How to Select the Best Refractive Index

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Outline

- Laser Diffraction Calculations
- Importance of Refractive Index
- Choosing Refractive Index
- Comparing Methods for Choosing Refractive Index

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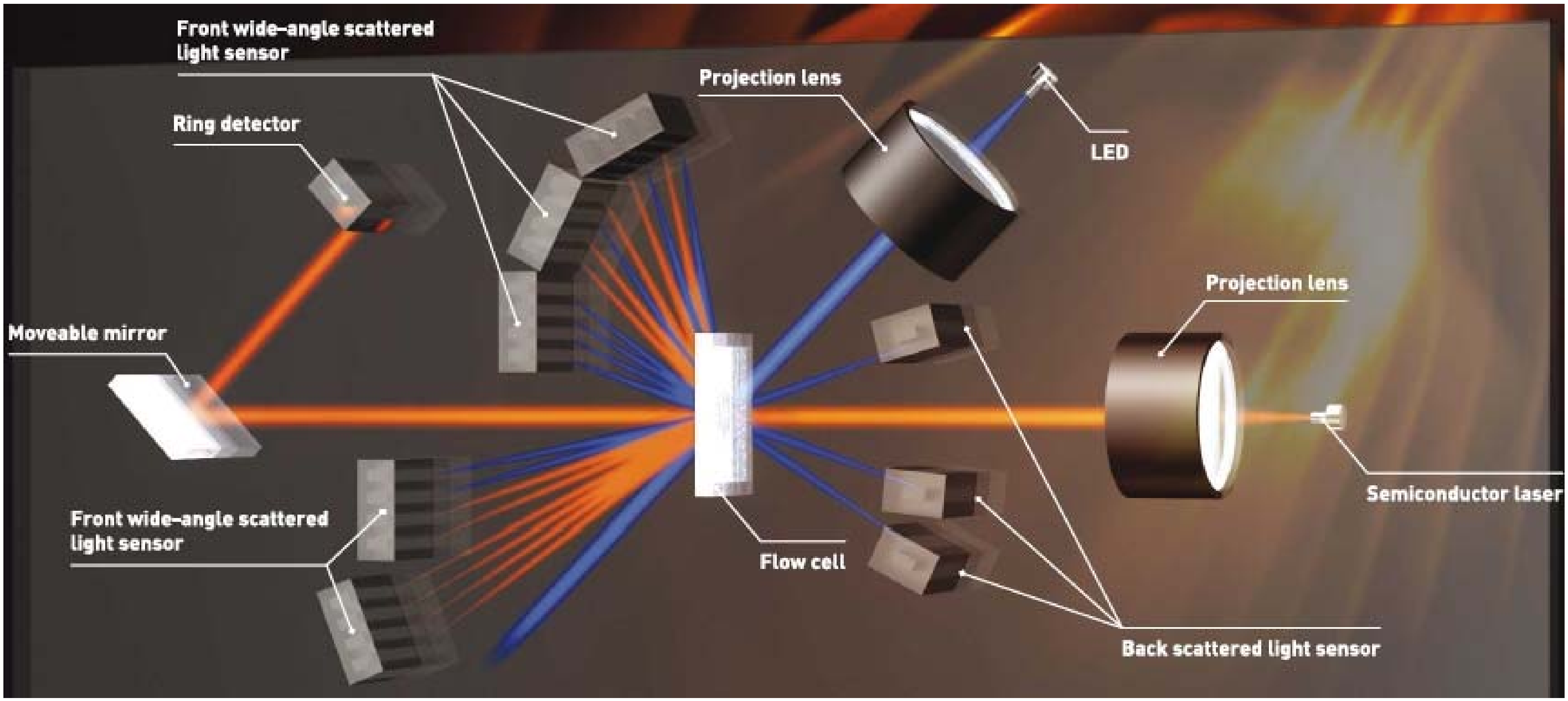
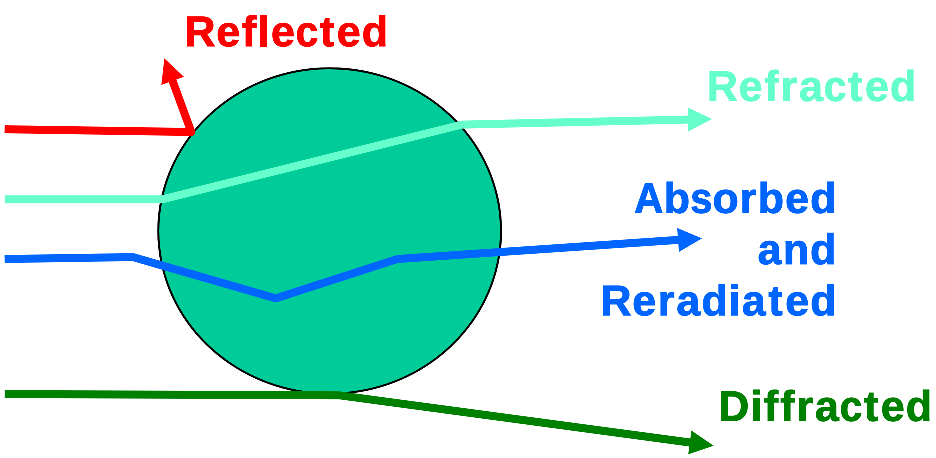
LA-950 Optics



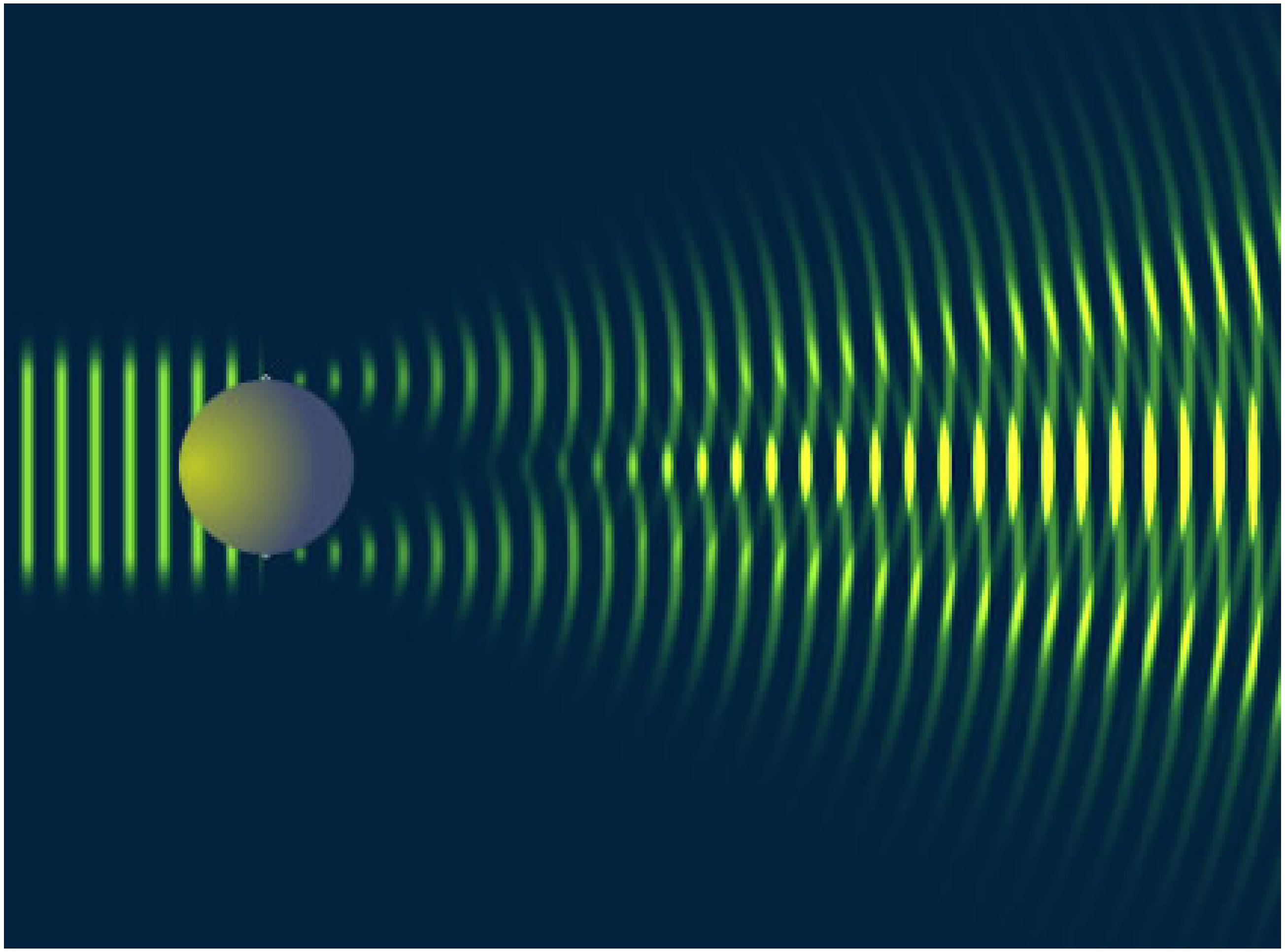
When a Light beam Strikes a Particle

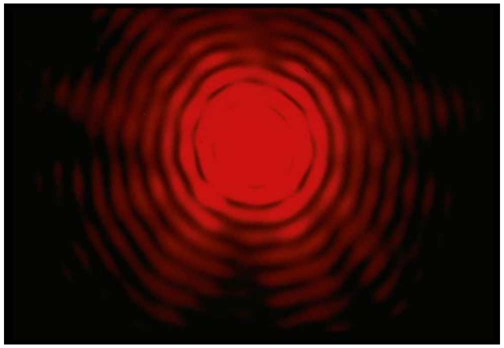
- Some of the light is:
  - Diffracted
  - Reflected
  - Refracted
  - Absorbed and Reradiated



- Small particles require knowledge of optical properties:
  - Real Refractive Index (bending of light)
  - 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

Diffraction Pattern





Using Models to Interpret Scattering

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

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

The Calculations

- There is no need to know all of the details.
- The LA-950 software handles all of the calculations with minimal intervention.

Laser Diffraction Models

- Large particles -> Fraunhofer
  - More straightforward math
  - Large, opaque particles
  - Use this to develop intuition

- All particle sizes -> Mie
  - Messy calculations
  - All particle sizes

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. Rephrased, results are insensitive to refractive index choice.

Mie Scattering

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

Use an existing computer program for the calculations!

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

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

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

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

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

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

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>.

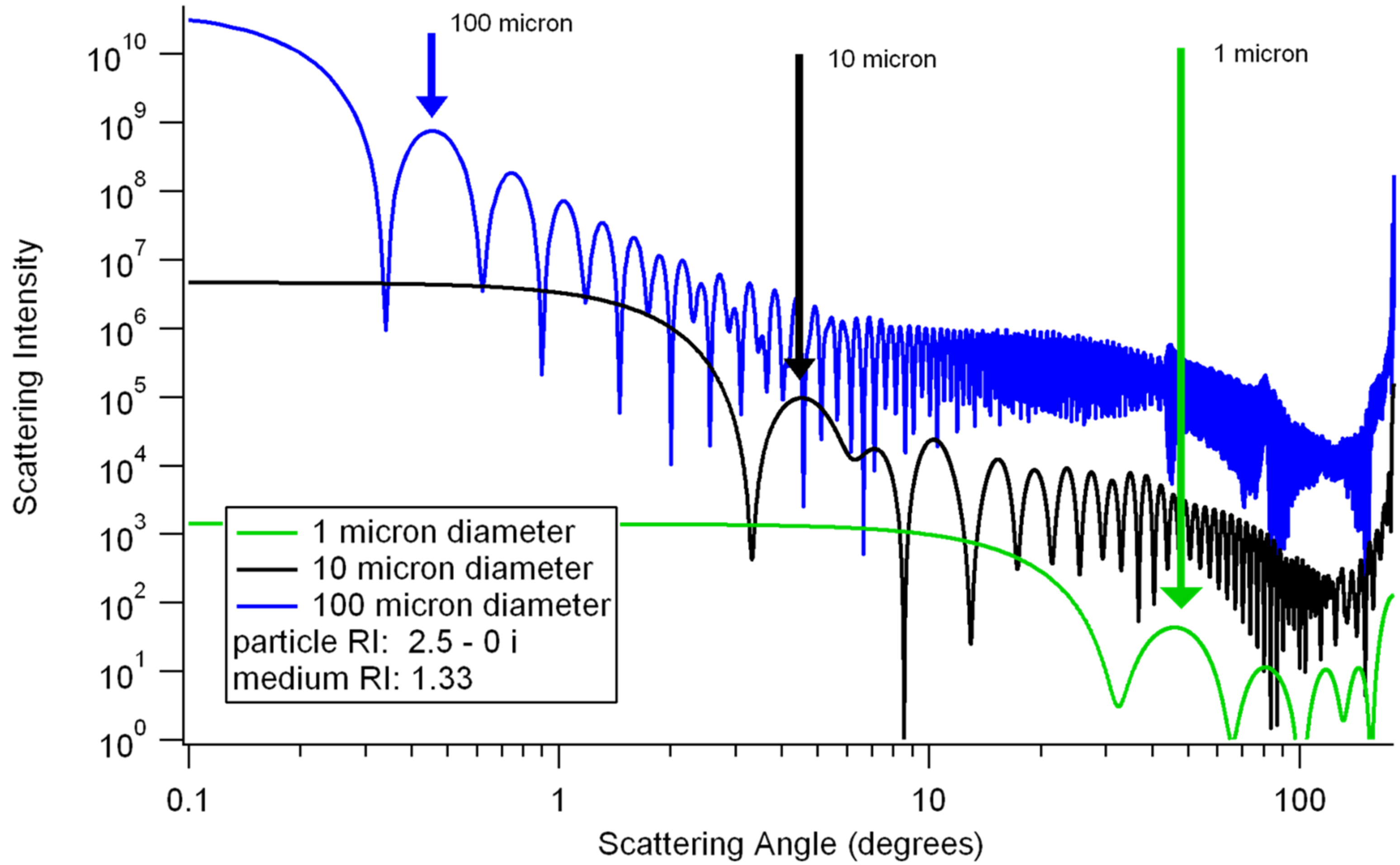
$$m = n_p / n_m$$

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

$$\theta$$

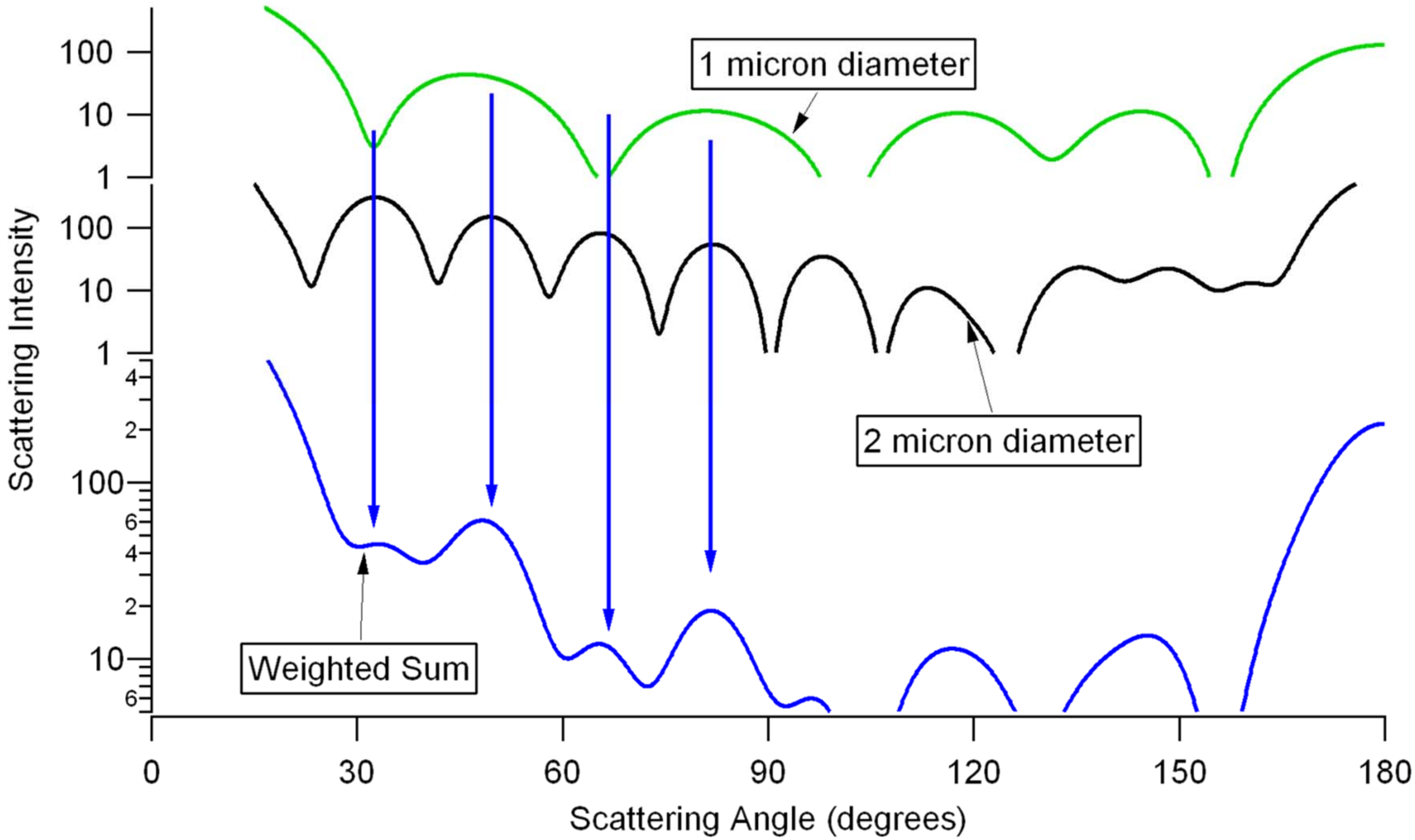
Scattering Angle

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.

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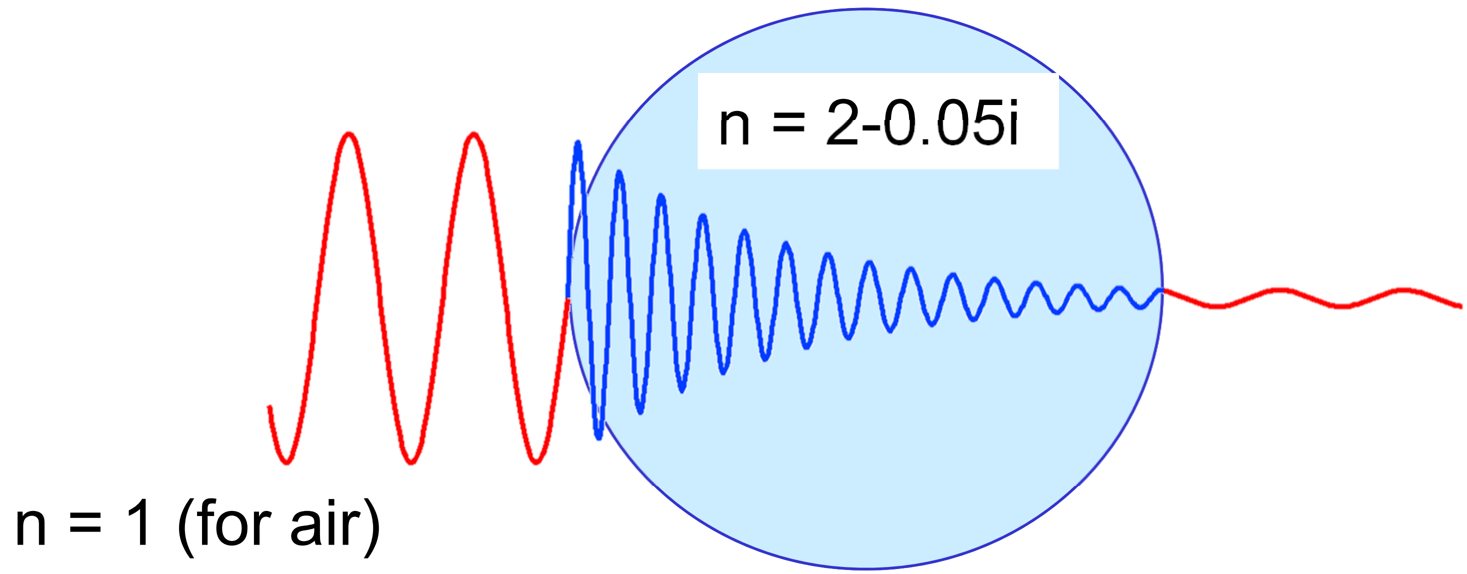
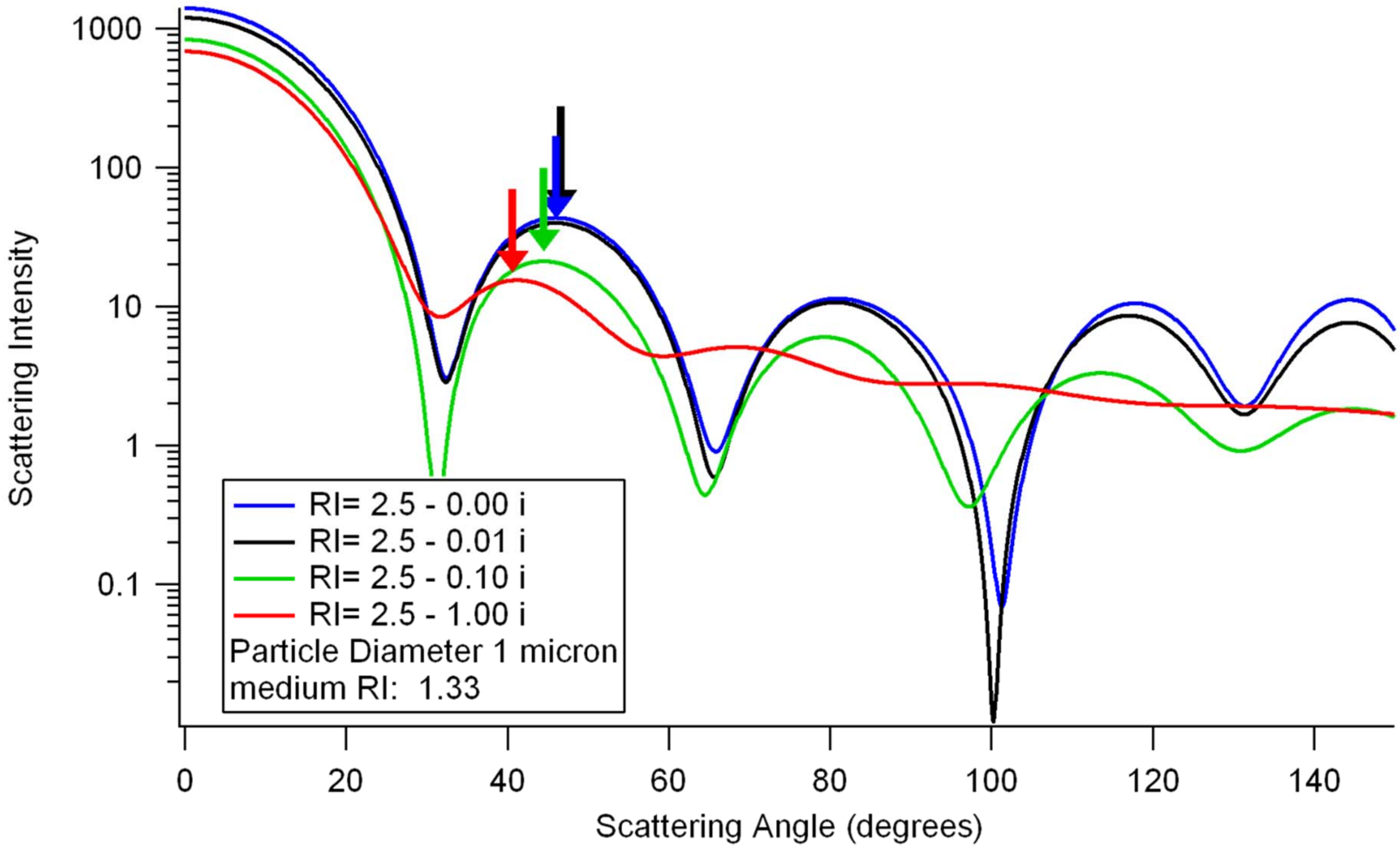
What do we mean by RI?

- Optical properties of particle different from surrounding medium
- Note that intensity and wavelength of light changes in particle (typical dispersants do not show significant absorption)
- Wavelength changes are described by real component
- Intensity changes are described by imaginary component

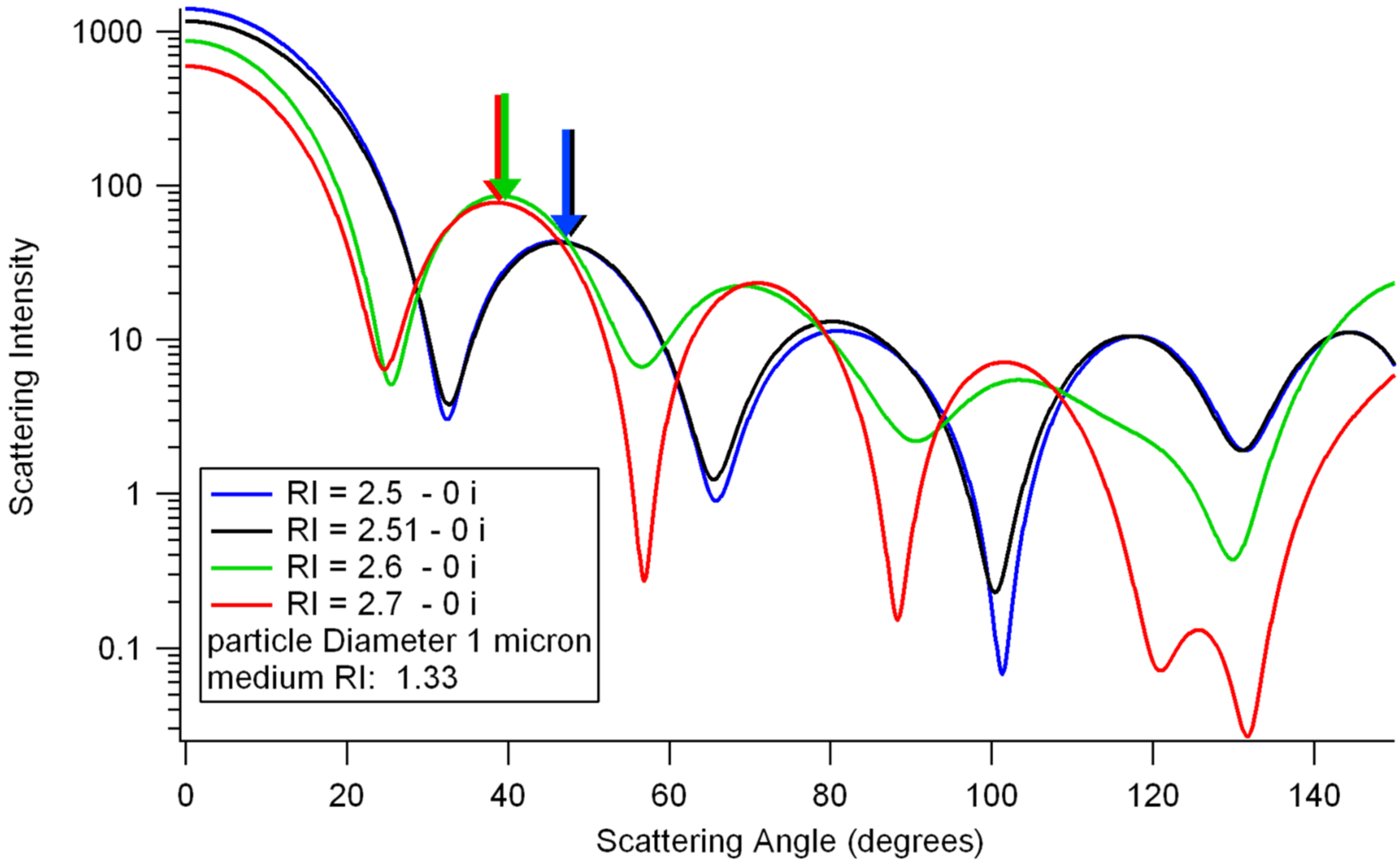


Effect of RI: imaginary term



As imaginary term (absorption) increases location of first peak shifts to smaller angle.

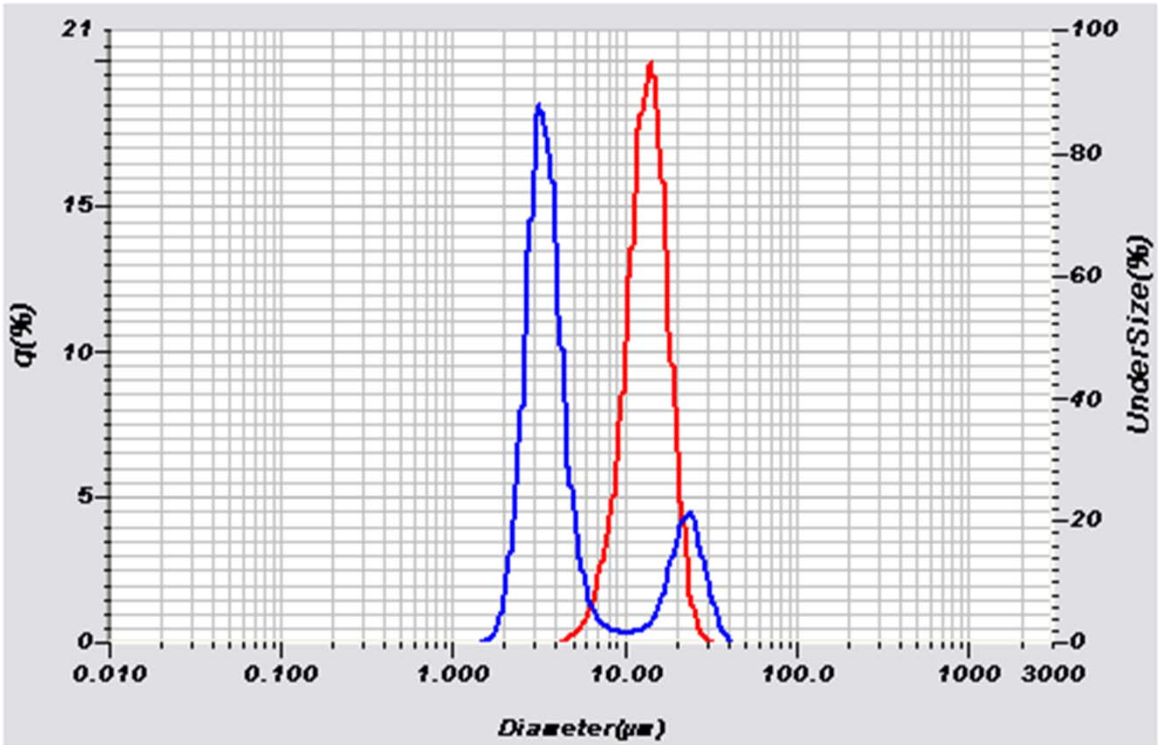
Effect of RI: Real Term



It depends….

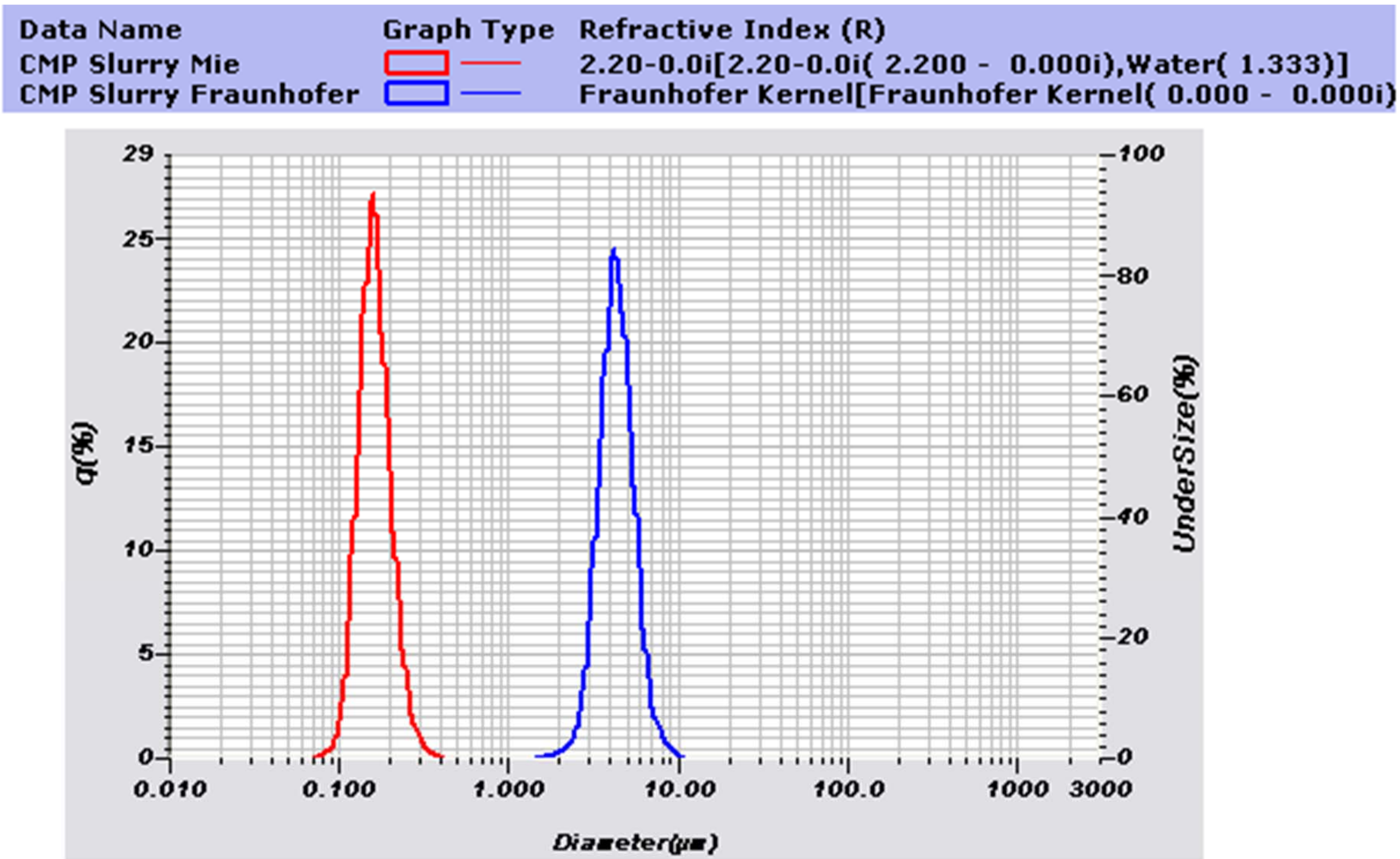
Practical Application: Glass Beads

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]

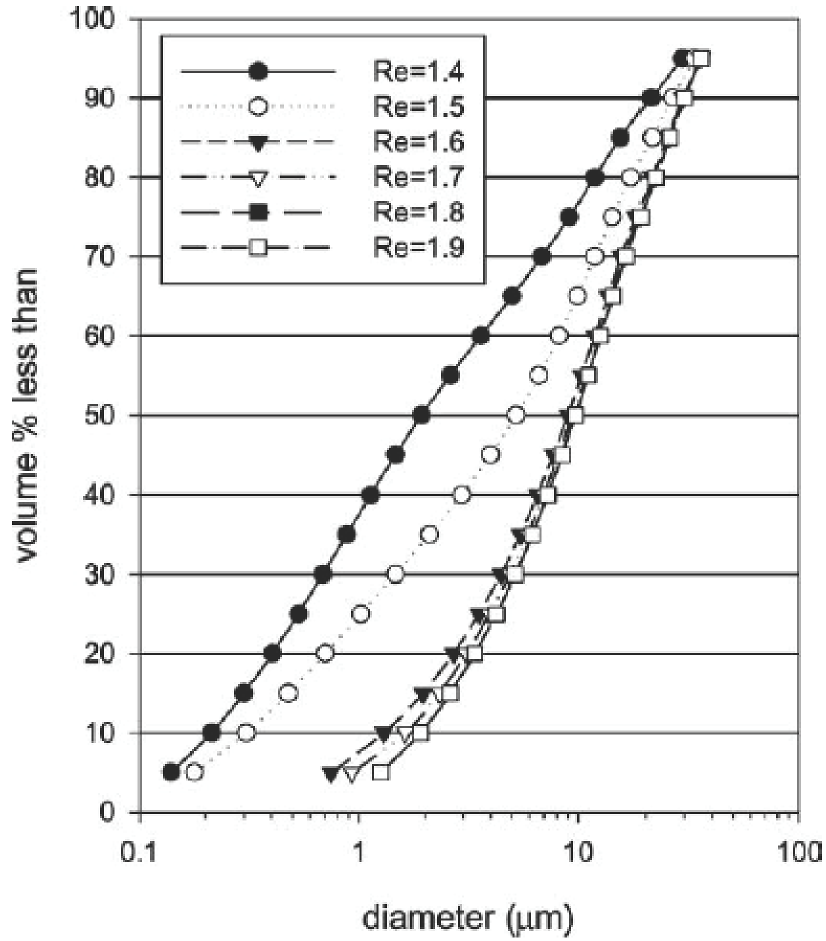


Graph Type	D(v,0.1)	D(v,0.5)	D(v,0.9)
red	8.98783(μm)	13.47741(μm)	18.8536
blue	2.58072(μm)	3.62044(μm)	22.3174

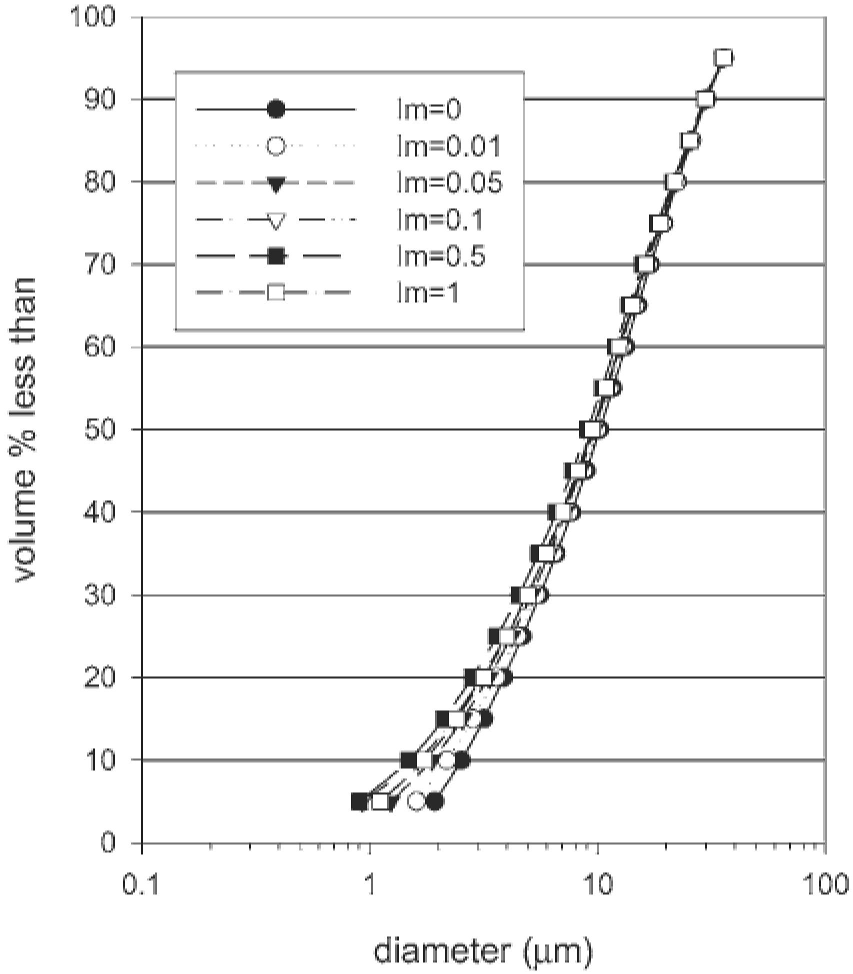
Practical Application: CMP Slurry



Effect of RI: Cement



Fixed absorbance, vary real



Fixed real, vary absorbance

Refractive Index Effect

Most pronounced when:

- Particles are spherical
- Particles are transparent
- RI of particle is close to RI of fluid
- Particle size is close to wavelength of light source

Least pronounced when:

- Particles are not spherical
- Particles are opaque
- RI of particle is larger than RI of the fluid
- Particle size is much larger than wavelength of the light source

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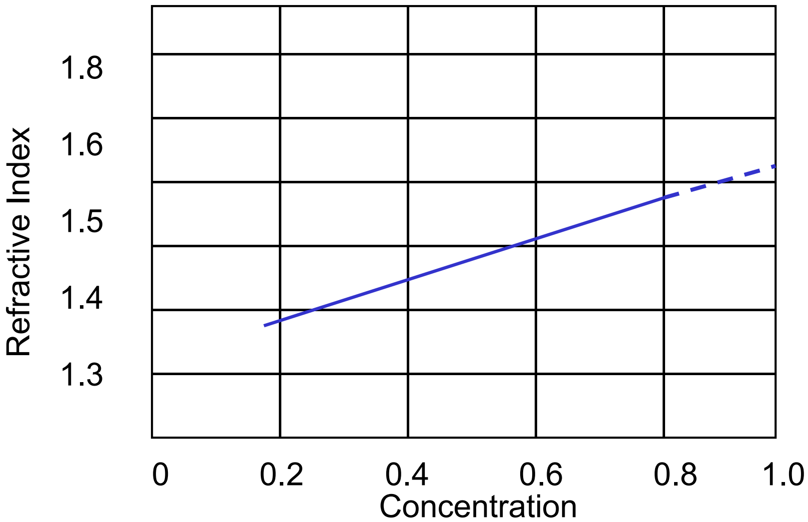
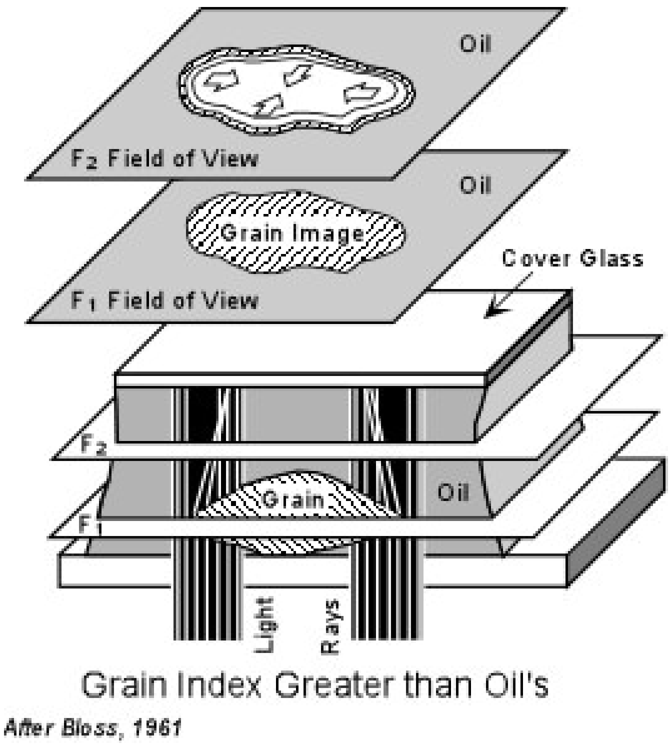
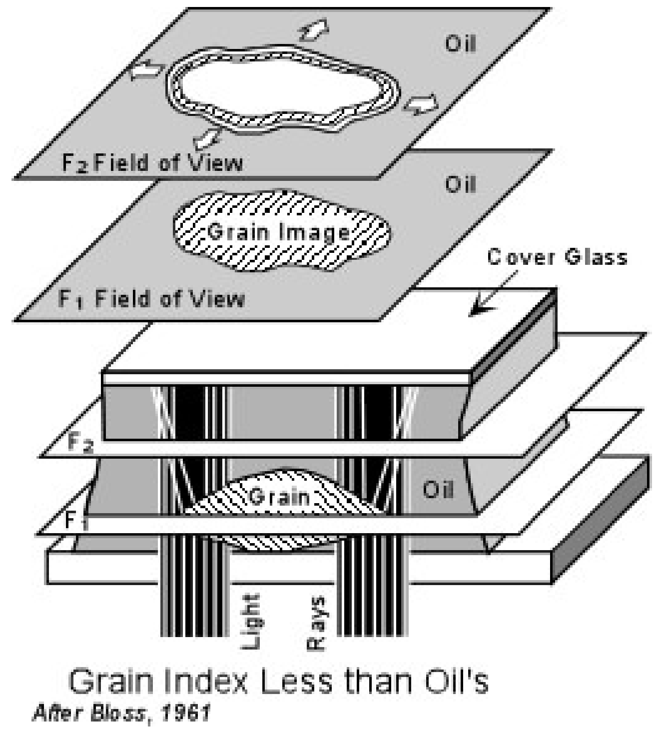
Abbe Refractometer

- Dissolve sample at different concentrations
- Plot conc. vs. RI
- Extrapolate to infinite concentration



Becke Lines

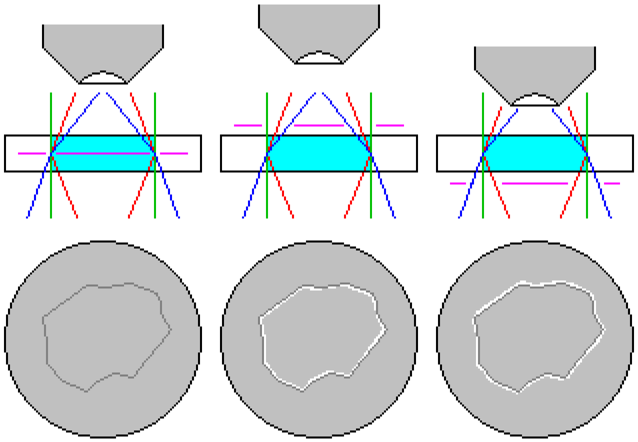




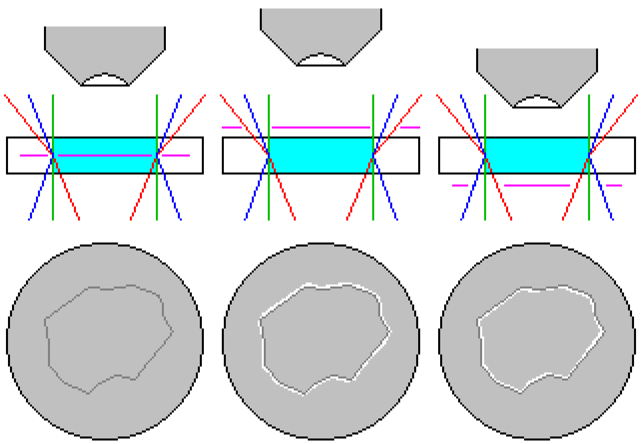
Bright line is called the ***Becke line*** and will always occur closest to the substance with a higher refractive index

Becke Line Test

As you move *away* from the thin section (raising the objective or lowering the stage), the Becke Line appears to move *into the material with greater refractive index.*



A particle that has greater refractive index than its surroundings will refract light inward like a crude lens.



A particle that has lower refractive index than its surroundings will refract light outward like a crude diverging lens.

Becke Line Test

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Refractive Index (Matching) Liquids

Also see our **Specialized Optical Coupling Liquids**

Cargille Refractive Index Liquids have become standard items in many laboratories as their applications have expanded from routine mineralogical identifications and quality control. New and broader uses in many more fields such as chemicals, engineering, medical, forensic, optics, instrumentation are continuously discovered. Many special requirements for specific applications have created a need for more technical data, new formulations, extended ranges, smaller increments and higher degrees of precision.

Price Schedule

All Refractive Index Values are standardized at 5893 angstroms and 25°C.
For Custom Made Liquids please fill in our **Optical Liquids Worksheet**
All of the Refractive Index Liquid Sets are sold in 7.4cc bottles (1/4 fl oz)

COMBINED SETS: n_D 1.400-1.700

The range of many minerals, most chemicals and virtually all biological materials are covered by the three Certified Series AA, A and B. These three Series are available as complete sets:

Cat. #		Price
18001	RF-1..........Full Set; Intervals 0.002; 151 liquids	$1,865.00
18002	RF-1/2.......Half Set; Intervals 0.004; 76 liquids	1,025.00
18005	RF-1/5.......Fifth Set; Intervals 0.01; 31 liquids	415.00

Individual Series, fractions of Series or selected liquids in the Standard Group may also be purchased separately.

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Index of Refraction

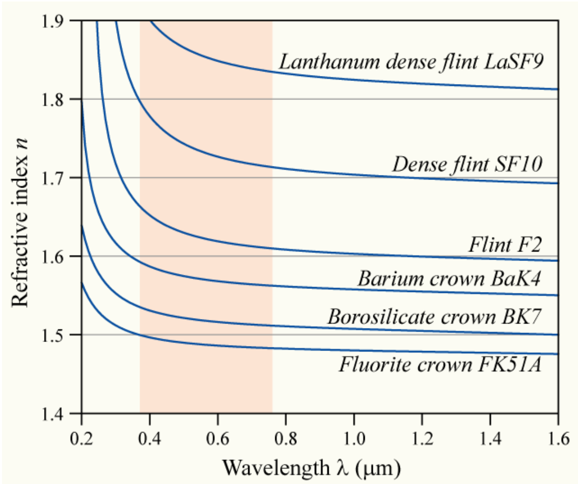
- Return the refractive index of a substance at a given wavelength, λ (nm). Further information in addition to the index of refraction also may be given.
- Luxpop returns the absolute refractive index (i.e. with resp. to vacuum), unless stated otherwise. Click here for more index of refraction terminology.
- To facilitate search, select the input box and type in the first letter of the desired substance. Contact Luxpop to request more materials.
- See also our long list of Index of Refraction Values (A-Z)... for other materials.

Substance: ZnO λ: 650 nm temperature (certain substances only) 25 deg C go

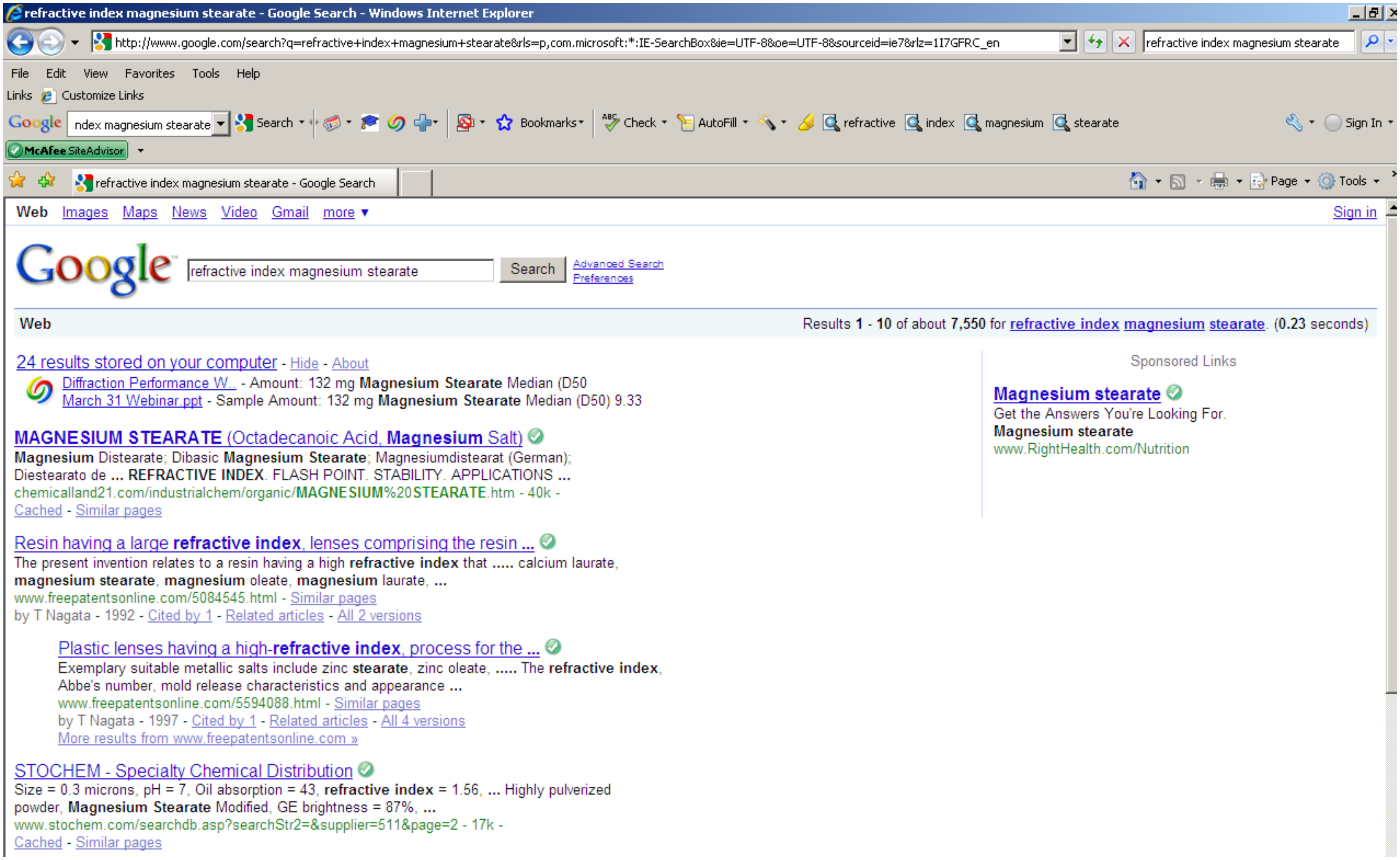
At a wavelength of 650 nm (1.908 eV), the index of refraction of ZnO is
n = 1.98, k = 0.000.

At a wavelength of 405 nm (3.061 eV), the index of refraction of ZnO is
n = 2.23, k = 0.010.

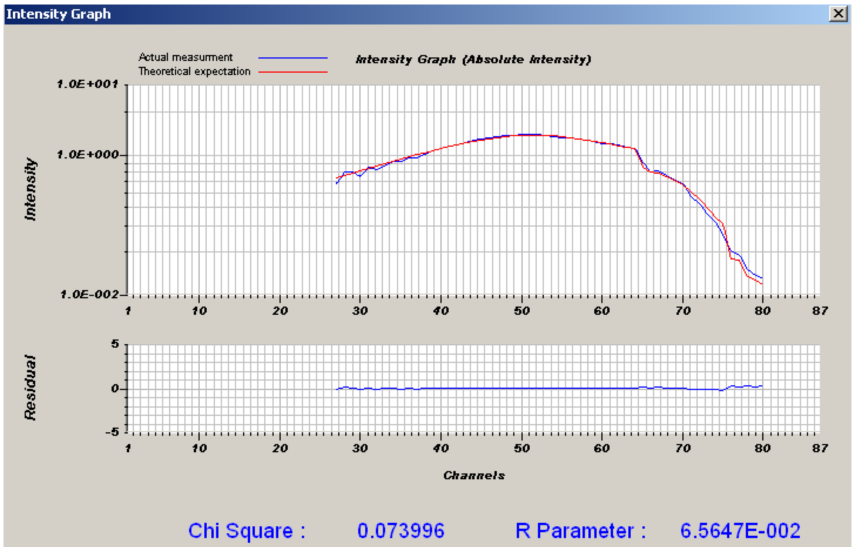
Note RI is dependent on wavelength of light.
Can adjust RI for red & blue light, but only need to for small, absorbing particles.

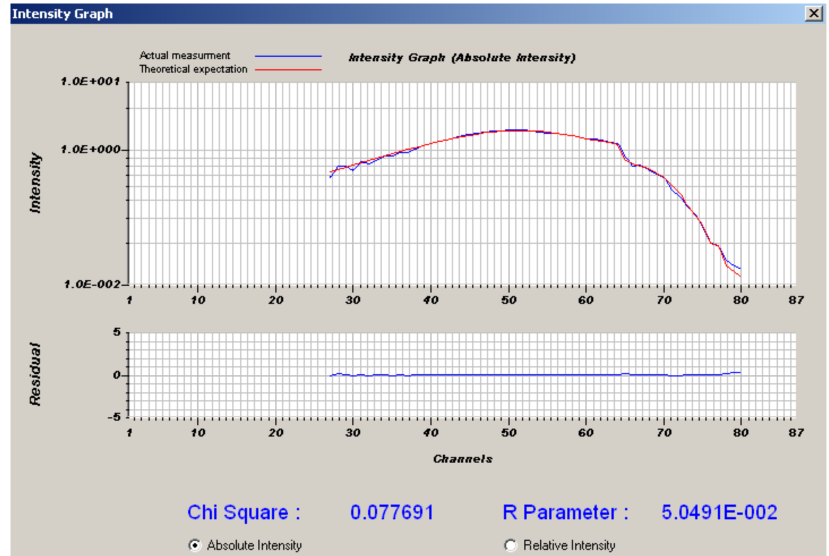


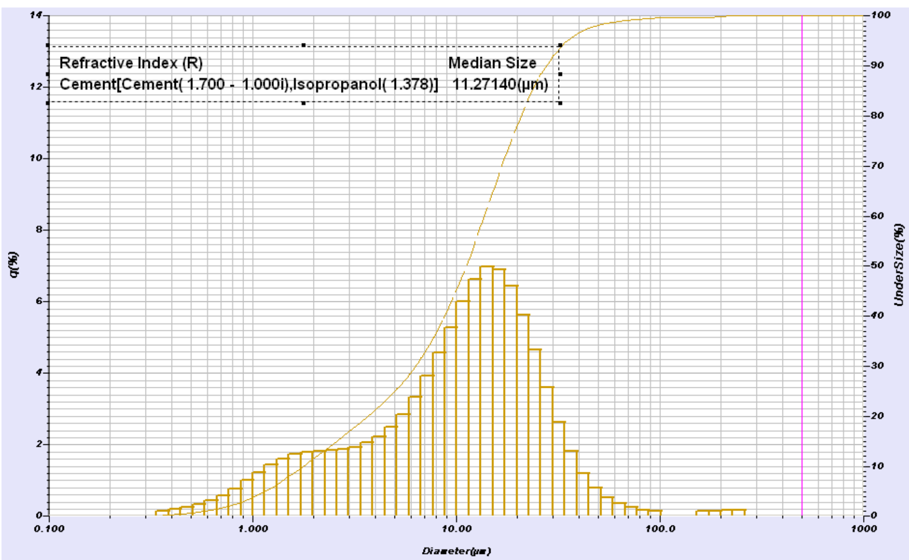
Google Search

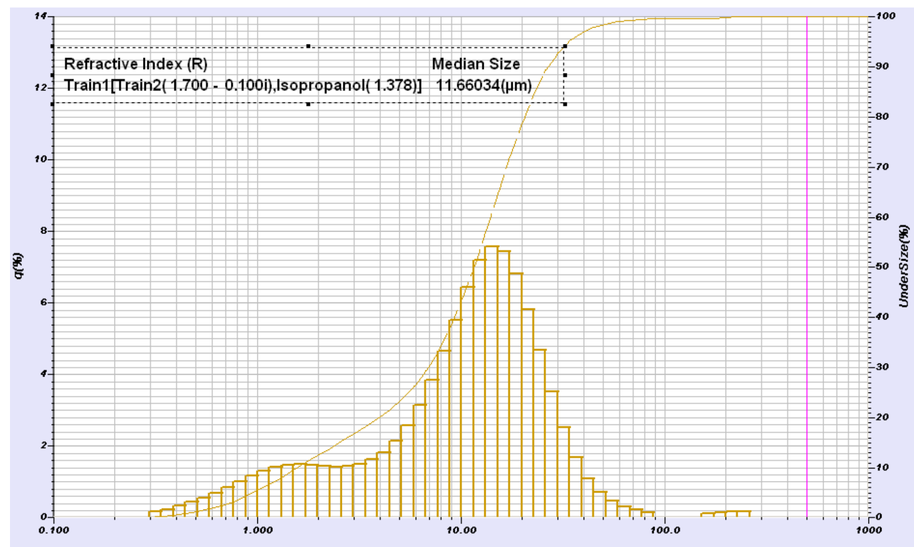


Using R Value for i









What is R parameter?

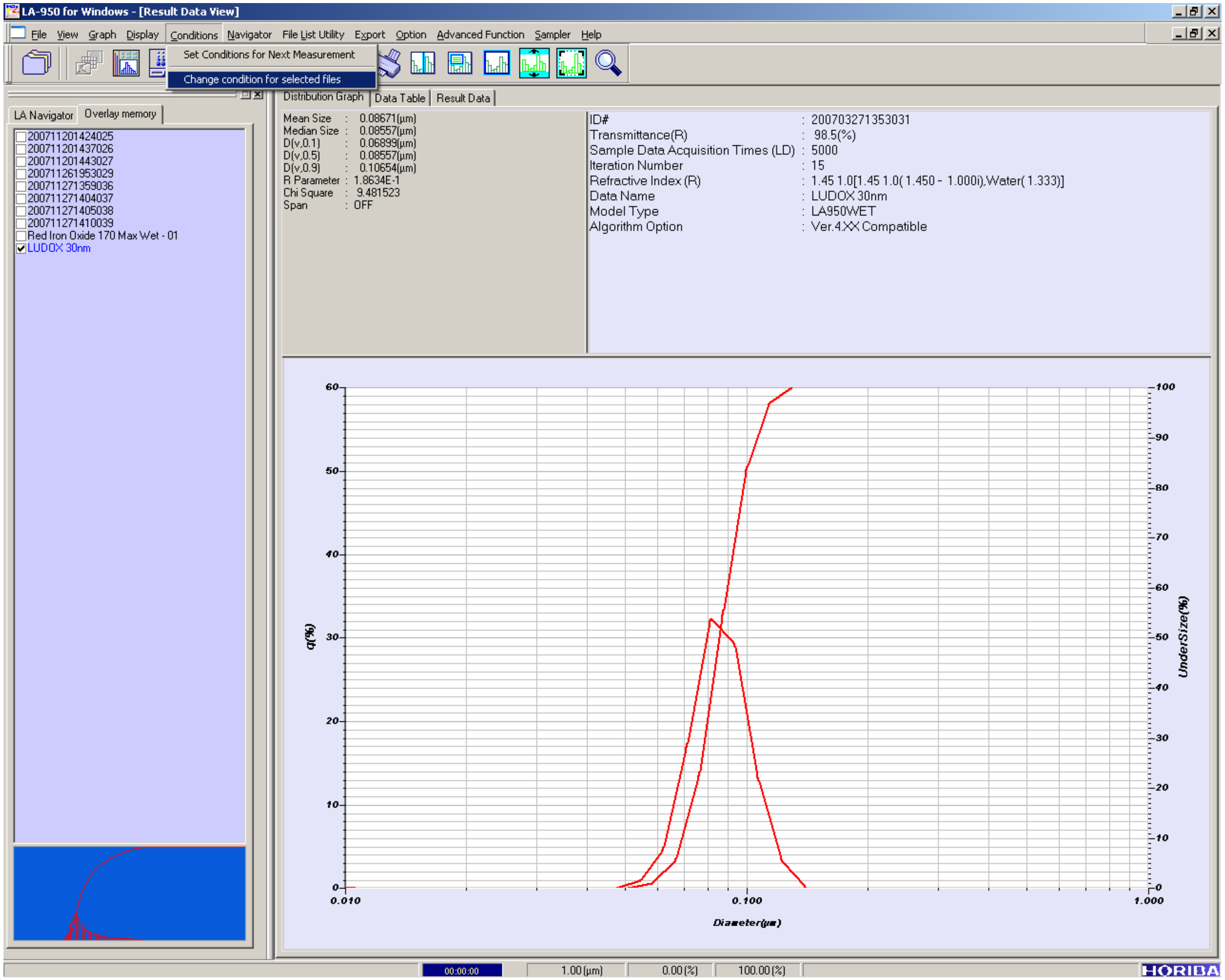
$$R = \frac{1}{N}\sum_{i=1}^{N}\frac{|y_i - y(x_i)|}{y(x_i)}$$

y_i is the measured scattering at detector I

$y(x_i)$ is the scattering data at detector i calculated from the size distribution

N is the number of detector channels used in the calculation.

Changing RI



LA-950 for Windows - [Result Data View]
File View Graph Display Conditions Navigator File List Utility Export Option Advanced Function Sampler Help
Set Conditions for Next Measurement
Change condition for selected files
LA Navigator
Overlay memory
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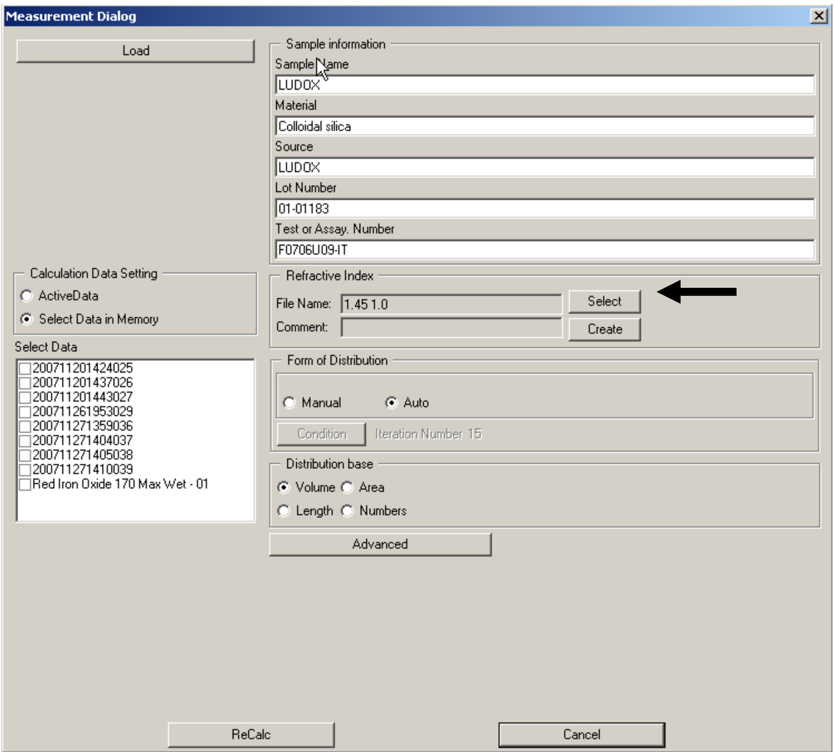
200711201437026
200711201443027
200711261953029
200711271359036
200711271404037
200711271405038
200711271410039
Red Iron Oxide 170 Max Wet - 01
LUDOX 30nm
Distribution Graph
Data Table
Result Data
Mean Size : 0.08671(µm)
Median Size : 0.08557(µm)
D(v,0.1) : 0.06899(µm)
D(v,0.5) : 0.08557(µm)
D(v,0.9) : 0.10654(µm)
R Parameter : 1.8634E-1
Chi Square : 9.481523
Span : OFF
ID# : 200703271353031
Transmittance(R) : 98.5(%)
Sample Data Acquisition Times (LD) : 5000
Iteration Number : 15
Refractive Index (R) : 1.45 1.0[1.45 1.0(1.450 - 1.000i),Water(1.333)]
Data Name : LUDOX 30nm
Model Type : LA950WET
Algorithm Option : Ver.4.XX Compatible
q(%)
UnderSize(%)
Diameter(µm)
0.010
0.100
1.000
1.00 (µm)
0.00 (%)
100.00 (%)

Changing RI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Source
LUDOX
Lot Number
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Test or Assay. Number
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ActiveData
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Select Data
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200711201437026
200711201443027
200711261953029
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200711271404037
200711271405038
200711271410039
Red Iron Oxide 170 Max Wet - 01
Refractive Index
File Name: 1.45 1.0
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Manual
Auto
Condition
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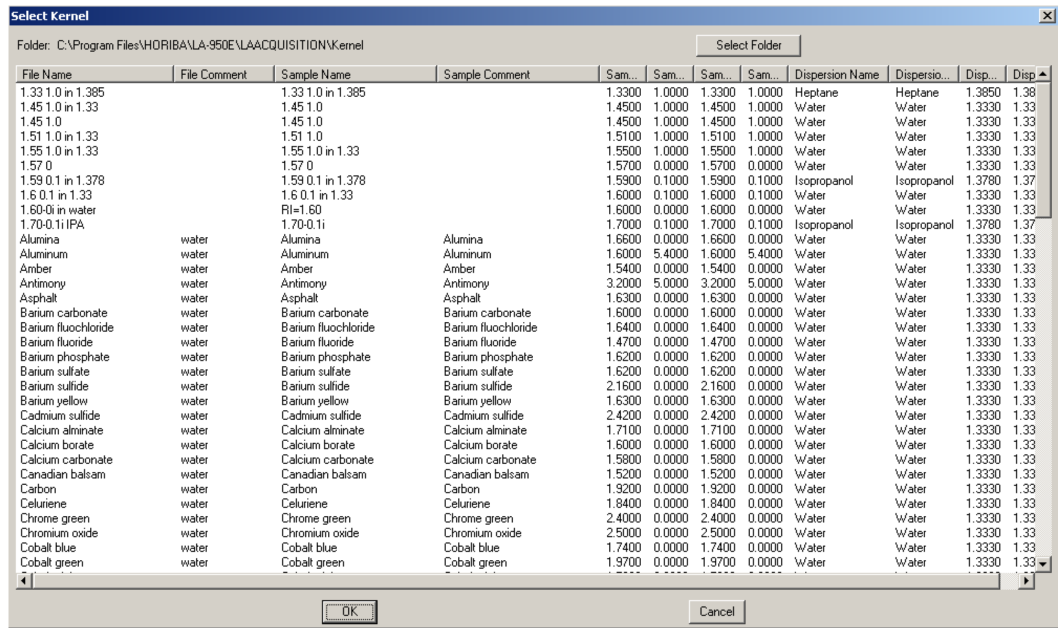
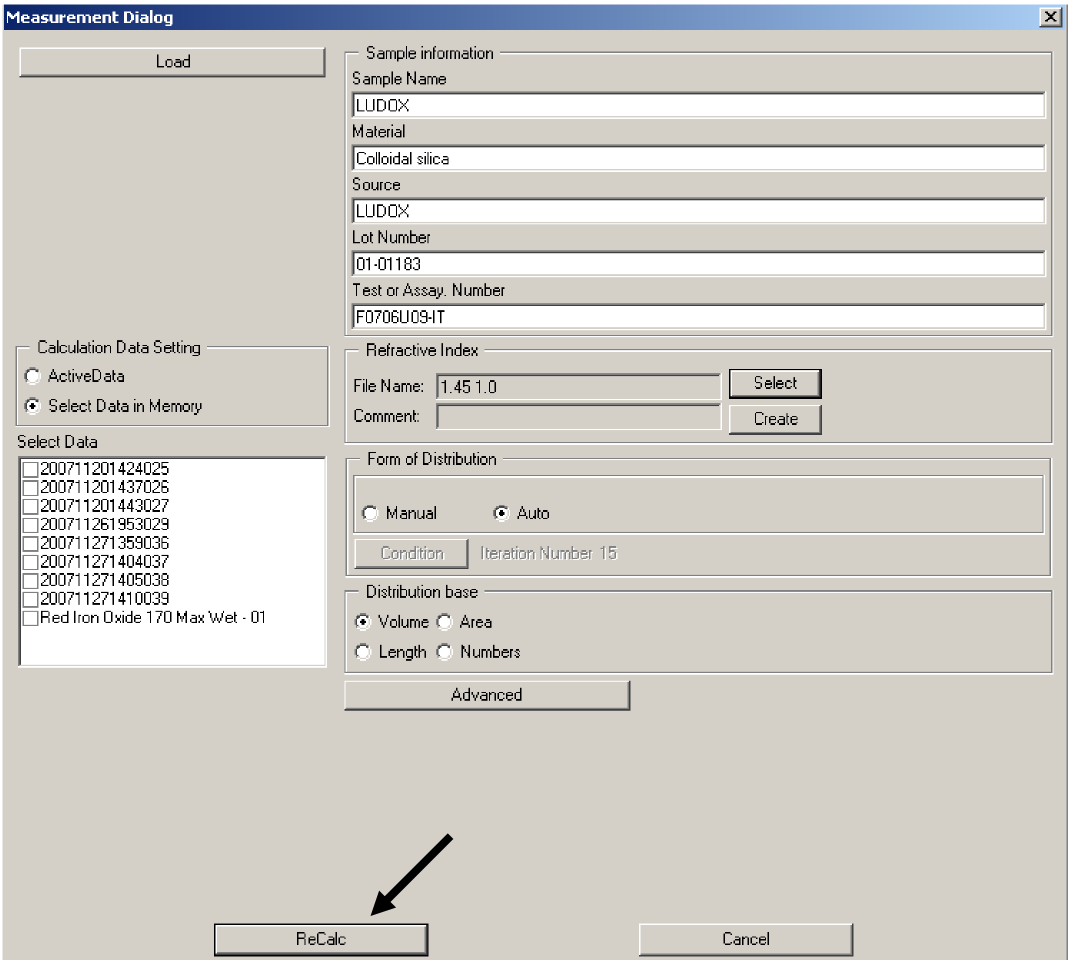
Distribution base
Volume
Area
Length
Numbers
Advanced
ReCalc
Cancel


Select Kernel
Folder: C:\Program Files\HORIBA\LA-950E\LAACQUISITION\Kernel
Select Folder
File Name | File Comment | Sample Name | Sample Comment | Sam... | Sam... | Sam... | Sam... | Dispersion Name | Dispersio... | Disp... | Disp
1.33 1.0 in 1.385 | 1.33 1.0 in 1.385 | 1.3300 1.0000 1.3300 1.0000 Heptane Heptane 1.3850 1.38
1.45 1.0 in 1.33 | 1.45 1.0 | 1.4500 1.0000 1.4500 1.0000 Water Water 1.3330 1.33
1.45 1.0 | 1.45 1.0 | 1.4500 1.0000 1.4500 1.0000 Water Water 1.3330 1.33
1.51 1.0 in 1.33 | 1.51 1.0 | 1.5100 1.0000 1.5100 1.0000 Water Water 1.3330 1.33
1.55 1.0 in 1.33 | 1.55 1.0 in 1.33 | 1.5500 1.0000 1.5500 1.0000 Water Water 1.3330 1.33
1.57 0 | 1.57 0 | 1.5700 0.0000 1.5700 0.0000 Water Water 1.3330 1.33
1.59 0.1 in 1.378 | 1.59 0.1 in 1.378 | 1.5900 0.1000 1.5900 0.1000 Isopropanol Isopropanol 1.3780 1.37
1.6 0.1 in 1.33 | 1.6 0.1 in 1.33 | 1.6000 0.1000 1.6000 0.1000 Water Water 1.3330 1.33
1.60-0i in water | RI=1.60 | 1.6000 0.0000 1.6000 0.0000 Water Water 1.3330 1.33
1.70-0.1i IPA | 1.70-0.1i | 1.7000 0.1000 1.7000 0.1000 Isopropanol Isopropanol 1.3780 1.37
Alumina water Alumina Alumina 1.6600 0.0000 1.6600 0.0000 Water Water 1.3330 1.33
Aluminum water Aluminum Aluminum 1.6000 5.4000 1.6000 5.4000 Water Water 1.3330 1.33
Amber water Amber Amber 1.5400 0.0000 1.5400 0.0000 Water Water 1.3330 1.33
Antimony water Antimony Antimony 3.2000 5.0000 3.2000 5.0000 Water Water 1.3330 1.33
Asphalt water Asphalt Asphalt 1.6300 0.0000 1.6300 0.0000 Water Water 1.3330 1.33
Barium carbonate water Barium carbonate Barium carbonate 1.6000 0.0000 1.6000 0.0000 Water Water 1.3330 1.33
Barium fluochloride water Barium fluochloride Barium fluochloride 1.6400 0.0000 1.6400 0.0000 Water Water 1.3330 1.33
Barium fluoride water Barium fluoride Barium fluoride 1.4700 0.0000 1.4700 0.0000 Water Water 1.3330 1.33
Barium phosphate water Barium phosphate Barium phosphate 1.6200 0.0000 1.6200 0.0000 Water Water 1.3330 1.33
Barium sulfate water Barium sulfate Barium sulfate 1.6200 0.0000 1.6200 0.0000 Water Water 1.3330 1.33
Barium sulfide water Barium sulfide Barium sulfide 2.1600 0.0000 2.1600 0.0000 Water Water 1.3330 1.33
Barium yellow water Barium yellow Barium yellow 1.6300 0.0000 1.6300 0.0000 Water Water 1.3330 1.33
Cadmium sulfide water Cadmium sulfide Cadmium sulfide 2.4200 0.0000 2.4200 0.0000 Water Water 1.3330 1.33
Calcium alminate water Calcium alminate Calcium alminate 1.7100 0.0000 1.7100 0.0000 Water Water 1.3330 1.33
Calcium borate water Calcium borate Calcium borate 1.6000 0.0000 1.6000 0.0000 Water Water 1.3330 1.33
Calcium carbonate water Calcium carbonate Calcium carbonate 1.5800 0.0000 1.5800 0.0000 Water Water 1.3330 1.33
Canadian balsam water Canadian balsam Canadian balsam 1.5200 0.0000 1.5200 0.0000 Water Water 1.3330 1.33
Carbon water Carbon Carbon 1.9200 0.0000 1.9200 0.0000 Water Water 1.3330 1.33
Celuriene water Celuriene Celuriene 1.8400 0.0000 1.8400 0.0000 Water Water 1.3330 1.33
Chrome green water Chrome green Chrome green 2.4000 0.0000 2.4000 0.0000 Water Water 1.3330 1.33
Chromium oxide water Chromium oxide Chromium oxide 2.5000 0.0000 2.5000 0.0000 Water Water 1.3330 1.33
Cobalt blue water Cobalt blue Cobalt blue 1.7400 0.0000 1.7400 0.0000 Water Water 1.3330 1.33
Cobalt green water Cobalt green Cobalt green 1.9700 0.0000 1.9700 0.0000 Water Water 1.3330 1.33
OK
Cancel

Changing RI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LUDOX
Material
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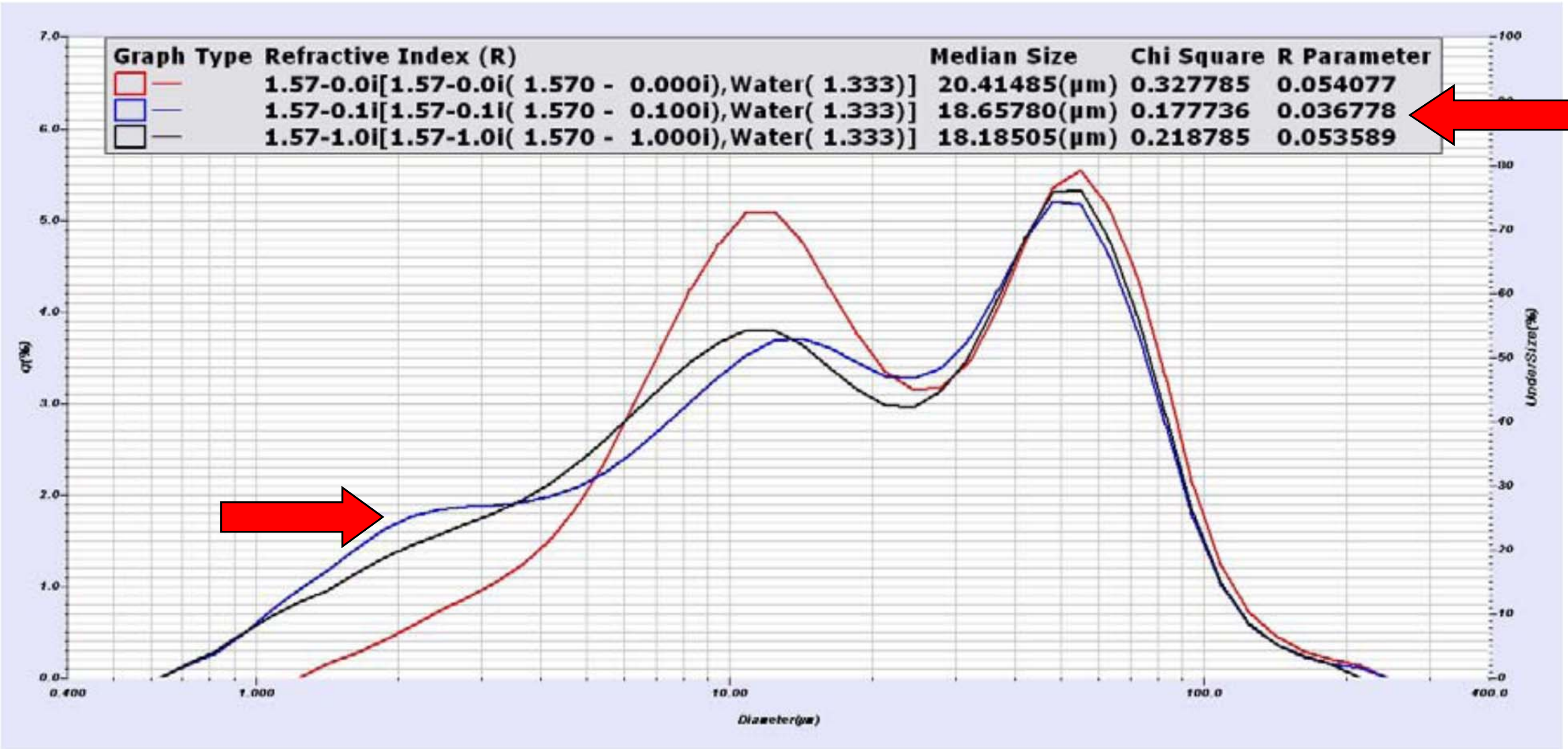
Source
LUDOX
Lot Number
01-01183
Test or Assay. Number
F0706U09-IT
Calculation Data Setting
ActiveData
Select Data in Memory
Select Data
200711201424025
200711201437026
200711201443027
200711261953029
200711271359036
200711271404037
200711271405038
200711271410039
Red Iron Oxide 170 Max Wet - 01
Refractive Index
File Name:
1.45 1.0
Select
Comment:
Create
Form of Distribution
Manual
Auto
Condition
Iteration Number 15
Distribution base
Volume
Area
Length
Numbers
Advanced
ReCalc
Cancel

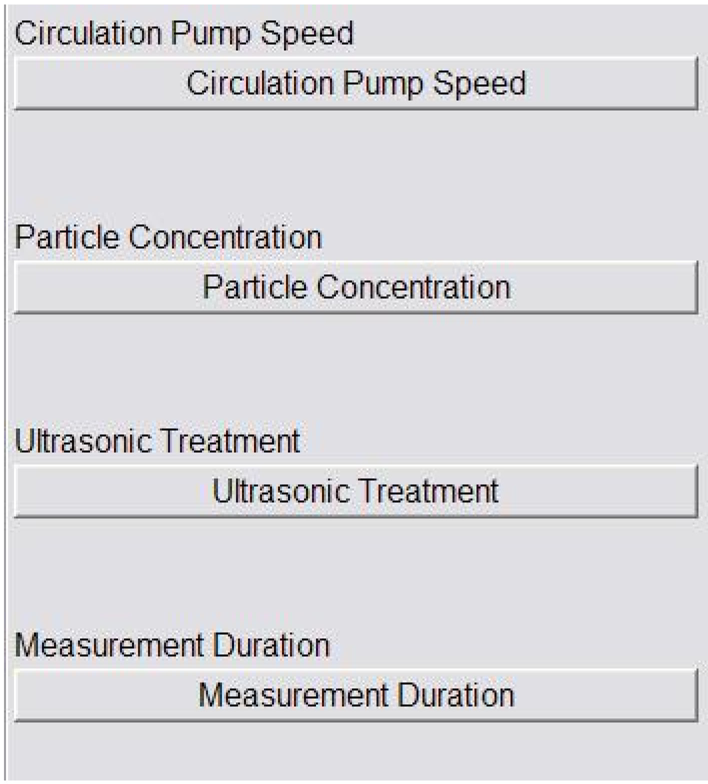
Using R Value for i

Real component = 1.57 via Becke line
Vary imaginary component, minimize Chi square & R parameter



Automation by Method Expert

Analytical conditions



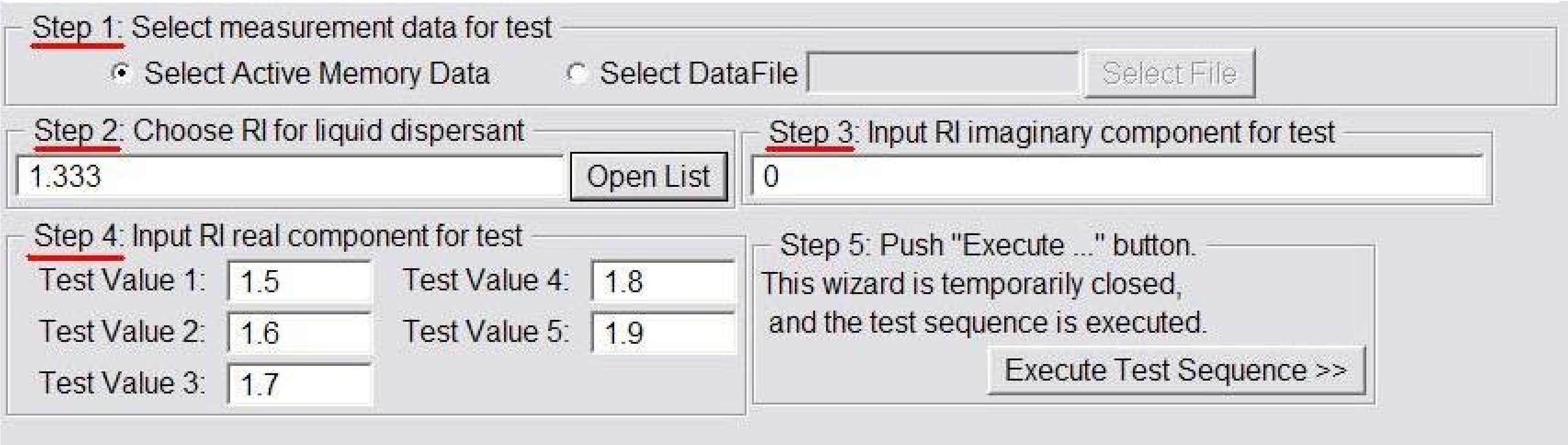
Calculation conditions

View Method Expert webinar TE004 in Download Center

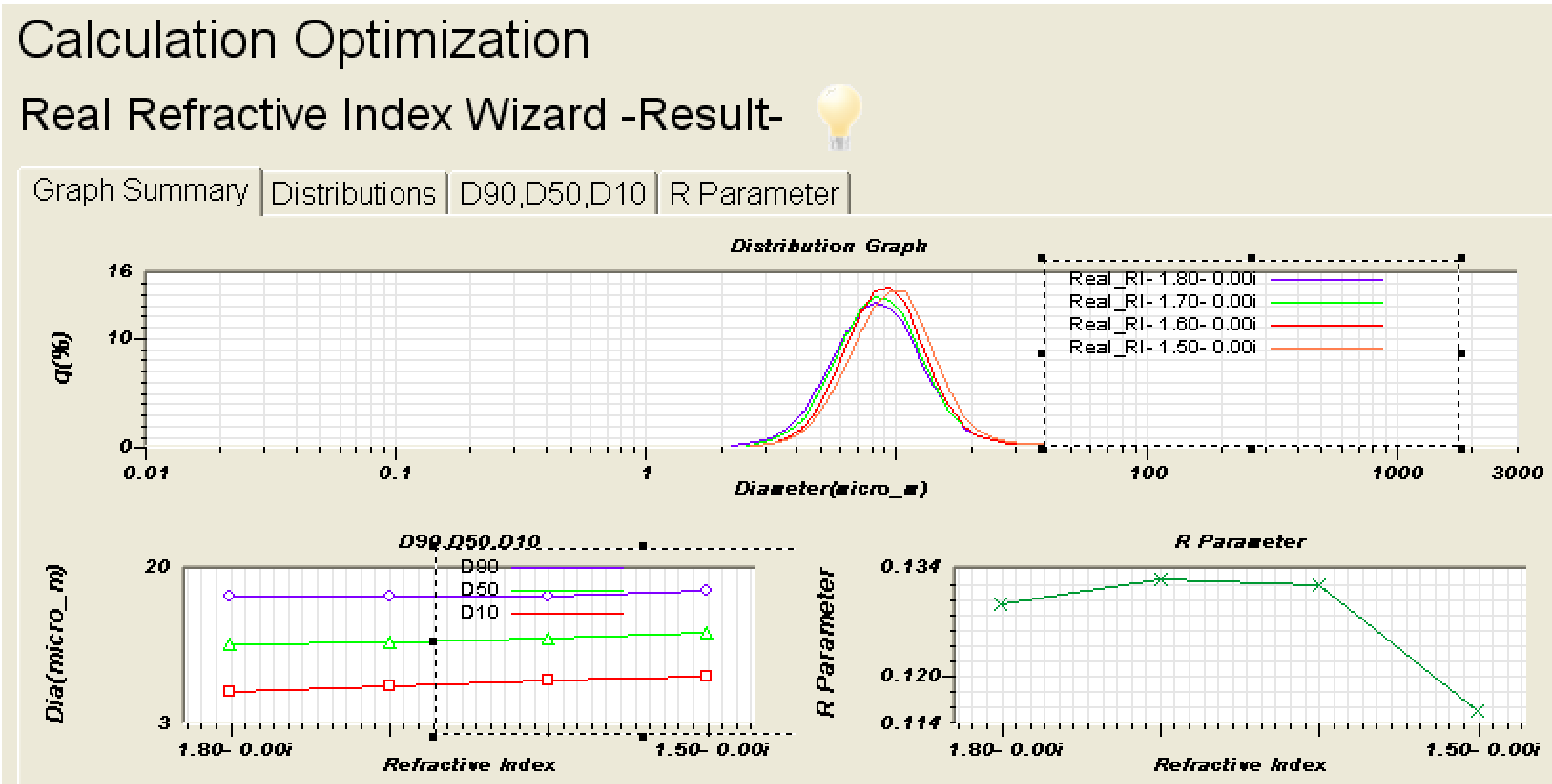
Automated RI Computation

Real part study

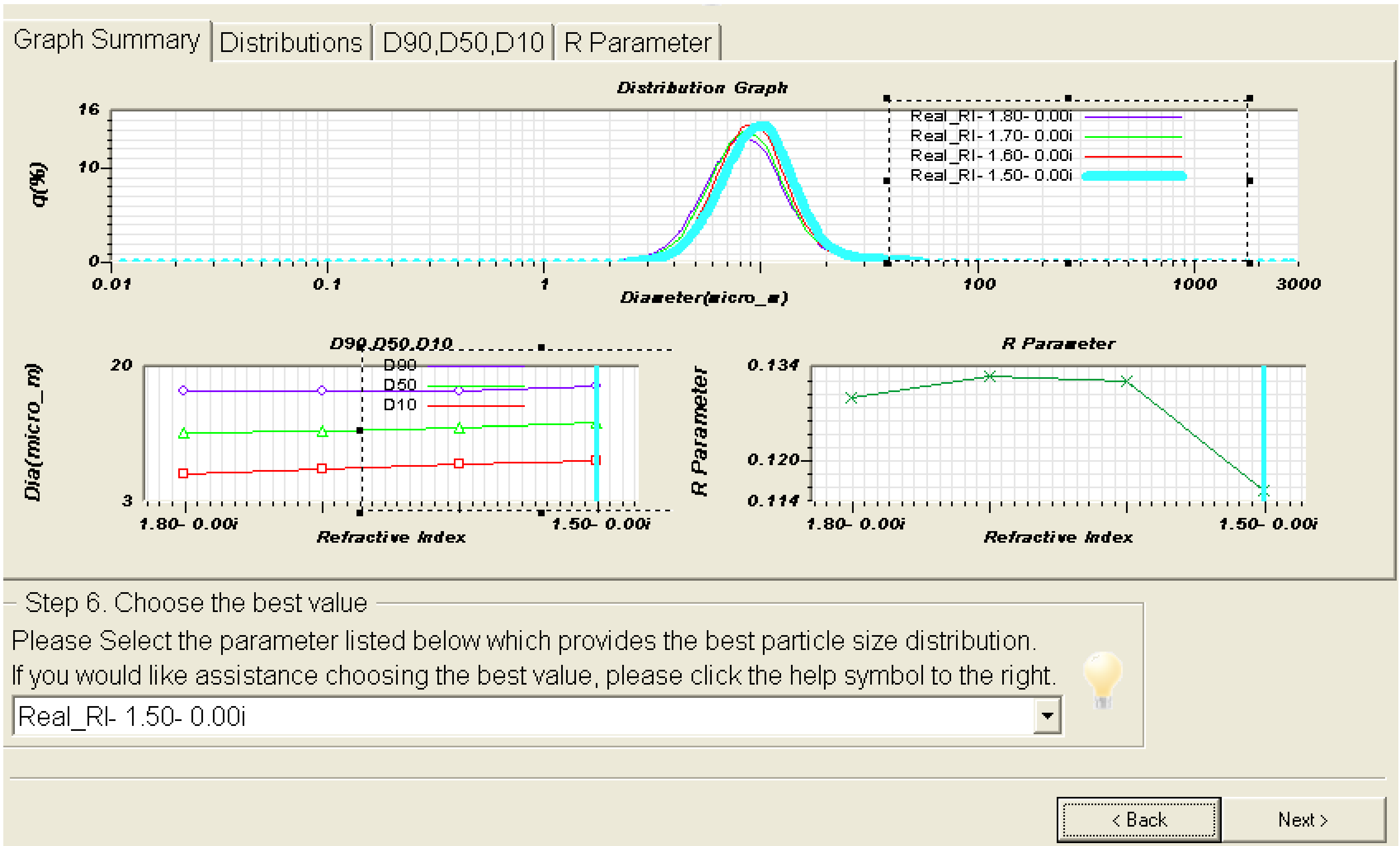
- Need to fix imaginary part
- Set up to 5 real parts
- Software will compute all RI and display R parameter variation with RI selection



Automated RI Computation



Automated RI Computation



Summary

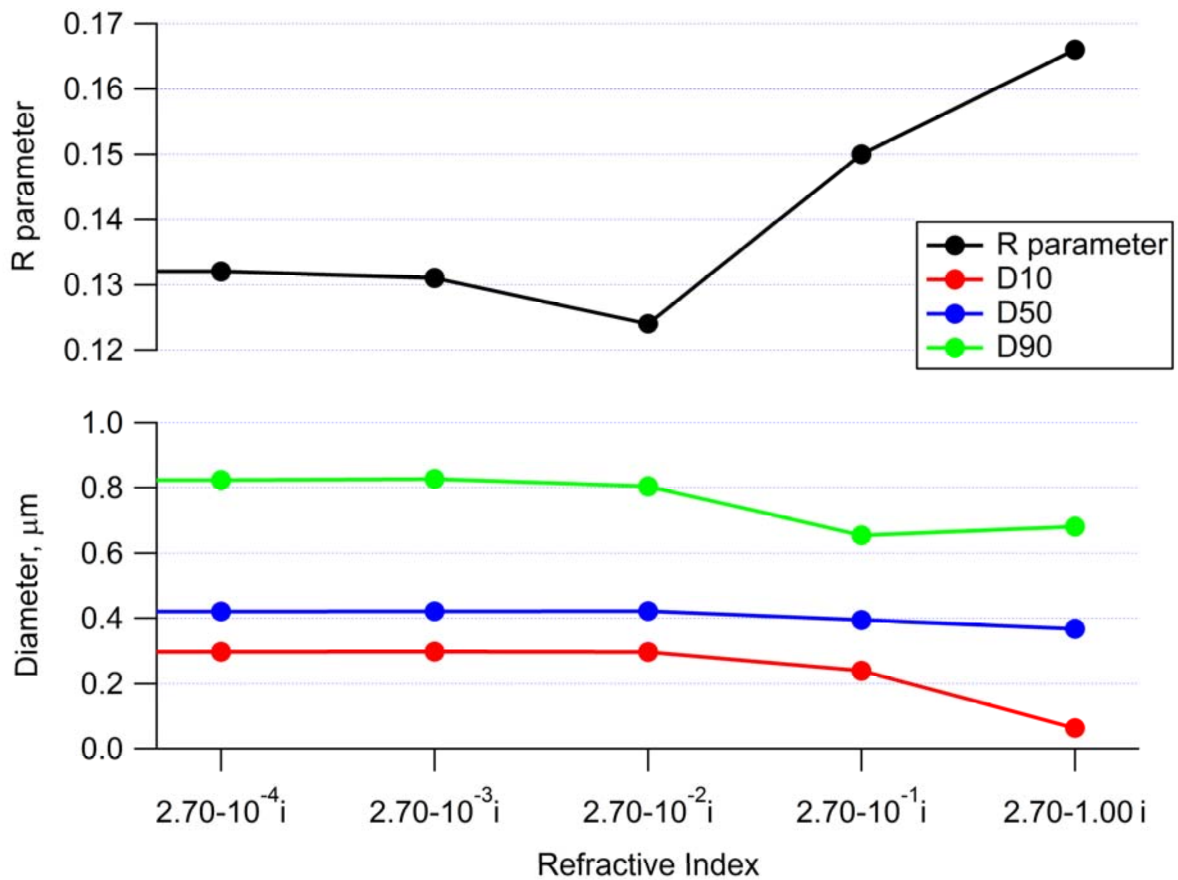
- Measure sample, recalculate w/different RI – see how important it is
- Use one of the described approaches to determine the real component
- Recalculate using different imaginary component
- Choose result that minimizes R parameter, but also check if result makes sense
- You wish you had Method Expert by your side

Outline

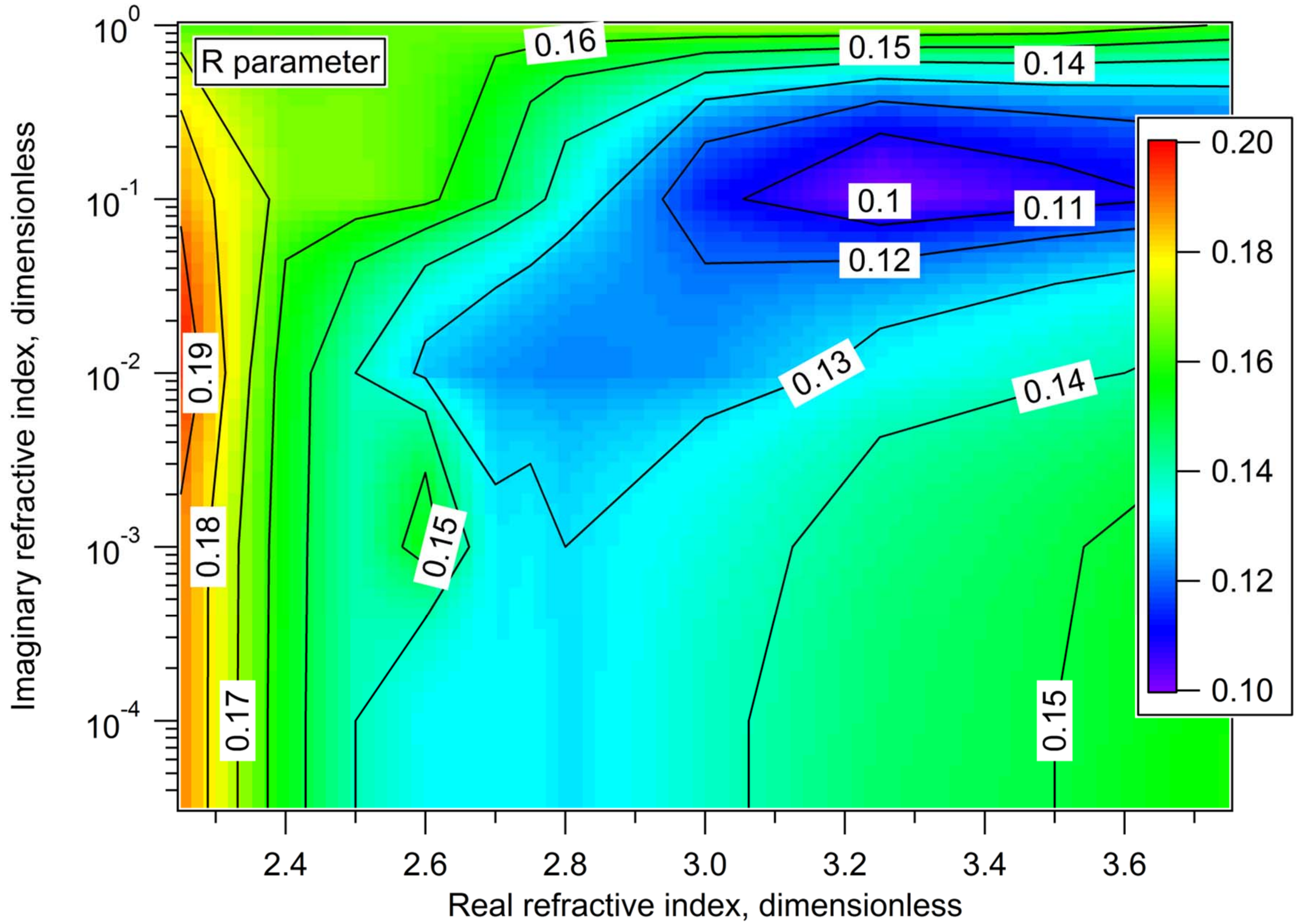
- Laser Diffraction Calculations
- Importance of Refractive Index
- Choosing Refractive Index
- Comparing Methods for Choosing Refractive Index

Study on TiO_2

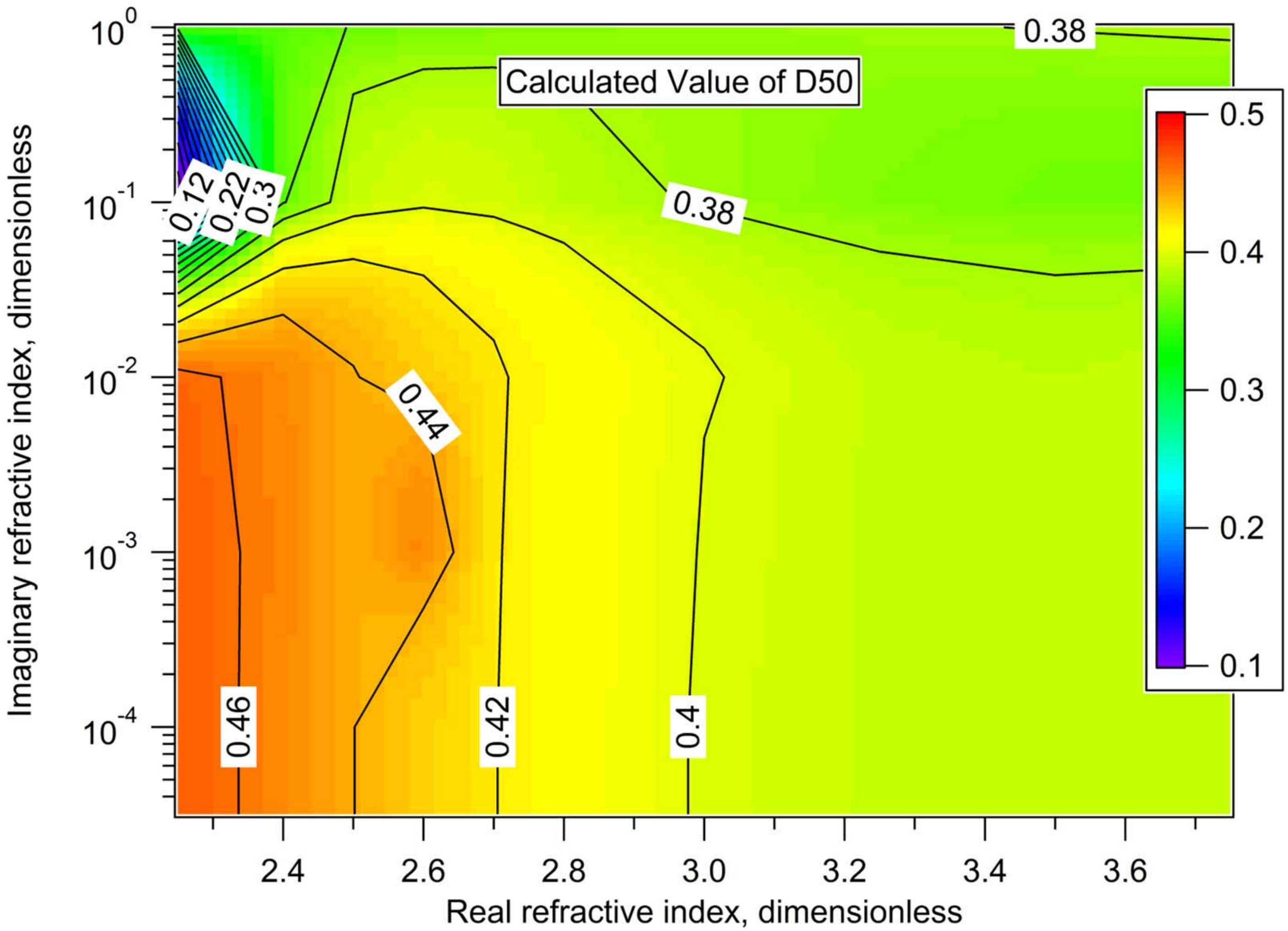
Look up real refractive index, use R parameter to find imaginary.



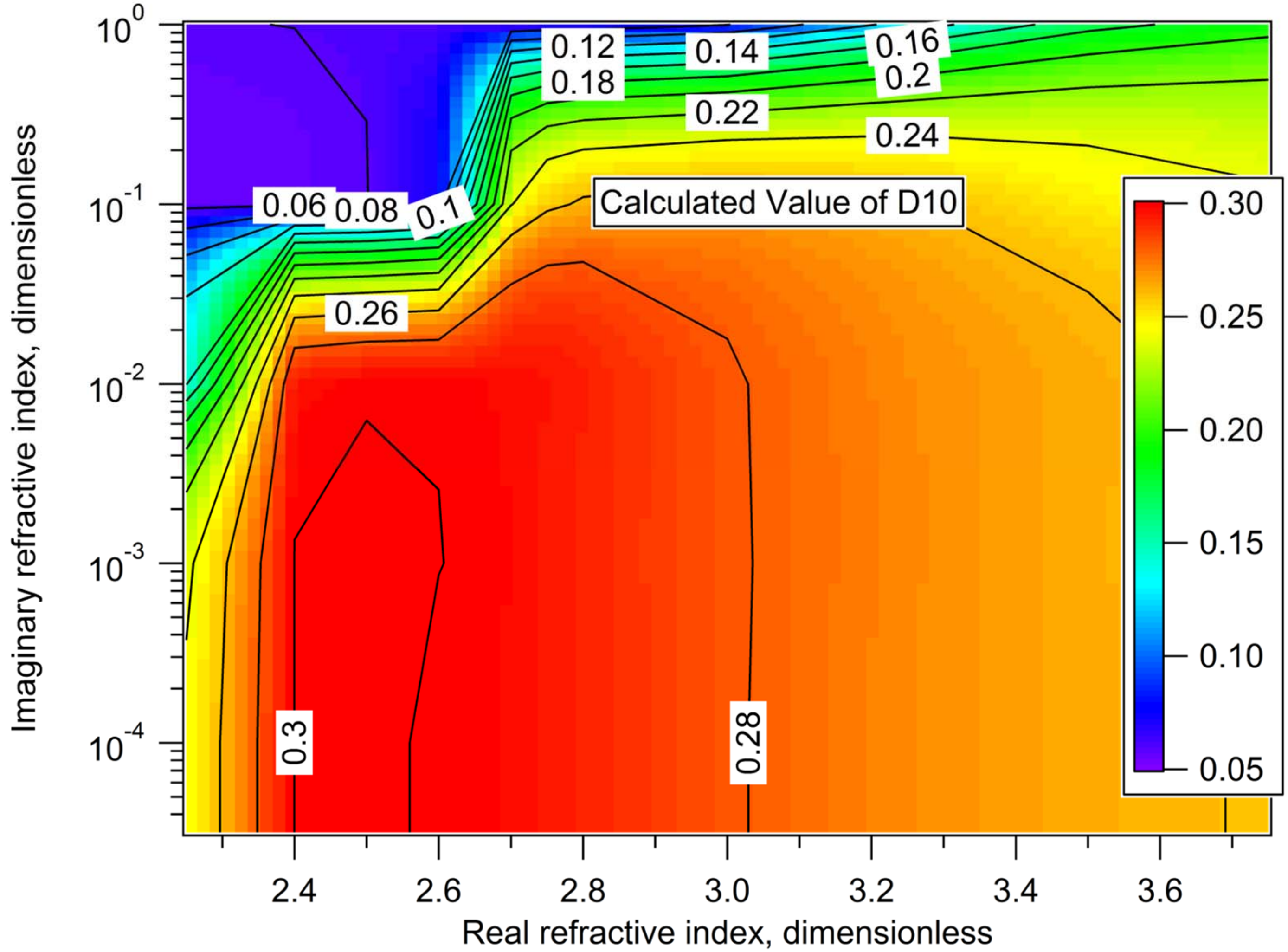
Effect of RI on R parameter



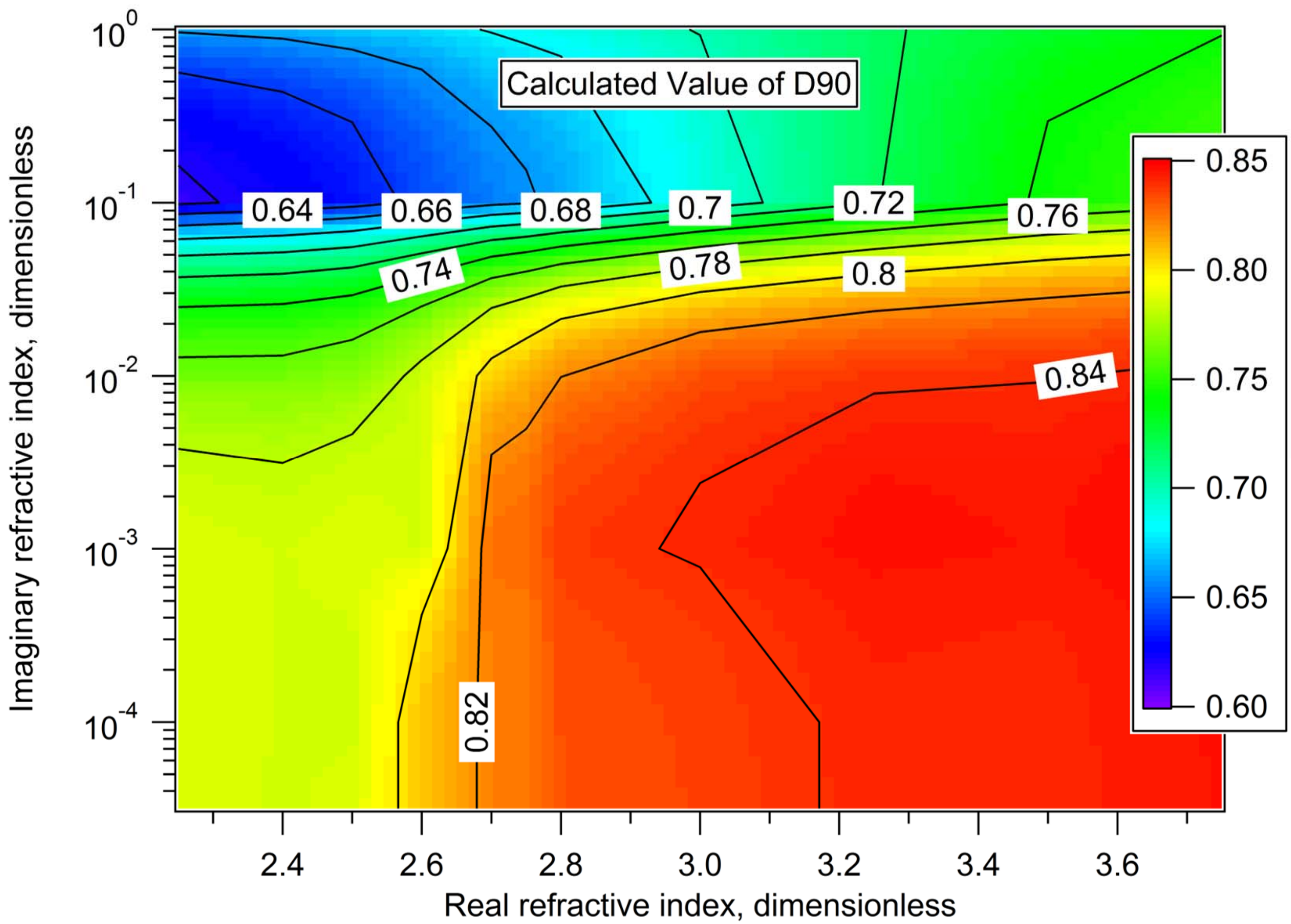
Effect of RI on measured D50

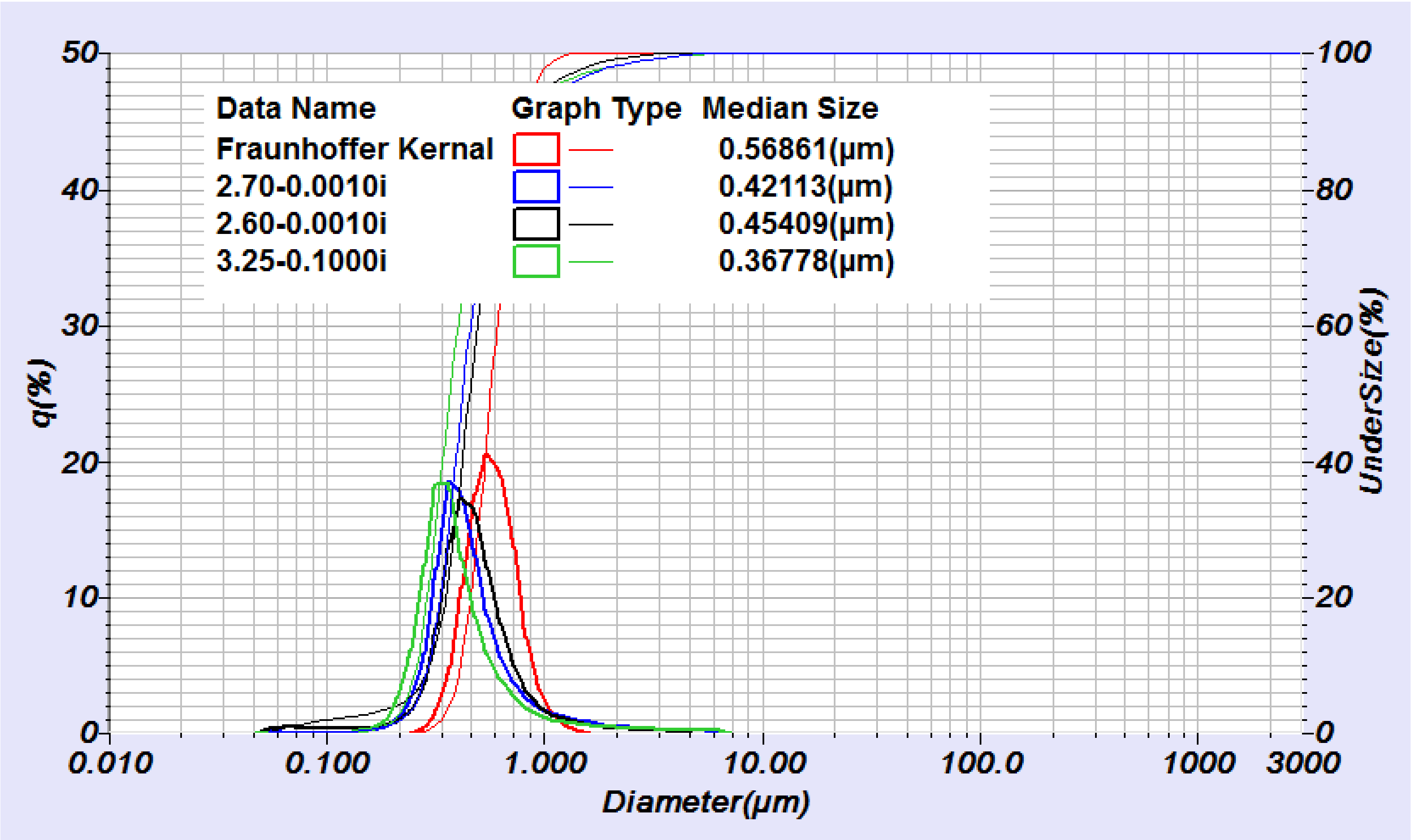


Effect of RI on measured D10



Effect of RI on measured D90




Data Name
Graph Type
Median Size
Fraunhoffer Kernal
0.56861(μm)
2.70-0.0010i
0.42113(μm)
2.60-0.0010i
0.45409(μm)
3.25-0.1000i
0.36778(μm)
q(%)
UnderSize(%)
Diameter(μm)
0.010
0.100
1.000
10.00
100.0
1000
3000
0
10
20
30
40
50
20
40
60
80
100

Results

Model	D10, microns	Difference from correct value	D50, microns	Difference from correct value	D90, microns	Difference from correct value
2.7 - 0.001i (correct value)	0.30		0.42		0.80	
2.6 - 0.001i	0.30	0%	0.45	7.1%	0.78	2.5%
Fraunhofer	0.41	37%	0.57	36%	0.81	1.2%
Minimize R parameter (3.25 - 0.1i)	0.26	13%	0.37	12%	0.72	10%

Recommendations

- Use the Mie model when evaluating laser diffraction data.
- Search for literature for real and imaginary refractive index values or measure your sample yourself.
- If literature values are not available, use the data to estimate values, it is better than guessing or using the Fraunhofer model.
- Once you choose a refractive index value, stick with it.

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.

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

Thank-you

Thank you

HORIBA Scientific

Thank you

ありがとうございました

Dziękuję

Gracias

ขอบคุณครับ

谢谢

Cảm ơn

Grazie

اشْكُر

Σας ευχαριστούμε

धन्यवाद

நன்றி

Tacka

Danke

Merci

Obrigado

감사합니다

Большое спасибо