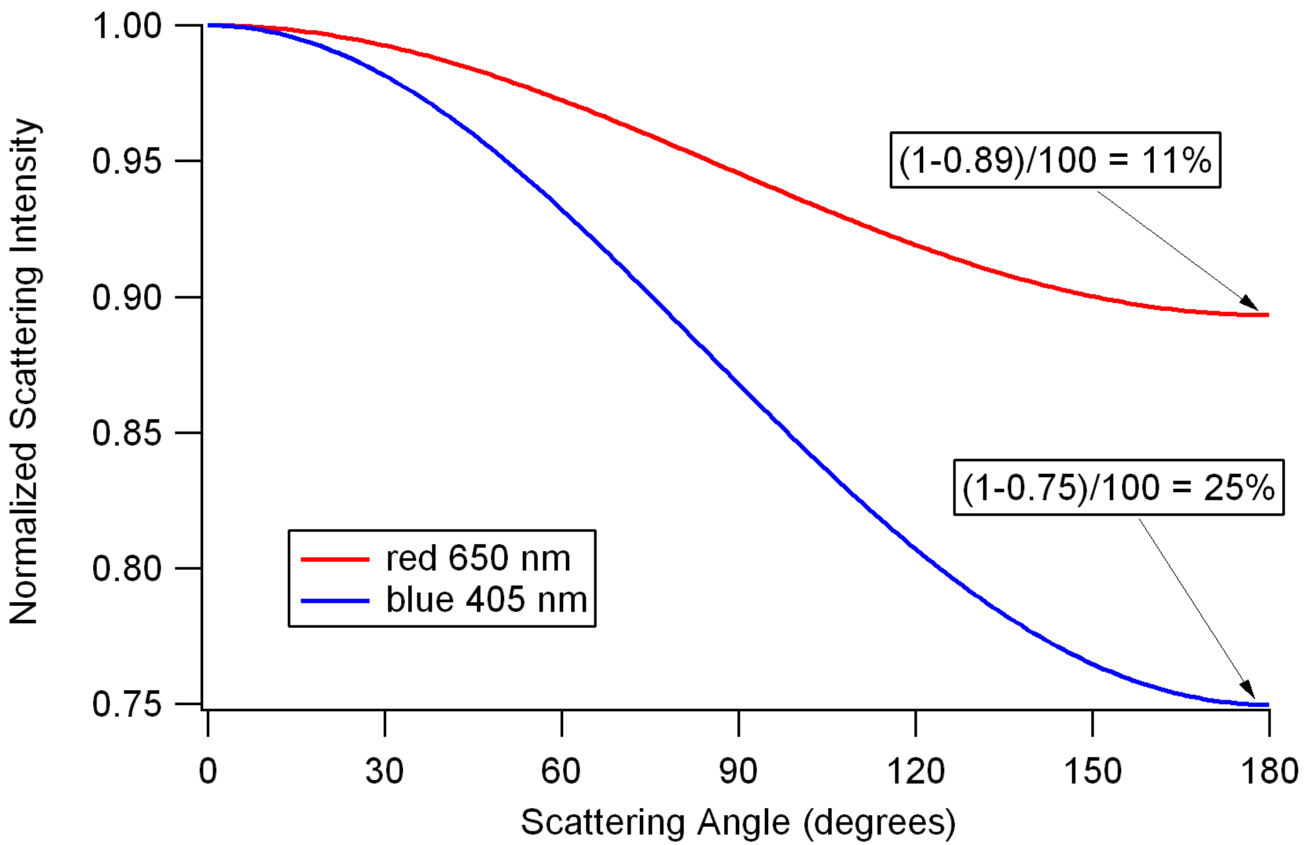
Small Particles -> Blue light



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.

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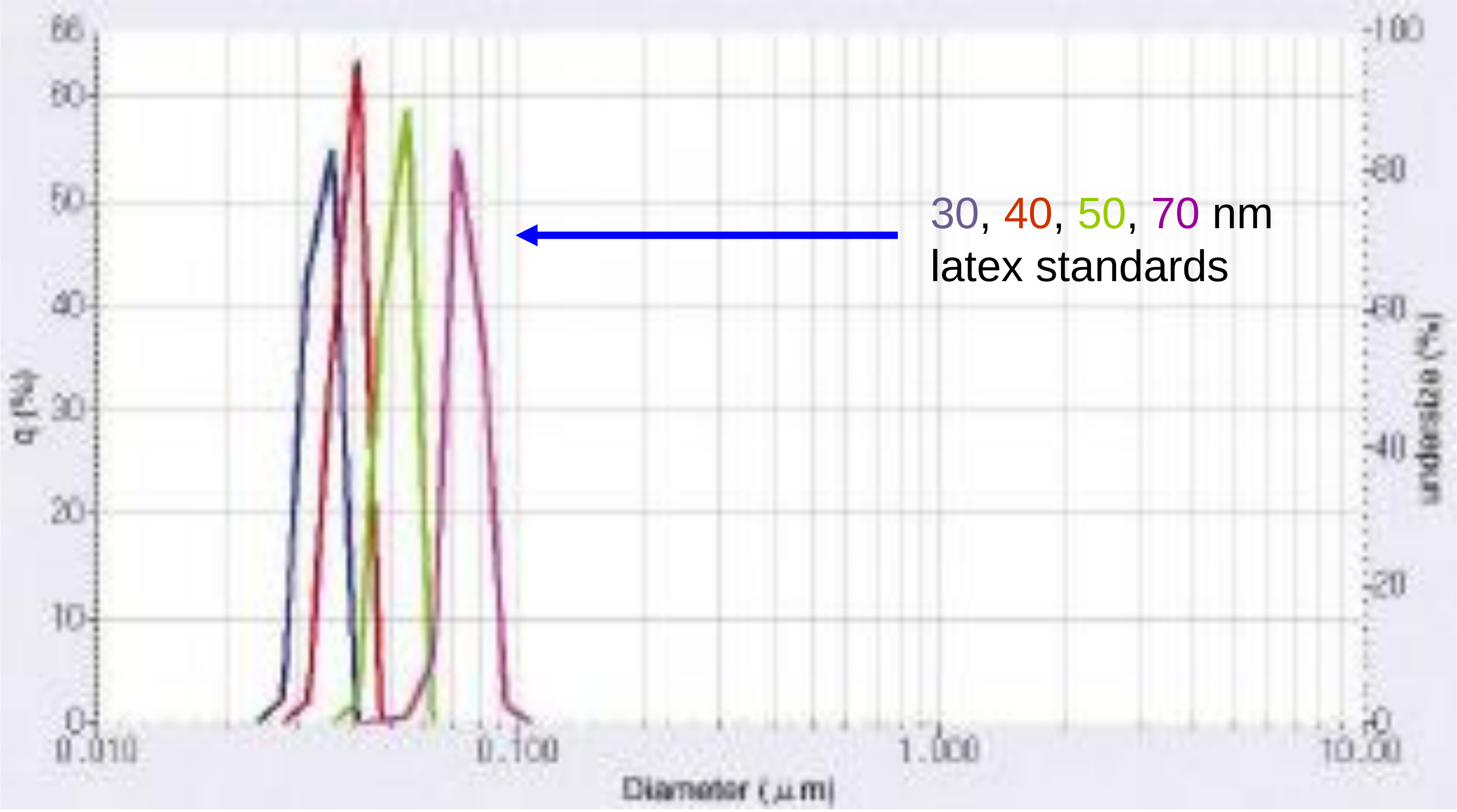
Example Results



30, 40, 50, 70 nm
latex standards

Data from very small particles.

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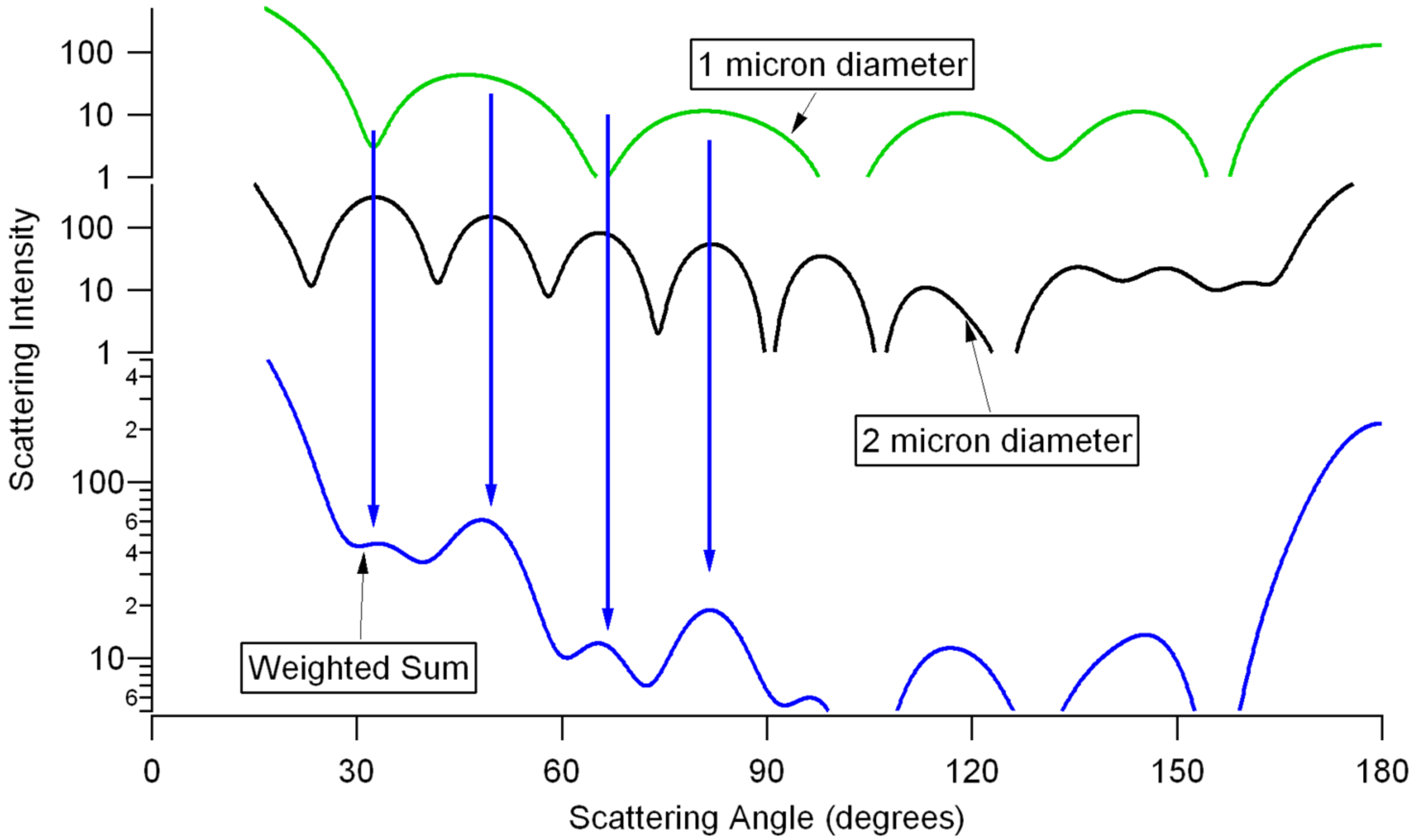
Mixing Particles? Just Add



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.

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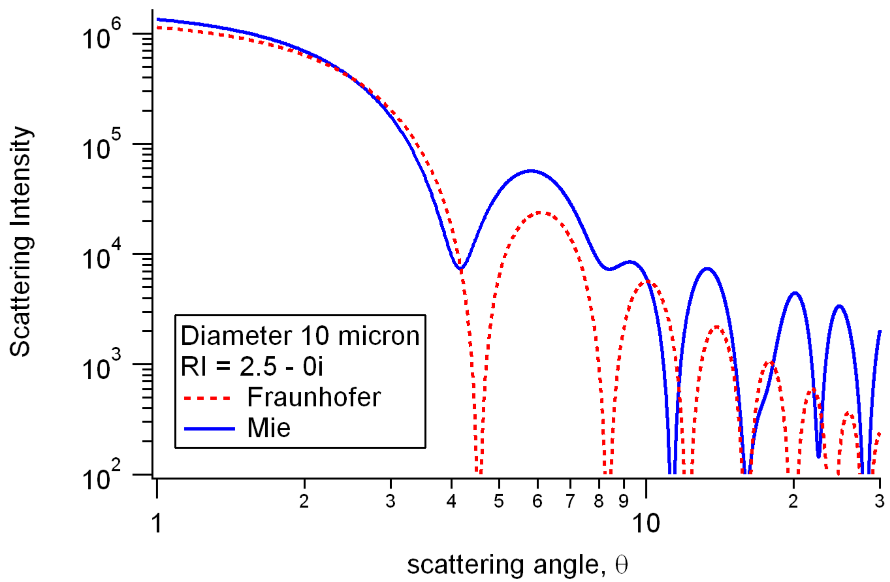
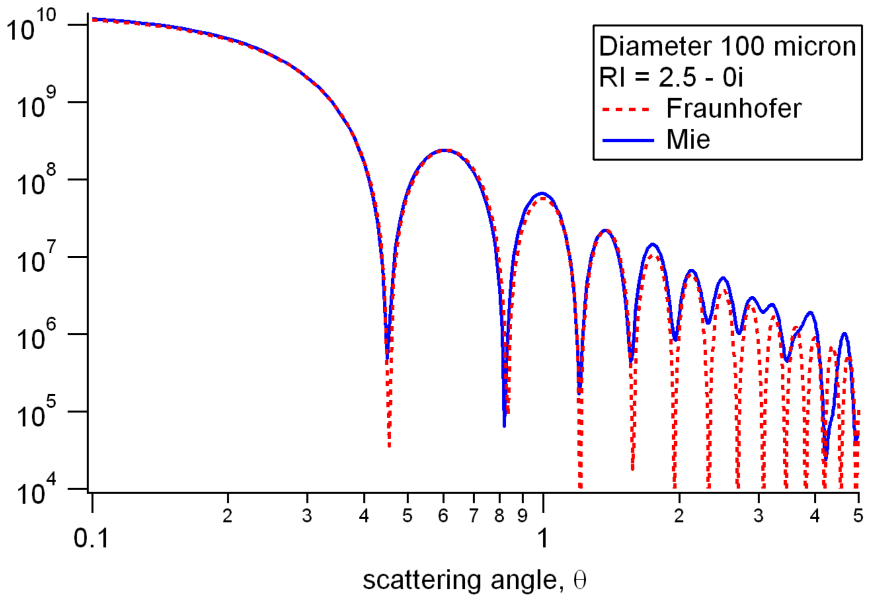
Mie vs Fraunhofer



For small particles, match is poor. Use Mie.



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

Computers are fast so no practical reason for Fraunhofer.

ISO-13320:2020, A.5: For most particles larger than about 50 μm with relative refractive index greater than 1,2, such knowledge may not be necessary, as the Mie theory and Fraunhofer approximation give similar results.

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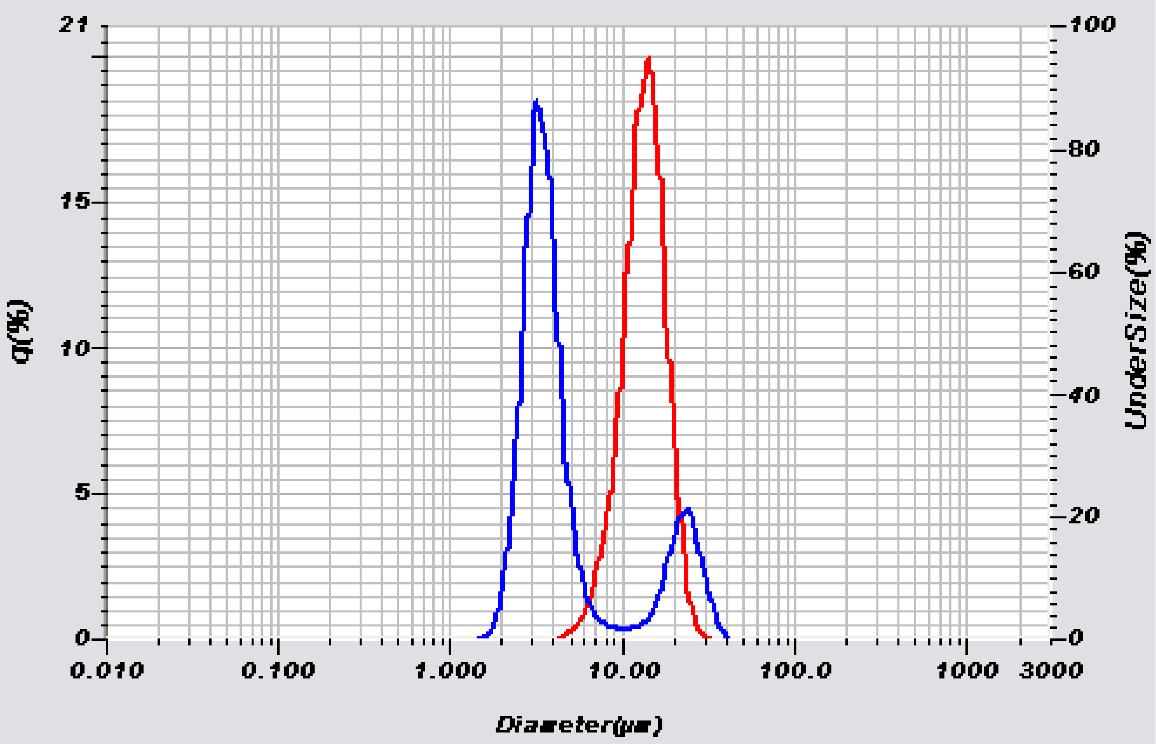
Glass Beads and Models

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

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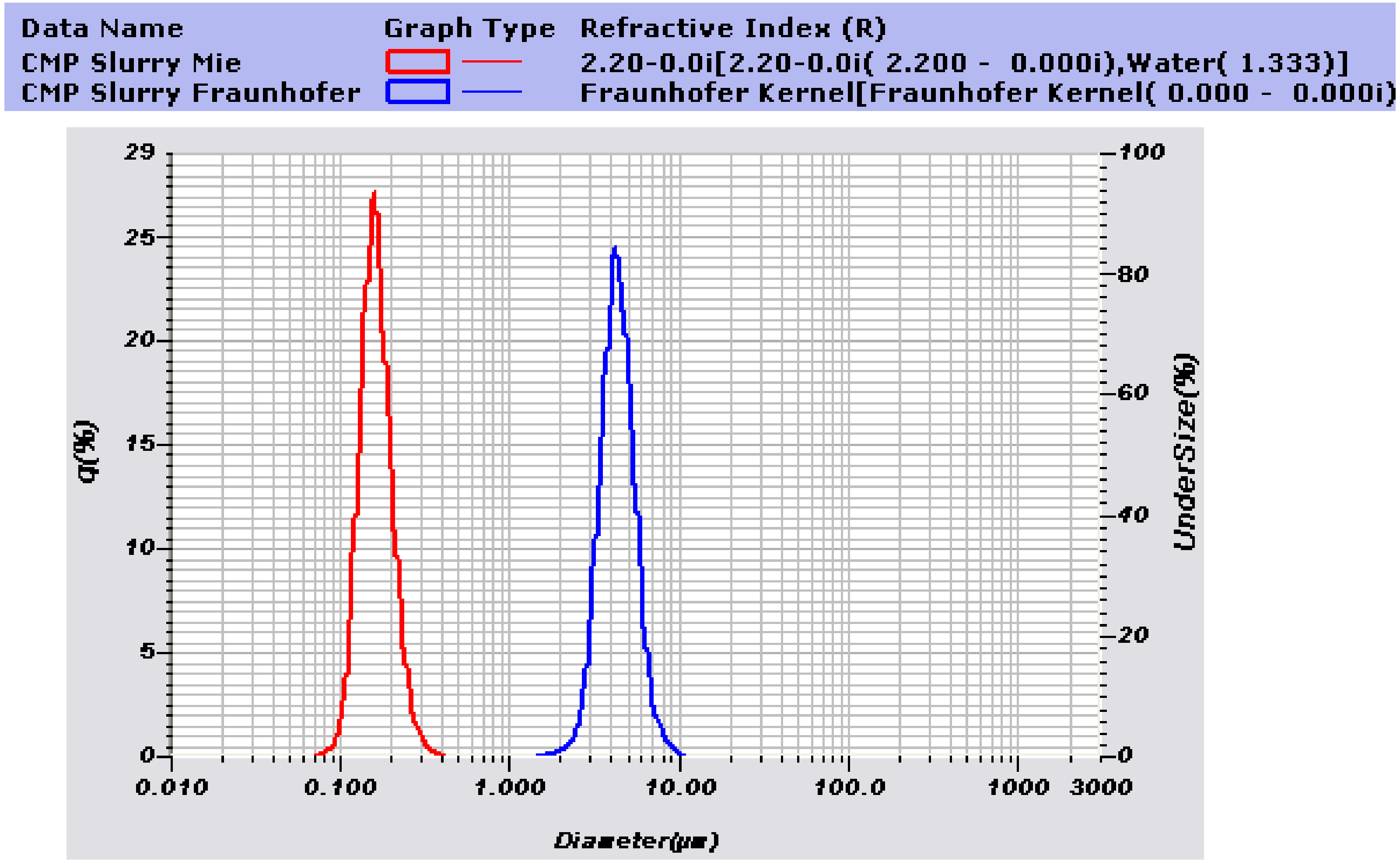
CMP Slurry



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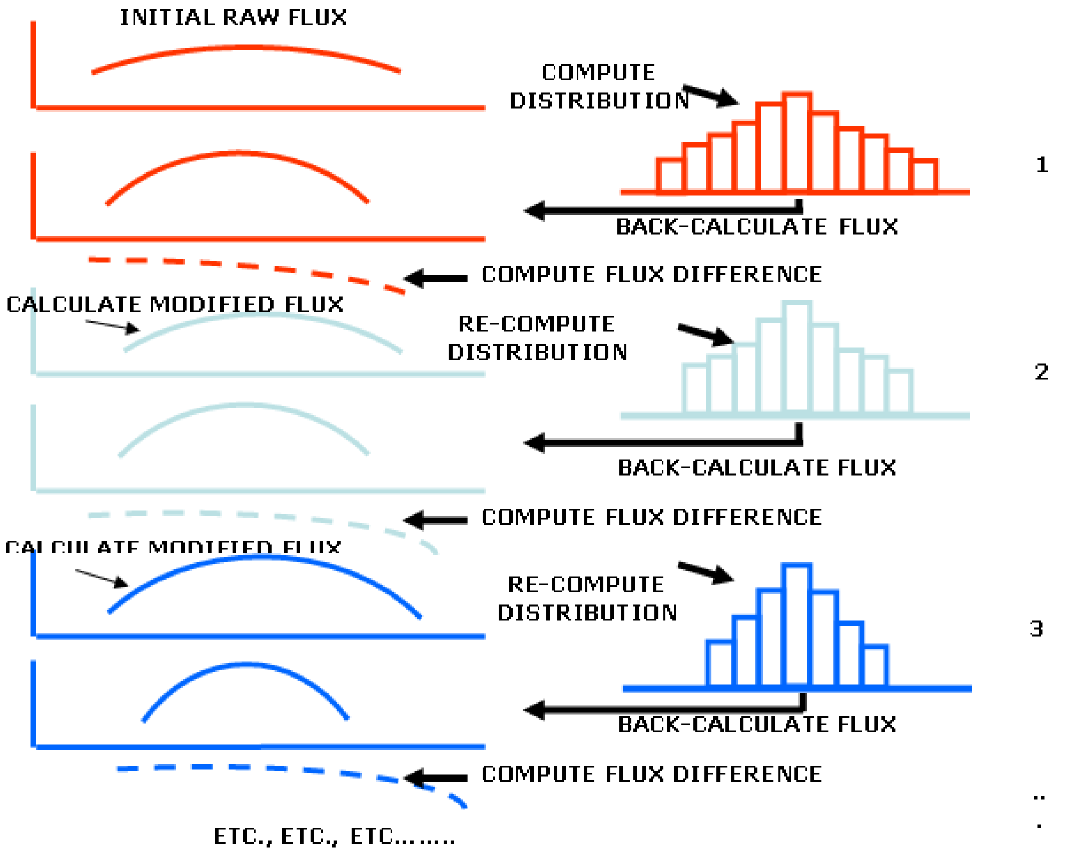
Analyzing data: convergence

You (or the instrument manufacturer) will need to decide how to treat “borderline” data. Else noise will overly distort your results.



ISO-13320:2020, A.9:

Formulae such as Formula (A.8) are described as ill-posed and ill-conditioned. Even the smallest errors due to measurement make direct inversion without constraint unviable.

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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

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Pop Quiz

What particle shape is used for laser diffraction calculations?

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

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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!

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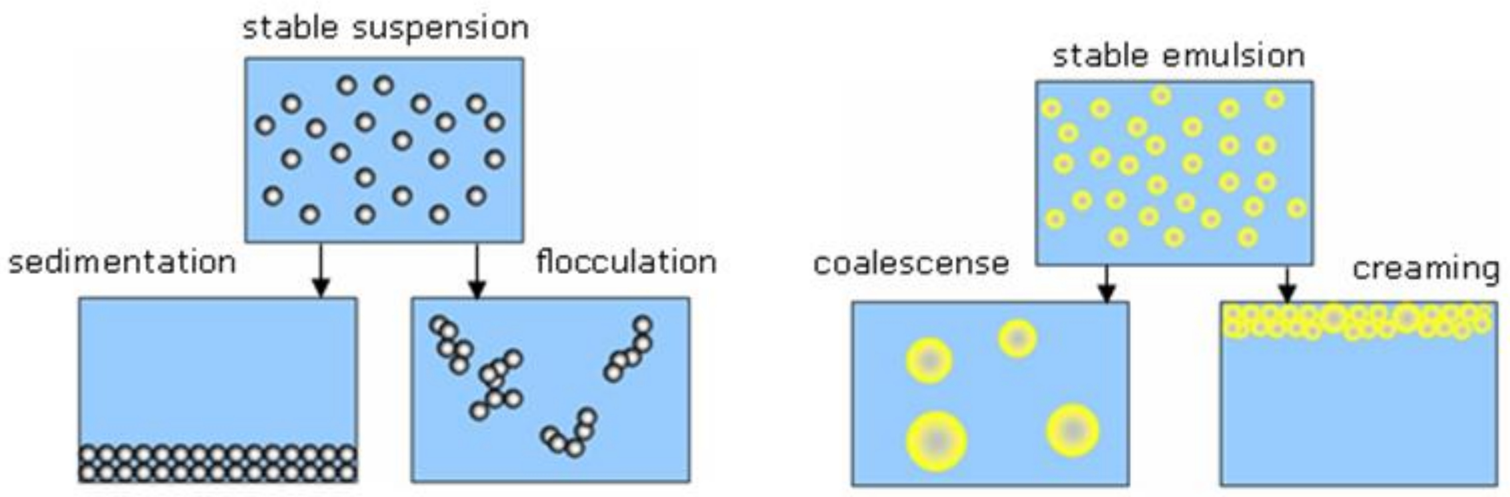
Measurement Workflow

Prepare the sample

Good sampling and dispersion a must!

May need to use surfactant or admixture



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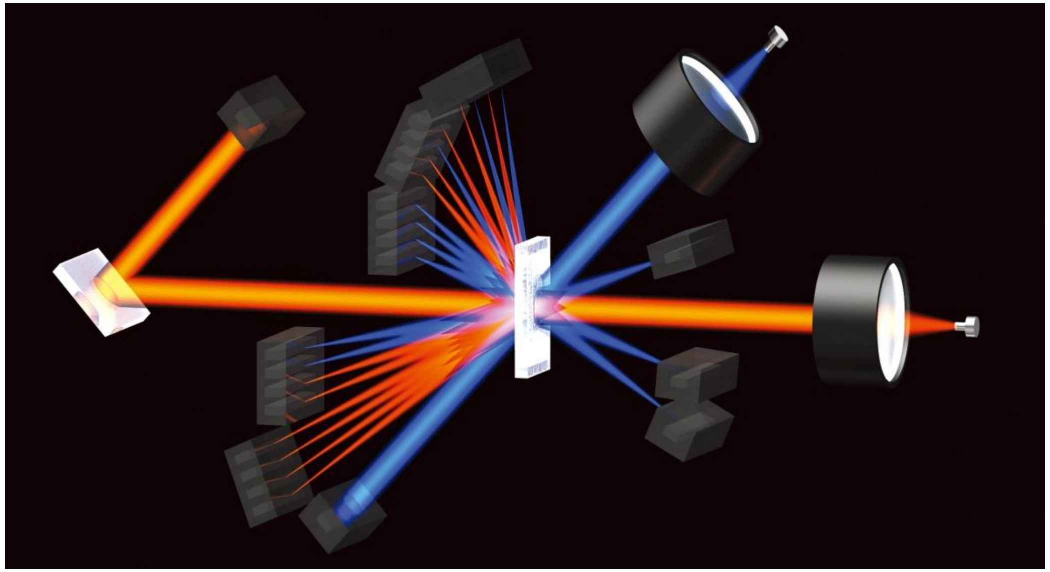
Measurement Workflow

Prepare the system

Align laser to maximize signal-to-noise

Acquire blank/background to reduce noise



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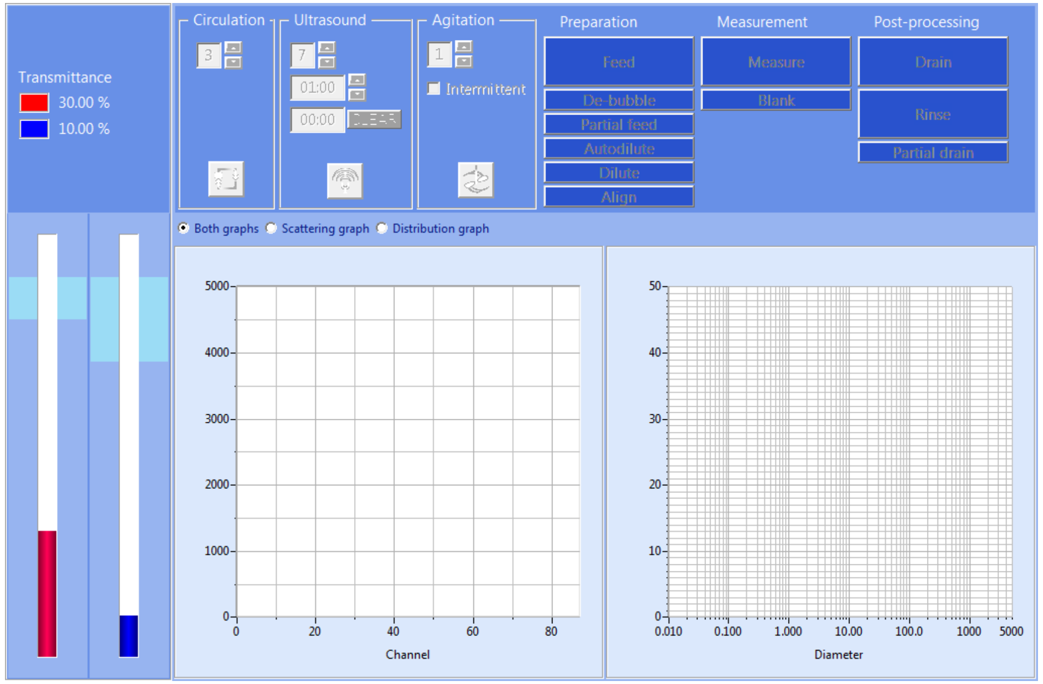
Measurement Workflow

Introduce sample

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



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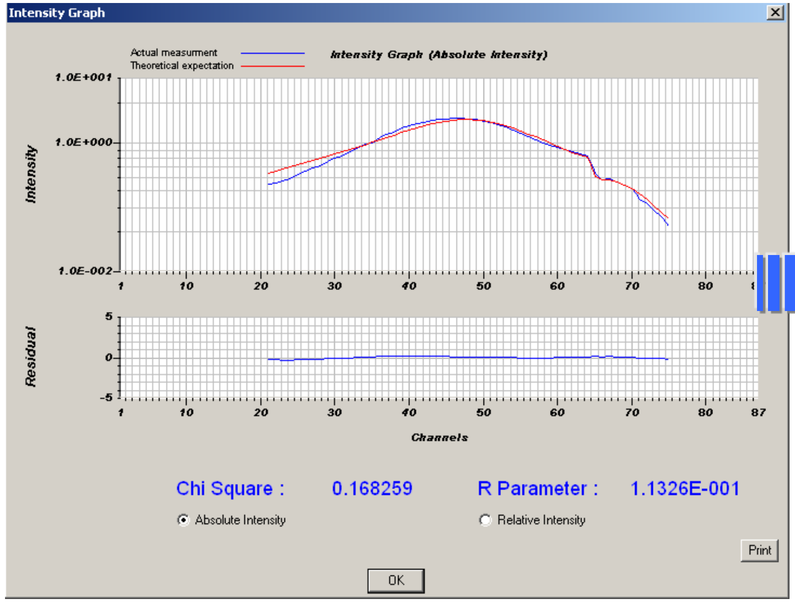
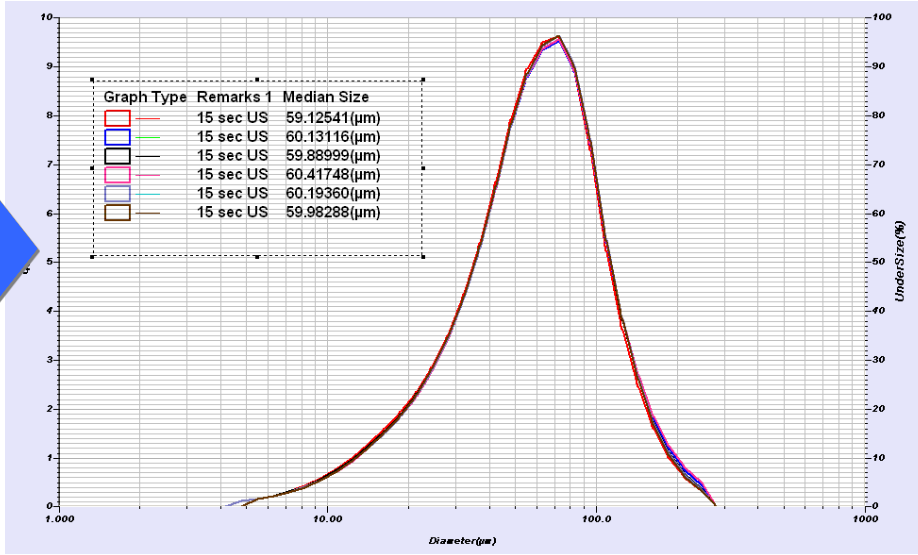
Measurement Workflow

Measurement

Click “Measure” button

- *Hardware* measures scattered light distribution
- *Software* then calculates size distribution





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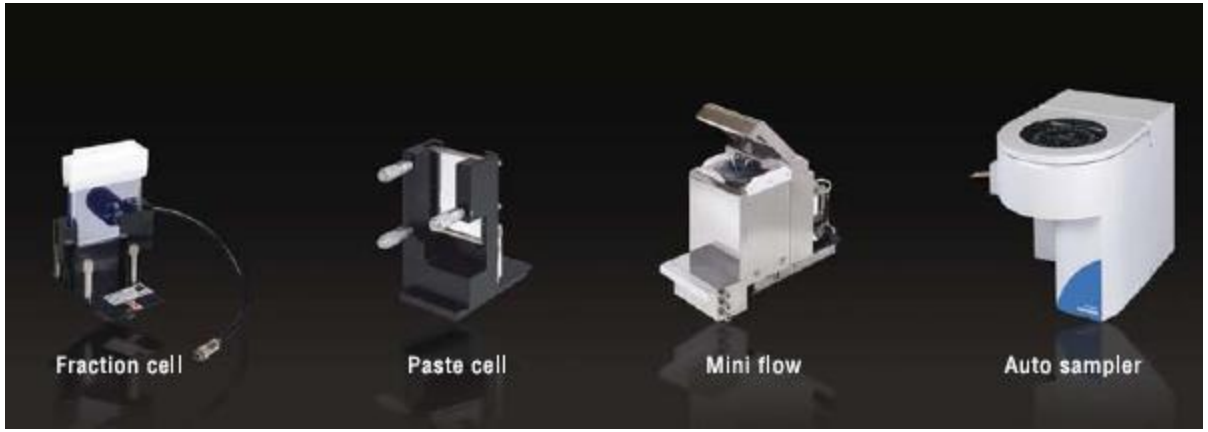
Flexible Sample Handlers



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

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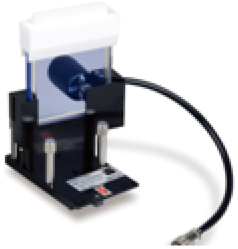
How much sample (wet)?

It depends on sample, but here are some examples.

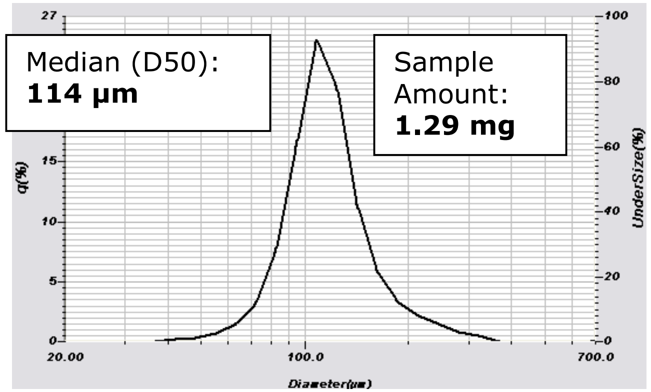
Larger, broad distributions require larger sample volume

Lower volume samplers for precious materials or solvents

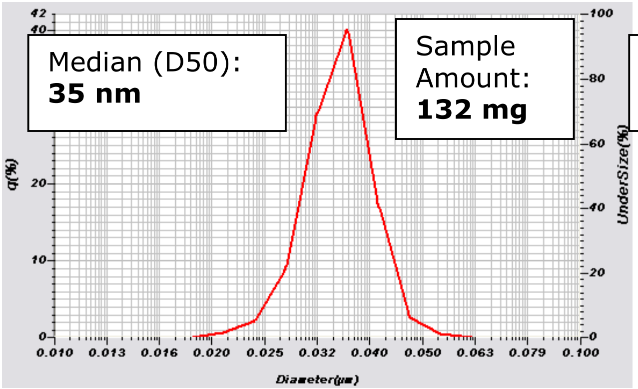
Sample Handlers	Dispersing Volume (mL)
Aqua/Solvo Flow	**180 - 330**
MiniFlow	**35 - 50**
Fraction Cell	**15**
Small Volume Fraction Cell	**10**



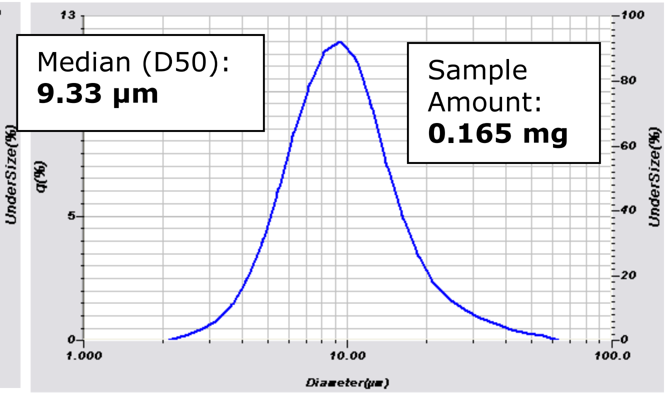
Note: Fraction cell has only magnetic stir bar, not for large or heavy particles



Bio polymer



Colloidal silica



Magnesium stearate

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Wet video

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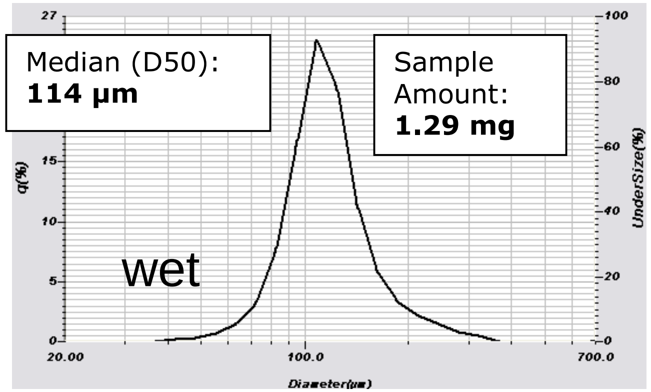
How much sample (dry)?

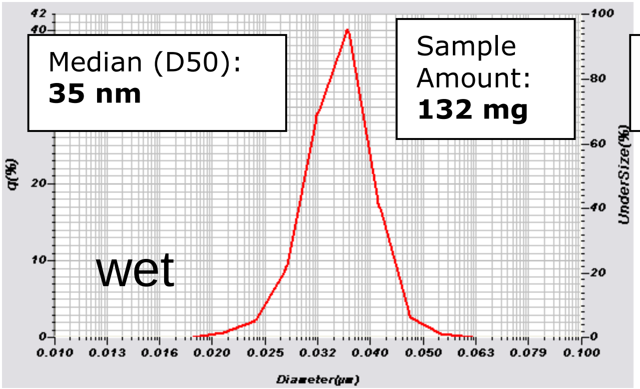
It depends on sample …..

Larger, broad distributions require larger sample quantity

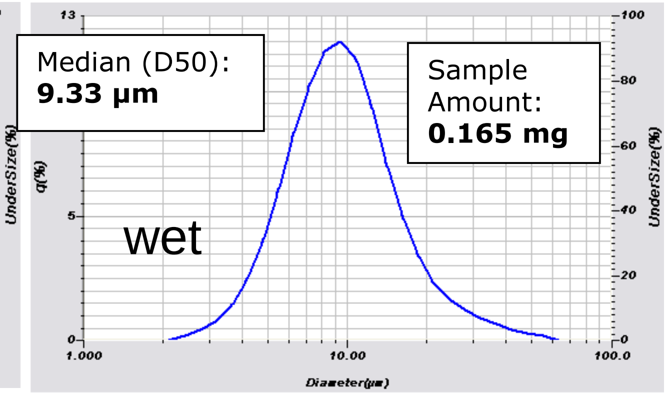
Can measure less than 5 mg (over a number of particle sizes).



Bio polymer



Colloidal silica



Magnesium stearate

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Dry video

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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

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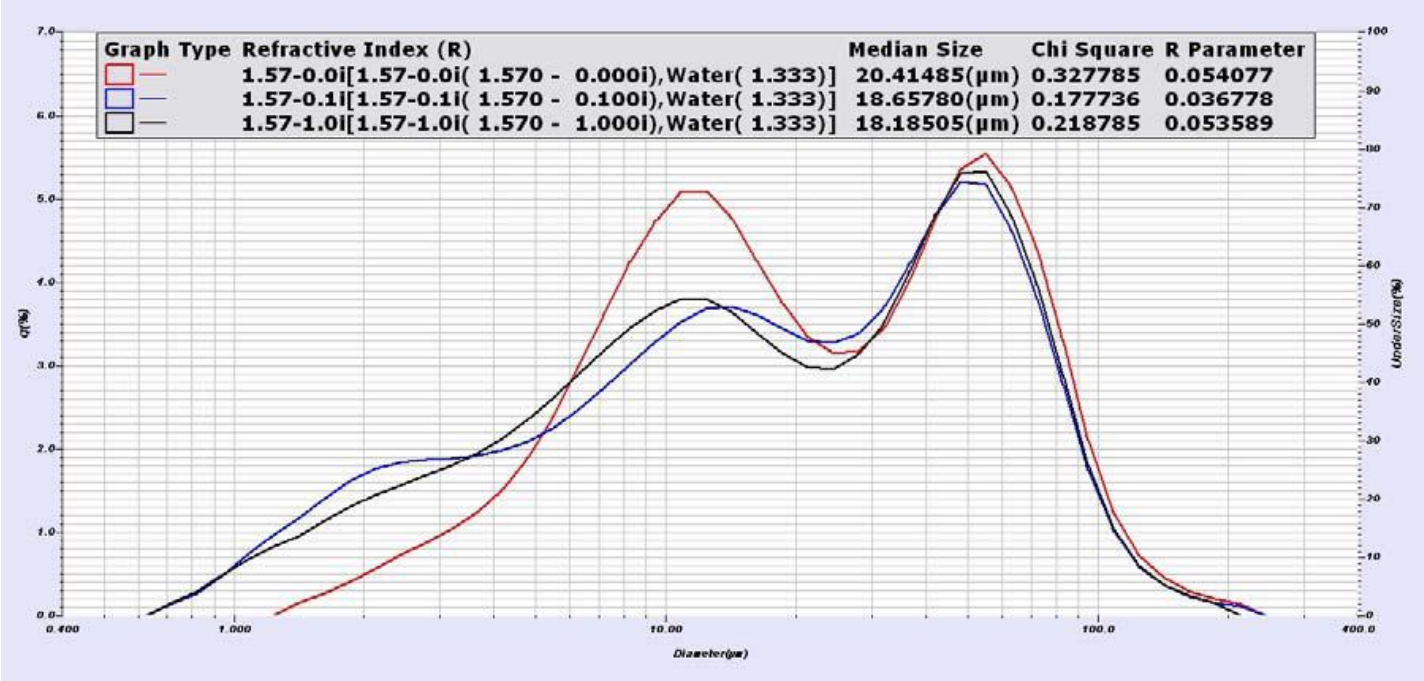
Determine Refractive Index

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



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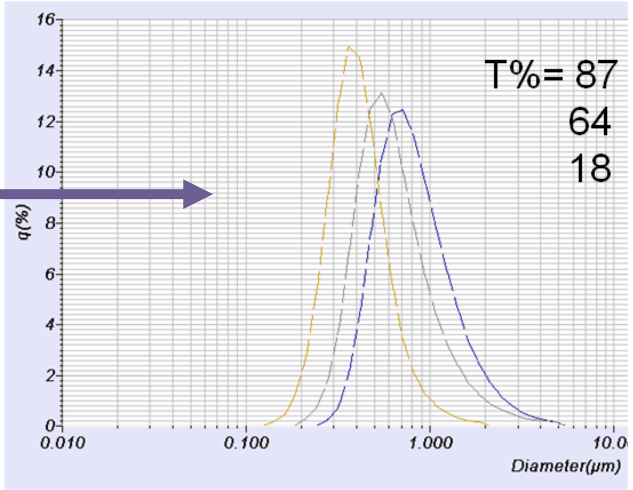
Concentration

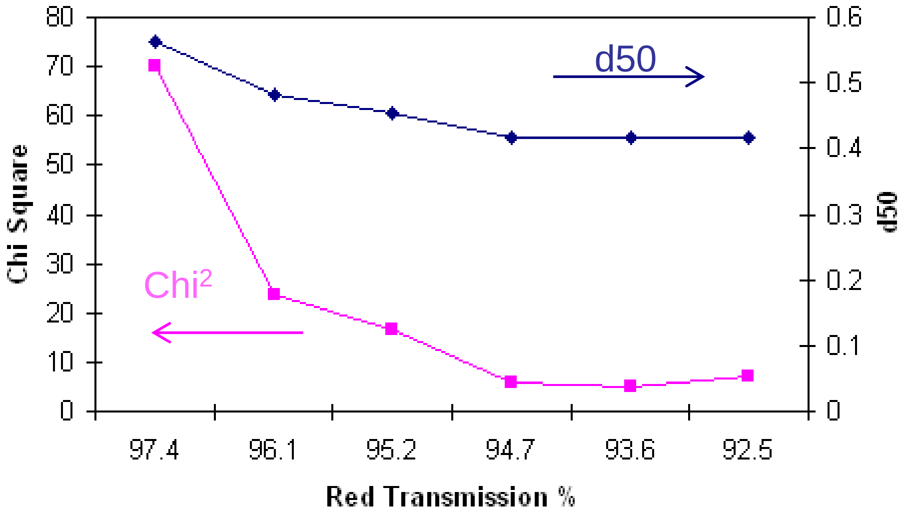
High enough for good S/N ratio

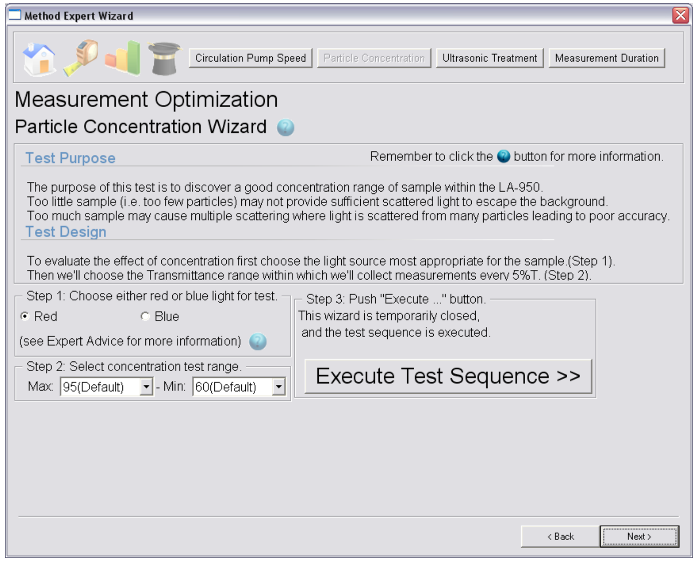
Low enough to avoid multiple scattering

Typically 95 – 80 %T

Measure at different T%, look at d50 result, Chi Square calculation







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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

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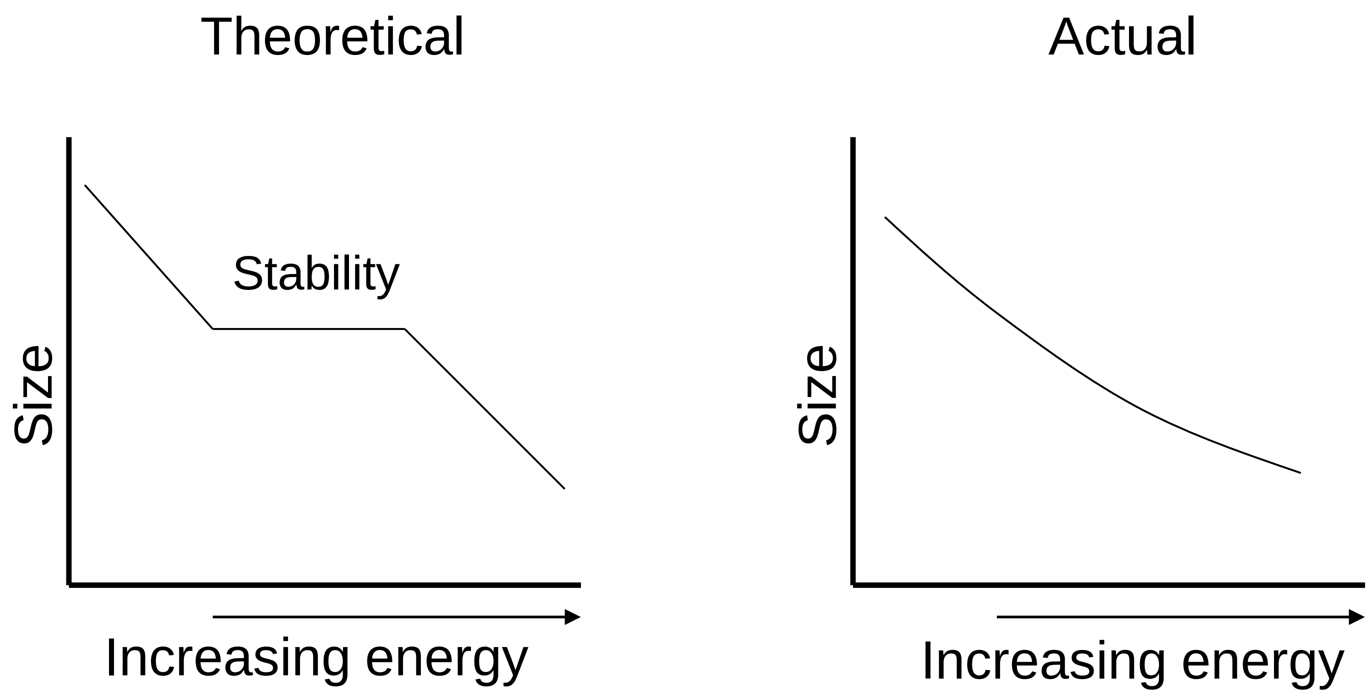
Dispersion vs. Breakage



Higher air pressure or longer ultrasound duration

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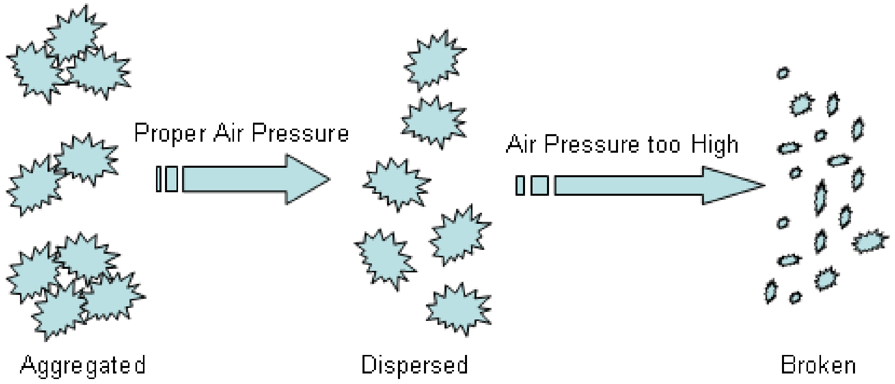
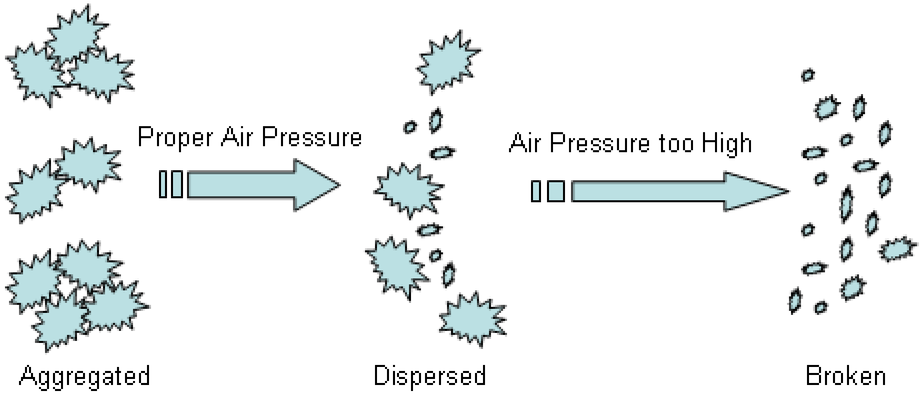
Dispersion vs. Breakage

Dispersion and milling can be parallel rather than sequential processes

Theoretical



Actual



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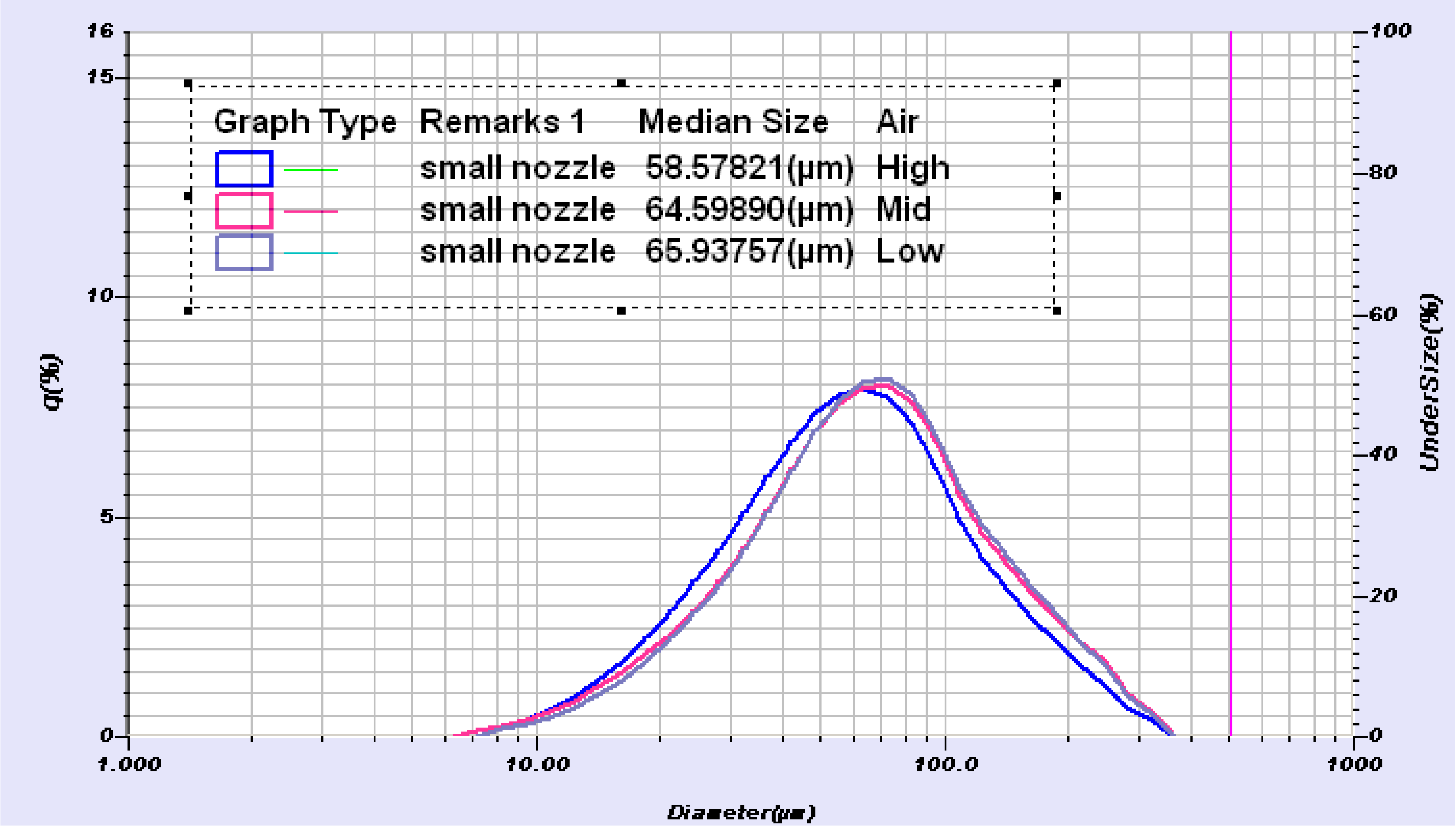
Effect of Air Pressure: MCC



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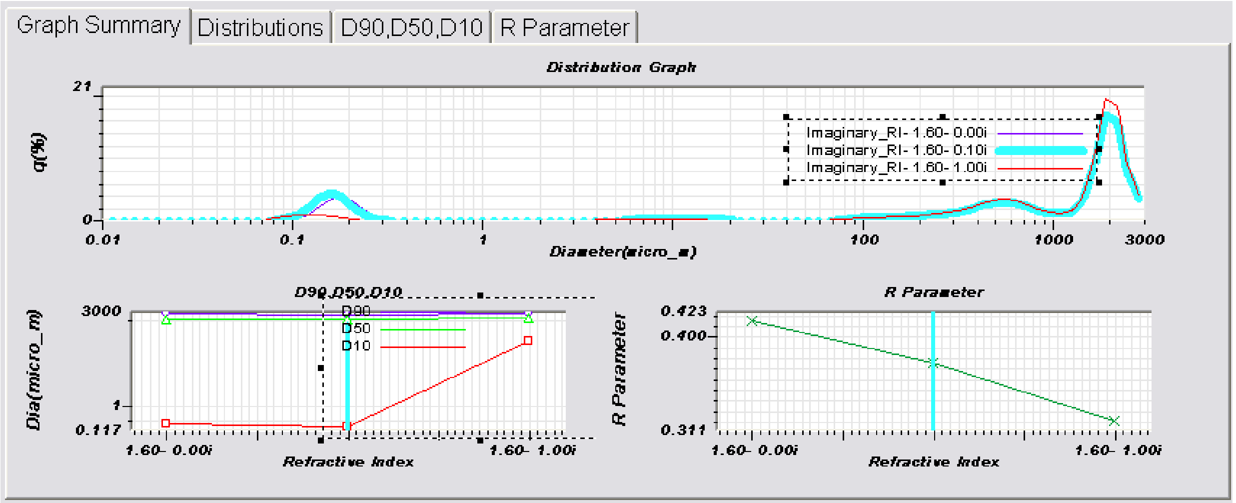
LA-960 Method Expert

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

Results displayed in multiple formats:

PSD, D50, R-parameter



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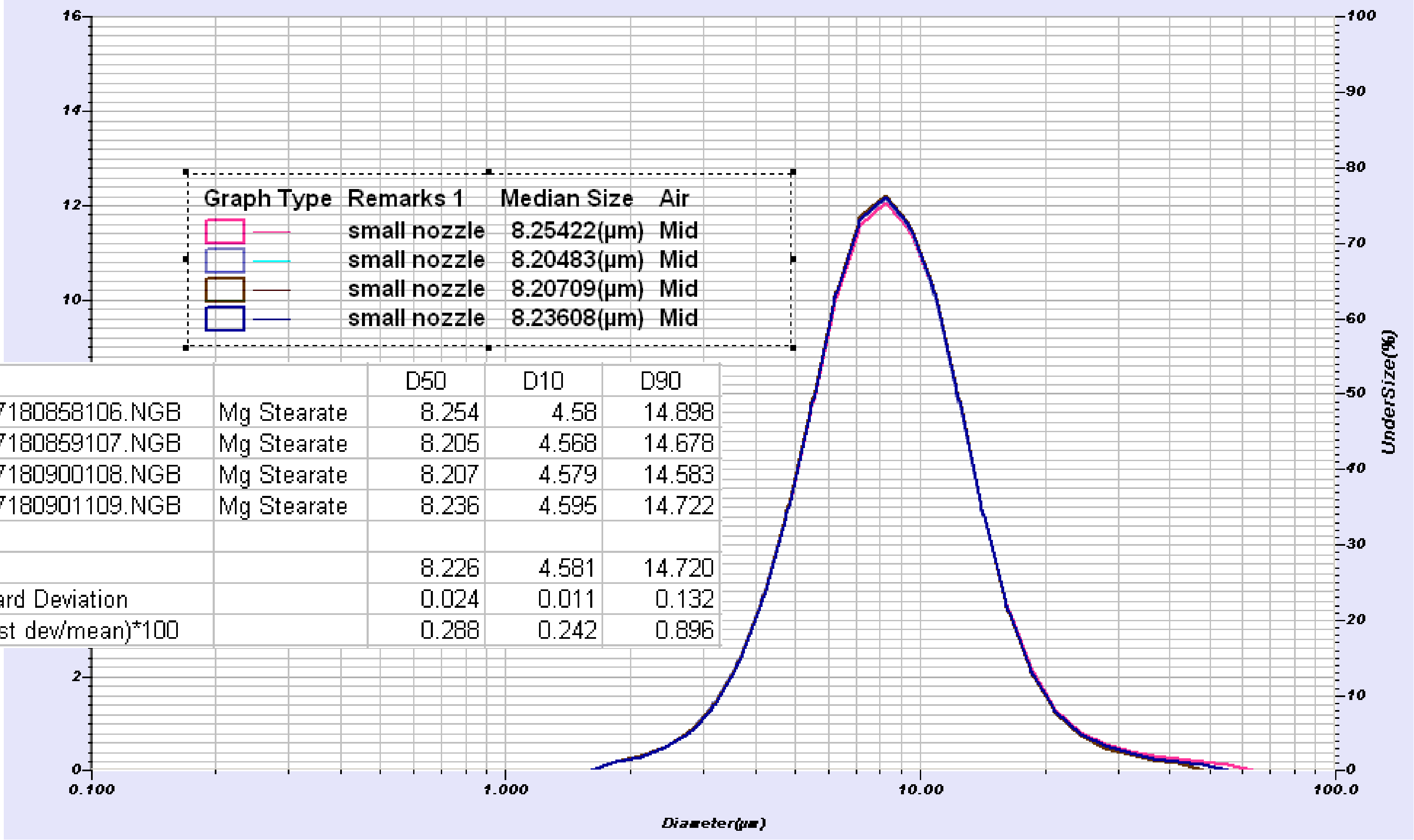
Reproducibility– Mg Stearate dry, 2 bar



		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

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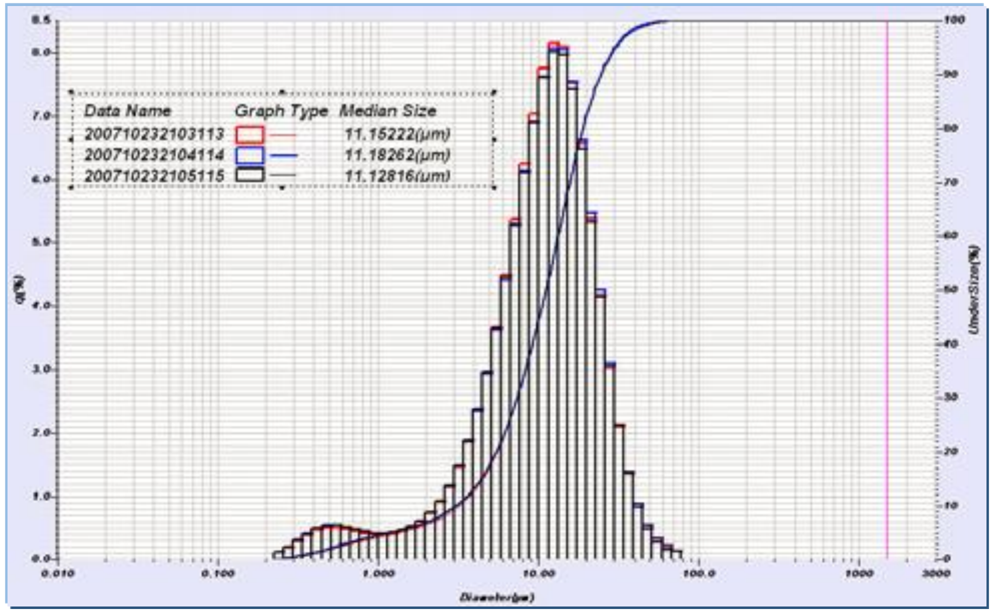
Cement Dry

	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



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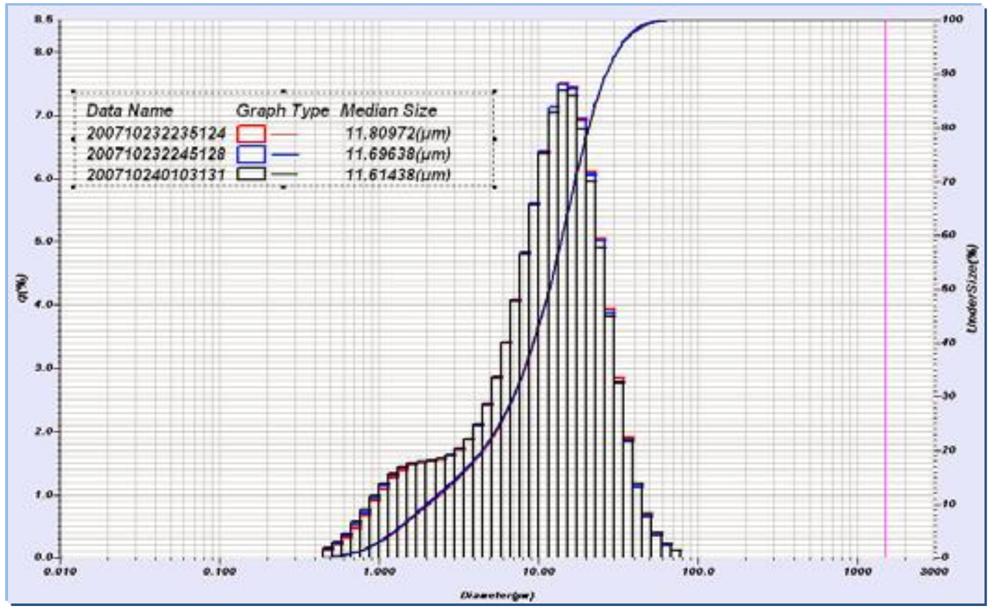
Cement Wet

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



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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			

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Instrument to instrument variation

Industrial Samples

	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.

	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.

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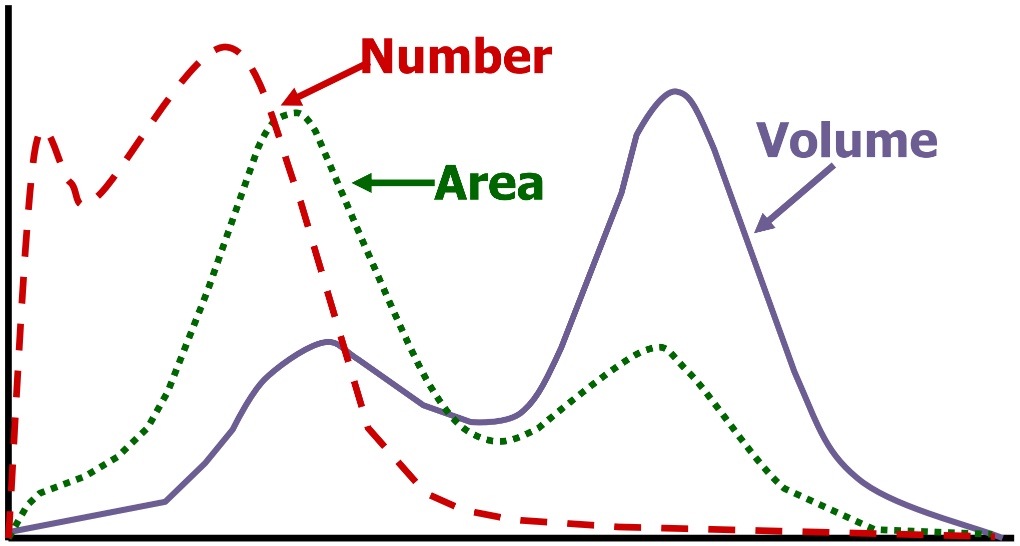
Diffraction Drawbacks

Volume basis by default

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

No shape information



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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

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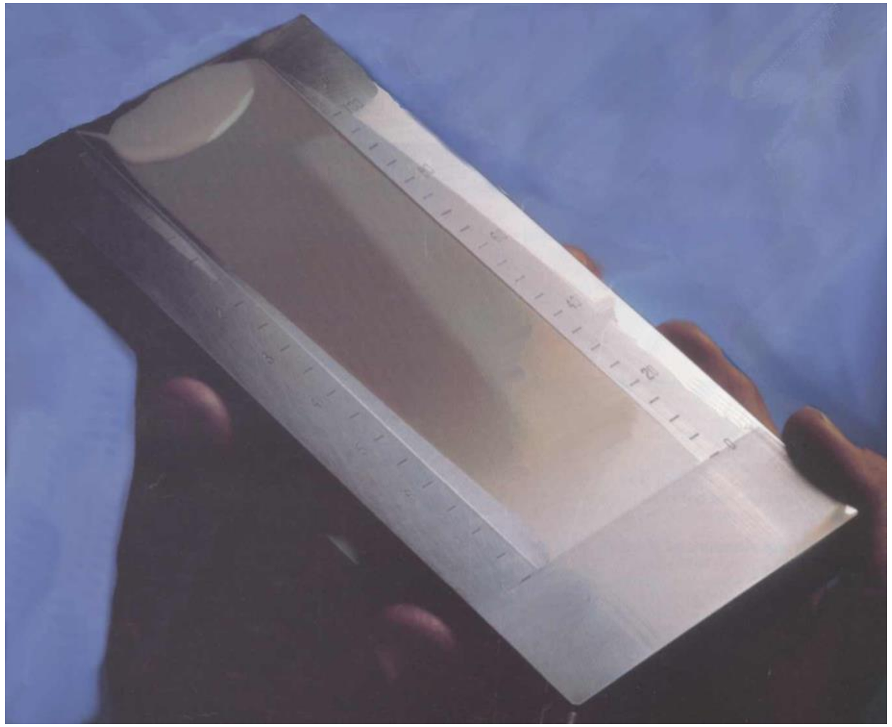
Hegman Gauge

Used in paint and coatings industry

- Device has tapered center channel
- Slurry is placed in channel, then straight edge is drawn across it
- “Hegman Number” is where particles disturb smooth surface of slurry
- **Information from largest particles only – no distribution**



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