The Importance of Refractive Index When using Laser Diffraction

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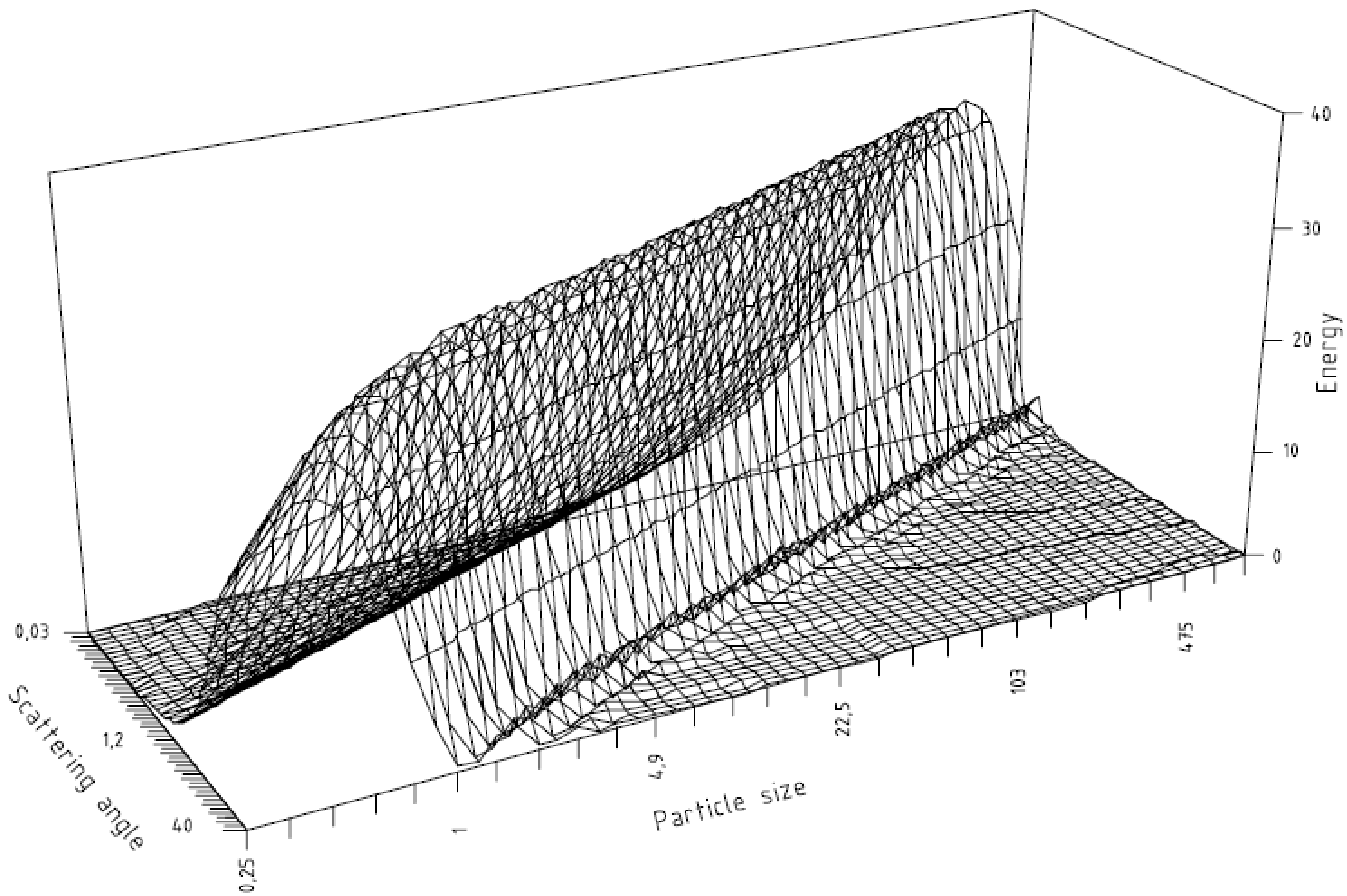
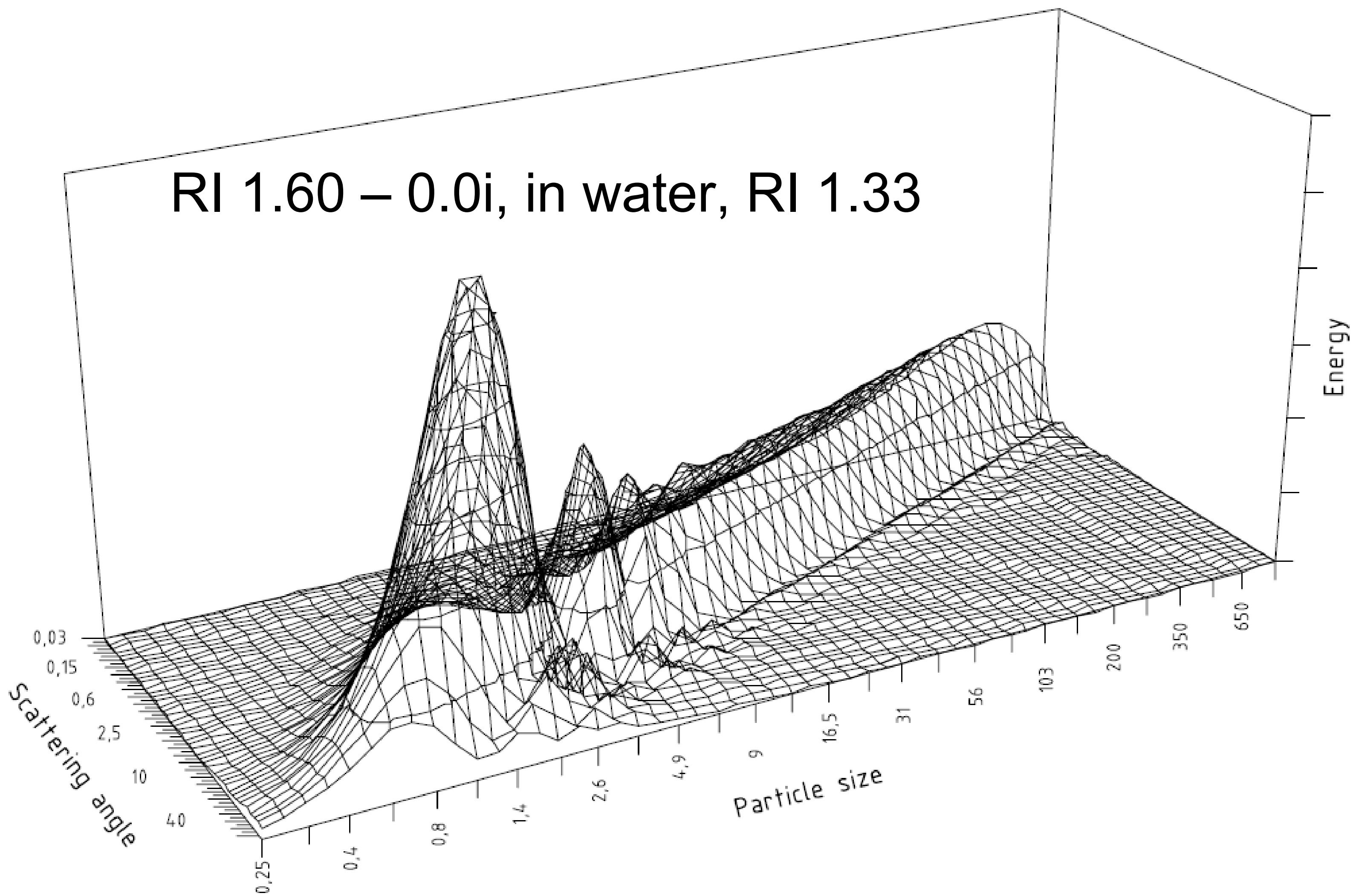
Fraunhofer Approximation



Mie Theory



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Mie vs. Fraunhofer

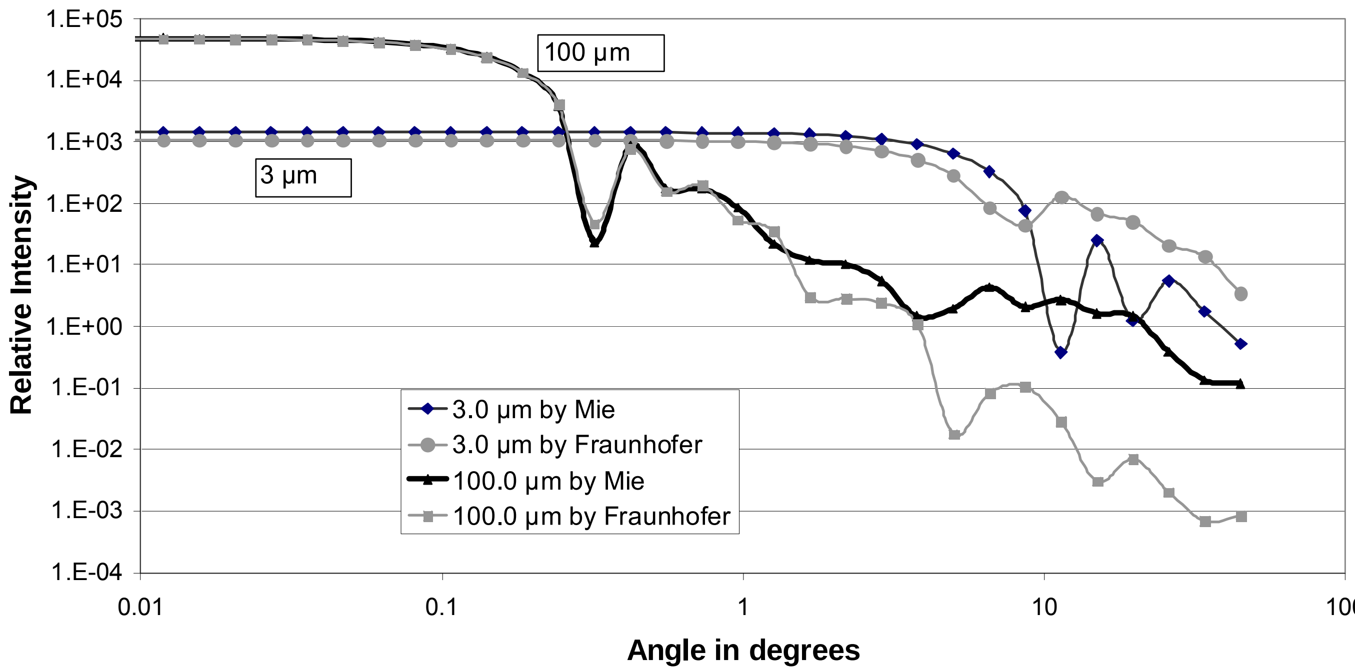
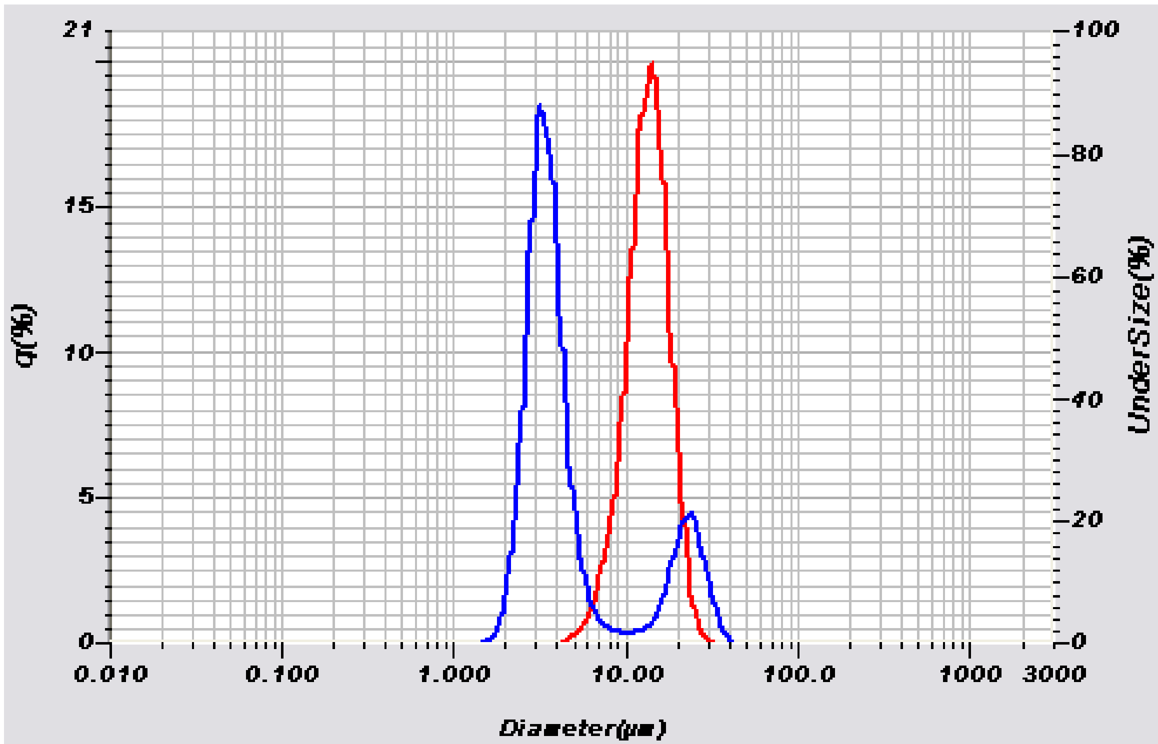


Figure A.3 -- Comparison of scattering patterns of non-absorbing particles according to Fraunhofer and Mie calculations (N_p = 1,59 – 0,0; n_{water} = 1,33; wavelength = 633 nm)

Practical Application of Theory: Mie vs. Fraunhofer for Glass Beads

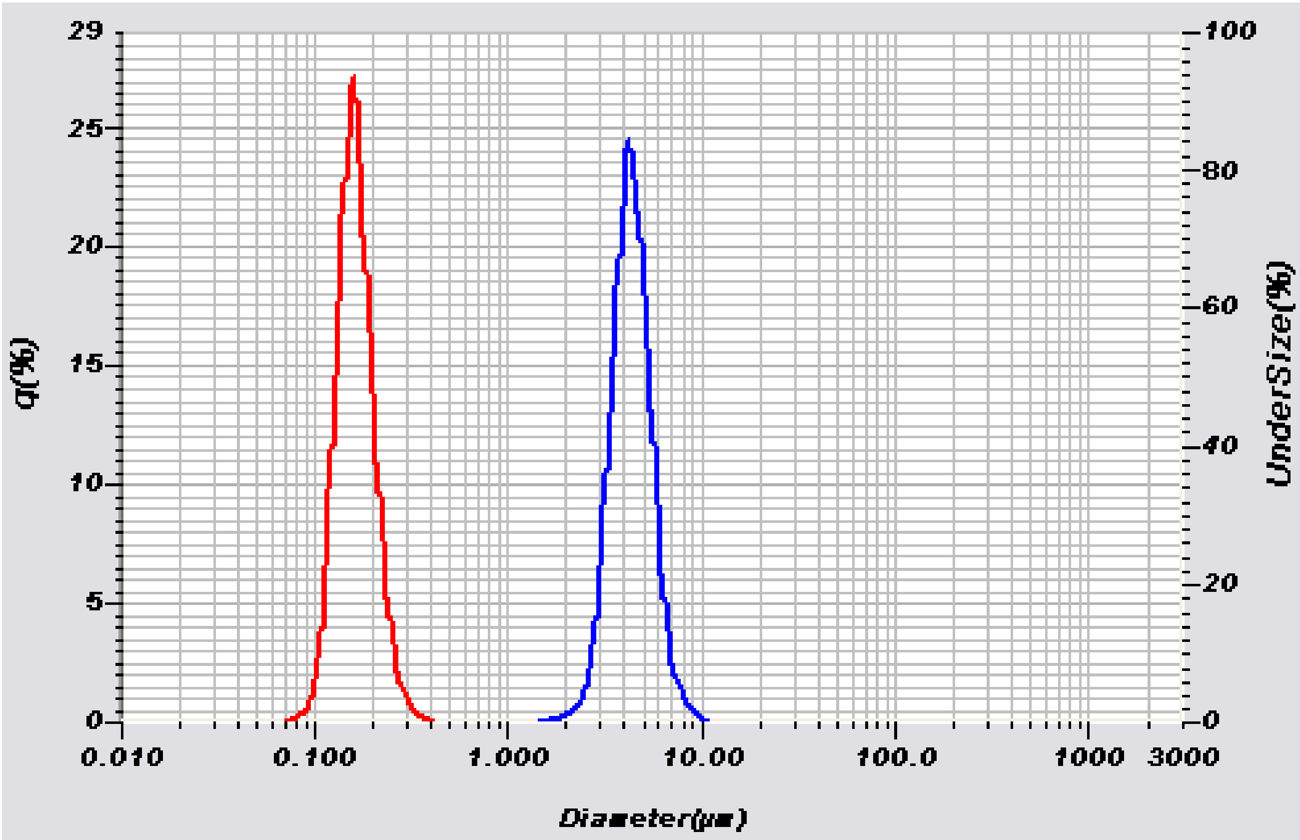
Data Name	Graph Type	Refractive Index (R)
Standard Glass Beads Mie	red	STD-GLASSBEADS[STD-GLASSBEADS(1.510 - 0.000i),'
Standard Glass Beads Fraunhofer	blue	Fraunhofer Kernel[Fraunhofer Kernel(0.000 - 0.000i]



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 of Theory: Mie vs. Fraunhofer for CMP Slurry

Data Name	Graph Type	Refractive Index (R)
CMP Slurry Mie	red	2.20-0.0i[2.20-0.0i(2.200 - 0.000i),Water(1.333)]
CMP Slurry Fraunhofer	blue	Fraunhofer Kernel[Fraunhofer Kernel(0.000 - 0.000i)



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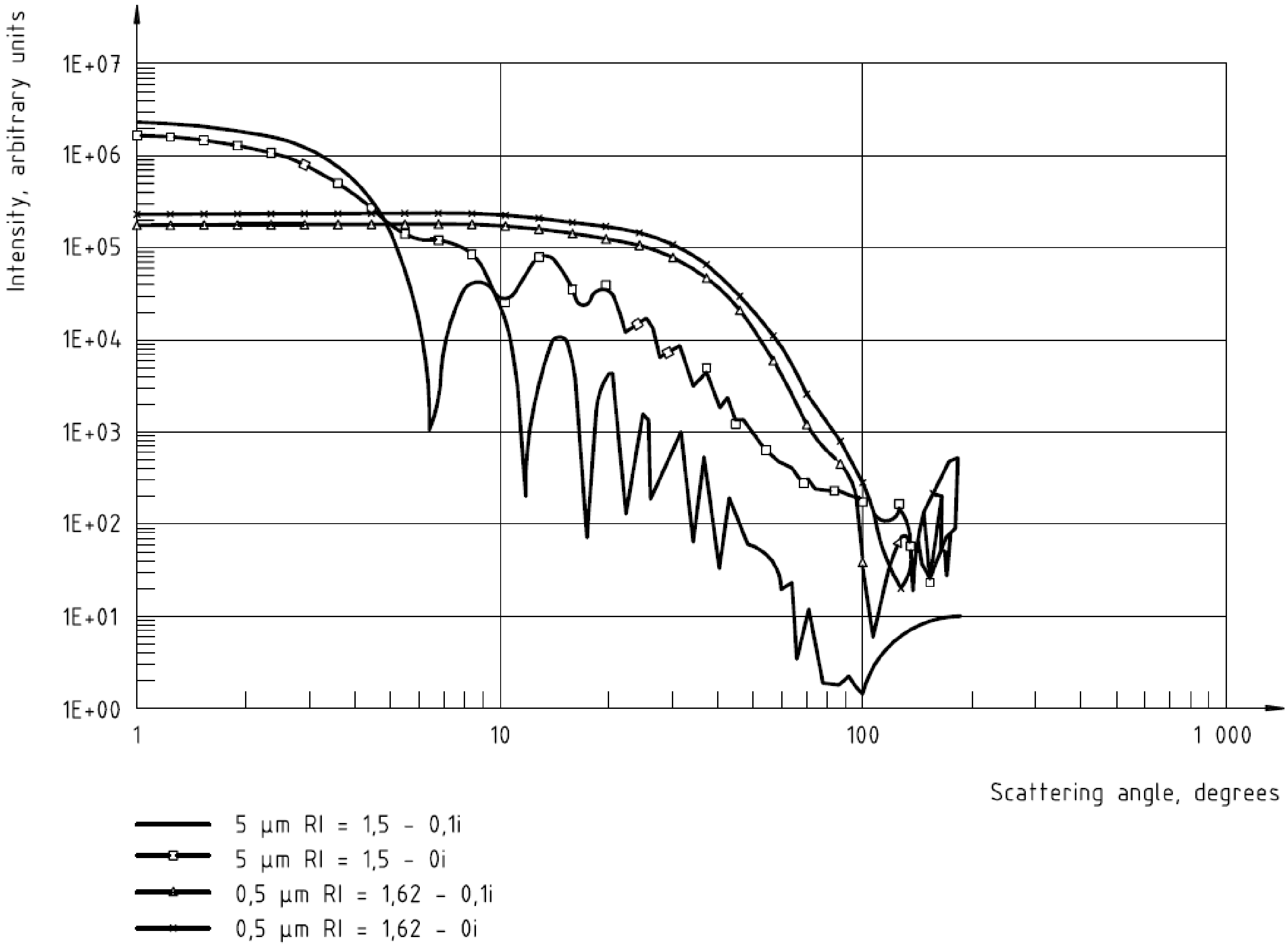
Influence of Particle Size on Angular Light Intensity Scattering Patterns



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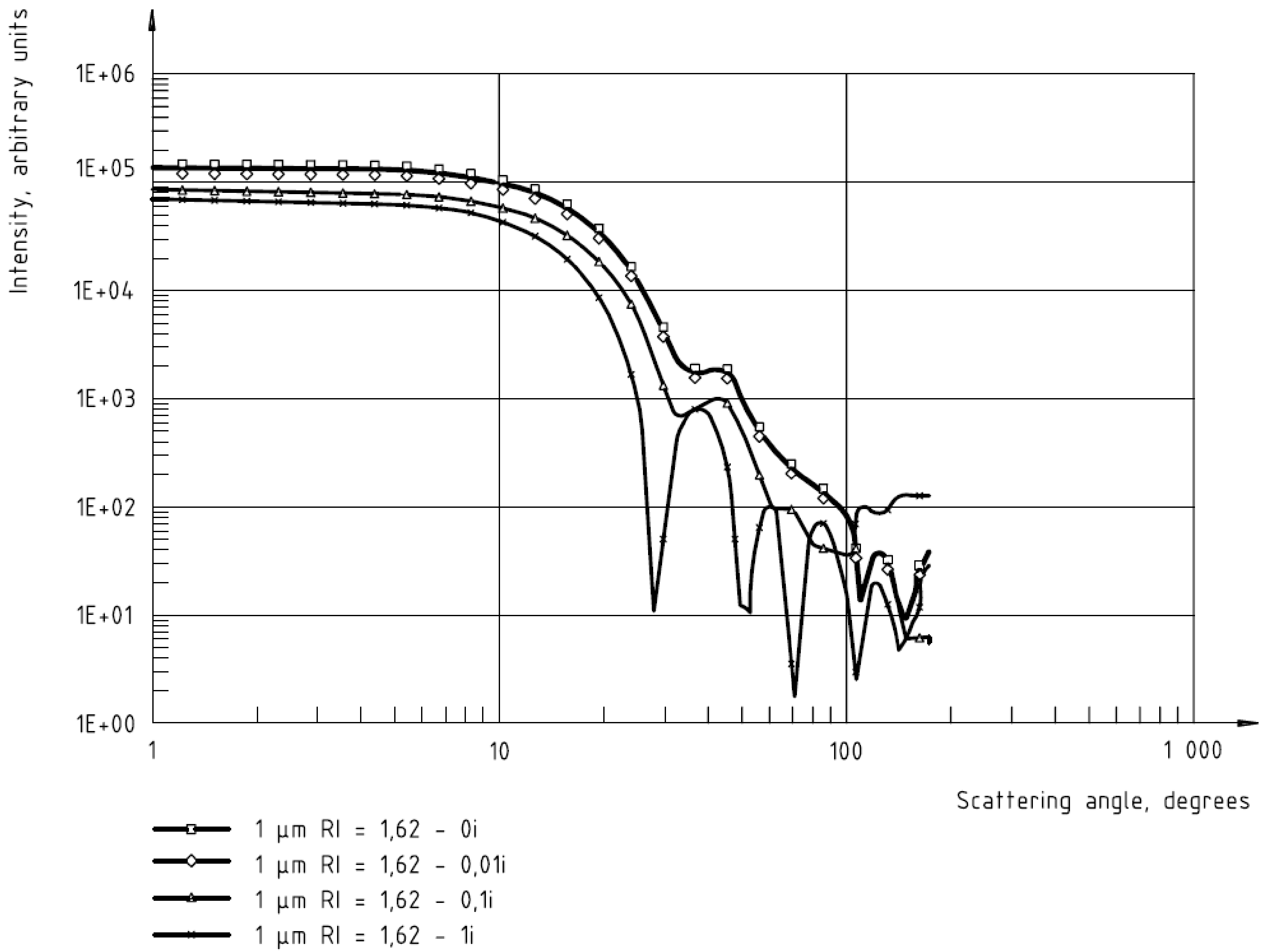
Influence of Imaginary Parts of RI (Absorbancies)



Refractive Index

- Refractive Index is defined by two components – Real and Imaginary

$$RI = n + ik$$

Where:

N = real component, velocity of light in a vacuum/ velocity of light in the particle

= c/v_p

c = speed of light in vacuum

Vp = speed of light in particle (liquid, air)

k = the extinction coefficient of the material

i = $\sqrt{-1}$

RI: Real Component

- Real component from published tables or measured using Snell's Law

$$n \sin \theta = n' \sin \theta'$$

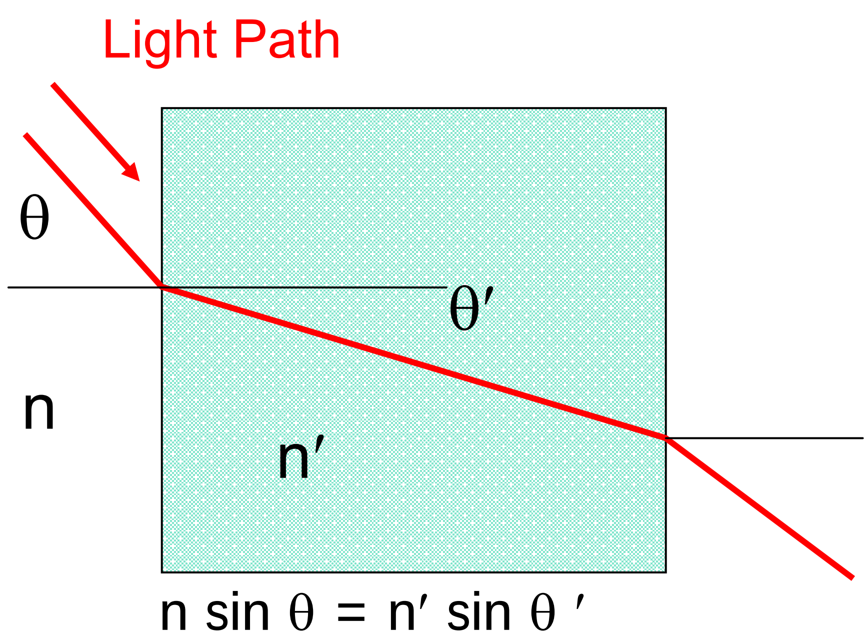
where:

n = RI of air

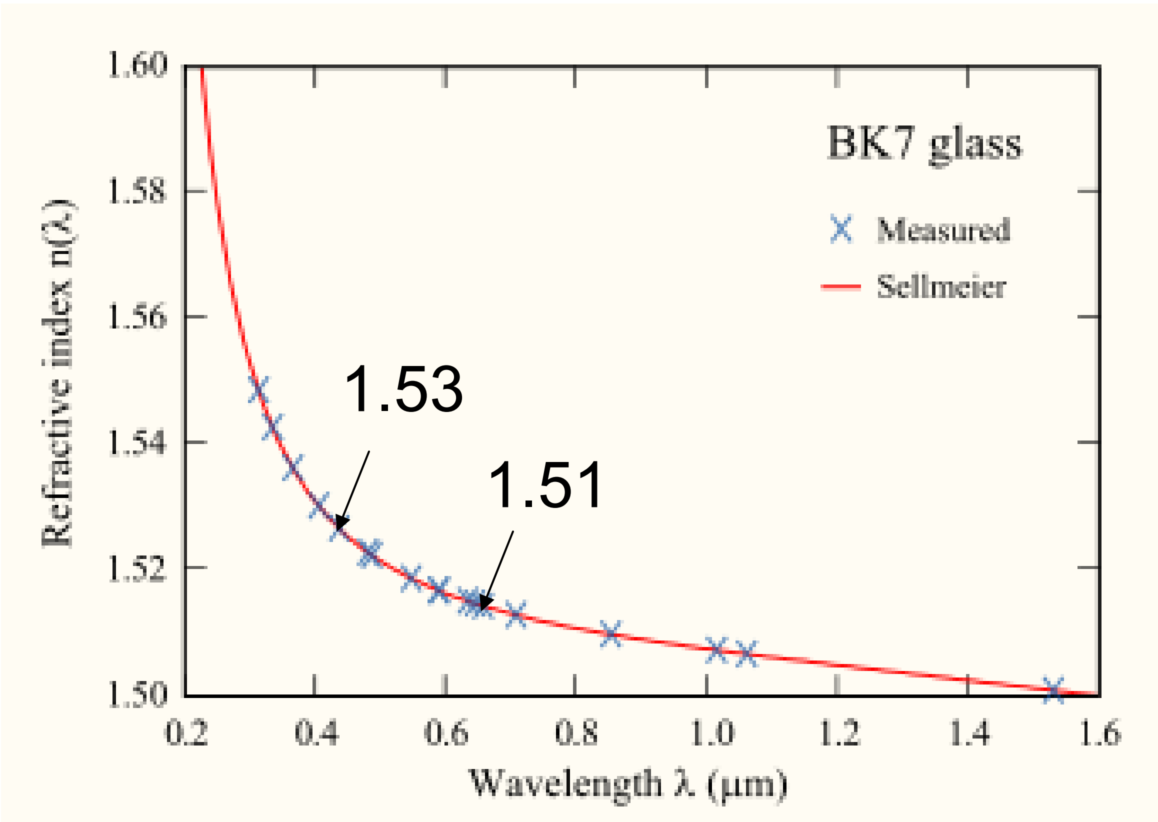
θ = angle of incidence

n' = RI of particle

θ' = angle of refraction



n is Frequency Dependent



Remember the
LA-950 has
two light sources
Red = 650 nm
Blue = 405 nm

In this example
1.53 vs. 1.51
Not very important

Could matter for
sub-micron pigments

Sellmeier equation

$$n^2(\lambda) = 1 + \frac{B_1\lambda^2}{\lambda^2 - C_1} + \frac{B_2\lambda^2}{\lambda^2 - C_2} + \frac{B_3\lambda^2}{\lambda^2 - C_3},$$

RI: Imaginary Component

- Imaginary component (k) in Mie equation is the extinction coefficient of the particle. Reduction of transmission of optical radiation caused by absorption and scattering of light.

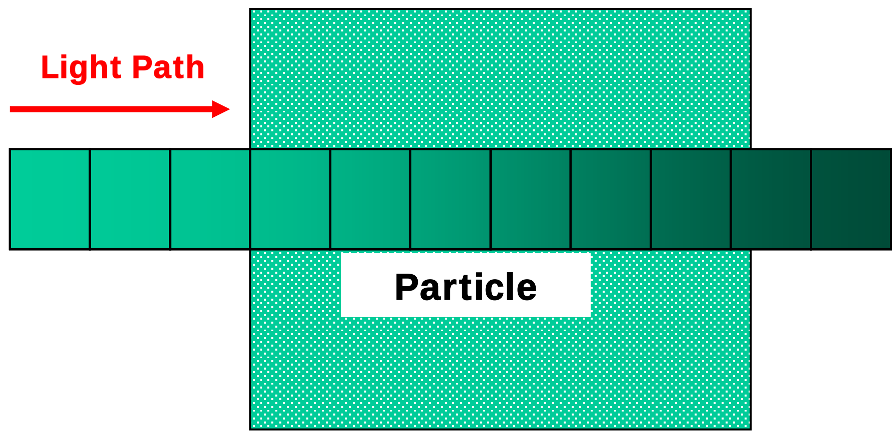
$$\mathbf{k} = (\lambda / 4\pi)\,\alpha$$

Where:

k = the extinction coefficient

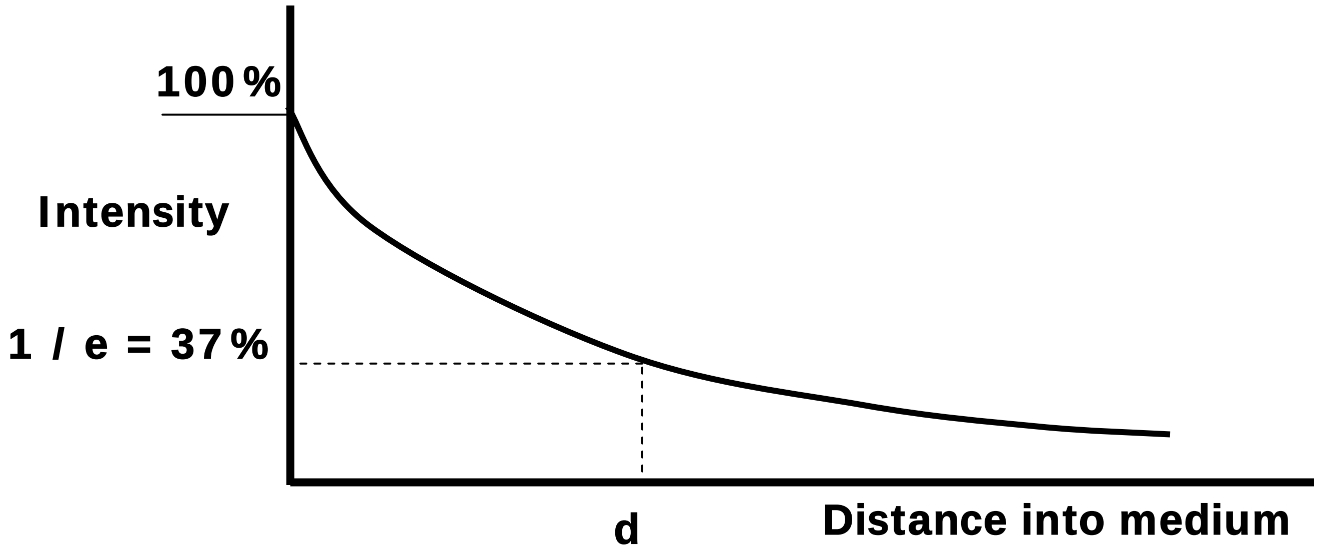
α = the absorption coefficient

λ = the wavelength of light used



- Absorption coefficient (α) = reciprocal distance light penetrates surface & be attenuated to 1/e of original intensity, about 37%. Opaque particles have high coefficient.

RI: Imaginary Component



- $1 / d = \alpha$
- $k = (\lambda / 4 \pi) \alpha$
- Example: for a value of k = 0.1
- $k = (\lambda / 4 \pi) [\alpha] = 0.05 \times [1 / d] = 0.1 = k$
- d = 0.05 / 0.1 = 0.5 micron

RI: Imaginary Component

- For transparent particles use 0 for the imaginary component
- For slightly opaque materials use 0.01 or 0.1
- For opaque materials use 1.0 or higher
- Values can exceed 1.0 (see below*)

Complex Index of Refraction Look-up Utility

Instructions

Choose a material from the drop down menu, enter the incident wavelength, and click on "Calculate." The material's index of refraction and extinction coefficient will appear below.

Index of Refraction Explanation

The Index of Refraction of a material is the ratio of phase velocity of an electromagentic wave in free space to the phase velocity in the material. The index of refraction of two materials can be used to predict how light will pass from one medium to the other. The Extinction Coefficient is the imaginary part of the index of refraction.

These optical constants are calculated via linear interpolation on the optical constant values reported in the book Handbook of Optical Constants of Solids by Edward D. Palik
The graphs and numerical data can be found on the Tabulated Optical Constants page.

Calculate

Material: Copper — Material Index: 1.6623006134 — Material Extinction Coefficient: 2.0176993865

Incident Wavelength: 650 (in nanometers)

*http://www.ee.byu.edu/photonics/opticalconstants.phtml

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

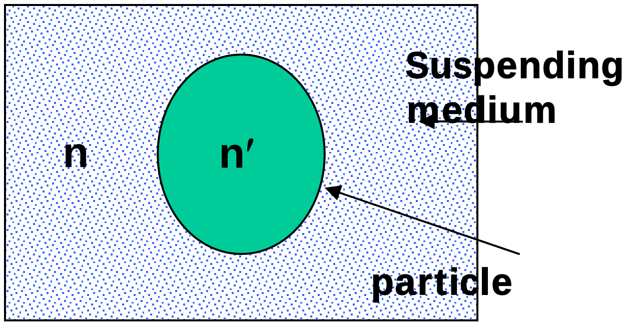
Older HORIBA Software: RI Kernels

If n = 1.33 (water) and n’ = 1.60 (particle)

Relative refractive index (RRI) : 1.60/1.33 = 1.203

Transparent particles: k = 0

Kernel function:120-000rri



Particles somewhat opaque: then k > 0

KERNEL function: 120-020rri

If powder, relative index:

n = 1.0 (air) and n’ = 1.60 (particle), RRI: 1.60/1.0 = 1.60

Kernel function: 160-000rri or 160-020rri

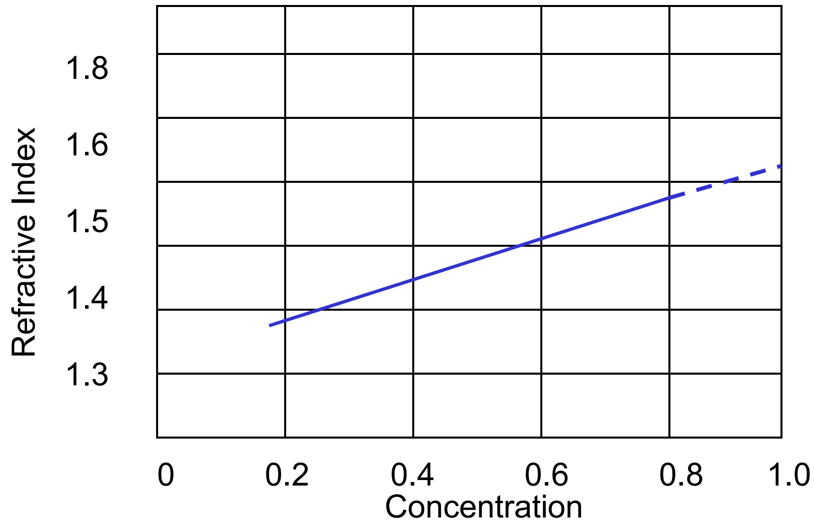
Practical Approach

- Measure sample once
- Change RI
- Does result change significantly?
- No: stop worrying
- Yes: keep working
- For LA-950 users: determine real component, vary imaginary component to minimize residual R value.

Oops, gave the plot away

Abbe Refractometer

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



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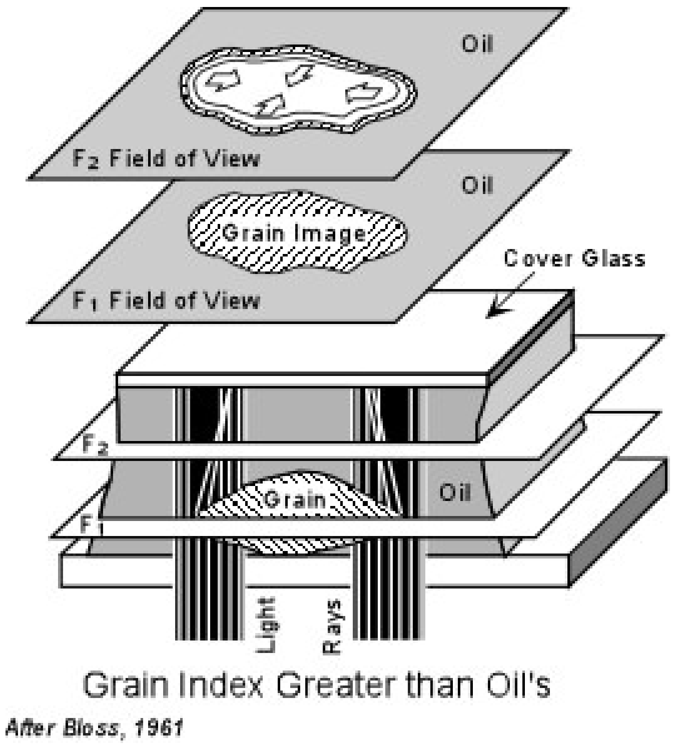
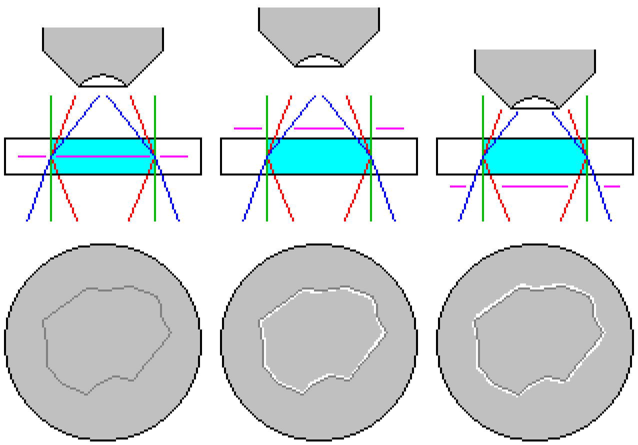
Becke Lines



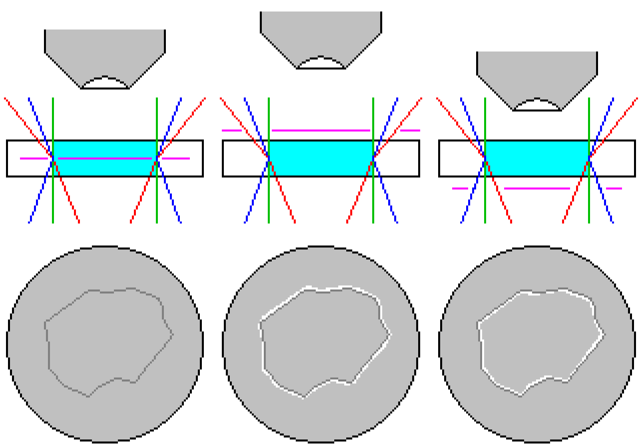
Bright line is called the ***Becke line*** and will always occur closest to the substance with a higher refractive index

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

Cargille Labs

Services to the sciences since 1924

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.

Luxpop.com

Index of Refraction

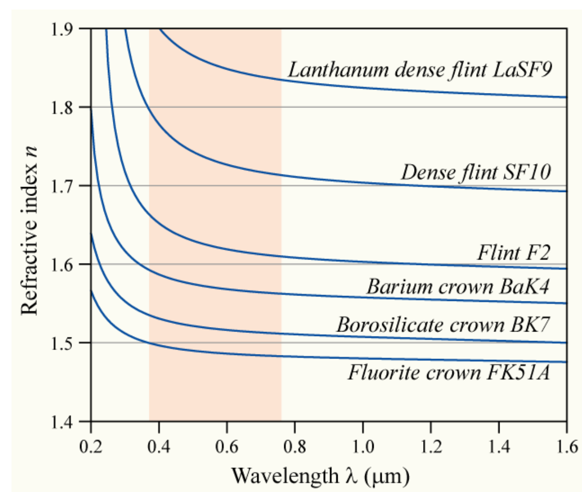
- Return the refractive index of a substance at a given wavelength, λ (nm). Further information in addition to the index of refraction also may be given.
- Luxpop returns the absolute refractive index (i.e. with resp. to vacuum), unless stated otherwise. Click here for more index of refraction terminology.
- 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.



RI of Polymers

http://www.texloc.com/closet/cl_refractiveindex.html

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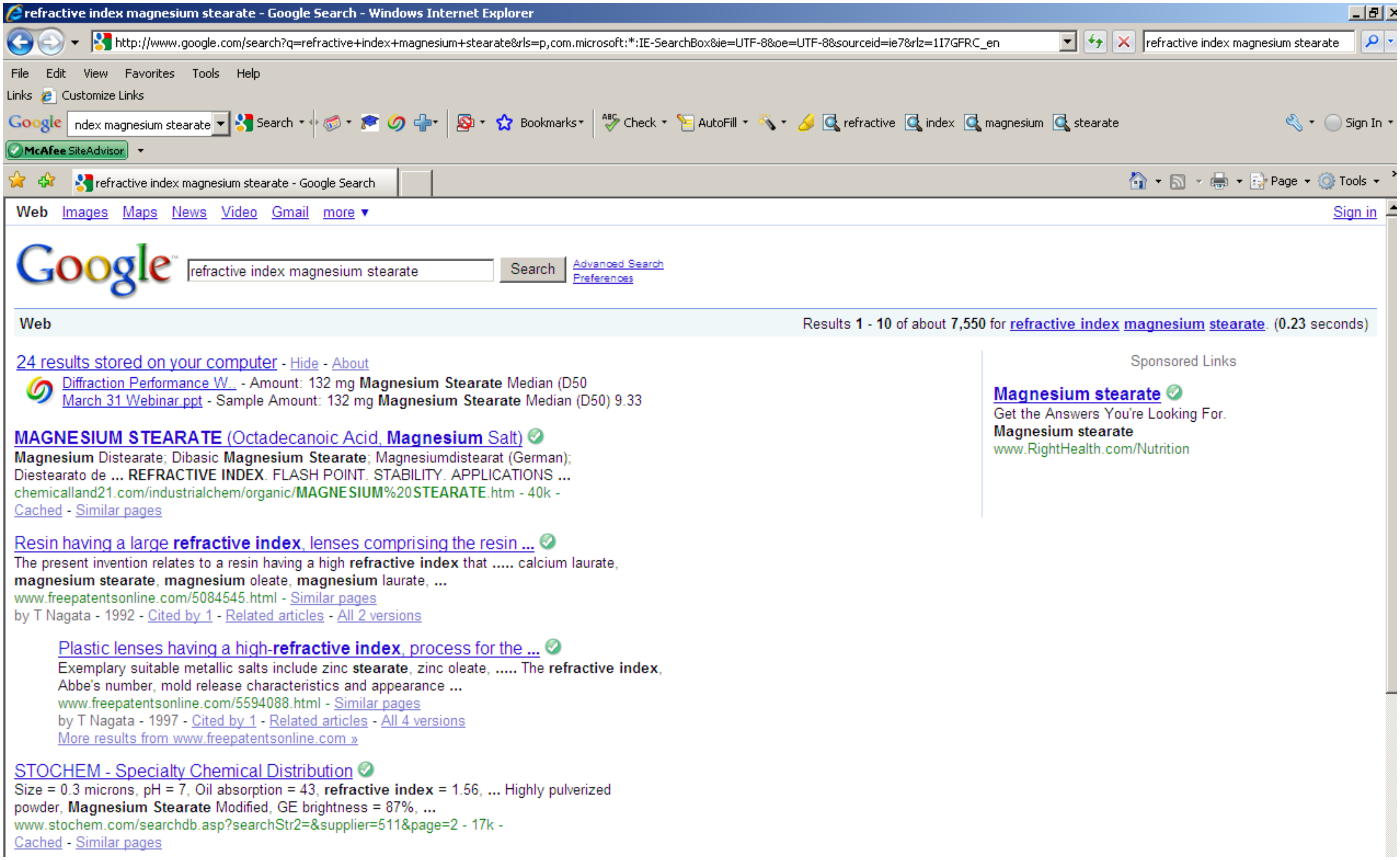
TexLoc Refractive Index of Polymers

NOTES:
Products supplied by TexLoc are designated in **bold green text.**

Water has a refractive index of 1.33.

PVDF	**Poly(vinylidene fluoride)**	**1.4200**
ECTFE	**Ethylene Chlorotrifluorotheylene**	**1.4470**
	Poly(trifluoroethyl methacrylate)	1.4370
	Poly(methyl octadecyl siloxane)	1.4430
	Poly(methyl hexyl siloxane)	1.4430
	Poly(methyl octyl siloxane)	1.4450
	Poly(isobutyl methacrylate)	1.4470
	Poly(vinyl isobutyl ether)	1.4507
	Poly(methyl hexadecyl siloxane)	1.4510
PEO	Poly(ethylene oxide)	1.4539
	Poly(vinyl ethyl ether)	1.4540
	Poly(methyl tetradecyl siloxane	1.4550
	Poly(ethylene glycol mono-methyl ether)	1.4555
	Poly(vinyl n-butyl ether)	1.4563
PPOX	Poly(propylene oxide)	1.4570
	Poly(3-butoxypropylene oxide)	1.4580
	Poly(3-hexoxypropylene oxide)	1.4590
	Poly(ethylene glycol)	1.4590
	Poly(vinyl n-pentyl ether)	1.4590

Google Search



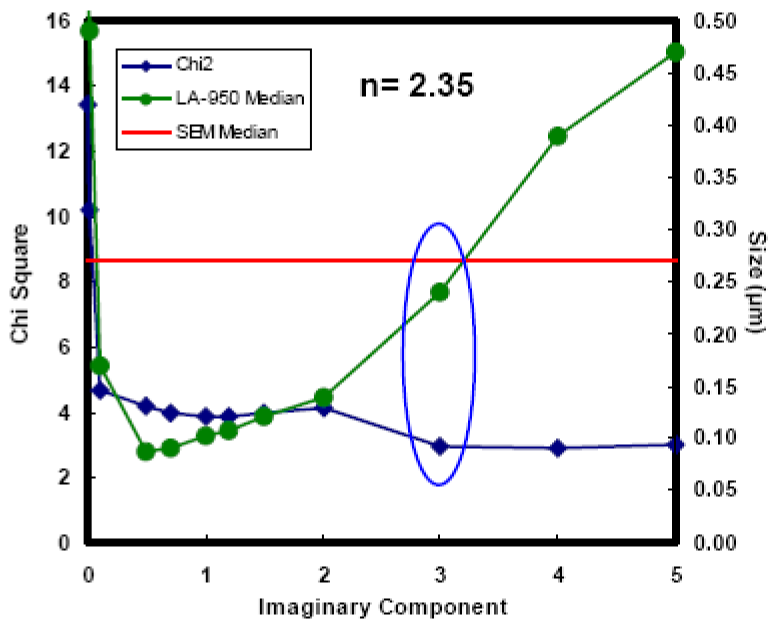
Mixtures

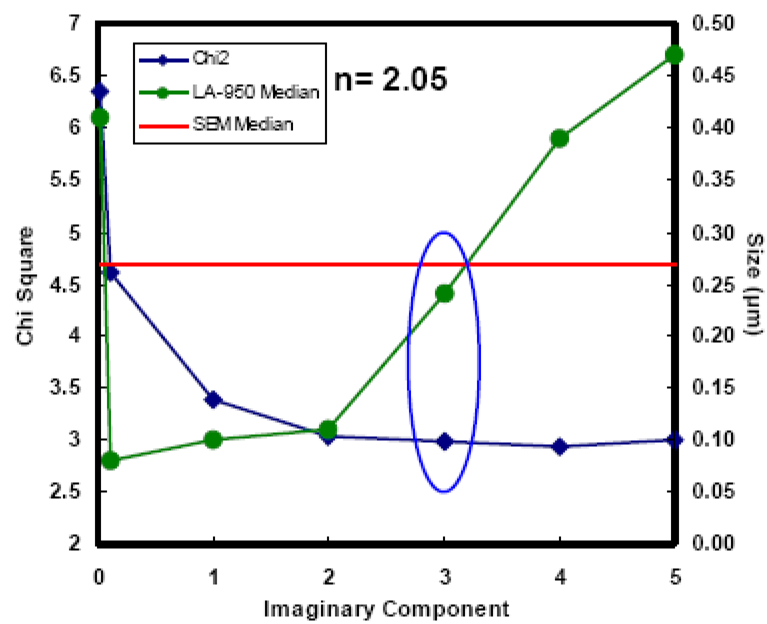
$$n_{mix} = \sum_{i=1}^{z} n_i V_i$$

$$n_{mix} = 1 + \rho_{mix} \sum_{i=1}^{z} m_i k_i$$

Where n_{mix} is the refractive index of the mixture, n_i is the refractive index of the ith component, V_i is the volume fraction of that component, and z is the total number of components. The real

The term m_i is the molar fraction of the component in the mixture and k_i is its Gladstone-Dale constant. These





Larsen, E.S., Berman, H., *The Microscopic Determination of the Non-Opaque Minerals, Second Edition*, United States Department of the Interior, Geological Survey Bulletin 848, 1934, US Government Printing Office, Washington, DC.

Mixtures

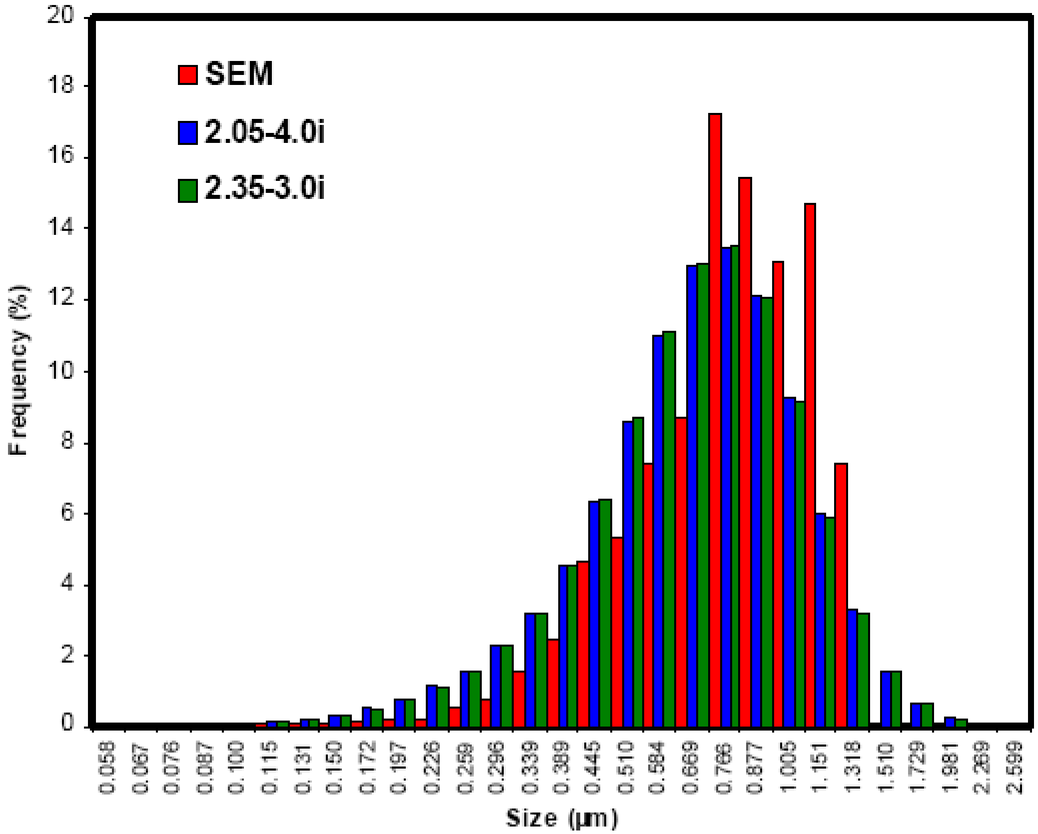


Table 1

	Median Size (µm)	
	Volume	Number
SEM	0.75	0.27
2.05-3.0i	0.64	0.24
2.35-3.0i	0.65	0.24

Anisotropy

Also called birefringence
Many crystals have different RI as inspected through different planes.
Use average, consider flow alignment

I would rather eat French food

Uniaxial vs. Biaxial Materials

Uniaxial materials, at 590 nm[3]

Material	n_o	n_e	Δn
beryl $Be_3Al_2(SiO_3)_6$	1.602	1.557	-0.045
calcite $CaCO_3$	1.658	1.486	-0.172
calomel Hg_2Cl_2	1.973	2.656	+0.683
ice H_2O	1.309	1.313	+0.004
lithium niobate $LiNbO_3$	2.272	2.187	-0.085
magnesium fluoride MgF_2	1.380	1.385	+0.006
quartz SiO_2	1.544	1.553	+0.009
ruby Al_2O_3	1.770	1.762	-0.008
rutile TiO_2	2.616	2.903	+0.287
peridot $(Mg, Fe)_2SiO_4$	1.690	1.654	-0.036
sapphire Al_2O_3	1.768	1.760	-0.008
sodium nitrate $NaNO_3$	1.587	1.336	-0.251
tourmaline (complex silicate)	1.669	1.638	-0.031
zircon, high $ZrSiO_4$	1.960	2.015	+0.055
zircon, low $ZrSiO_4$	1.920	1.967	+0.047

Biaxial materials, at 590 nm[3]

Material	n_α	n_β	n_γ
borax	1.447	1.469	1.472
epsom salt $MgSO_4 \cdot 7(H_2O)$	1.433	1.455	1.461
mica, biotite	1.595	1.640	1.640
mica, muscovite	1.563	1.596	1.601
olivine $(Mg, Fe)_2SiO_4$	1.640	1.660	1.680
perovskite $CaTiO_3$	2.300	2.340	2.380
topaz	1.618	1.620	1.627
ulexite	1.490	1.510	1.520

Biaxial birefringence, also known as trirefringence, describes an anisotropic material that has more than one axis of anisotropy

$$\Delta n = n_e - n_o$$

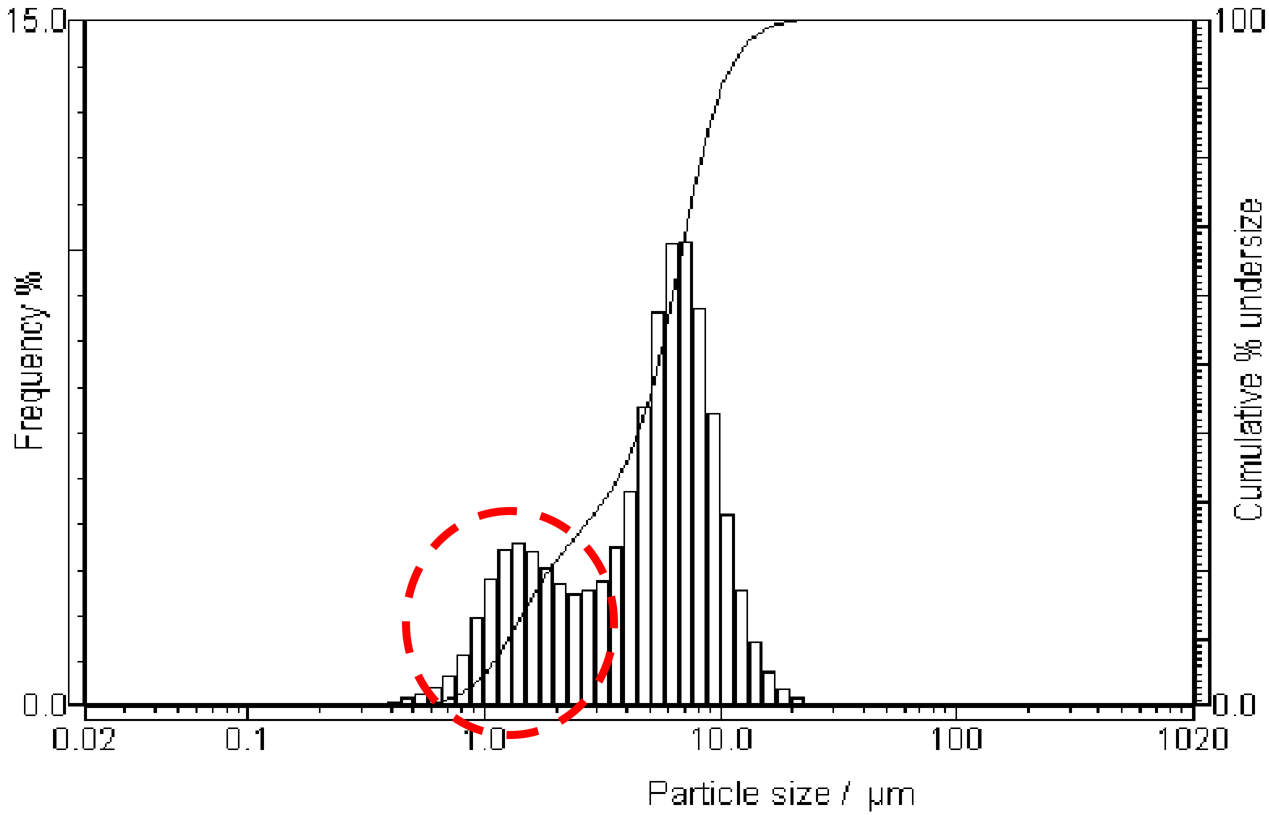
where n_o and n_e are the refractive indices for polarizations perpendicular (ordinary) and parallel (extraordinary) to the axis of anisotropy respectively.

3 Elert, Glenn. "Refraction". *The Physics Hypertextbook*. http://hypertextbook.com/physics/waves/refraction/.

Scary Example: Is the Small Peak Real?

Starch sample

Low imaginary

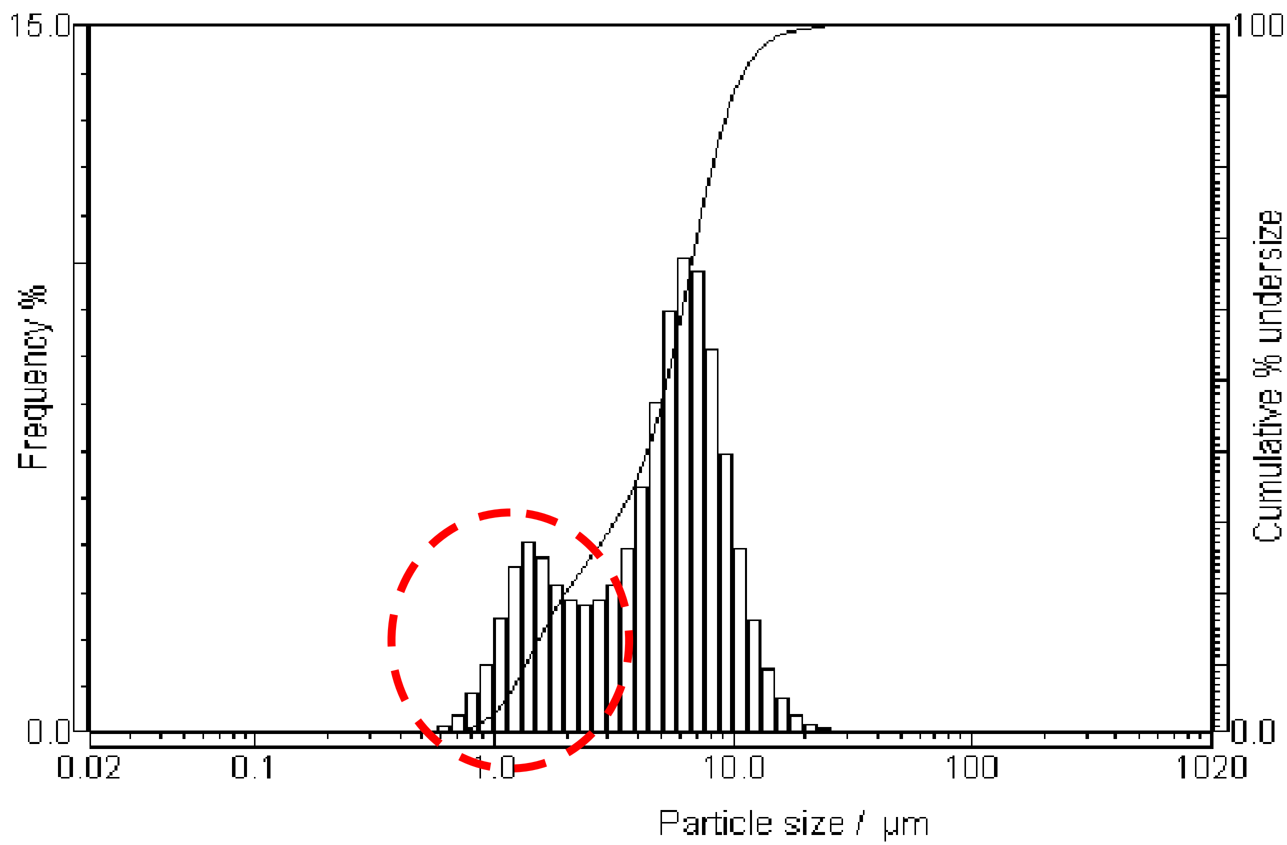


INDEX = 1.22 - 0.1i

Scary Example: Is the Small Peak Real?

Starch sample

High imaginary

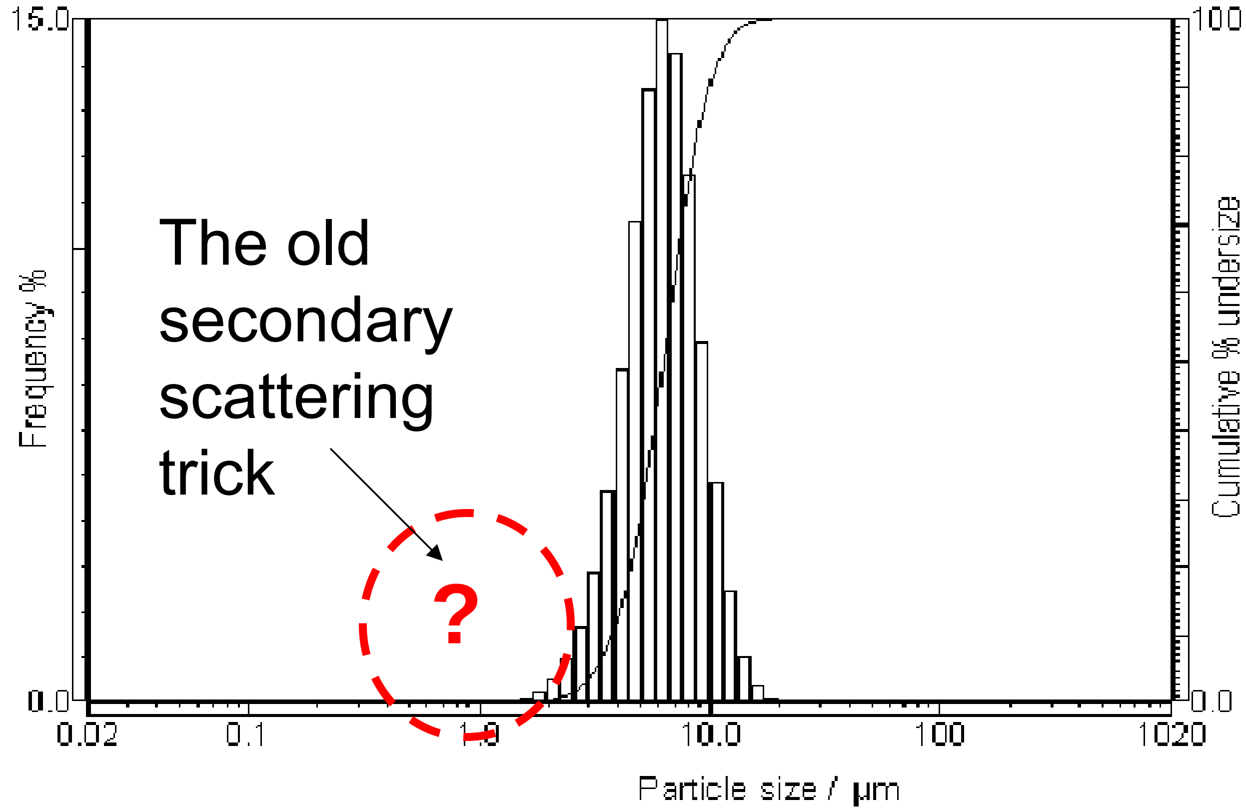


INDEX = 1.23 - 4.13i

Scary Example: Is the Small Peak Real?

Starch sample

Zero imaginary



INDEX = 1.22 - 0.0i

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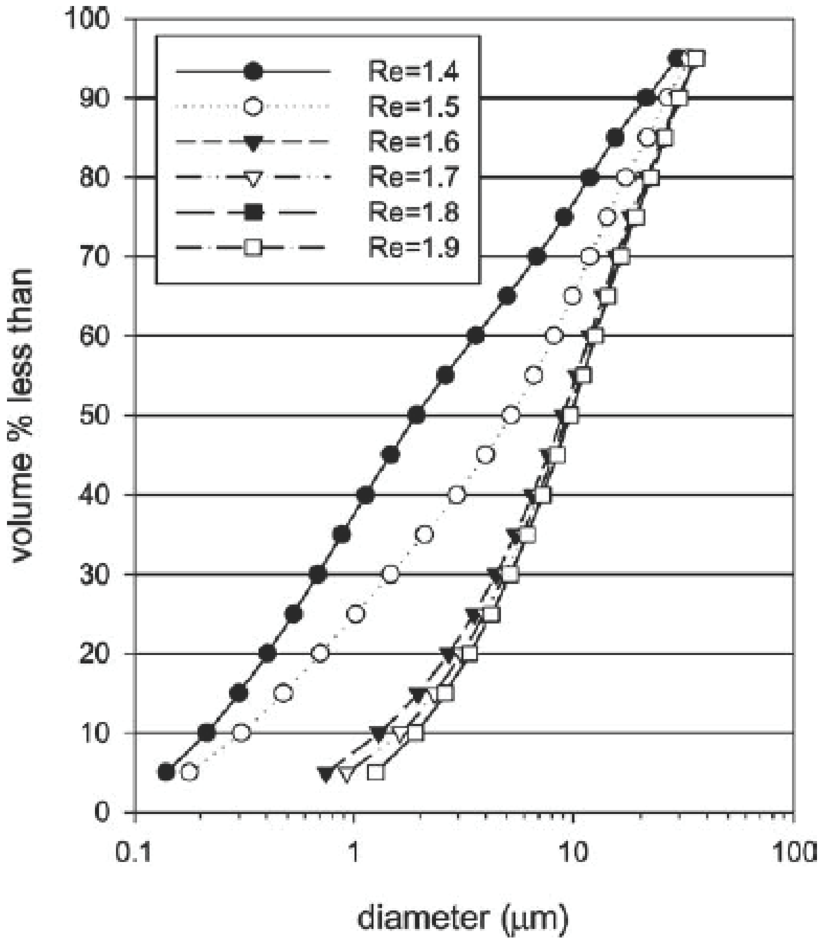
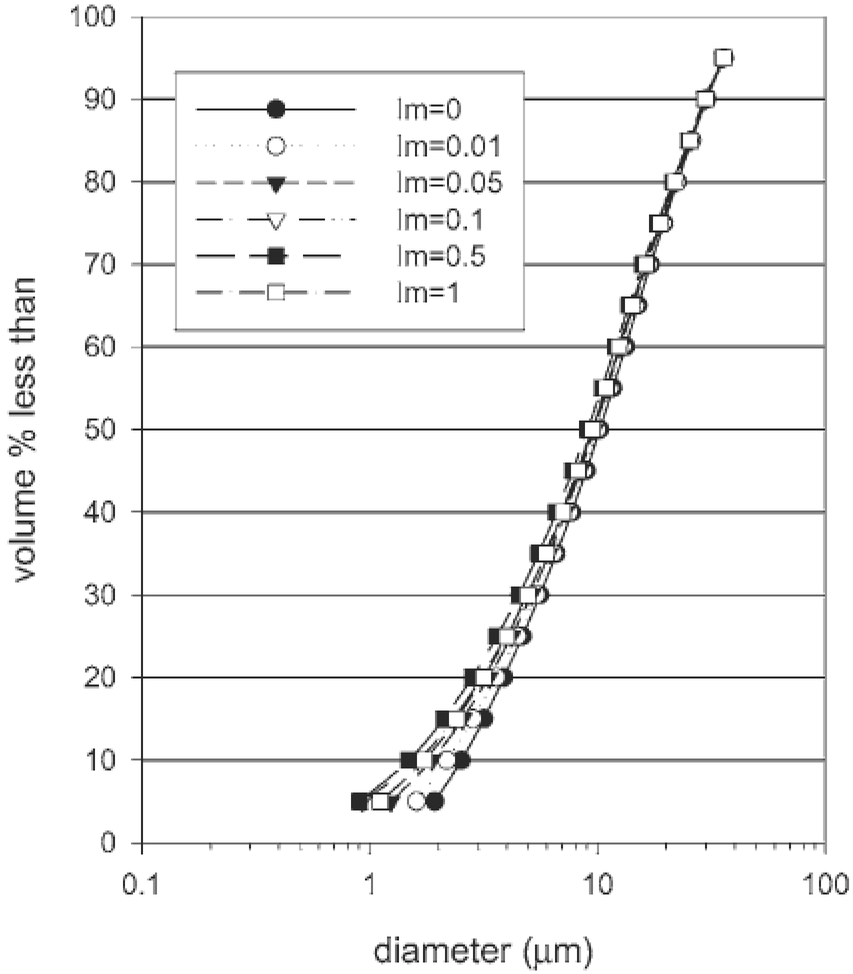
Effect of RI: Cement



Fixed absorbance, vary real



Fixed real, vary absorbance

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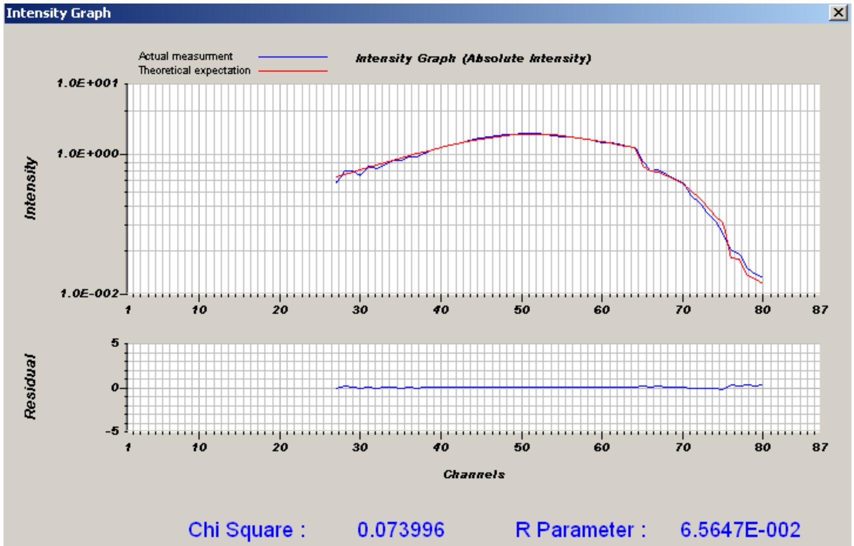
Chi Square and R Parameter

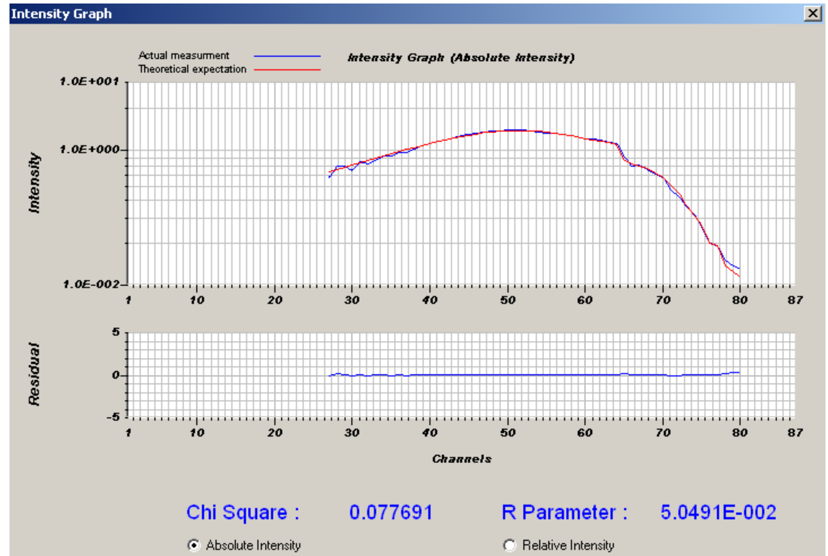
$$\chi^2 = \sum \left\{ \frac{1}{\sigma_i^2} [y_i - y(x_i)]^2 \right\}$$

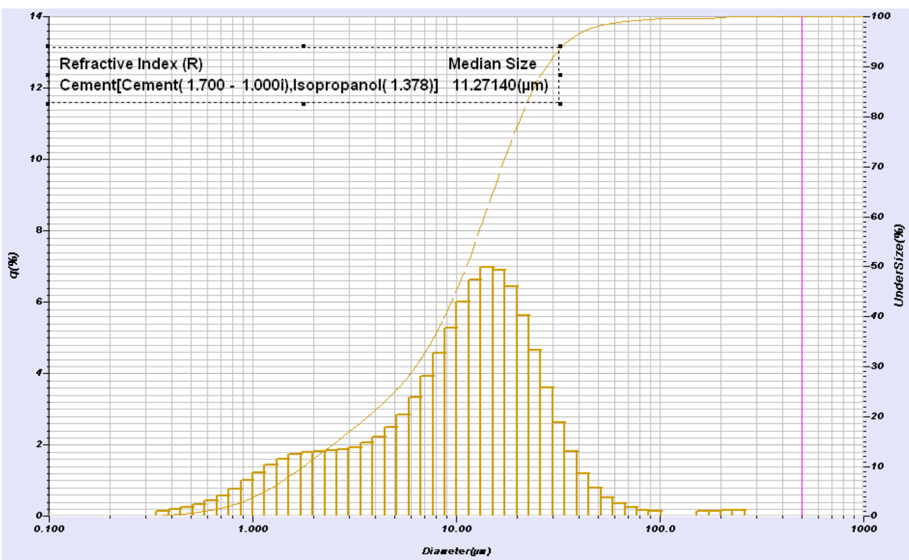
$$R = \frac{1}{N} \sum_{i=1}^{N} \left\{ \frac{1}{y_{(x_i)}} |y_i - y(x_i)| \right\}$$

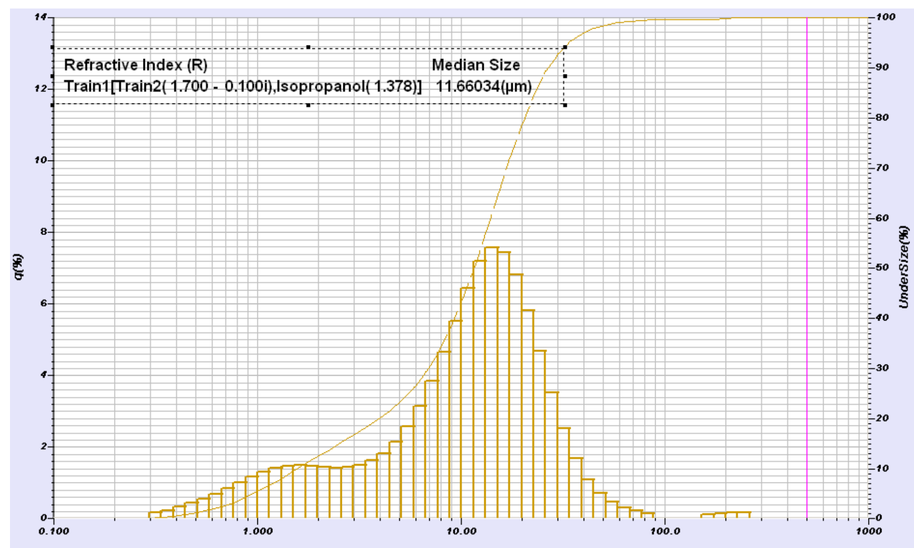
yi The measured scattered light at each channel (i) of the detector.
y (xi) The calculated scattered light at each channel (i) of the detector based on the chosen refractive index kernel and reported particle size distribution.
σi The standard deviation of the scattered light intensity at each channel (i) of the detector. A larger σi indicates lower reliability of the signal on a given detector.
N The number of detectors used for the calculation

Using R Value for i









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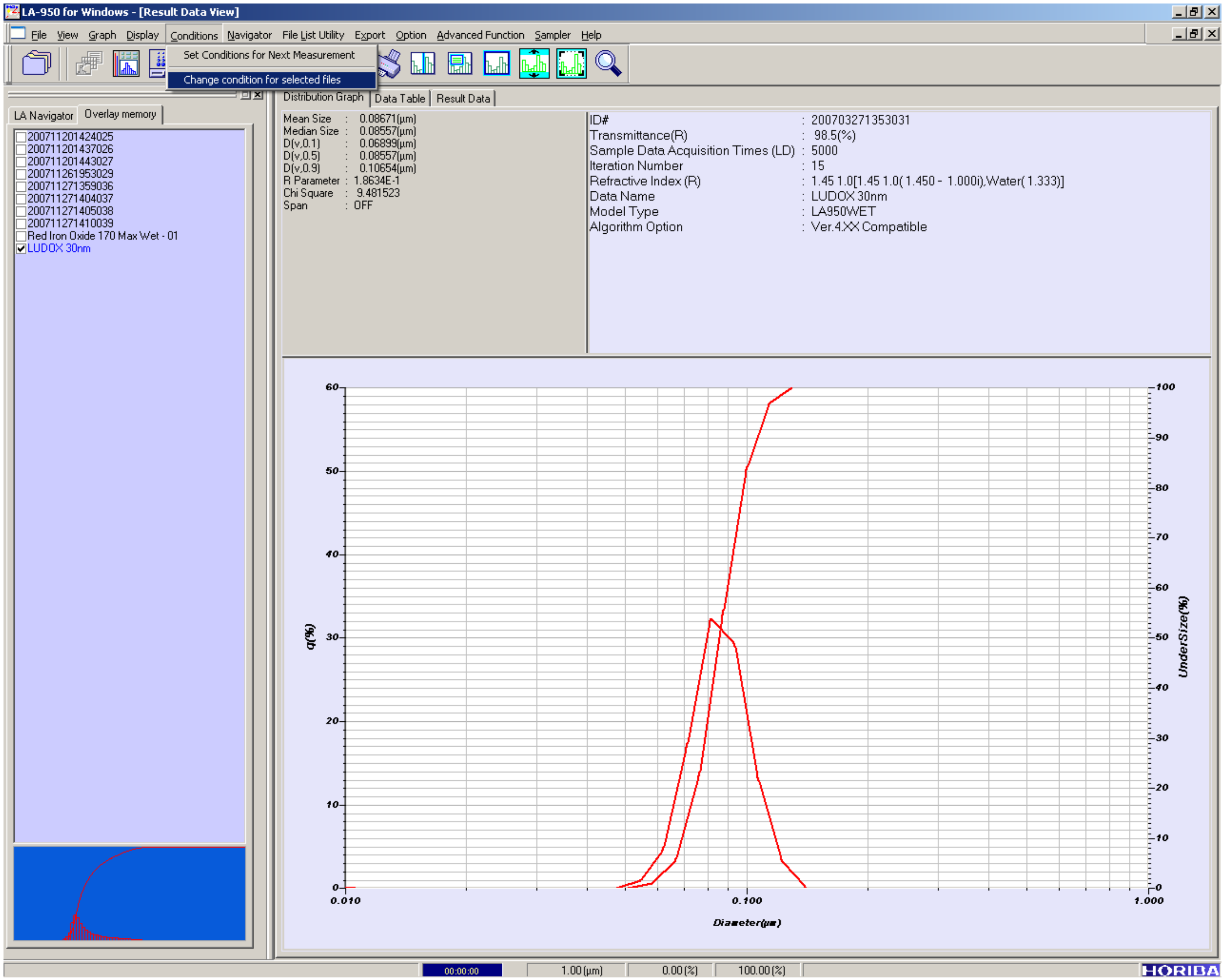
Changing RI


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
200711201424025
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
00:00:00
1.00 (µm)
0.00 (%)
100.00 (%)
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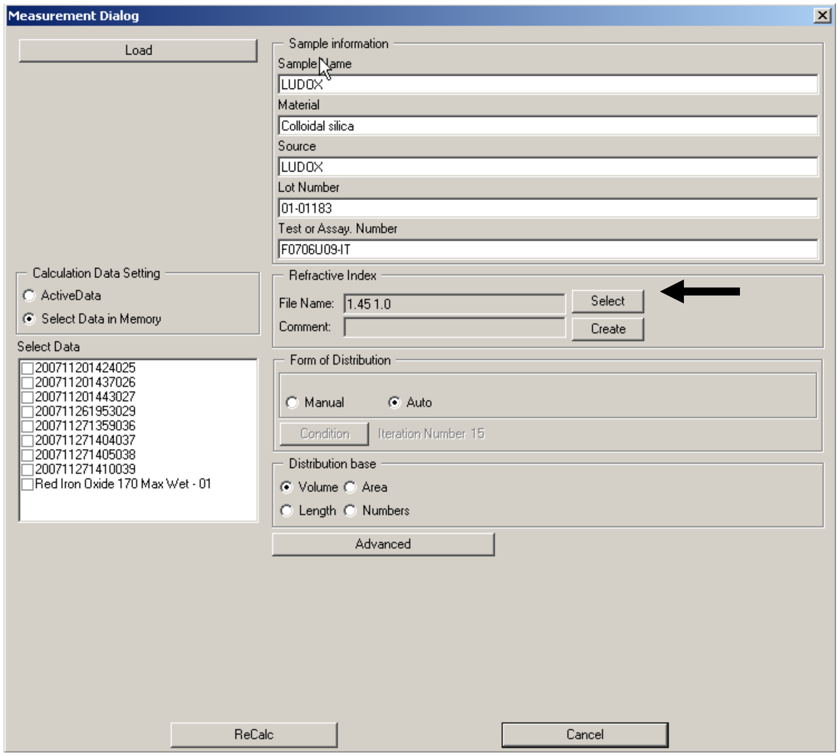
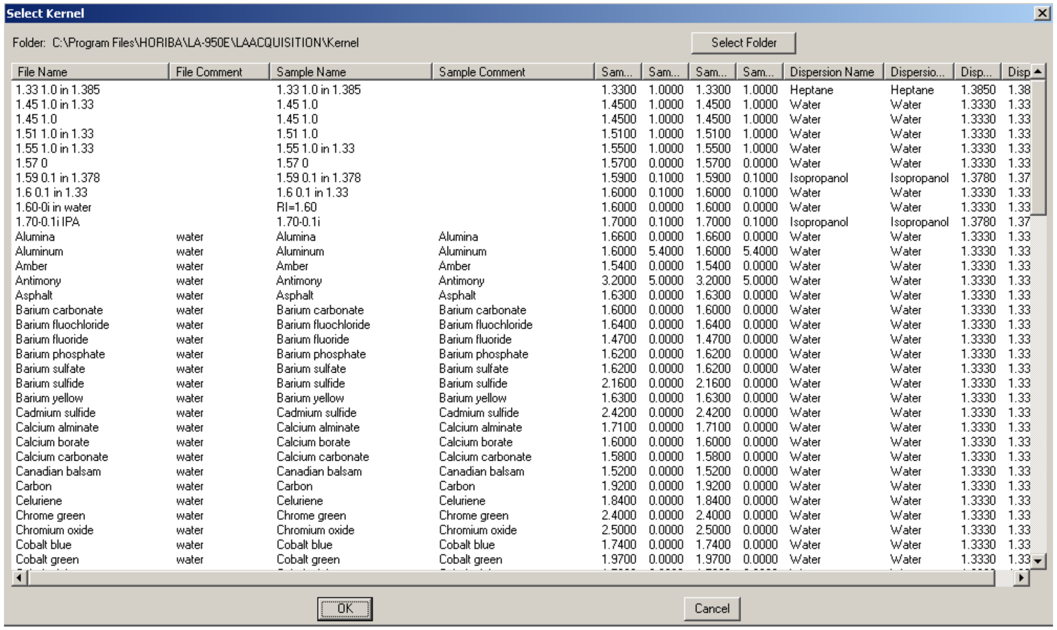
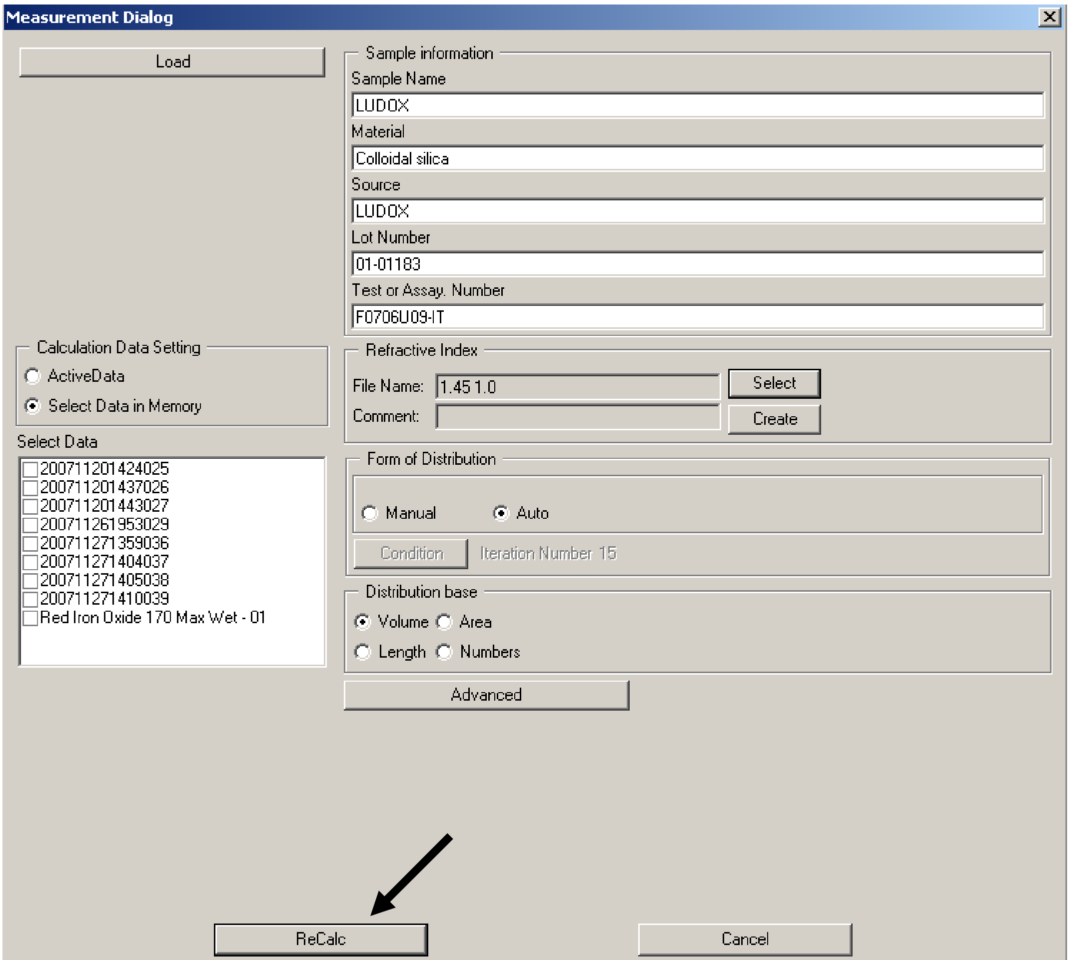
Changing RI


Measurement Dialog
Load
Sample information
Sample Name
LUDOX
Material
Colloidal silica
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


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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Material
Colloidal silica
Source
LUDOX
Lot Number
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Test or Assay. Number
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Calculation Data Setting
ActiveData
Select Data in Memory
Select Data
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200711271404037
200711271405038
200711271410039
Red Iron Oxide 170 Max Wet - 01
Refractive Index
File Name: 1.45 1.0
Select
Comment:
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Form of Distribution
Manual
Auto
Condition
Iteration Number 15
Distribution base
Volume
Area
Length
Numbers
Advanced
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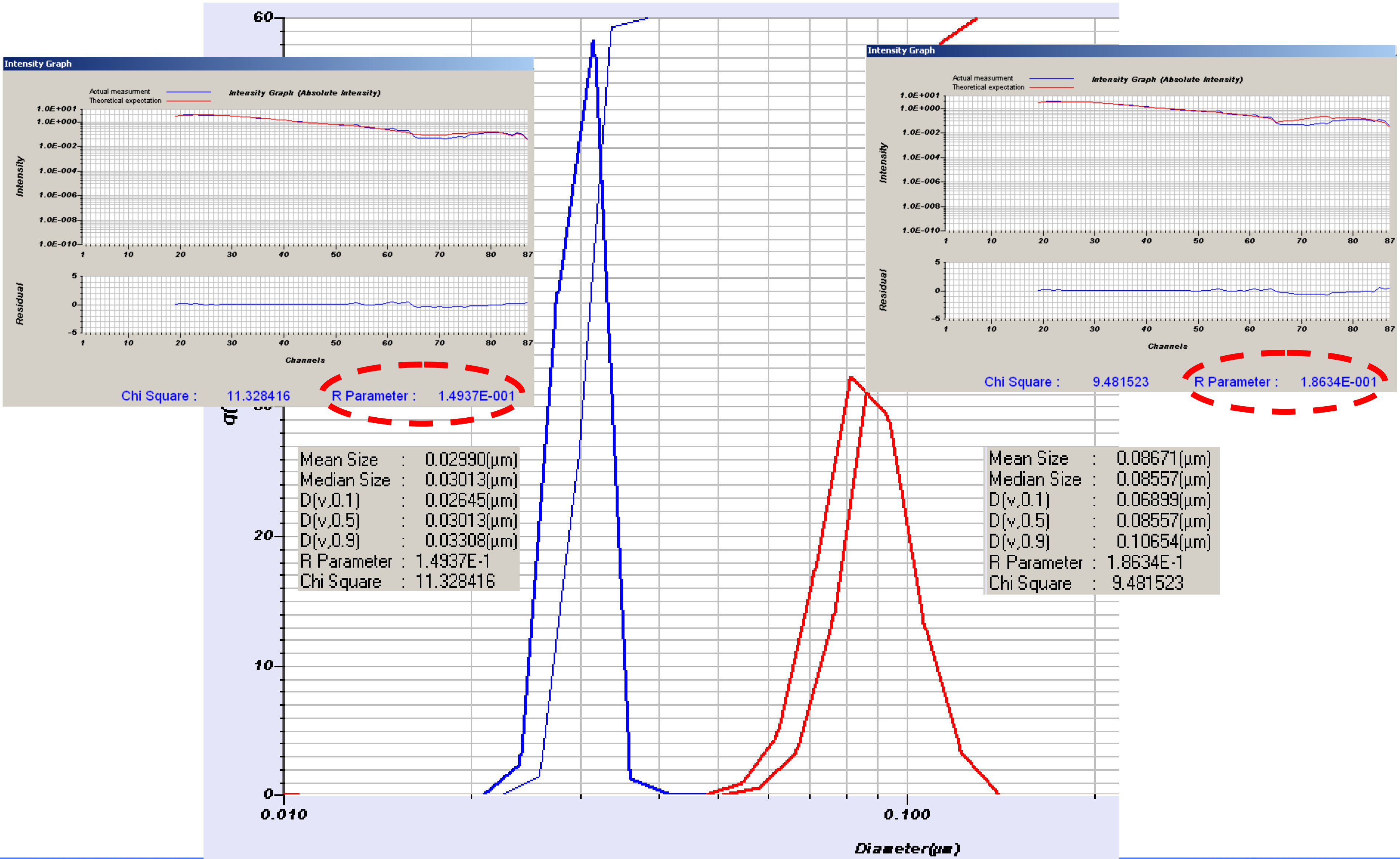
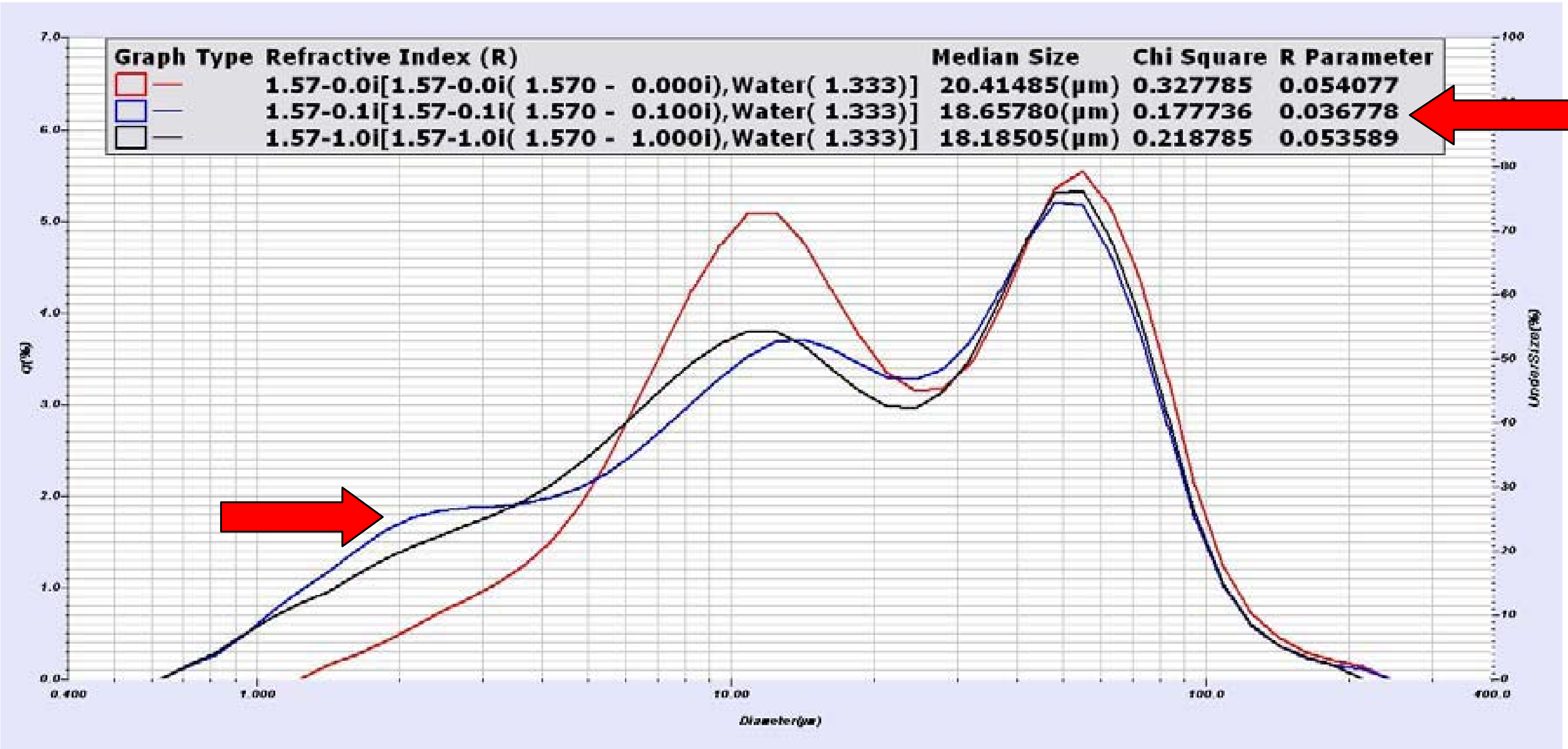
Cancel

Using R Value for i



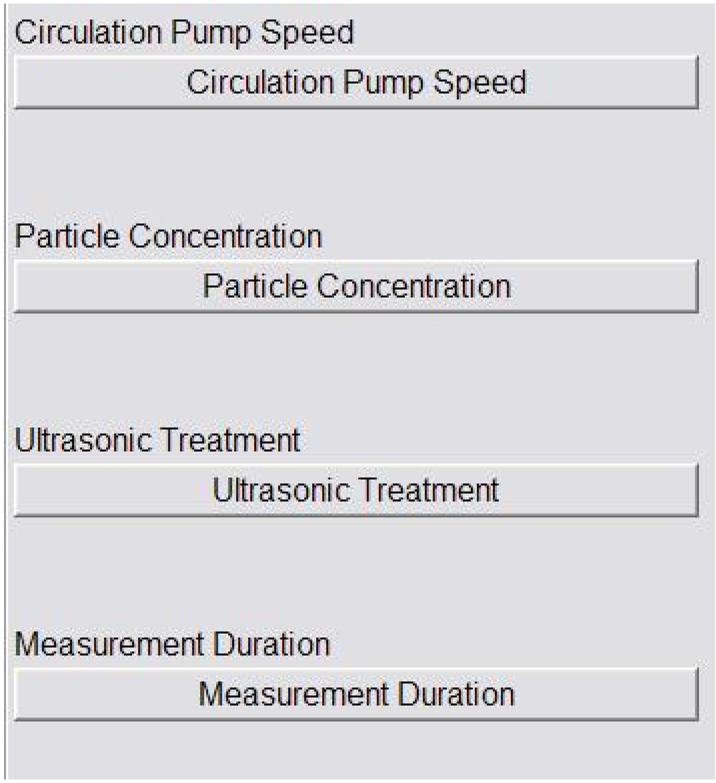
Using R Value for i

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



Automation by Method Expert

Analytical conditions



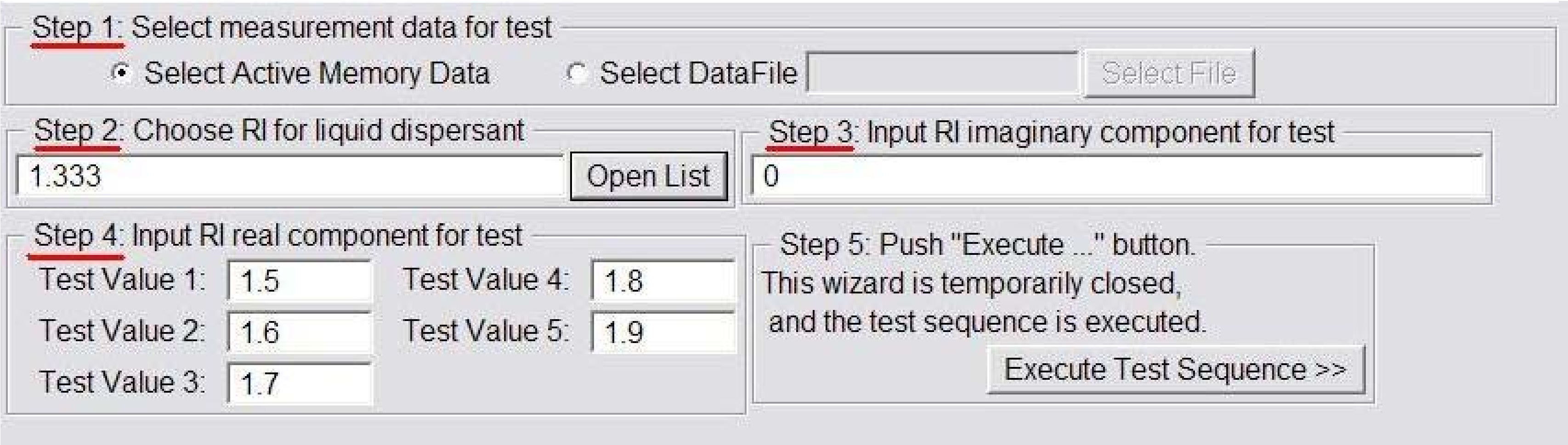
Calculation conditions

View Method Expert webinar TE004 in Download Center

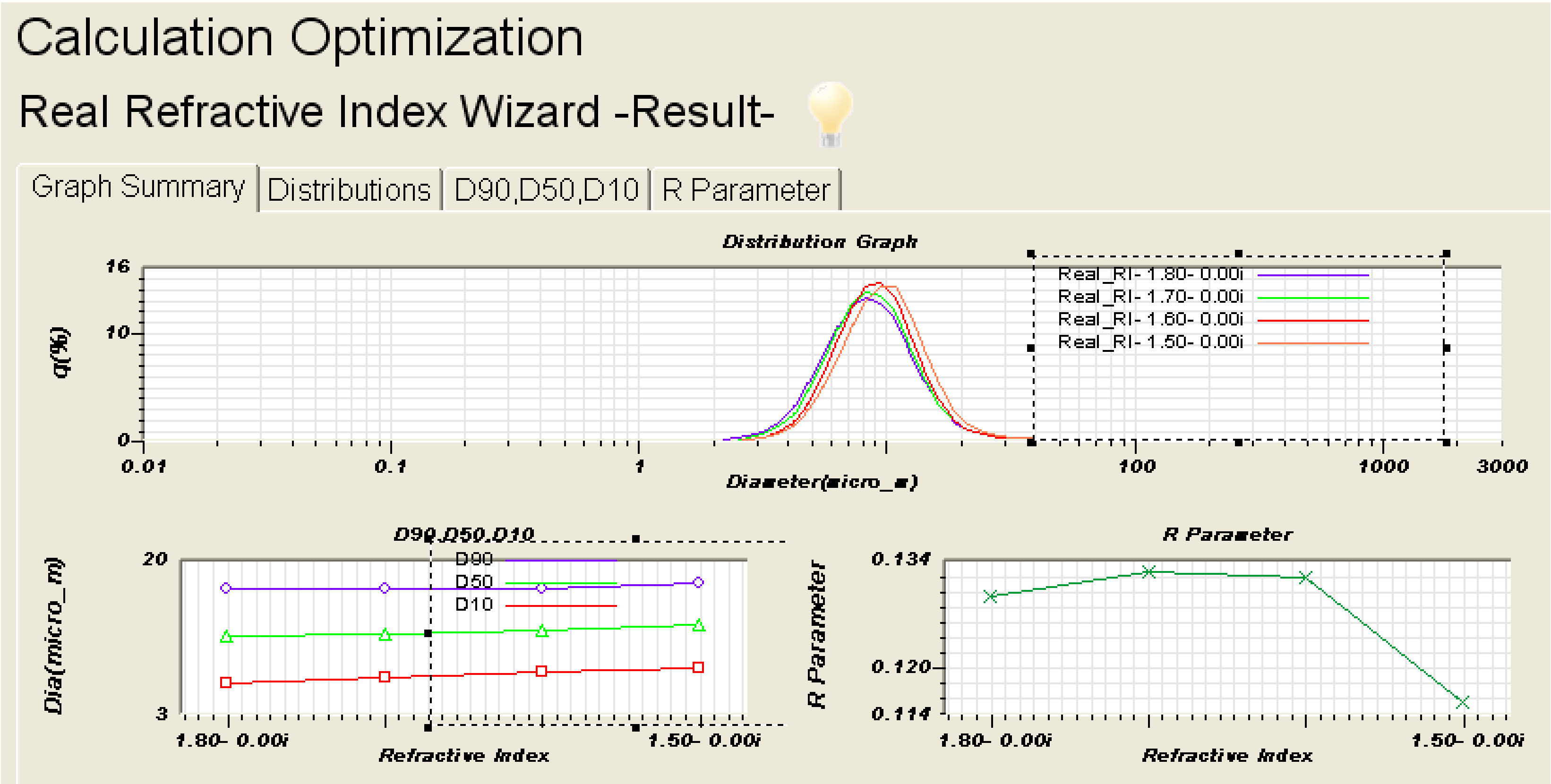
Automated RI Computation

Real part study

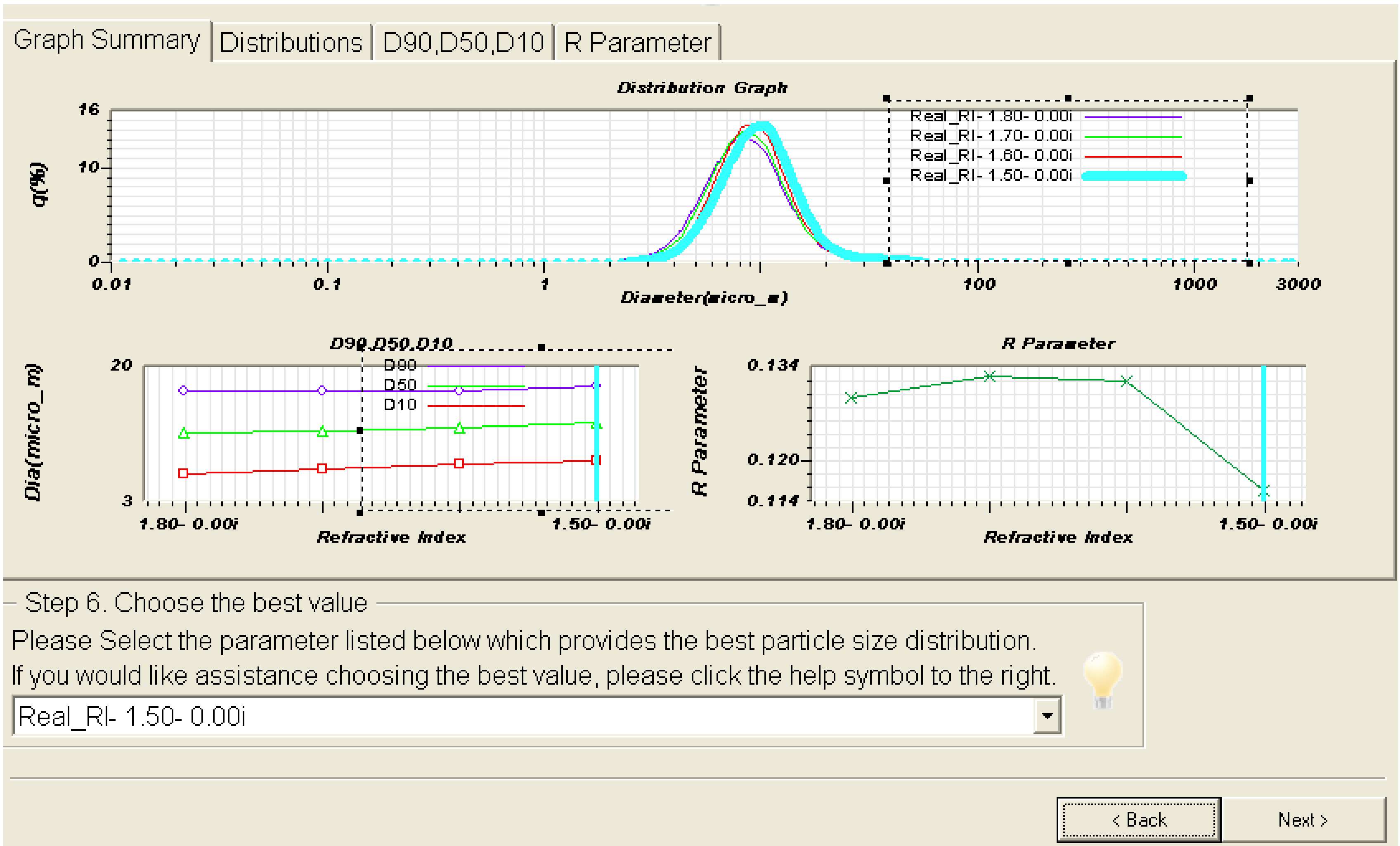
- Need to fix imaginary part
- Set up to 5 real parts
- Software will compute all RI and display R parameter variation with RI selection



Automated RI Computation



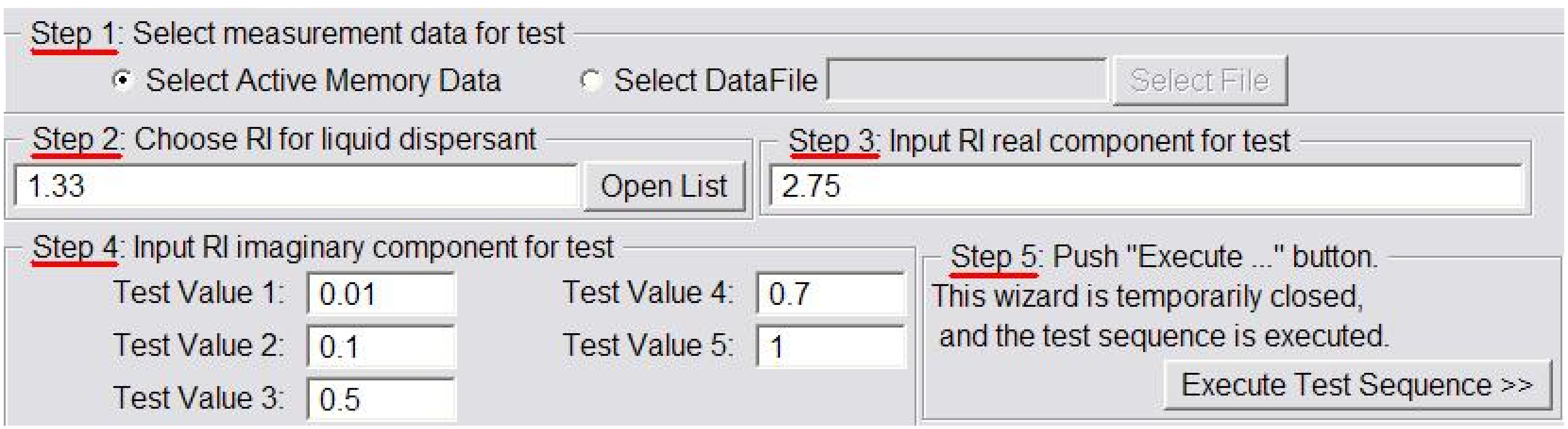
Automated RI Computation



Automated RI Computation

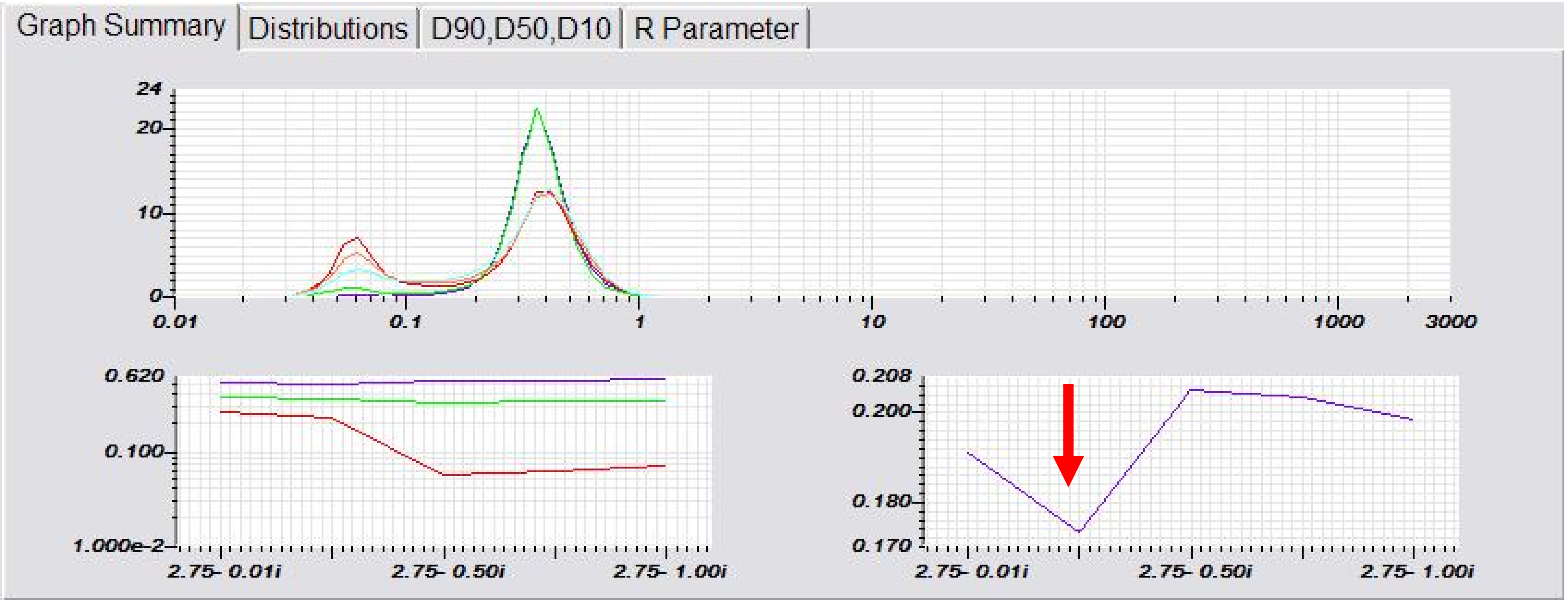
Imaginary part study

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



Automated RI Computation

Imaginary study



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

It's All on the Website

- Register to visit Download Center
- Application Notes
- Technical Notes
- Past webinars
- Bibliography
- And soon… today's webinar
- mark.bumiller@horiba.com
- ian.treviranus@horiba.com

Thank-you