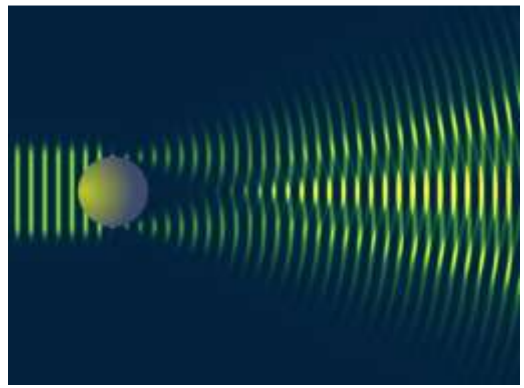
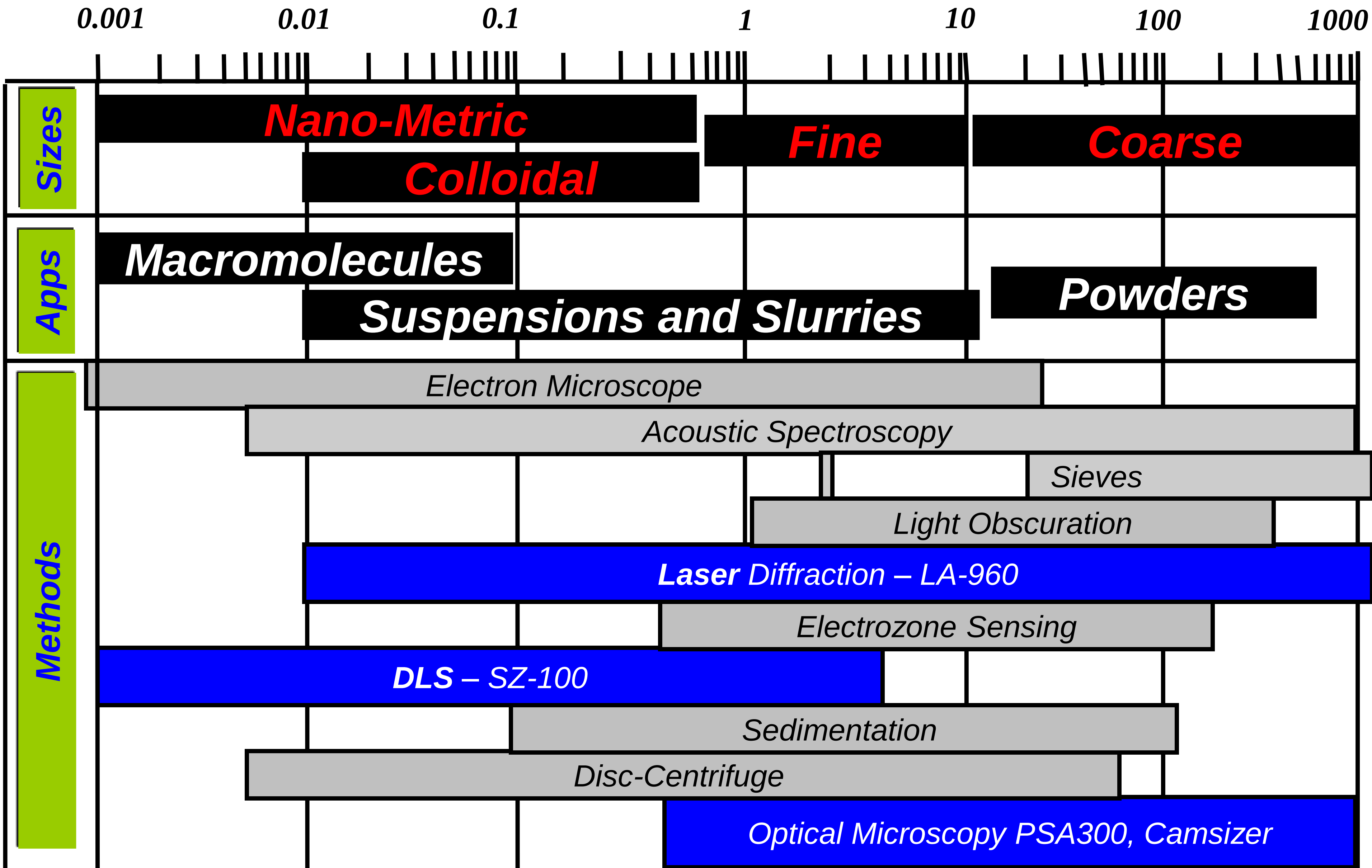
Introduction to Laser Diffraction



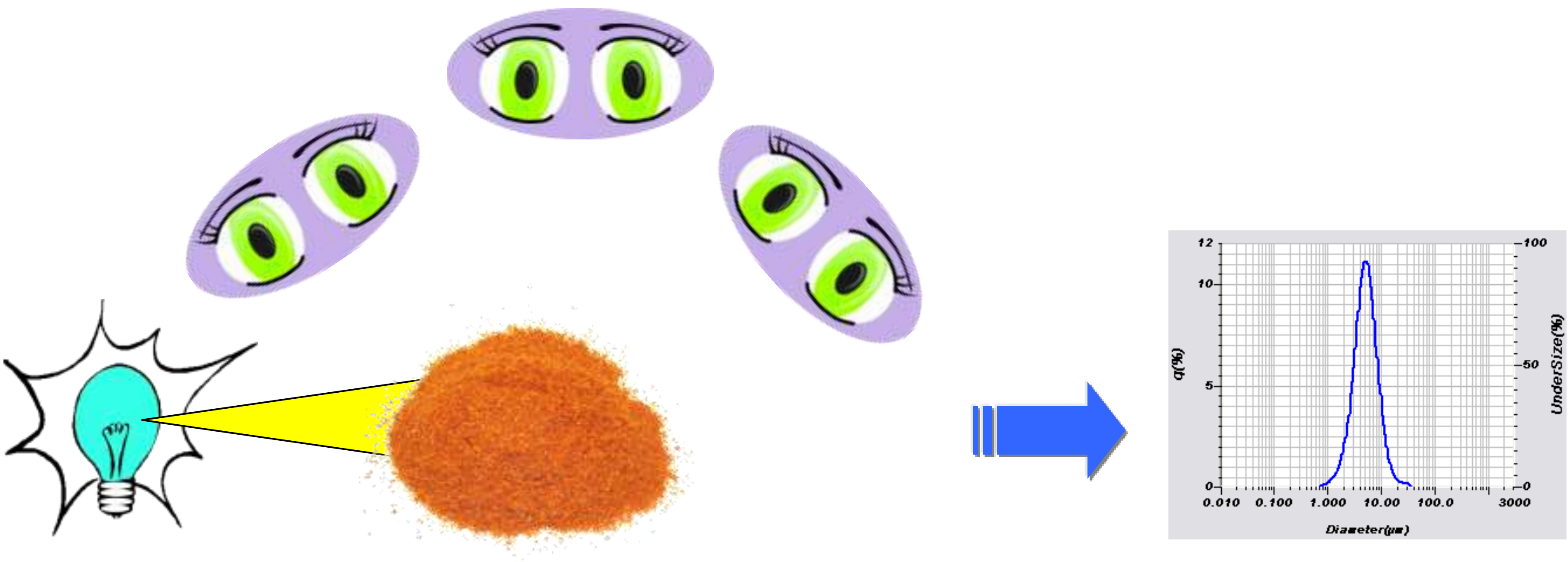
Jeffrey Bodycomb, Ph.D.
HORIBA Scientific
www.horiba.com/us/particle

Size: Particle Diameter (μm)



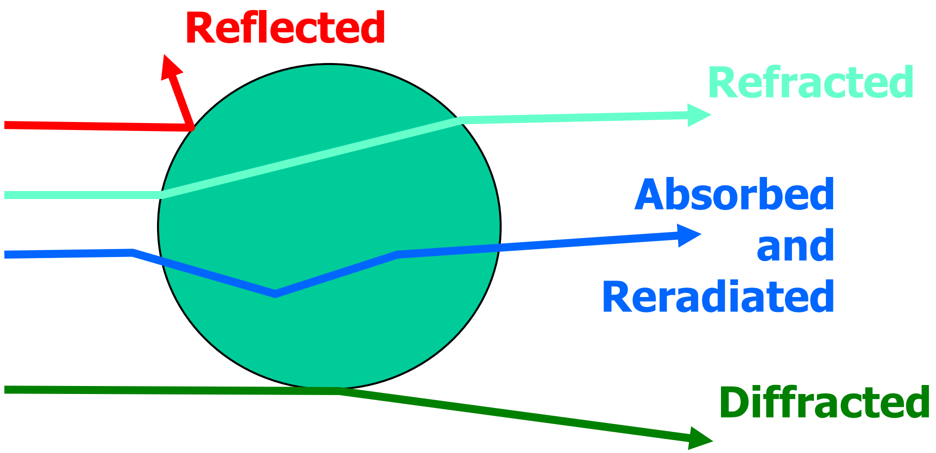
Core Principle

- Can investigate a particle with light and determine its size



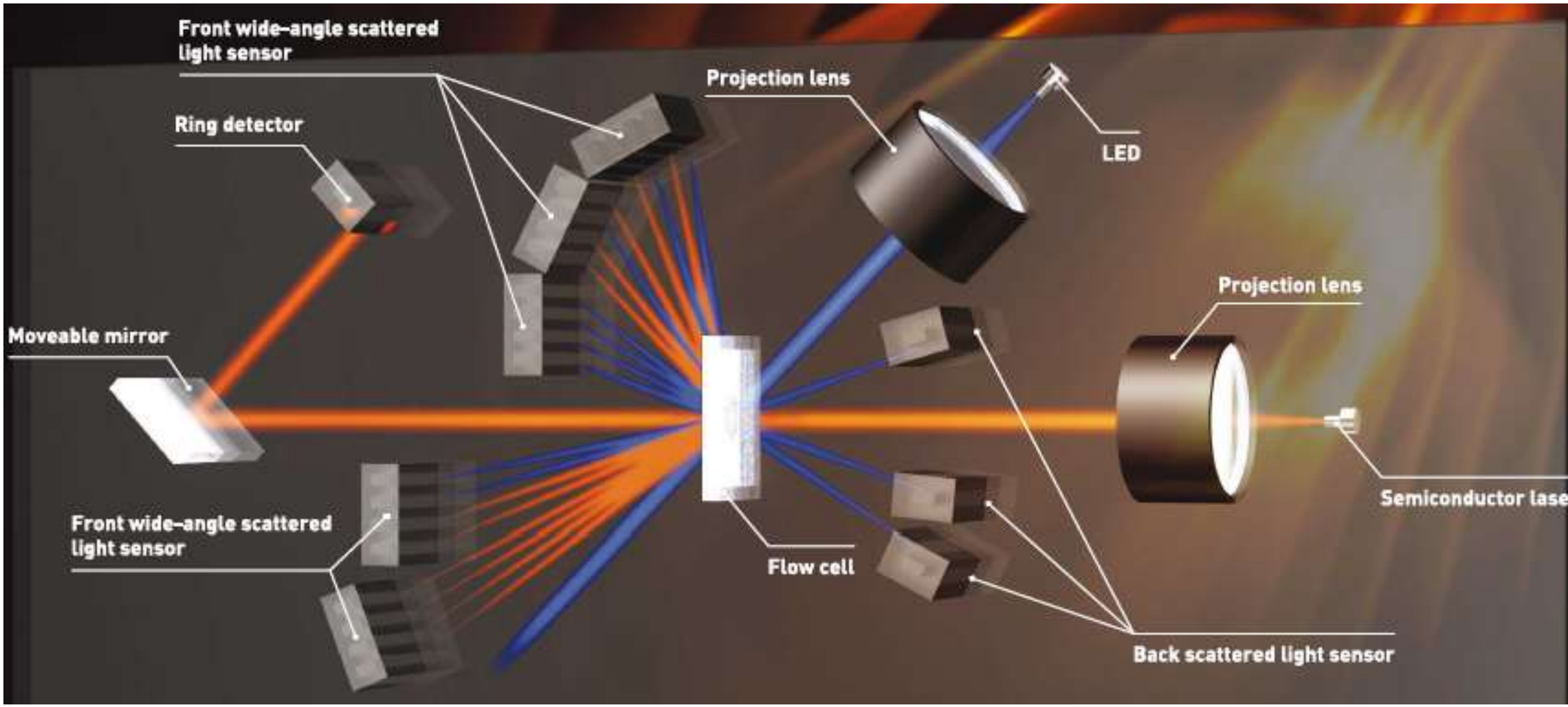
When a Light beam Strikes a Particle

- Some of the light is:
  - Diffracted
  - Reflected
  - Refracted
  - Absorbed and Reradiated

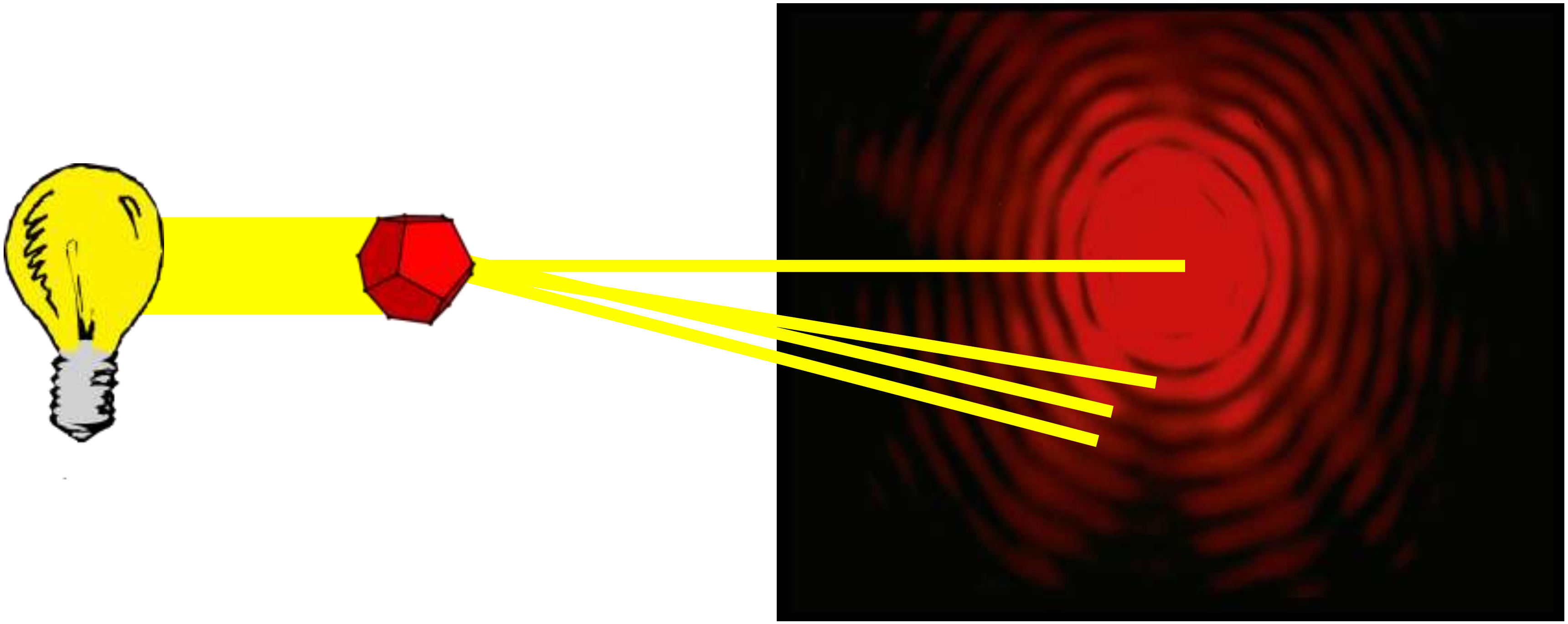


- Small particles require knowledge of optical properties:
  - Real Refractive Index (bending of light, wavelength of light in particle)
  - Imaginary Refractive Index (absorption of light within particle)
  - Refractive index values less significant for large particles
- Light must be collected over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

LA-960 Optics



Diffraction Pattern



Light

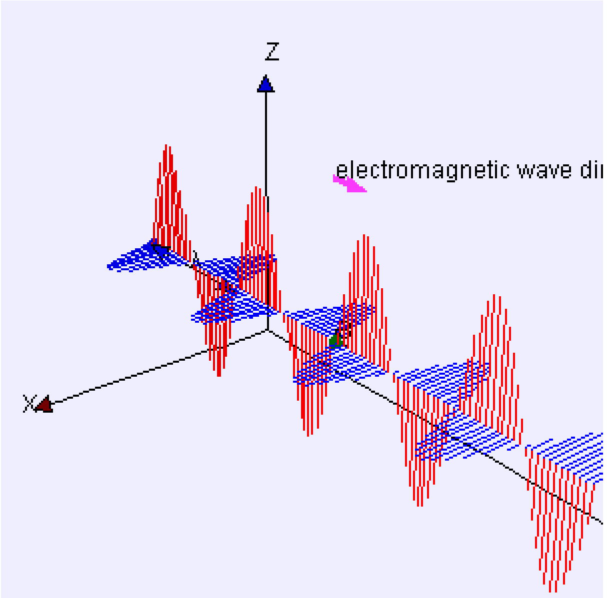
Expressed in just in y-direction

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

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

Oscillating electric field

Oscillating magnetic field (orthogonal to electric field)



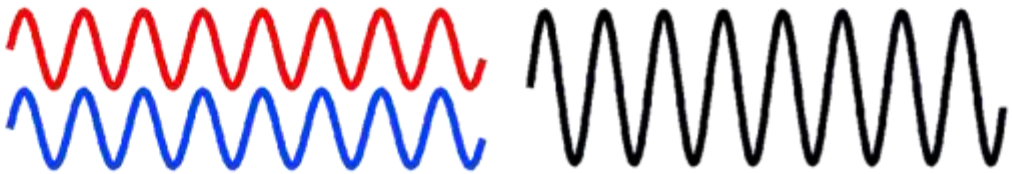
Complements of Lookang @ weelookang.blogspot.com

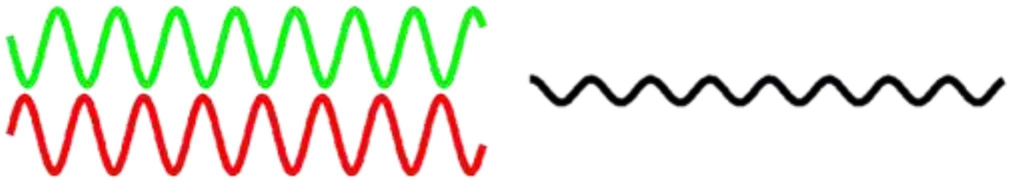
Light: Interference

Look at just the electric field.

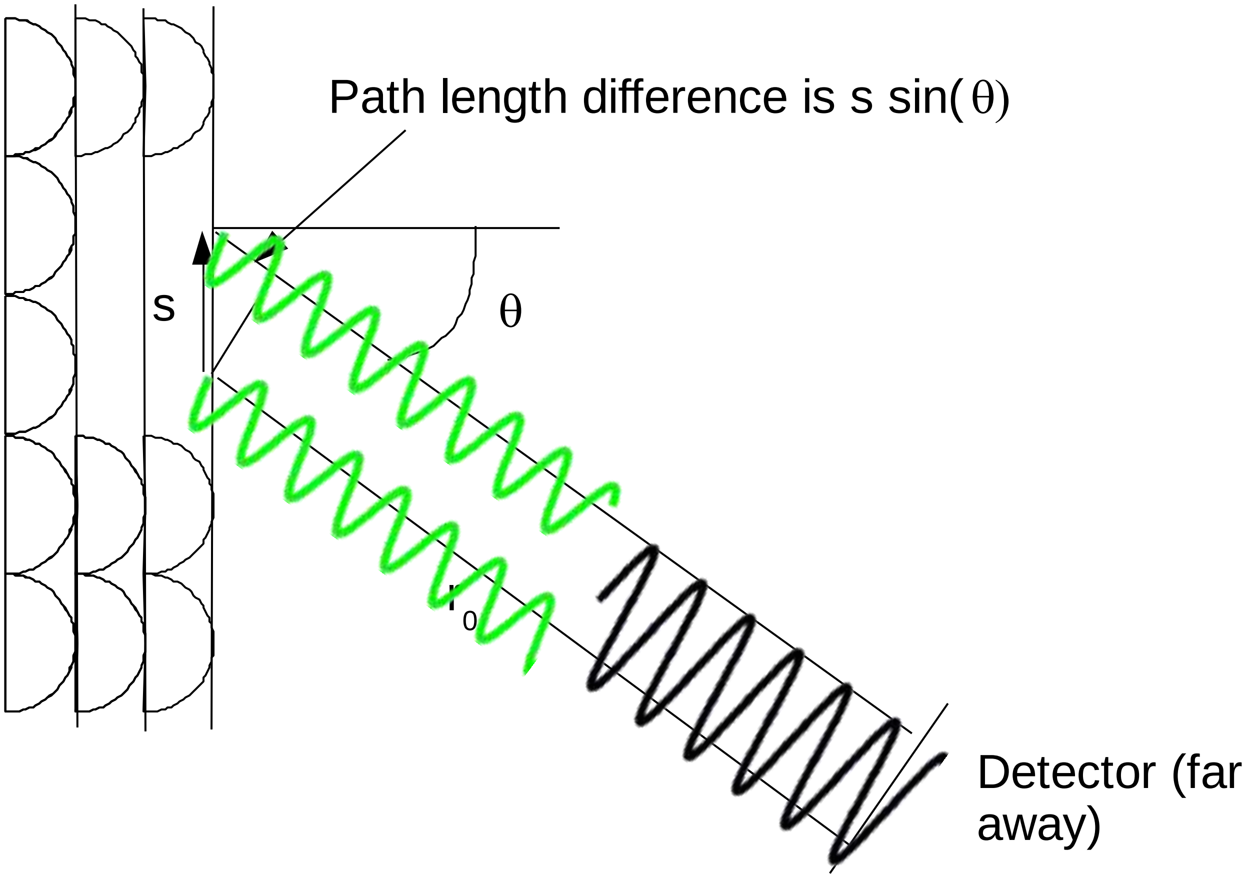
$$E = E_0 \sin(kx - \omega t + \phi)$$ Oscillating electric field

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





Path Length Difference



Using Models to Interpret Scattering

HORIBA Scientific

- 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

HORIBA Scientific

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

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

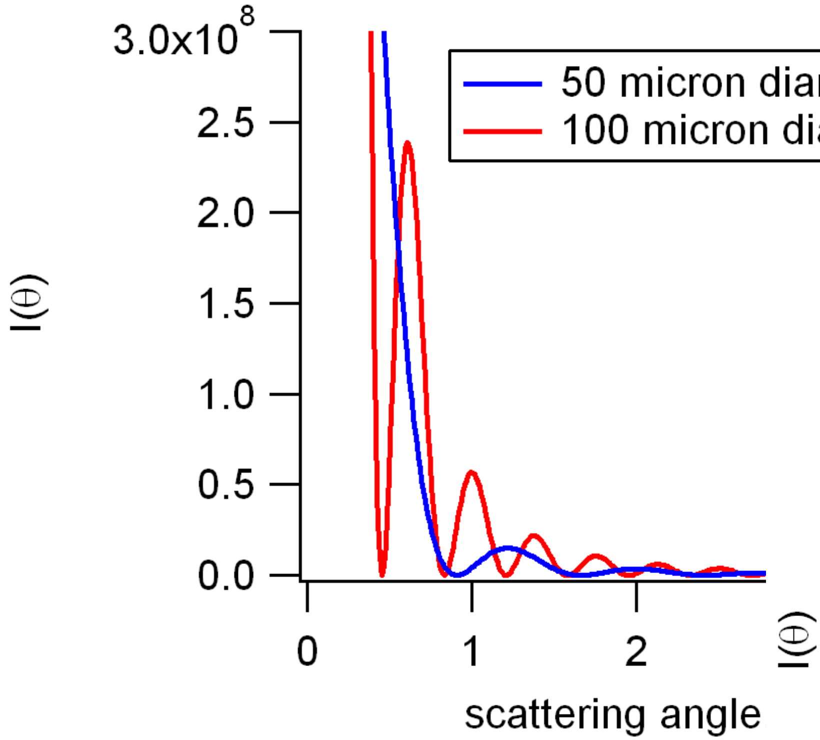
dimensionless size parameter $\alpha = \pi D/\lambda$;

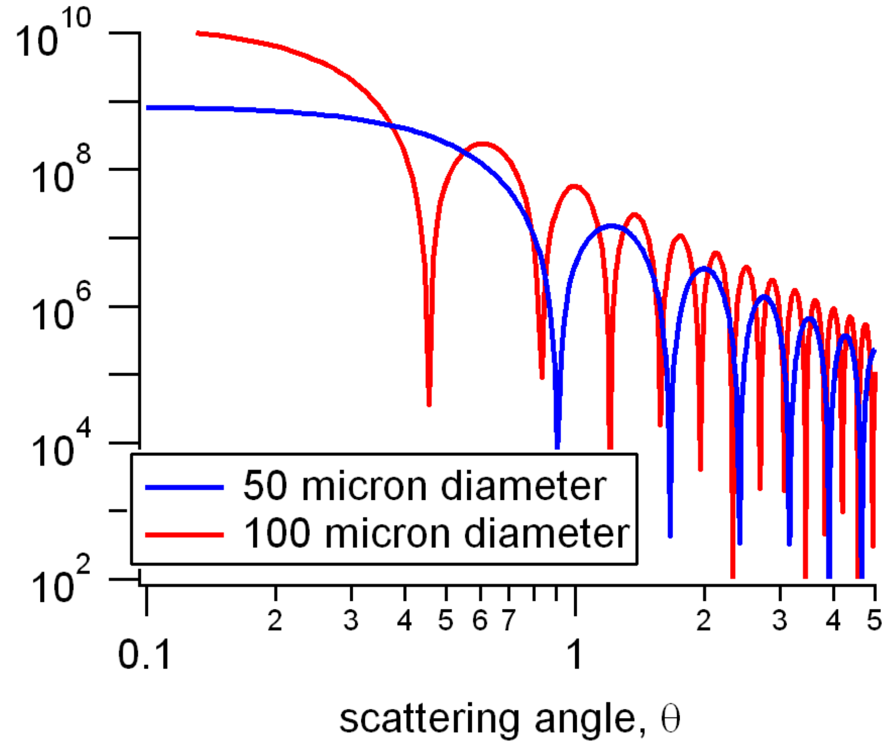
J_1 is the Bessel function of the first kind of order unity.

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 $\alpha >> 1$)*
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

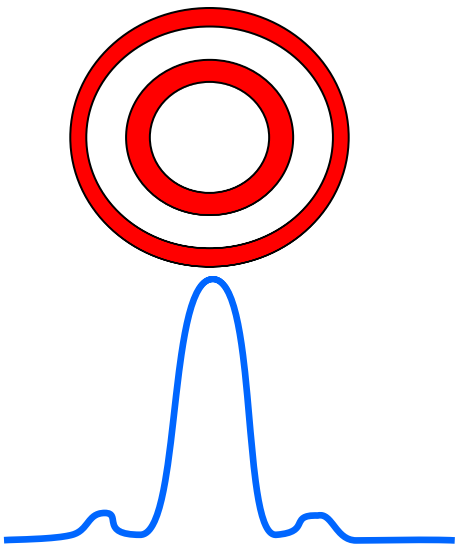




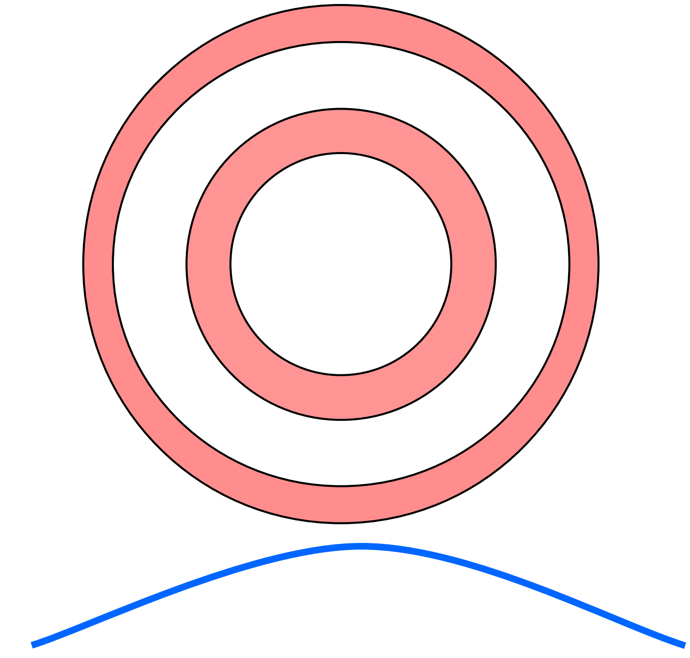
Diffraction Pattern: Large vs. Small Particles

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

HORIBA Scientific

- 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

HORIBA Scientific

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

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

Mie

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, <u>get a blue light source for small particles</u>.

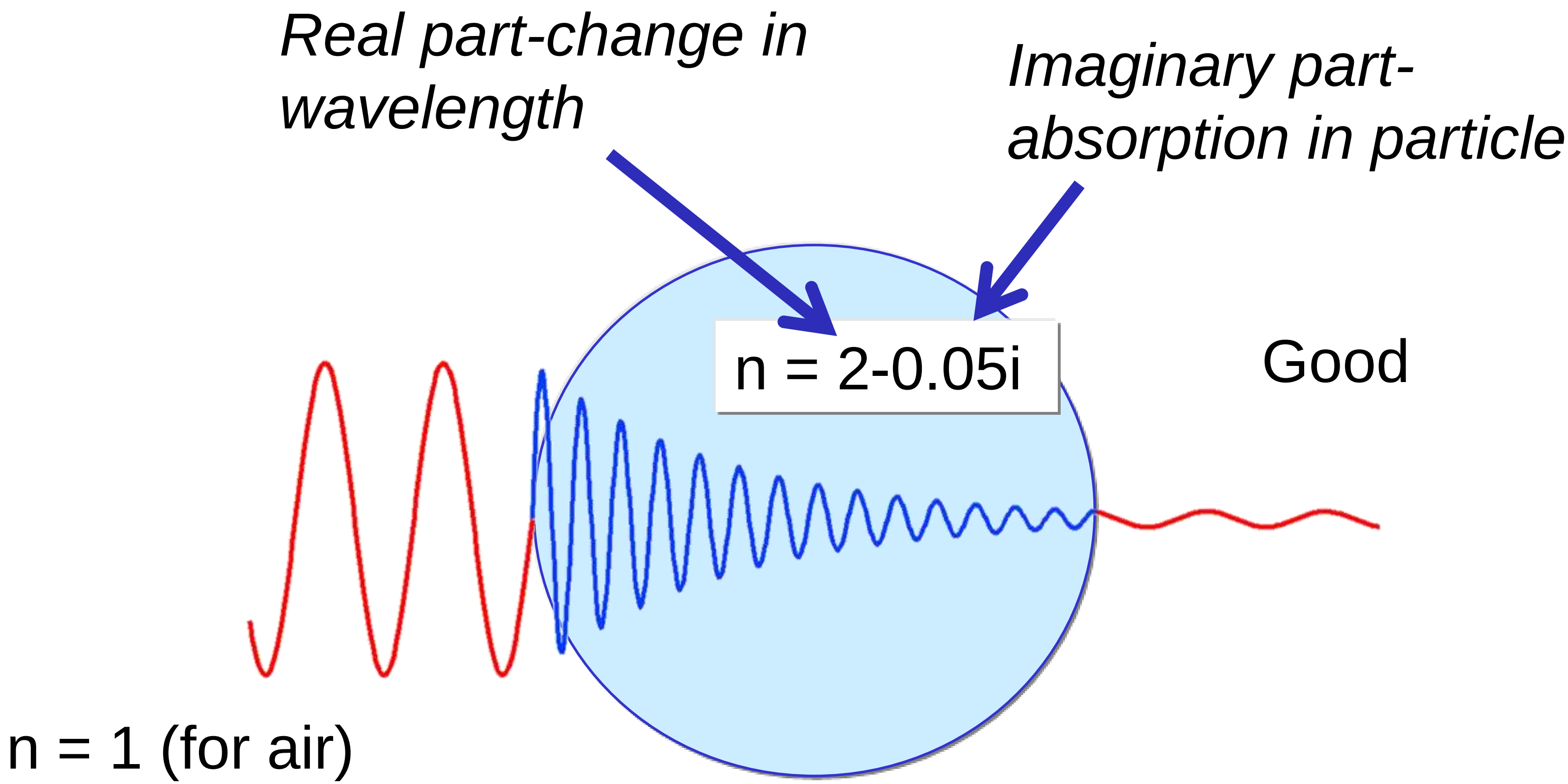
$$m = n_p / n_m$$

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

$$\theta$$

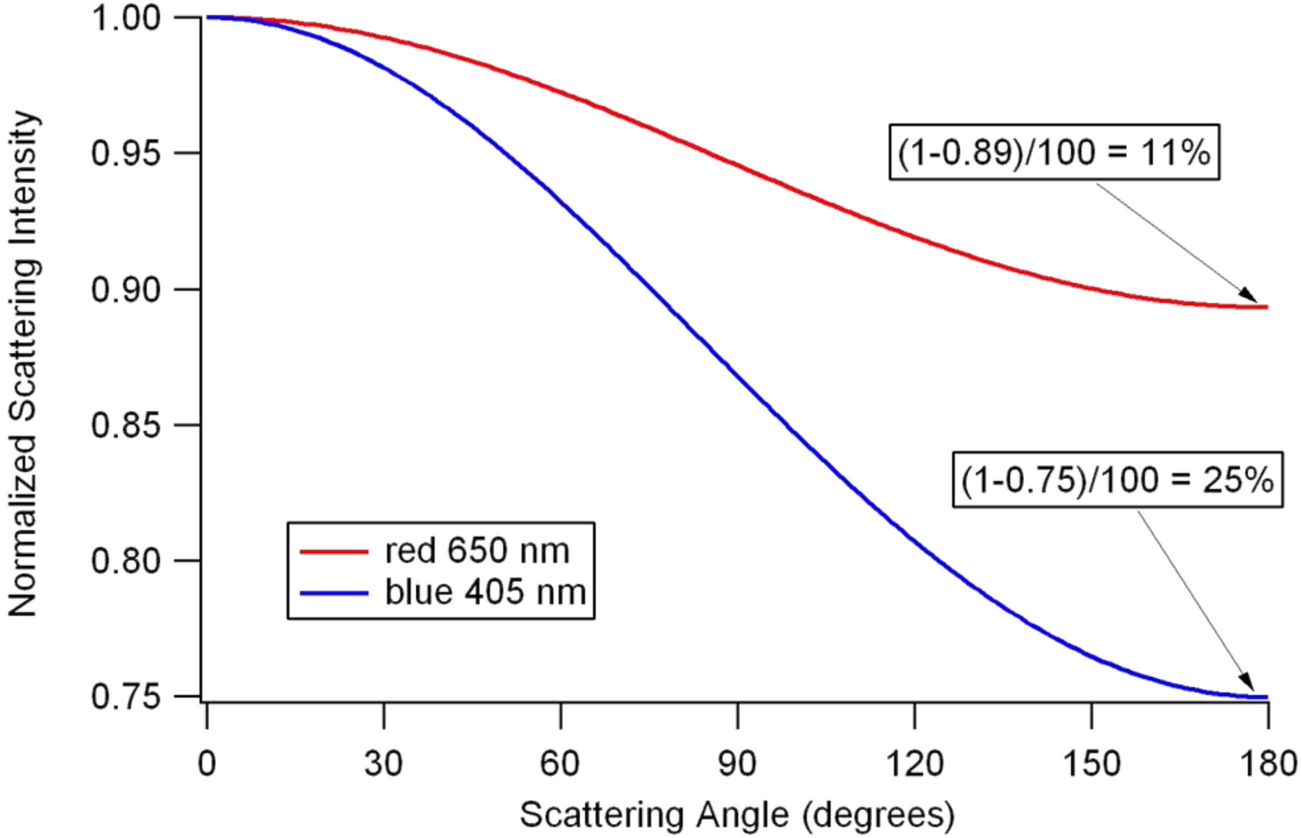
Scattering Angle

Refractive Index



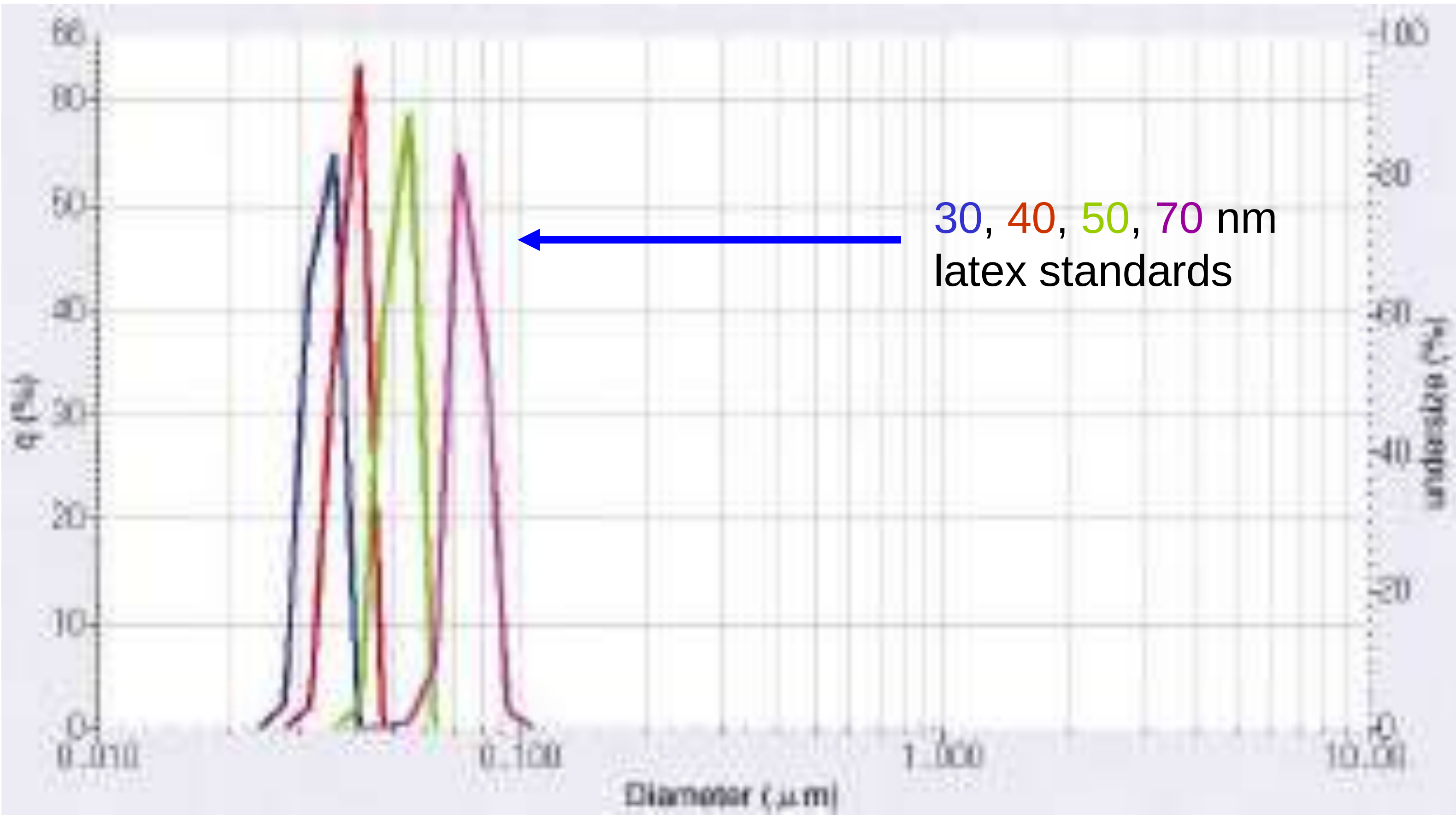
Short Wavelengths for Smallest Particles

HORIBA Scientific



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.

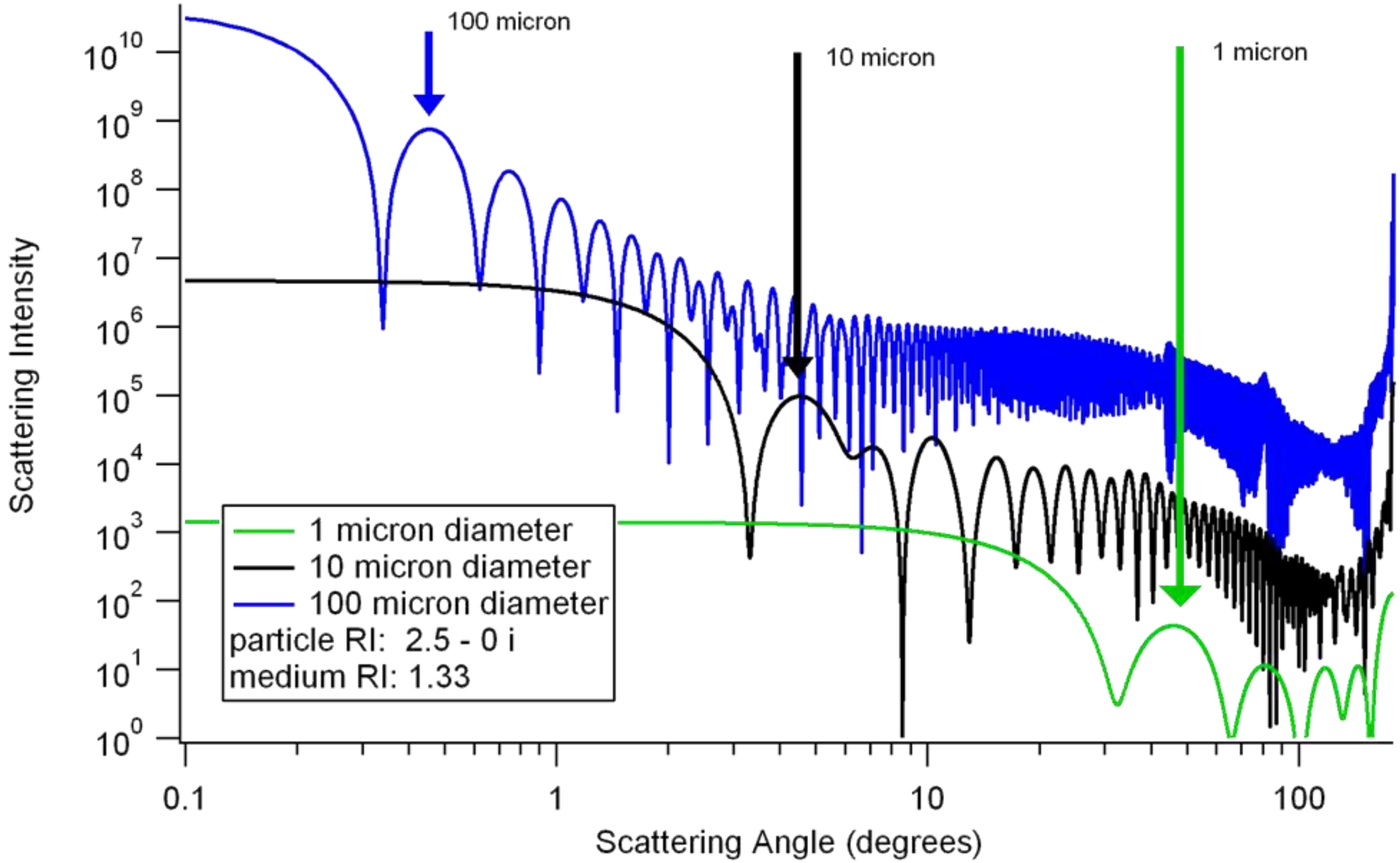
Why 2 Wavelengths?



Data from very small particles.

Effect of Size

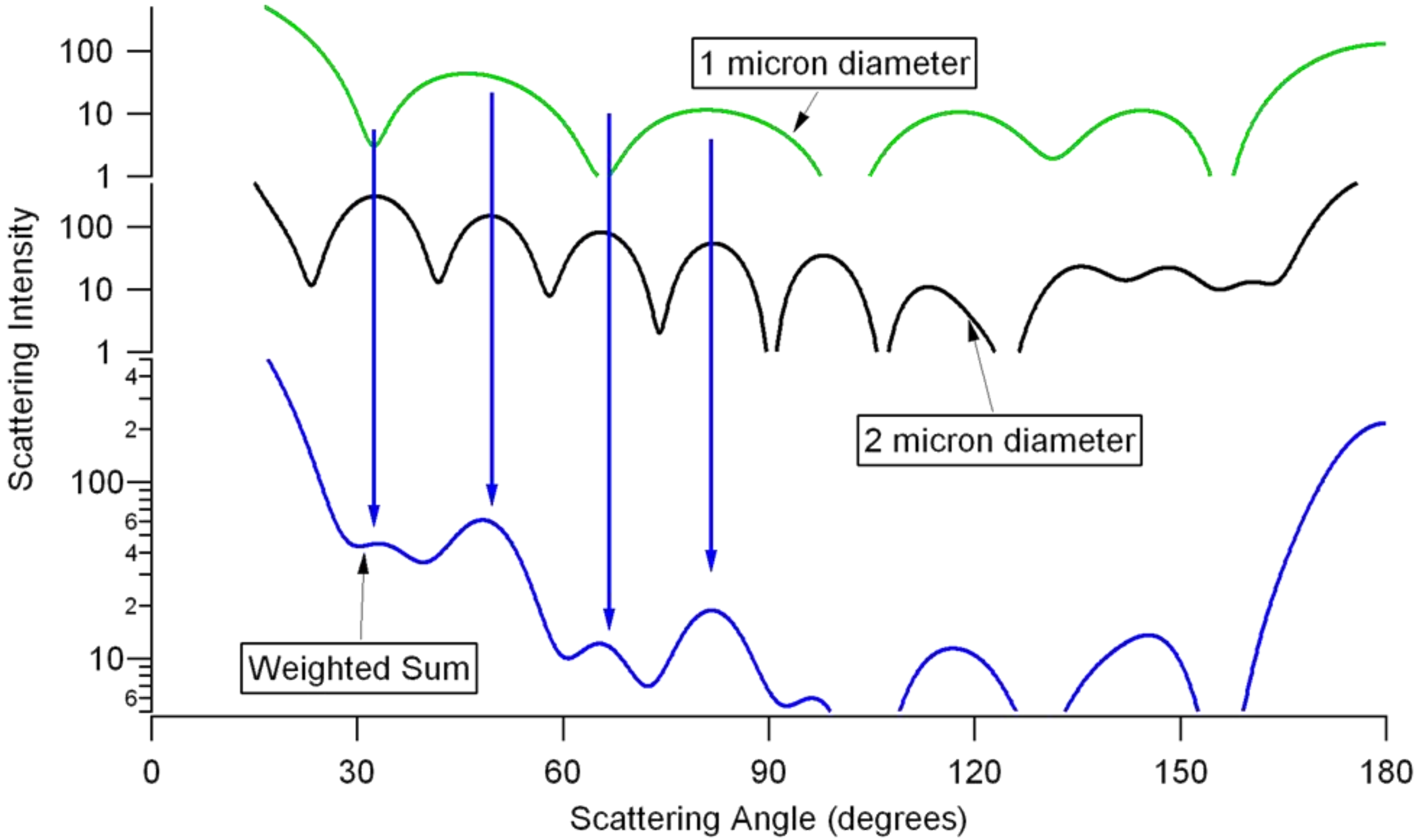
HORIBA Scientific



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

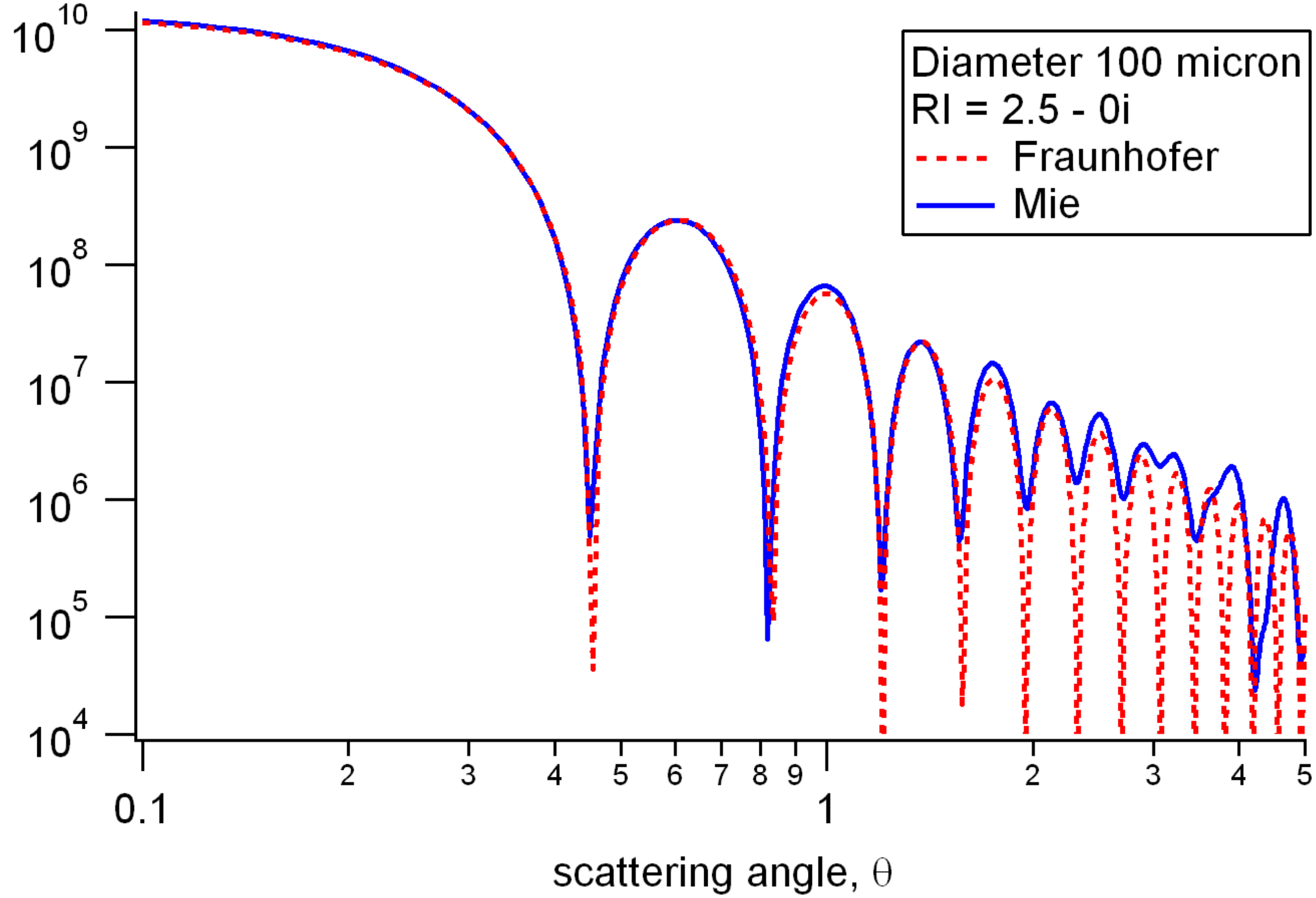
Mixing Particles? Just Add

HORIBA Scientific



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.

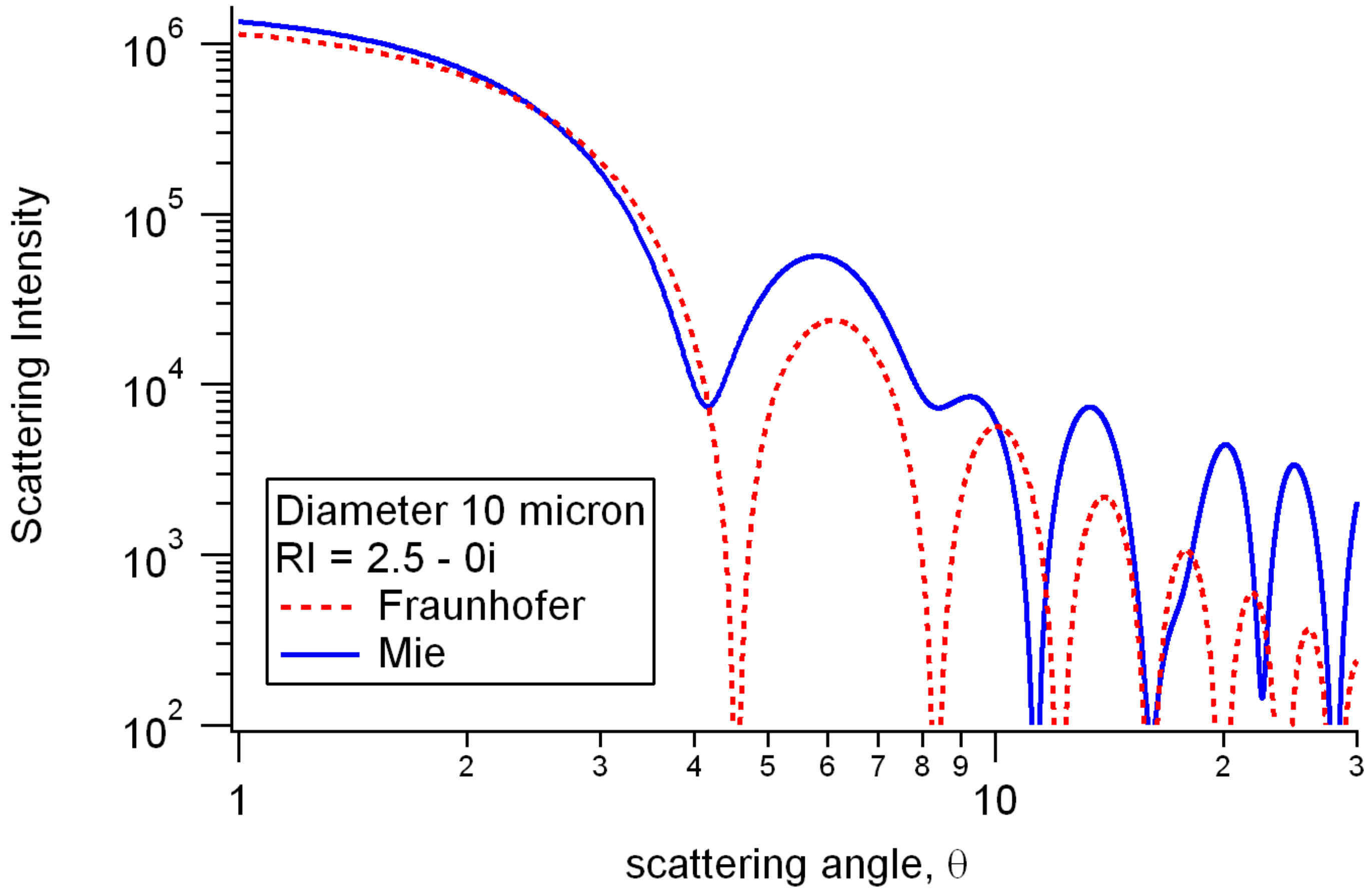
Comparison, Large Particles



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

Comparison, Small Particles

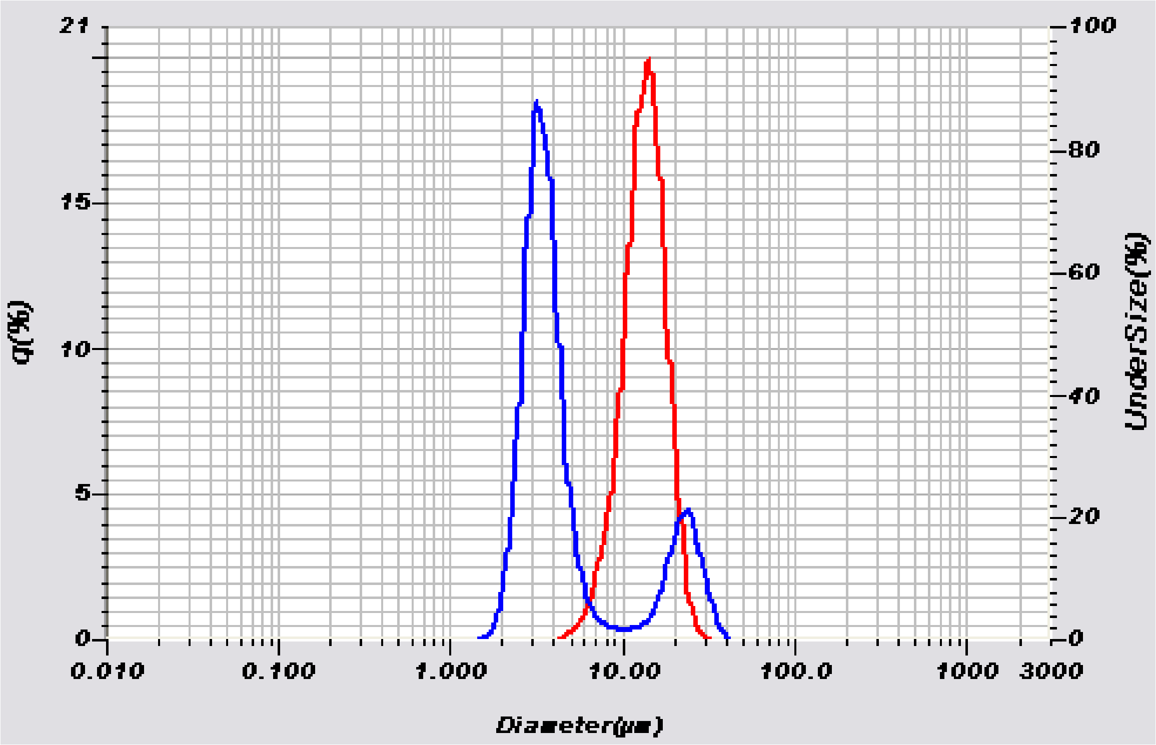
HORIBA Scientific



For small particles, match is poor. Use Mie.

Practical Application: Glass Beads

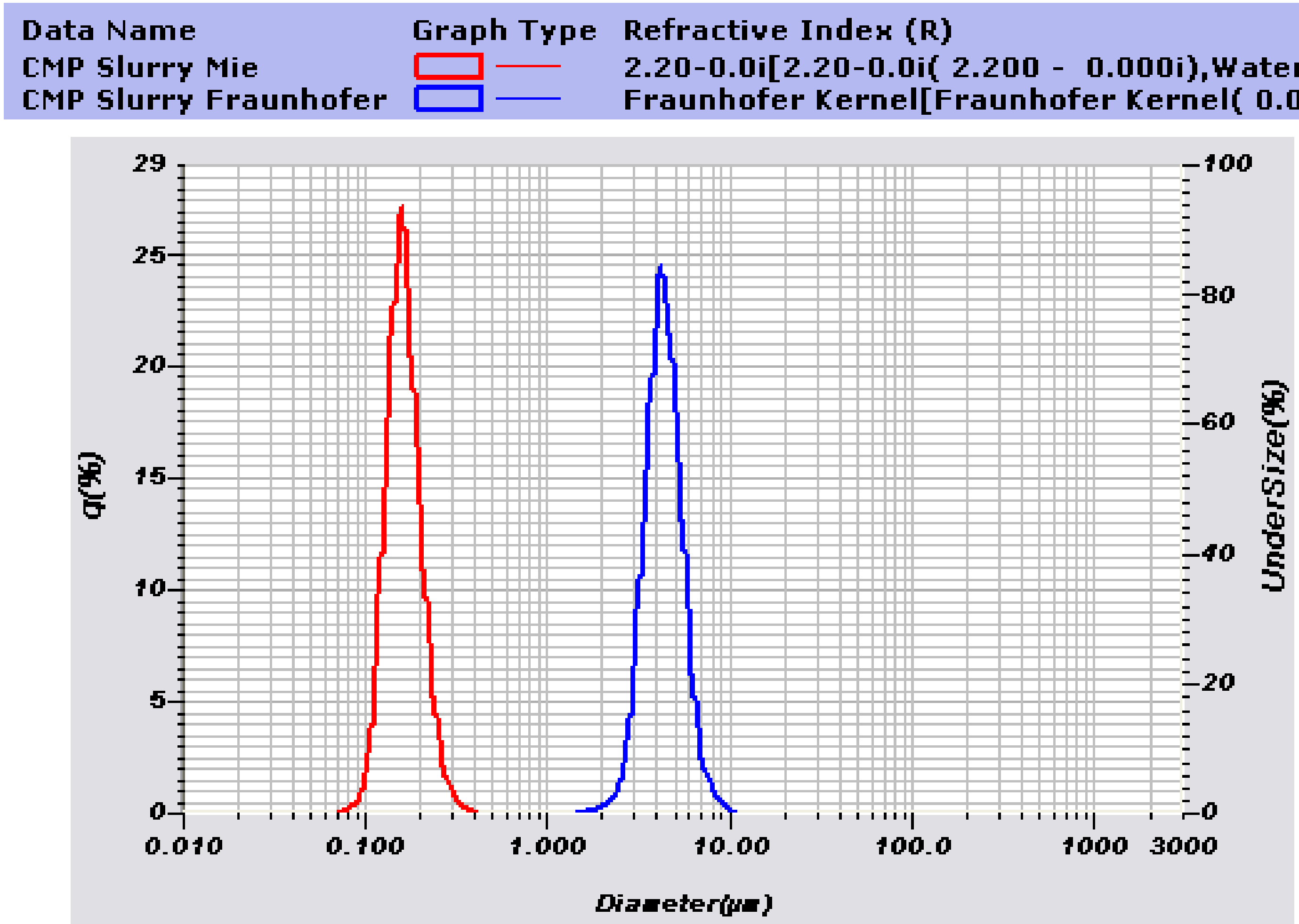
Data Name	Graph Type	Refractive Index (R)
Standard Glass Beads Mie	red	STD-GLASSBEADS[STD-GLASSBEADS(1.510 - 0.000i),'
Standard Glass Beads Fraunhofer	blue	Fraunhofer Kernel[Fraunhofer Kernel(0.000 - 0.000i]



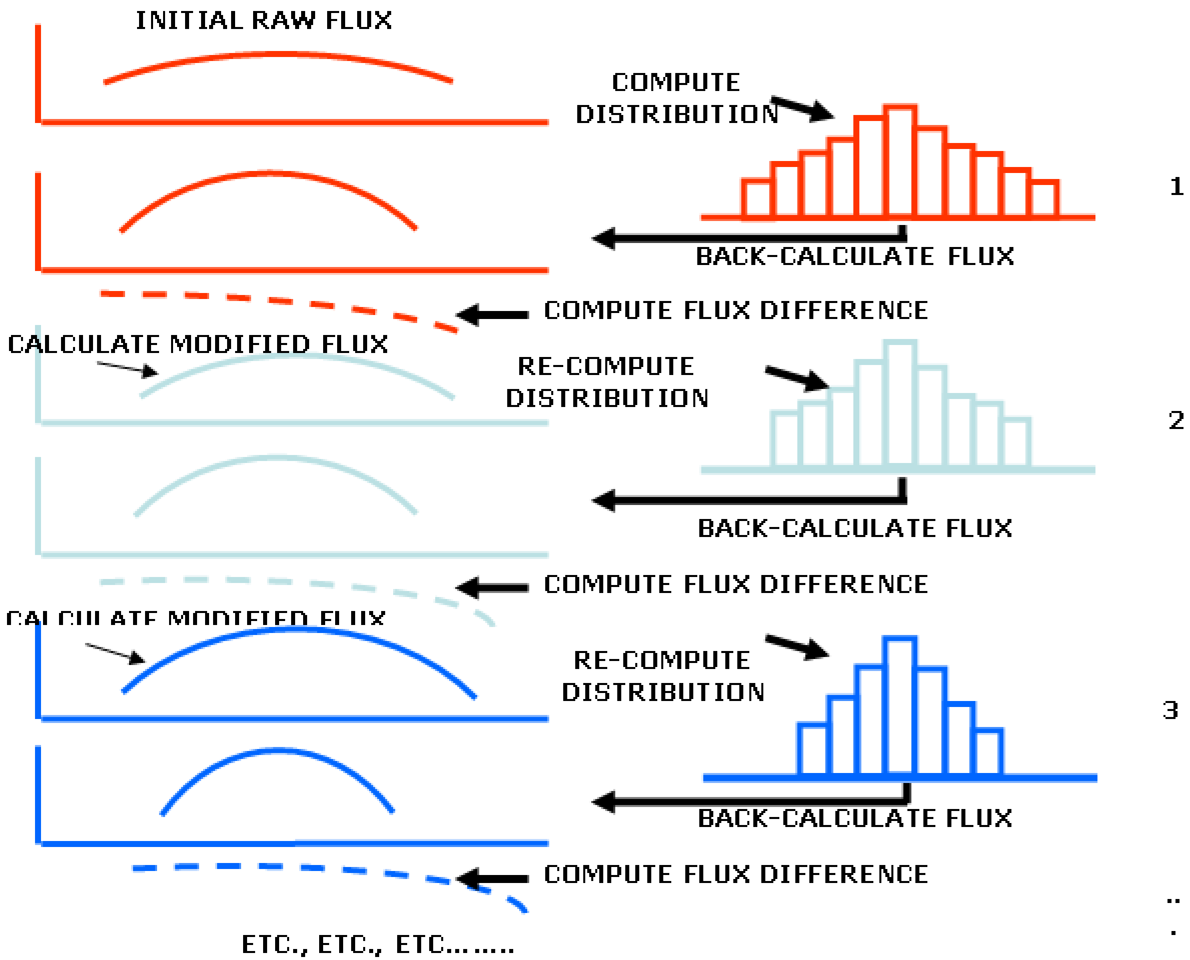
Graph Type	D(v,0.1)	D(v,0.5)	D(v,0.9)
red	8.98783(µm)	13.47741(µm)	18.8536
blue	2.58072(µm)	3.62044(µm)	22.3174

Practical Application: CMP Slurry

HORIBA Scientific



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

HORIBA Scientific

- What particle shape is used for laser diffraction calculations?

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

Pop Quiz

HORIBA Scientific

- What particle shape is used for laser diffraction calculations?

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

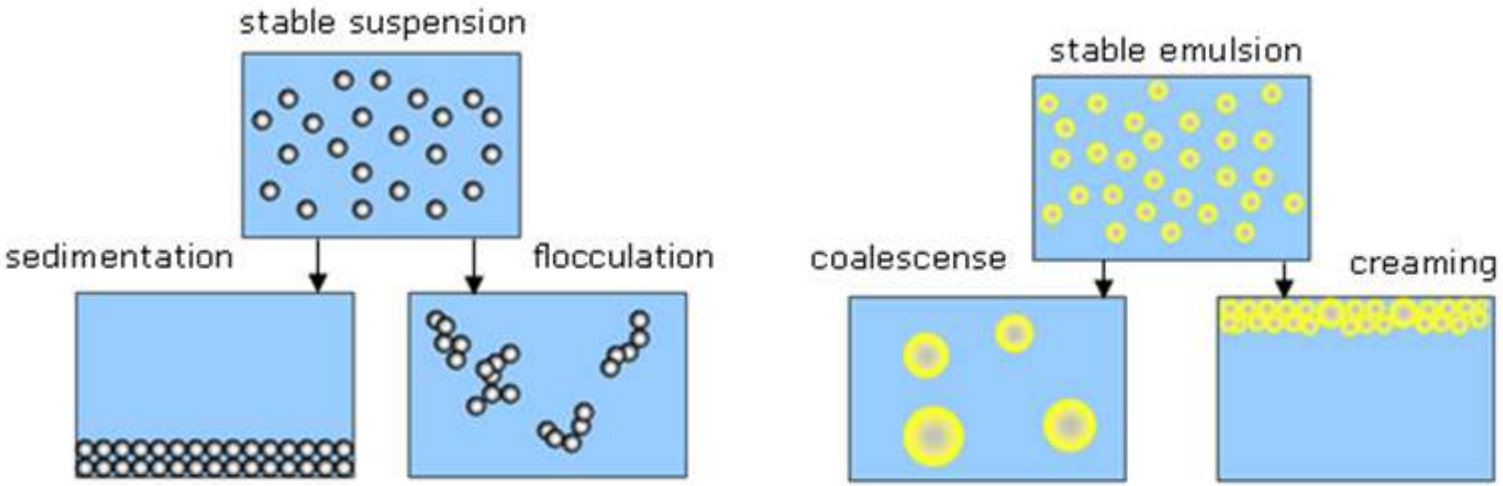
Either gets full credit!

Measurement Workflow

HORIBA Scientific

Prepare the sample

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

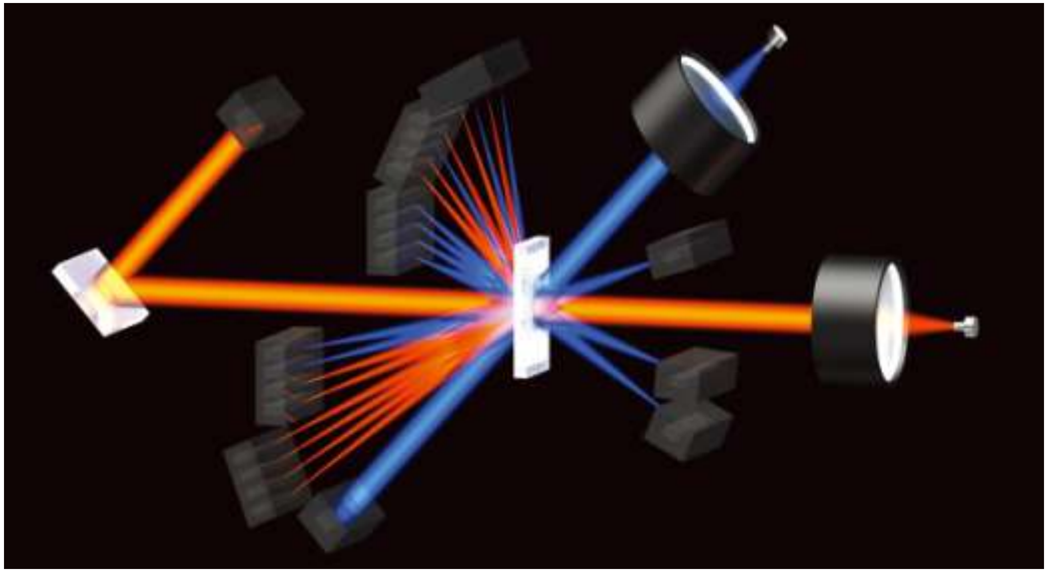


Measurement Workflow

HORIBA Scientific

Prepare the system

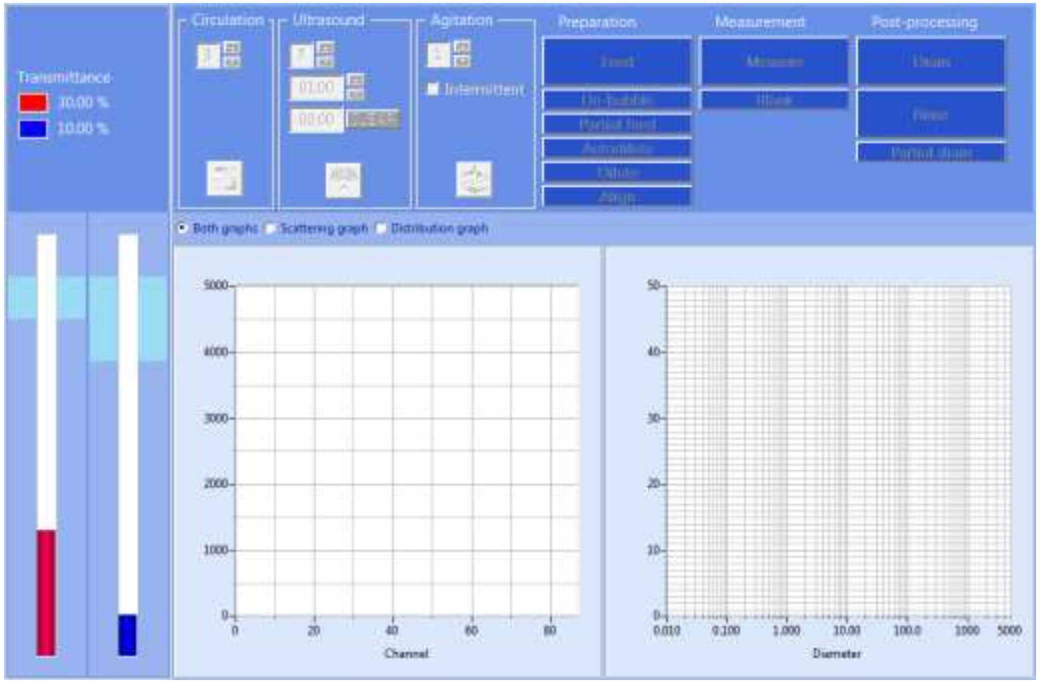
- Align laser to maximize signal-to-noise
- Acquire blank/background to reduce noise



Measurement Workflow

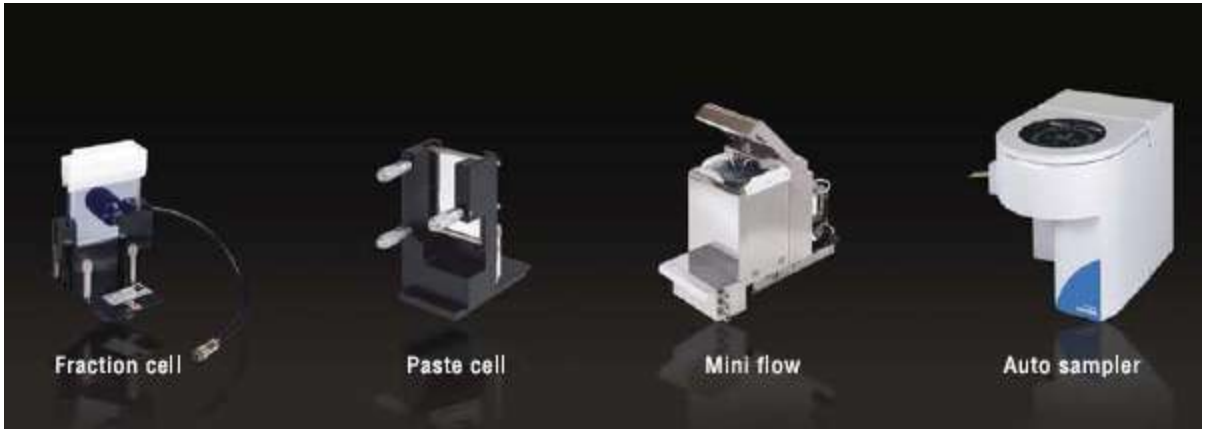
Introduce sample

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



Flexible Sample Handlers

HORIBA Scientific



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)?

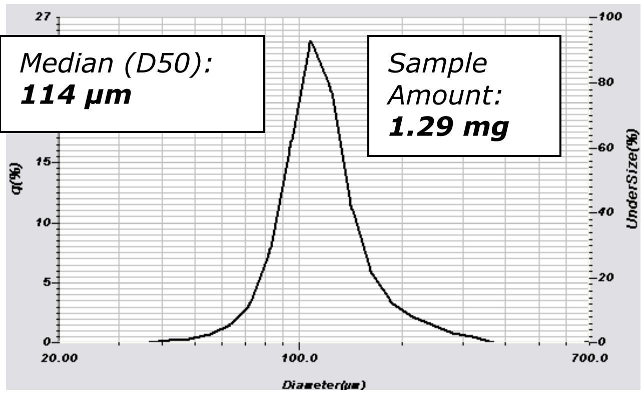
HORIBA Scientific

It depends on sample, but here are some examples.

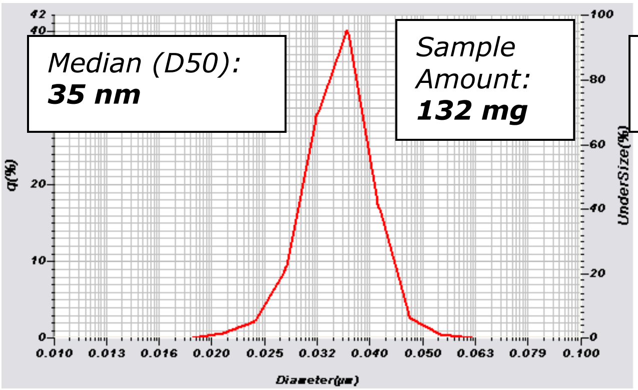
- Larger, broad distributions require larger sample volume
- Lower volume samplers for precious materials or solvents

LA-950 Sample Handlers	Dispersing Volume (mL)
Aqua/SolvoFlow	**180 - 330**
MiniFlow	**35 - 50**
Fraction Cell	**15**
Small Volume Fraction Cell	**10**

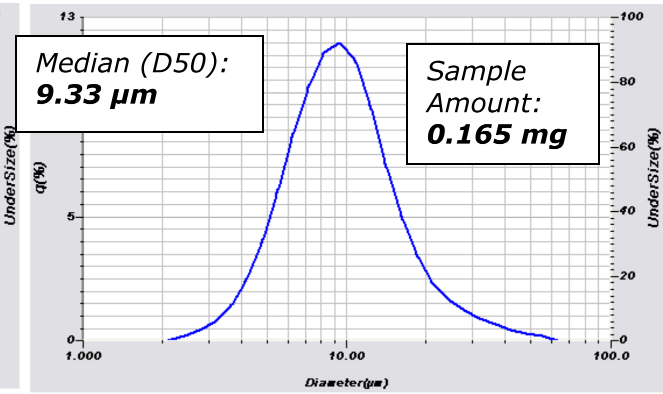
Note: Fraction cell has only magnetic stir bar, not for large or heavy particles



Bio polymer



Colloidal silica



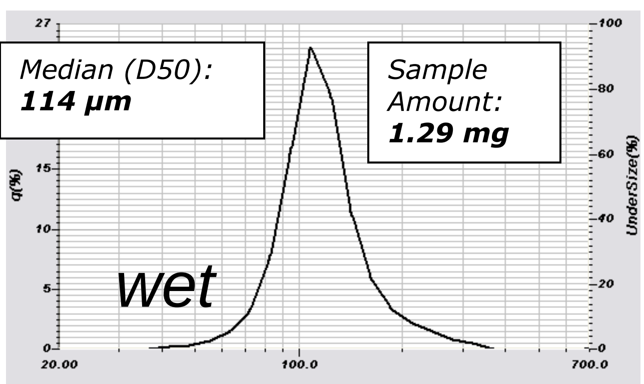
Magnesium stearate

How much sample (dry)?

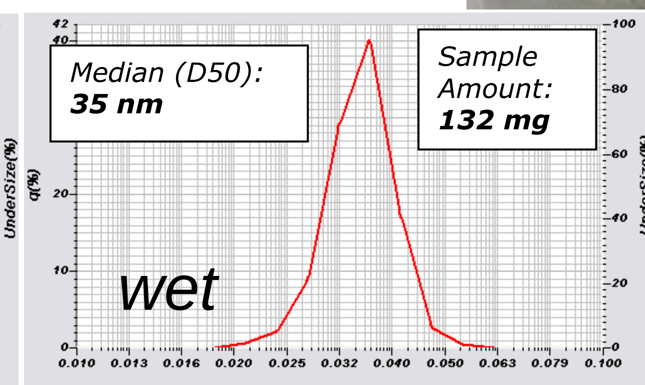
HORIBA Scientific

It depends on sample …..

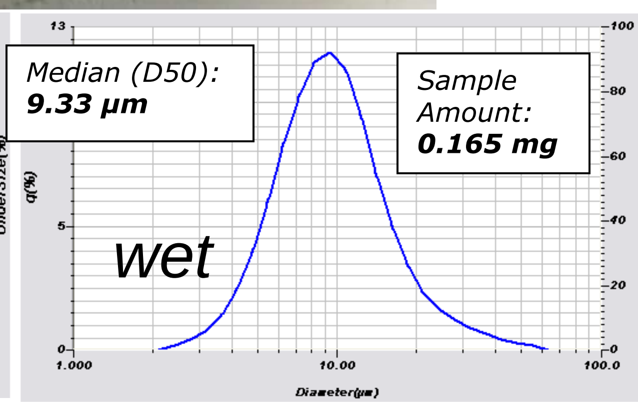
- Larger, broad distributions require larger sample quantity
- Can measure less than 5 mg (over a number of particle sizes).



Bio polymer



Colloidal silica



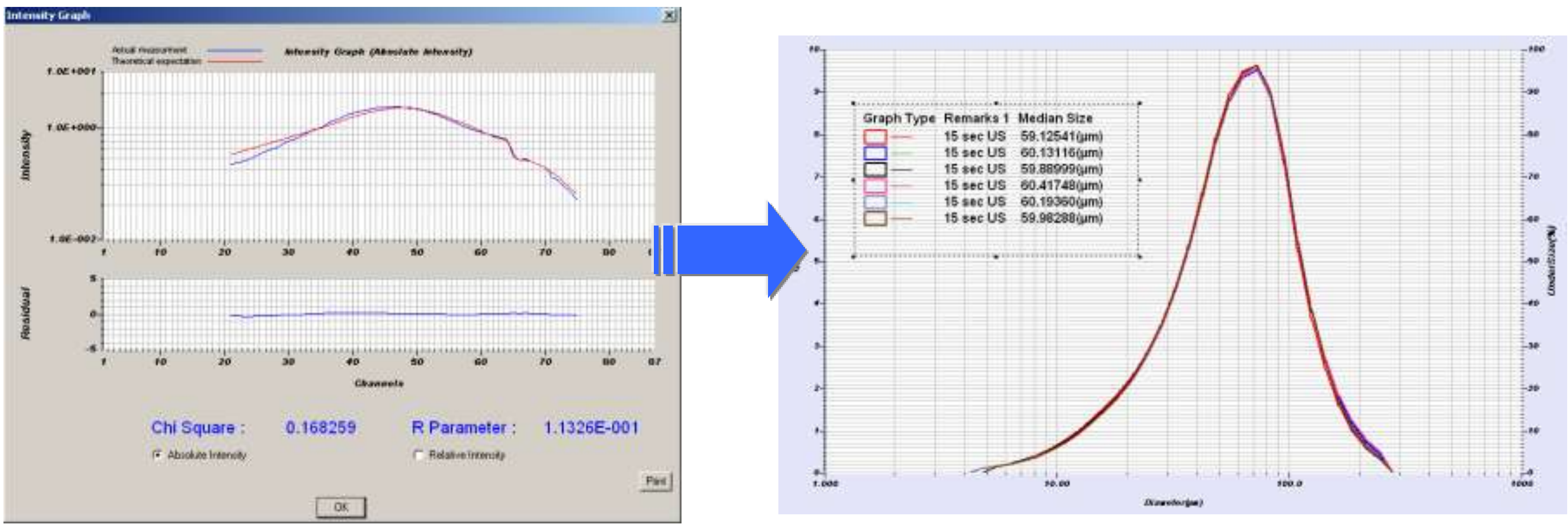
Magnesium stearate

Measurement Workflow

HORIBA Scientific

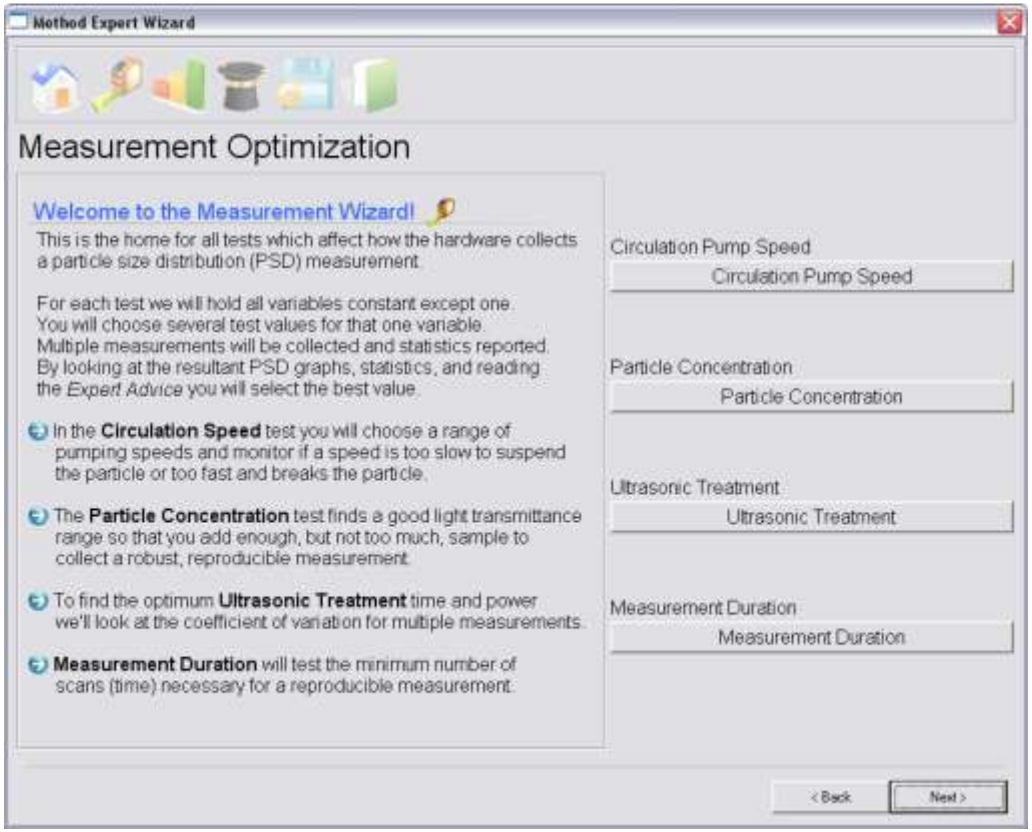
■ Measurement

- ●Click “Measure” button
  - – *Hardware* measures scattered light distribution
  - – *Software* then calculates size distribution



Pump? Dispersion? LA-960 Method Expert

There are four important tests…



Circulation

Concentration

Dispersion

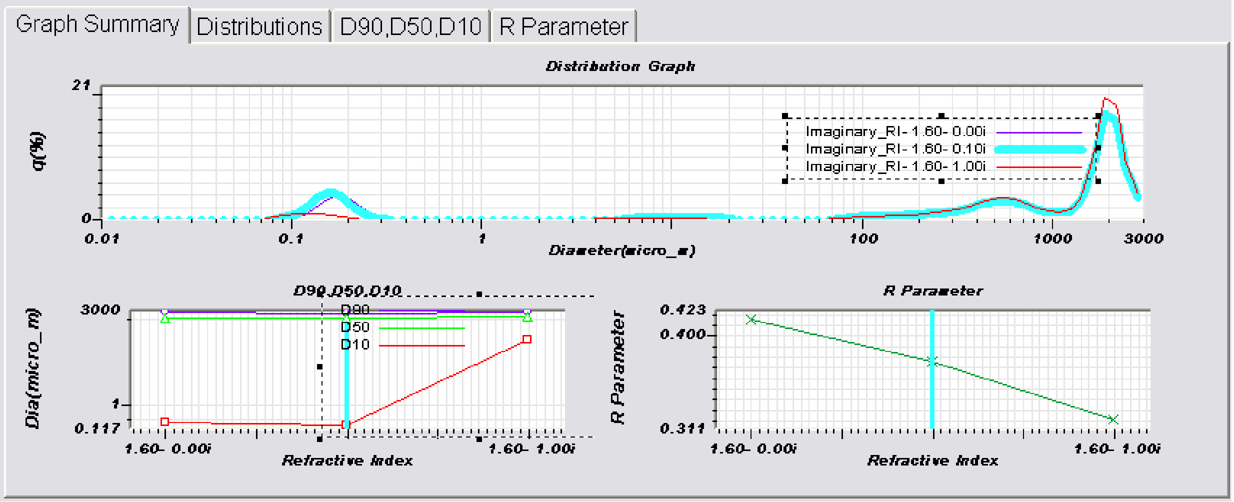
Duration

LA-960 Method Expert

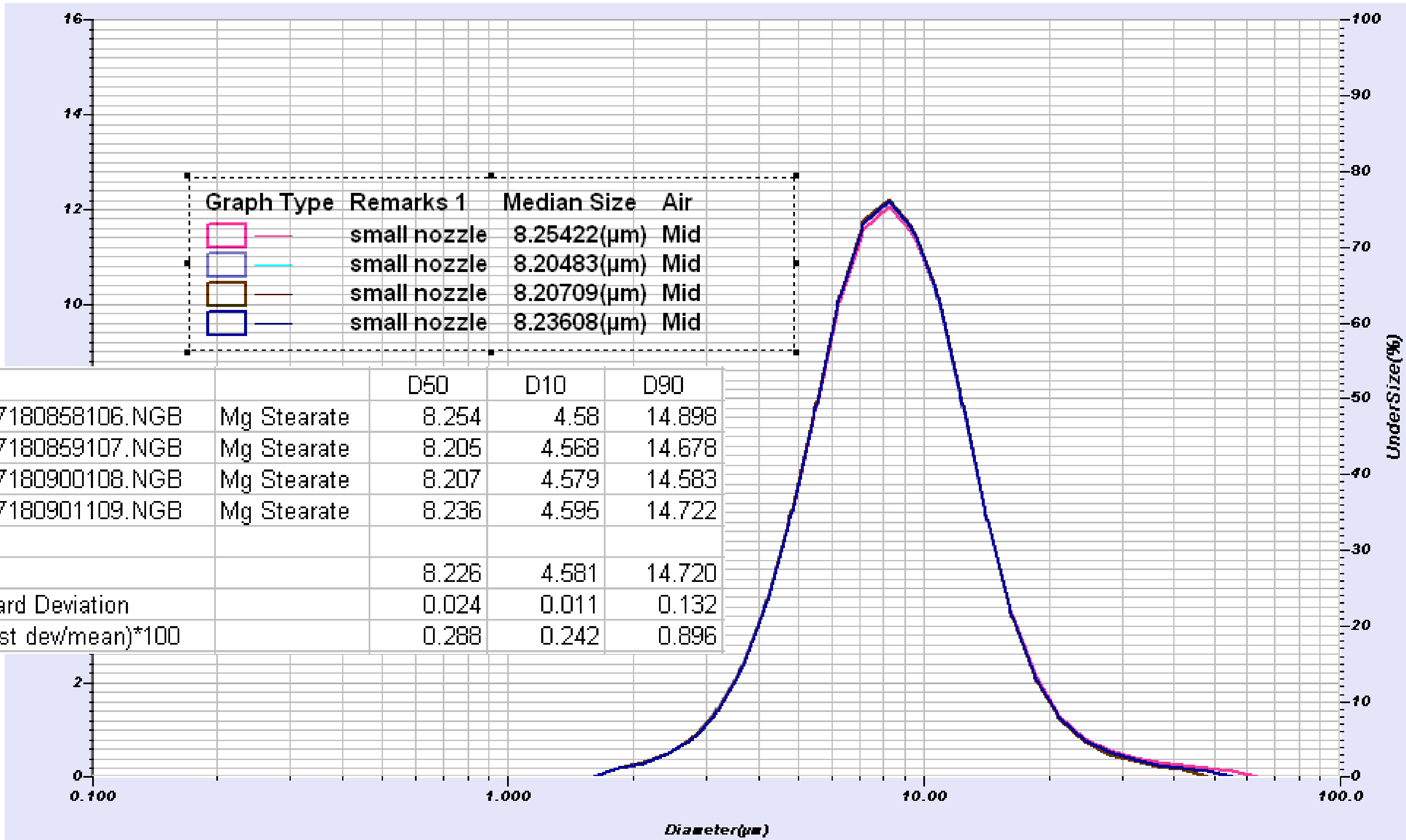
Method Expert guides user to prepare the LA-960 for each test

Results displayed in multiple formats:

PSD, D50, R-parameter

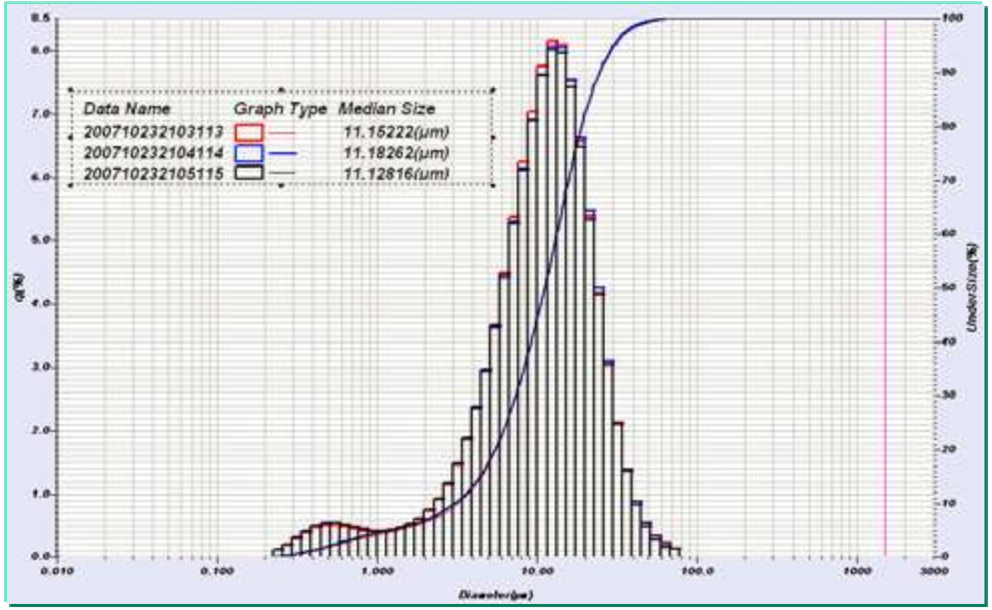


Reproducibility- Mg Stearate dry, 2 bar



		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

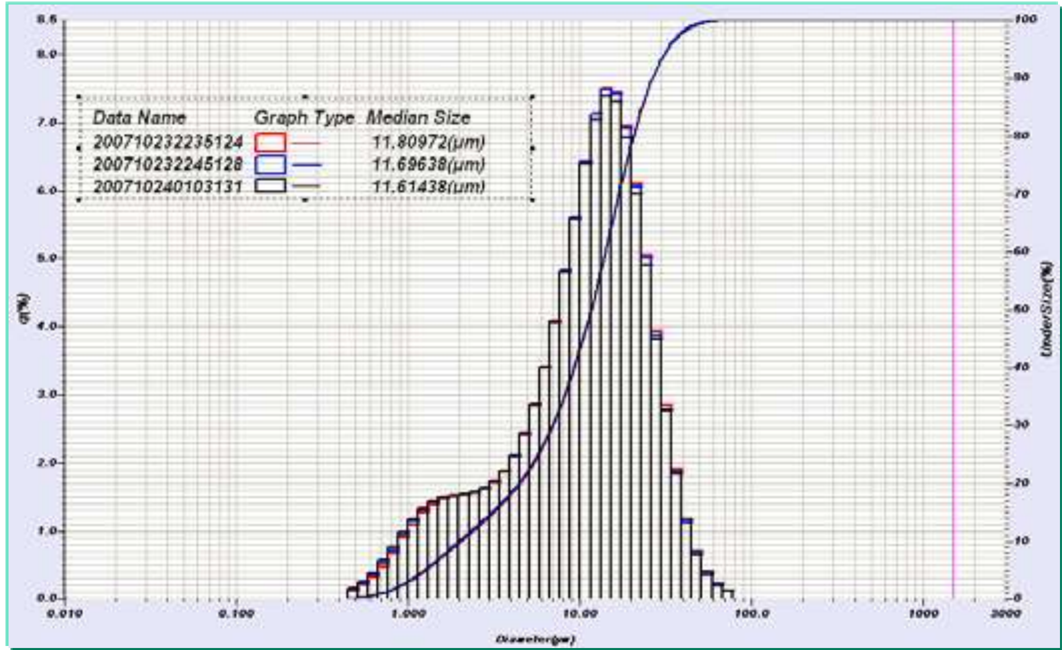


	D10	D50	d90
Portland Cement 1	3.255	11.152	24.586
Portland Cement 2	3.116	11.183	24.671
Portland Cement 3	3.112	11.128	24.92
Average	3.161	11.154	24.726
Std. Dev.	0.082	0.027	0.173
CV (%)	2.6	0.24	0.70

Cement Wet

HORIBA Scientific

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

HORIBA Scientific

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

HORIBA Scientific

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

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

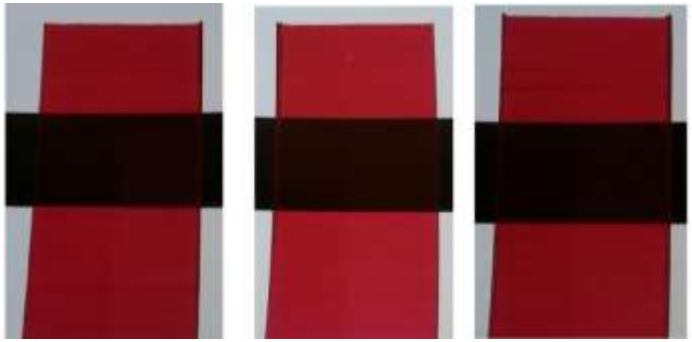
	Dmean	D5	D10	D50	D90	D95
Average (nm)	193	136	147	187	247	264
Std. Dev (nm)	1.5	0.5	0.4	0.6	0.4	1.1
CV (%)	0.8	0.4	0.3	0.3	0.2	0.4

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

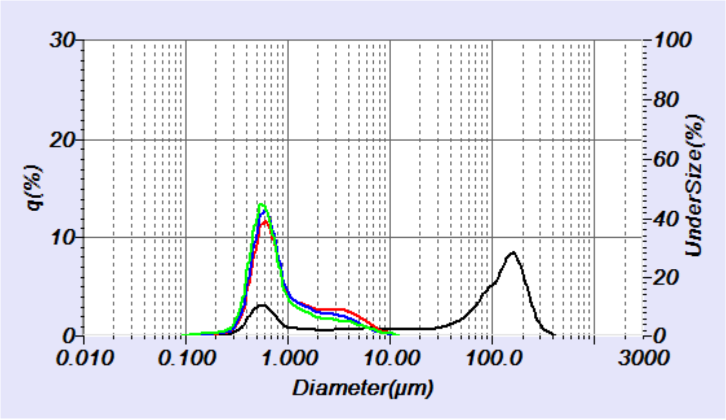
Application: Pigment Hiding Power

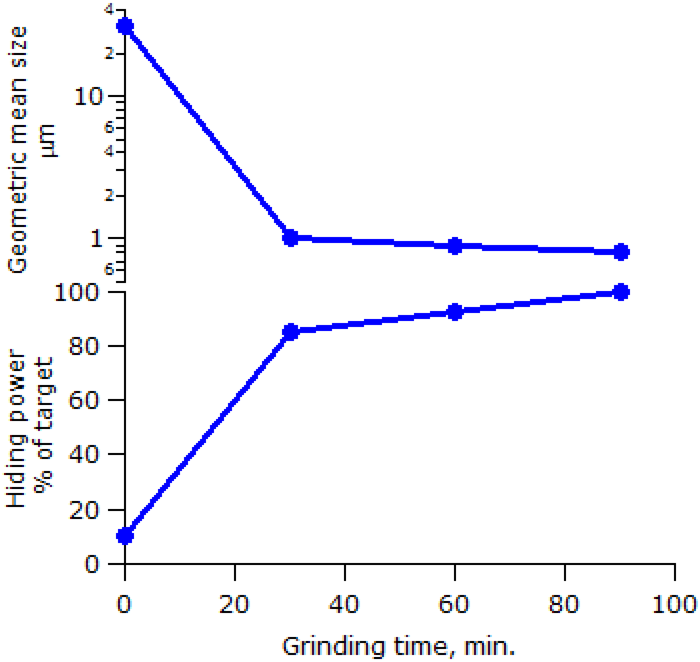
HORIBA Scientific

Operator dependent, need to wait for drying.



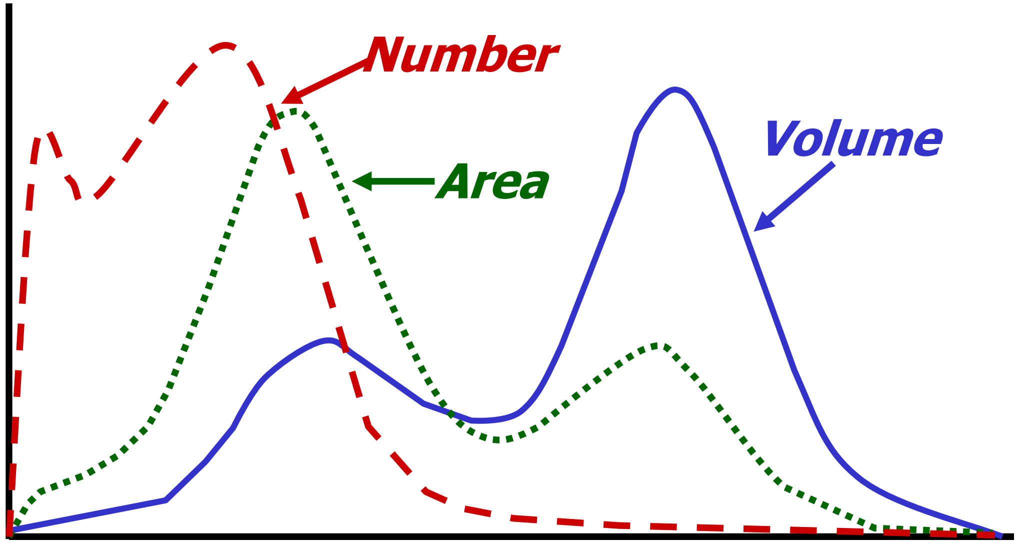
Operator independent, no need to wait for drying.





Diffraction Drawbacks

- Volume basis by default
  - Although excellent for mass balancing, cannot calculate number basis without significant error
- No shape information



The 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

Keep reading the monthly HORIBA Particle e-mail newsletter!

Visit the Download Center to find the video and slides from this webinar.

www.horiba.com/us/particle

Jeff Bodycomb, Ph.D.
P: 866-562-4698
E: jeff.bodycomb@horiba.com

Thank-you