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HORIBA Instruments

Particle Analysis

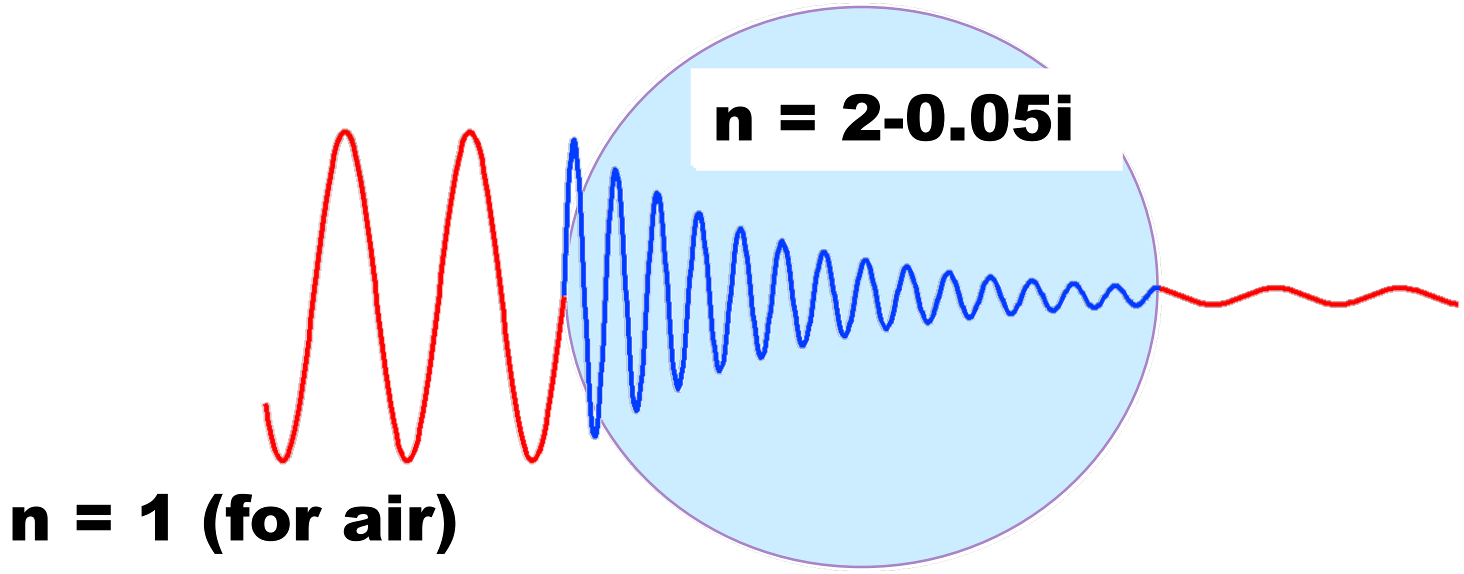
Jeff Bodycomb, Ph.D.

Refractive Index and Laser Diffraction

March 6, 2019

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



Why Worry about Refractive Index?

Light scattering is an optical measurement. Under certain conditions, one must include behavior of light inside the particulate material.

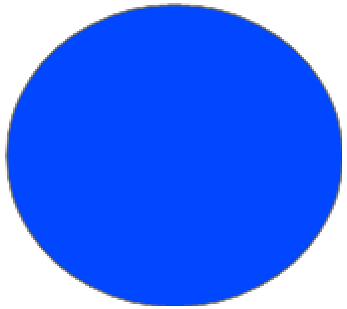
For larger particles; i. e., above approx. 26 micrometers, Fraunhofer Diffraction may be adequate to describe particle size and refractive index is less important.

When particle diameter is of the same approximate size as the wavelength of light used to make the measurement, a complex theory known as Mie Scattering Theory must be invoked. Refractive index describes the behavior of light inside the particle.

Mie vs. Fraunhofer

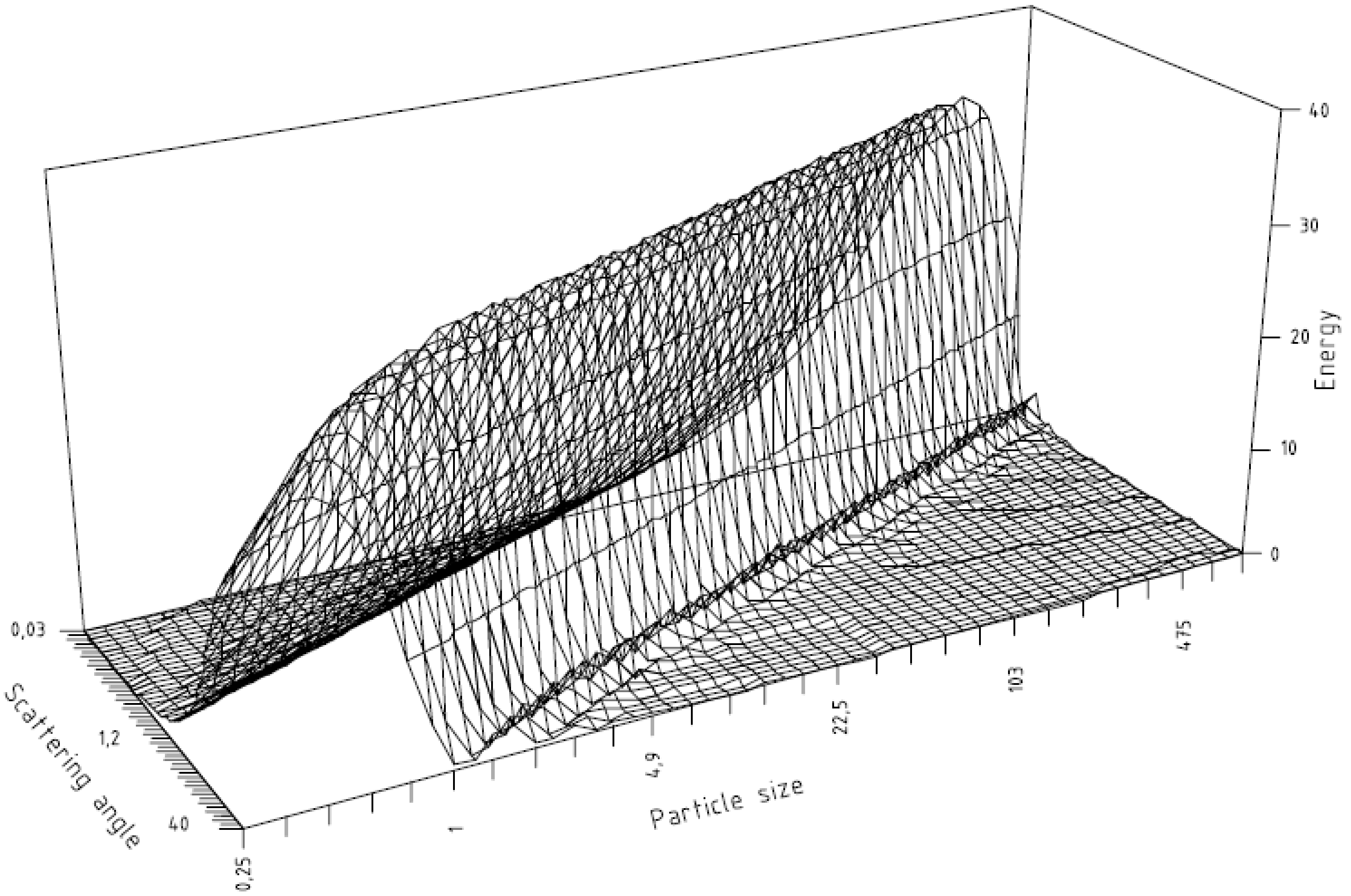
Mie: 3 dimensional particle (sphere)

Fraunhofer: 2 dimensional particle (disc)

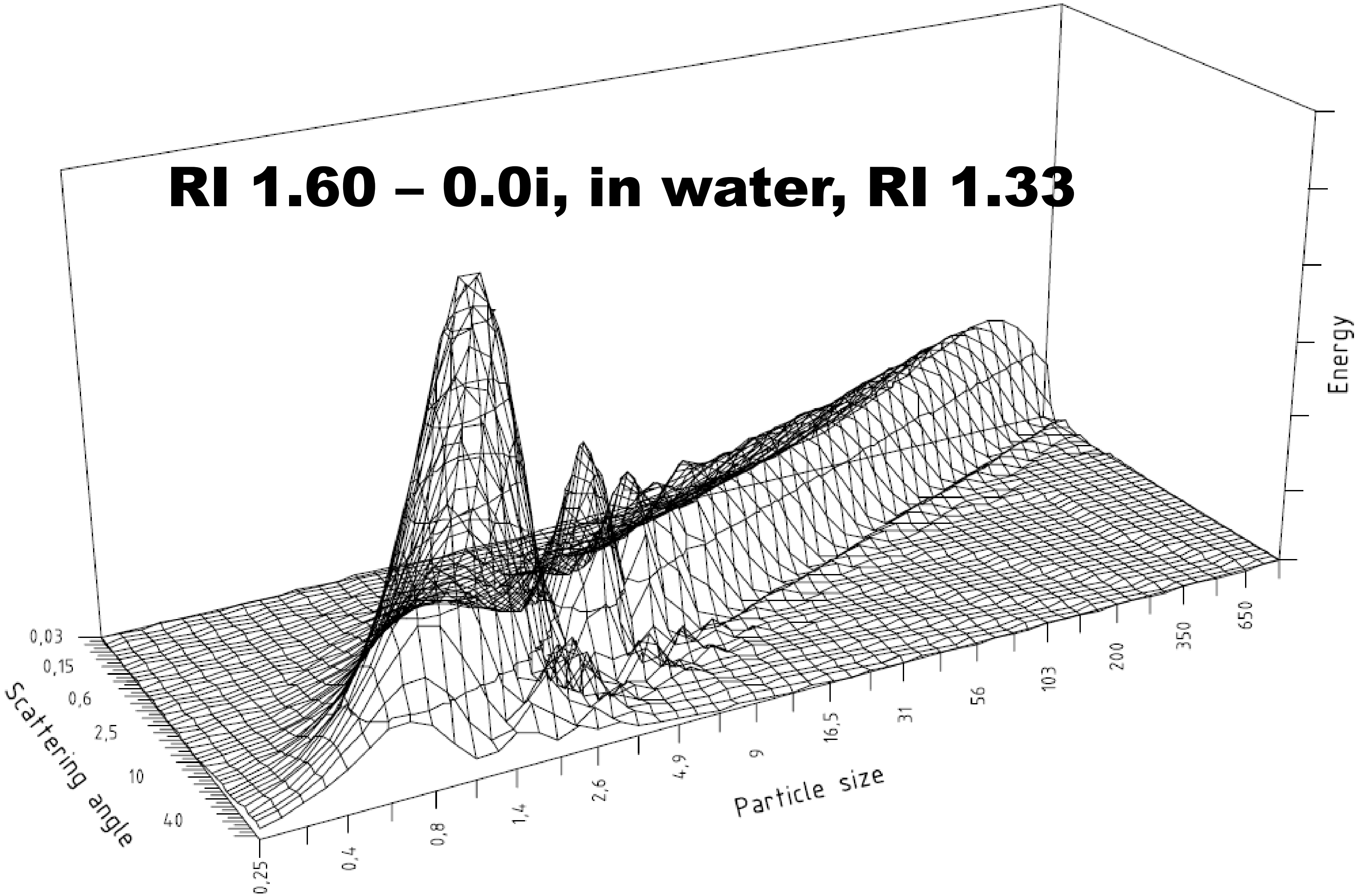


No longer a good idea to pretend world is 2-D and there is no need for refractive index.

Fraunhofer Approximation

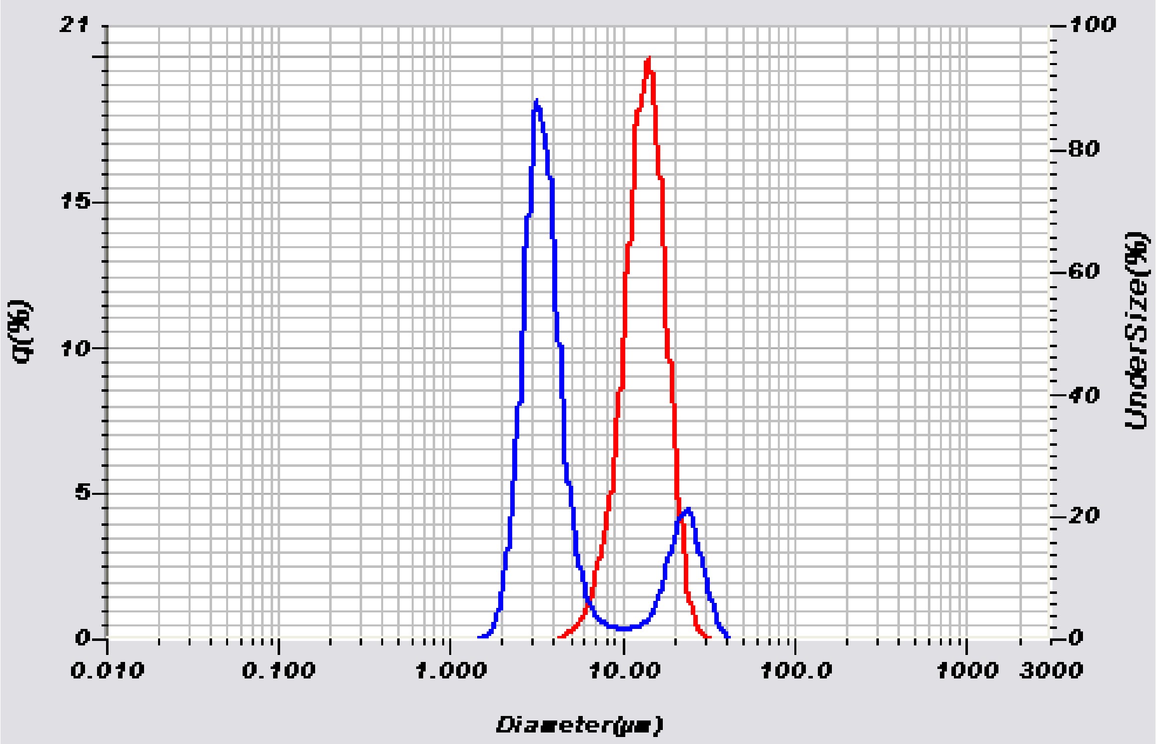


Mie Theory


RI 1.60 – 0.0i, in water, RI 1.33
Energy
Scattering angle
0,03
0,15
0,6
2,5
10
40
Particle size
0,25
0,4
0,8
1,4
2,6
4,9
9
16,5
31
56
103
200
350
650

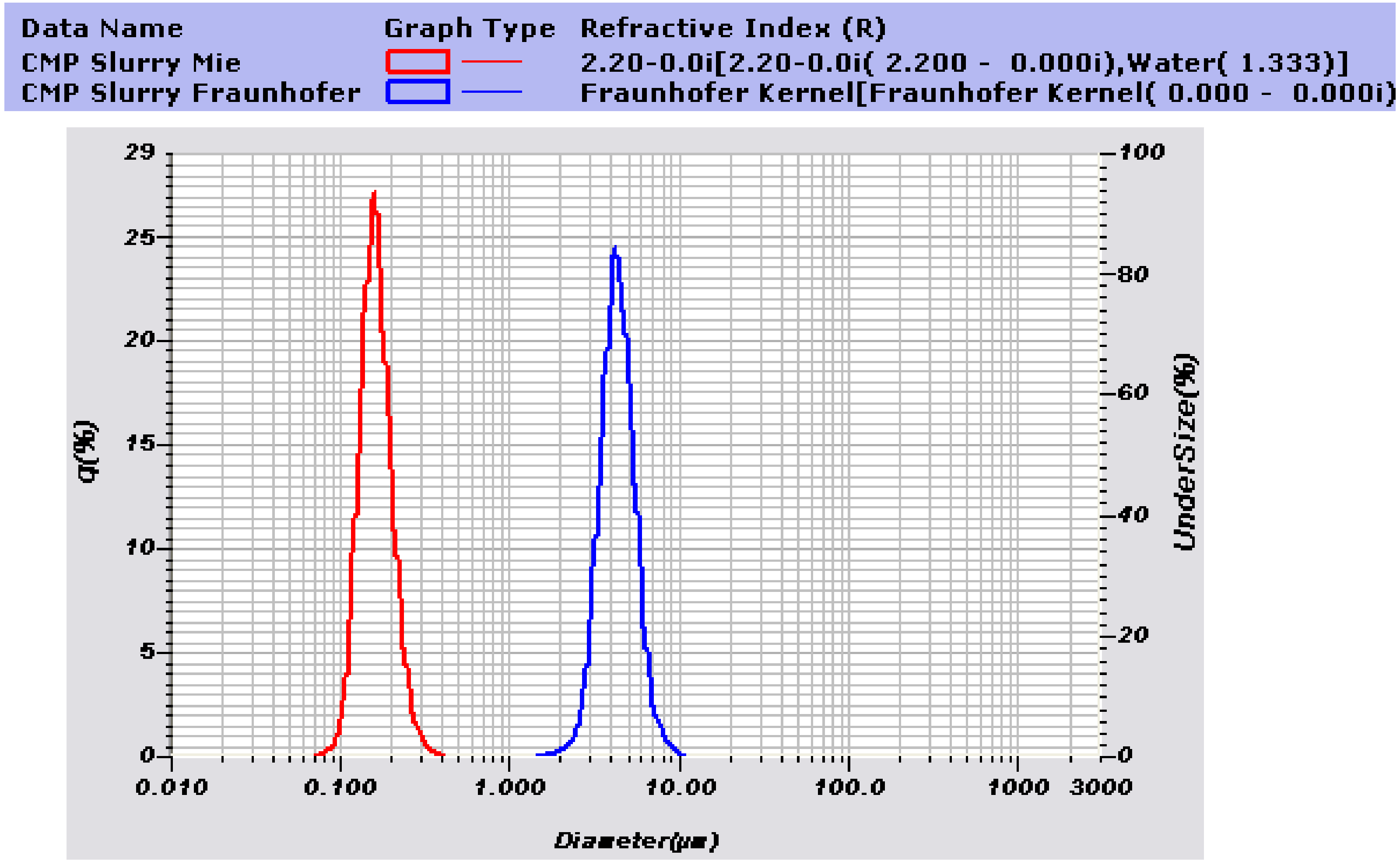
Practical Application: Glass Beads

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



More Details on Refractive Index

Refractive Index is defined by two components – REAL and IMAGINARY

RI = n + ik

Where:

n = the real component, which is the ratio of the velocity of light in a vacuum to the velocity of light in the material

= 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 = $\sqrt{-1}$

Example: typical soda-lime glass has a refractive index of 1.5, which means that in glass, light travels at 1 / 1.5 = 0.67 times the speed of light in a vacuum.

RI: Real Component

Real component can be determined from published tables or it can be measured using Snell's Law

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

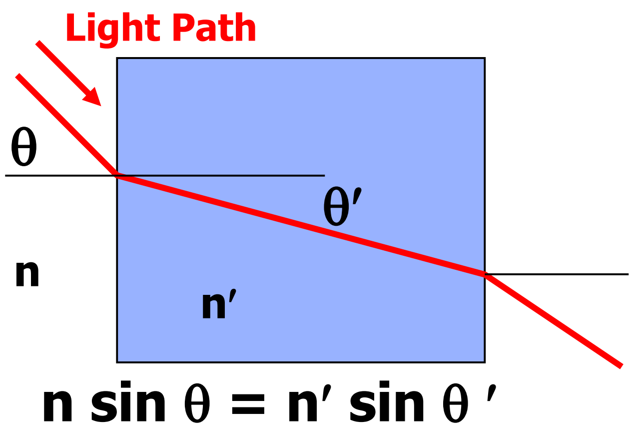
where:

n = refractive index (RI) of first substance (usually air)

θ = angle of incidence

n′ = refractive index of second substance (usually measured substance)

θ' = angle of refraction (deviation from original direction



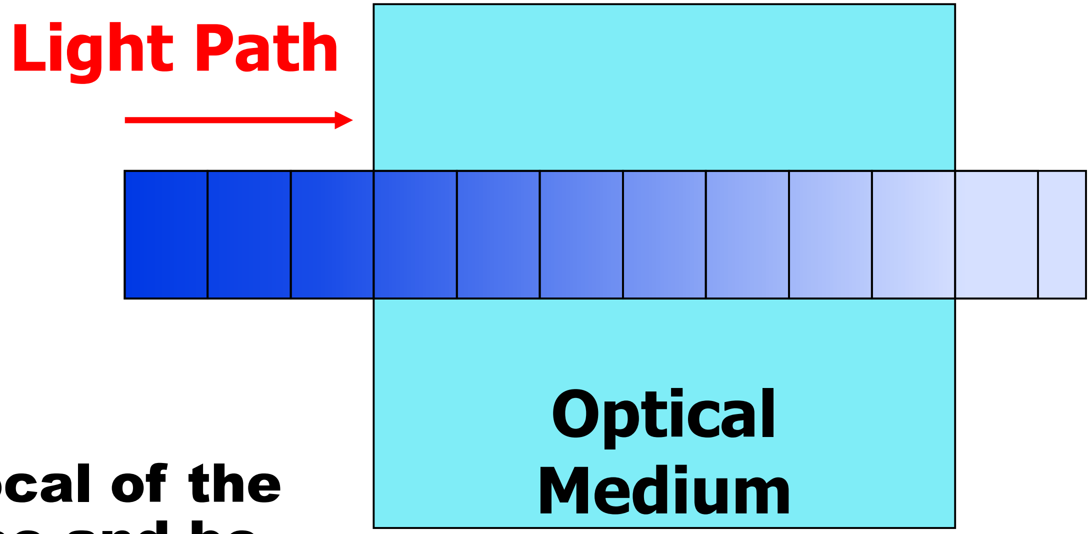
- **For particles with HIGH REAL INDICES, the reported size depends less on the imaginary component. As size increases, formula simplifies to Fraunhofer and becomes weak function of total refractive index**

RI: Imaginary Component

The imaginary component (k) in the Mie equation is the extinction coefficient of the material, defined as the reduction of transmission of optical radiation caused by absorption and scattering of light

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

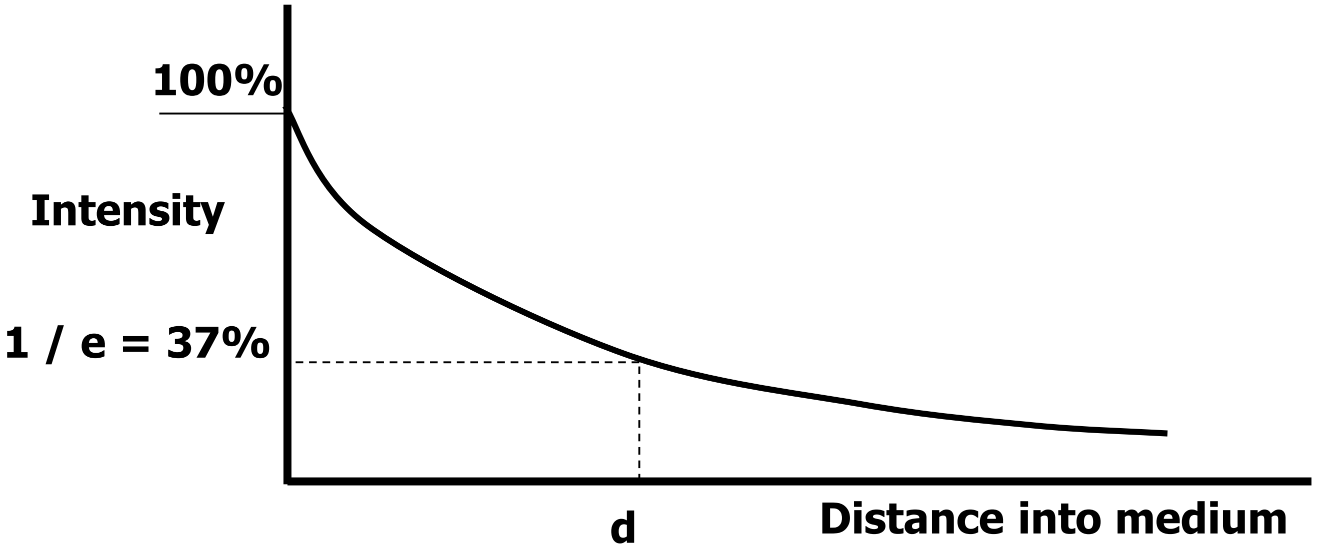
Where:
k = the extinction coefficient
α = the absorption coefficient
λ = the wavelength of light used



- **Absorption coefficient (α) is the reciprocal of the distance light will penetrate the surface and be attenuated to 1/e of its original intensity, about 37%. Opaque materials have high extinction coefficients.**

Refractive Index = n + ik

RI: Imaginary Component



$1 / d = \alpha$

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

Example: for a value of k = 0.1

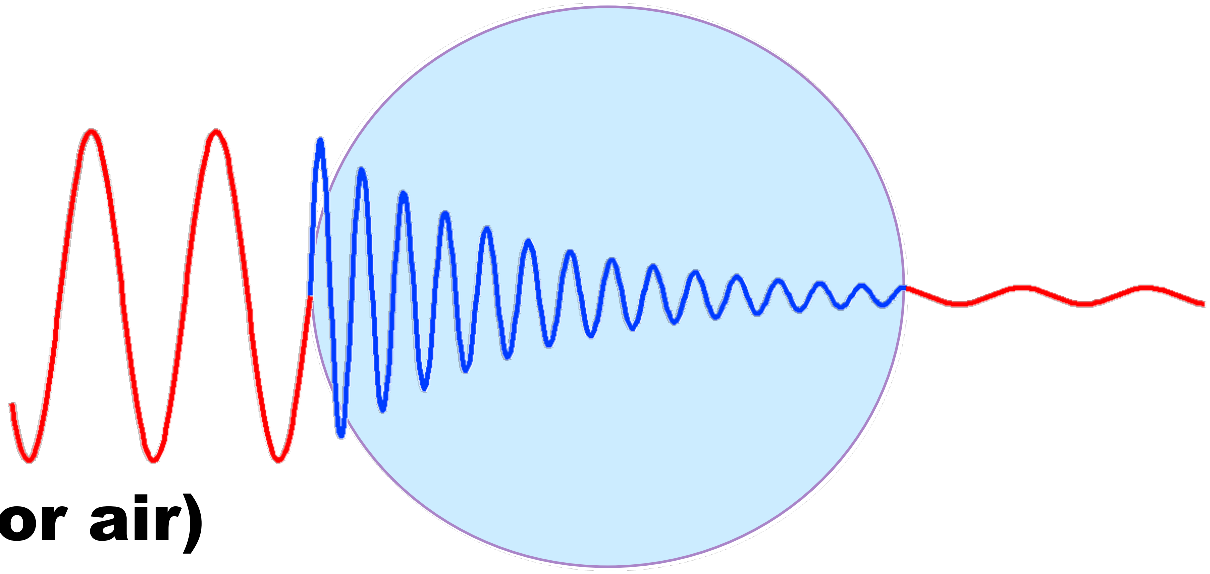
$k = (\lambda / 4\pi)\, [\alpha] = 0.05 \times [1 / d] = 0.1 = k$

$d = 0.05 / 0.1 = 0.5$ micron

What do we mean by RI?

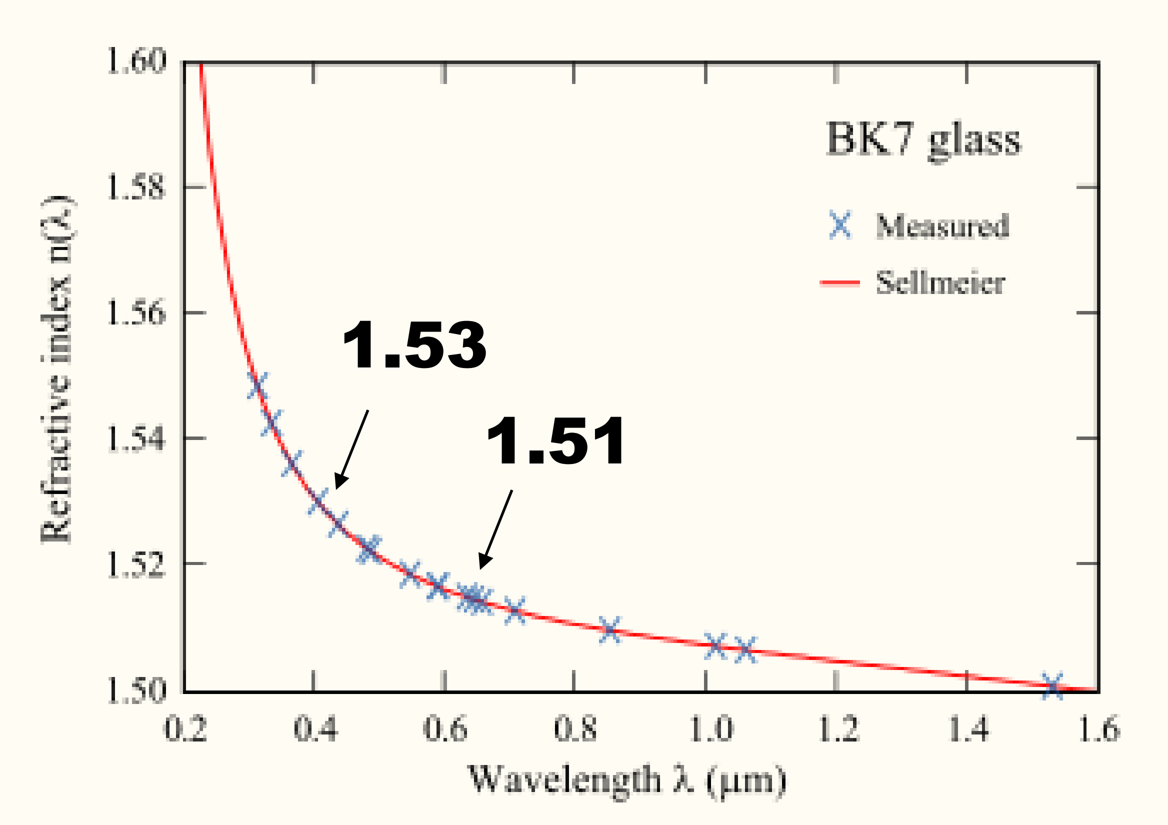
Real component is change in wavelength
Imaginary component is reduction in amplitude

n = 2-0.05i



n = 1 (for air)

n is Wavelength Dependent



Remember the LA-960 has two light sources
Red = 650 nm
Blue = 405 nm

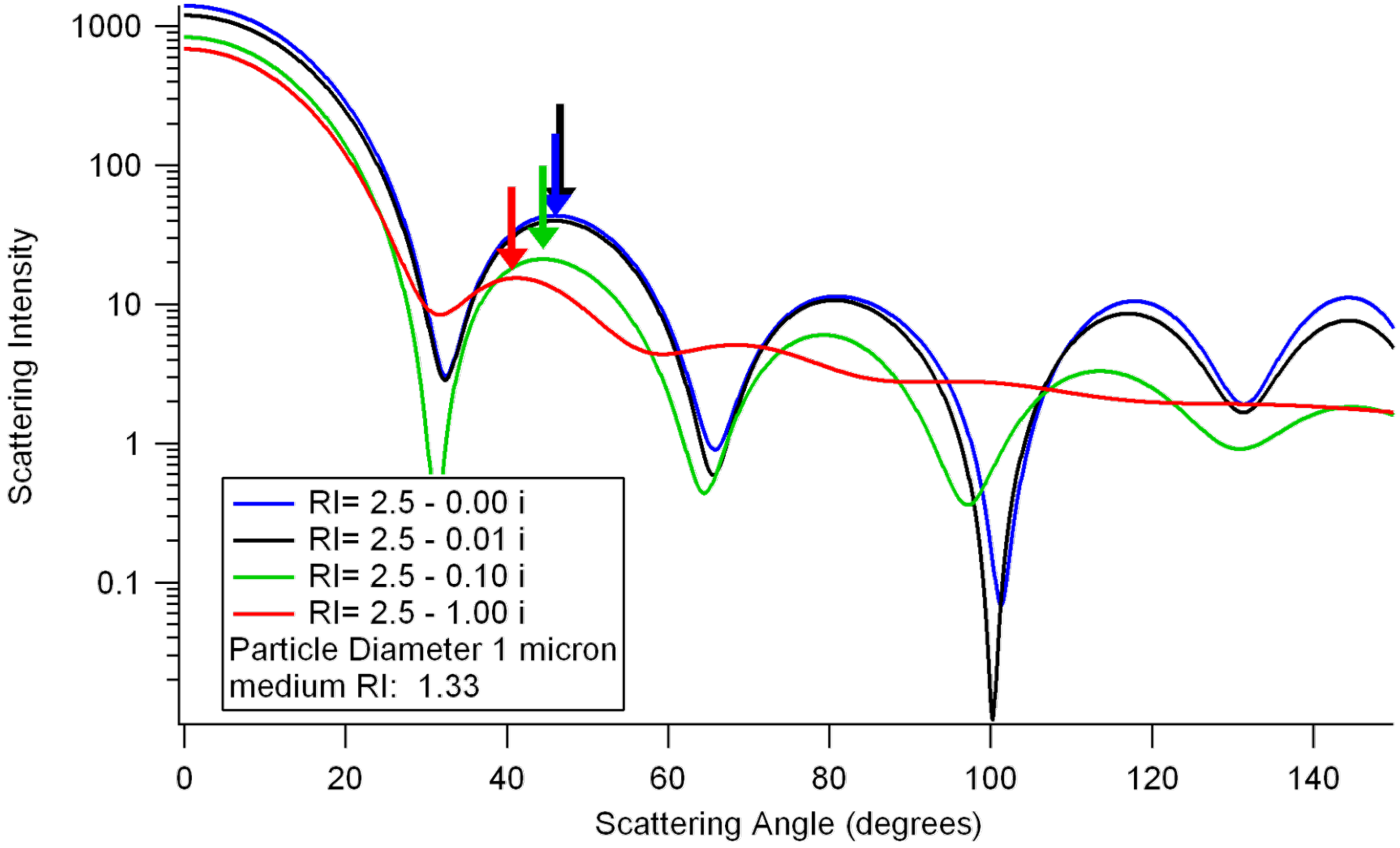
In this example
1.53 vs. 1.51
Not very important

Could matter for sub-micron pigments

Sellmeier equation

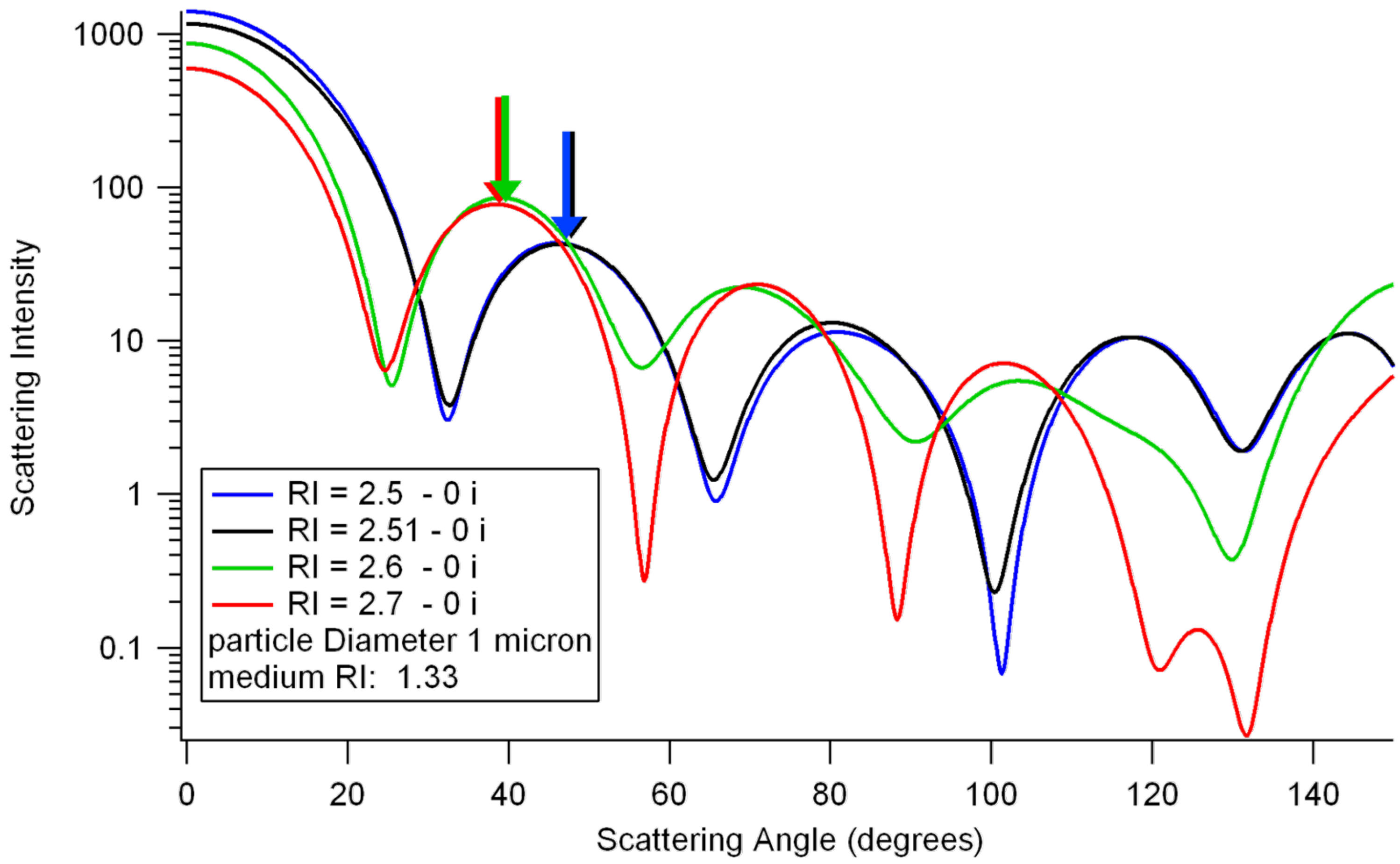
$$n^2(\lambda) = 1 + \frac{B_1\lambda^2}{\lambda^2 - C_1} + \frac{B_2\lambda^2}{\lambda^2 - C_2} + \frac{B_3\lambda^2}{\lambda^2 - C_3},$$

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….

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

RI effects are <u>most</u> 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

RI effects are <u>least</u> pronounced when:

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

Relative Refractive Index

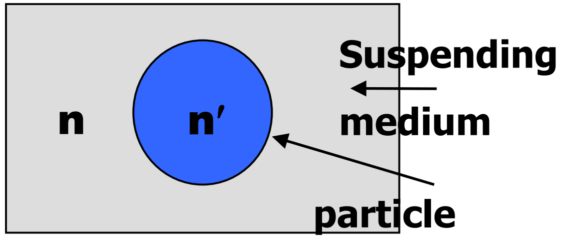
Legacy instruments and methods

If n = 1.33 (water) and n’ = 1.60 (particle), then <u>relative index is 1.60/1.33 = 1.203</u>

If particles are totally transparent, then <u>k = 0</u>

The selected <u>KERNEL function would be 120-000rri</u>

If n = 1.33 (water) and n’ = 1.60 (particle), then relative index is 1.60/1.33 = 1.203 s above. However, if particles are <u>somewhat opaque</u>, then <u>k > 0</u>



The selected KERNEL function would be 120-020rri

If material is being analyzed DRY, then the relative index is as follows:

If n = 1.0 (air) and n’ = 1.60 (particle), then relative index is 1.60/1.0 = 1.60

The selected KERNEL function would 160-000rri or 160-020rri depending on the degree of transparency of the particles.

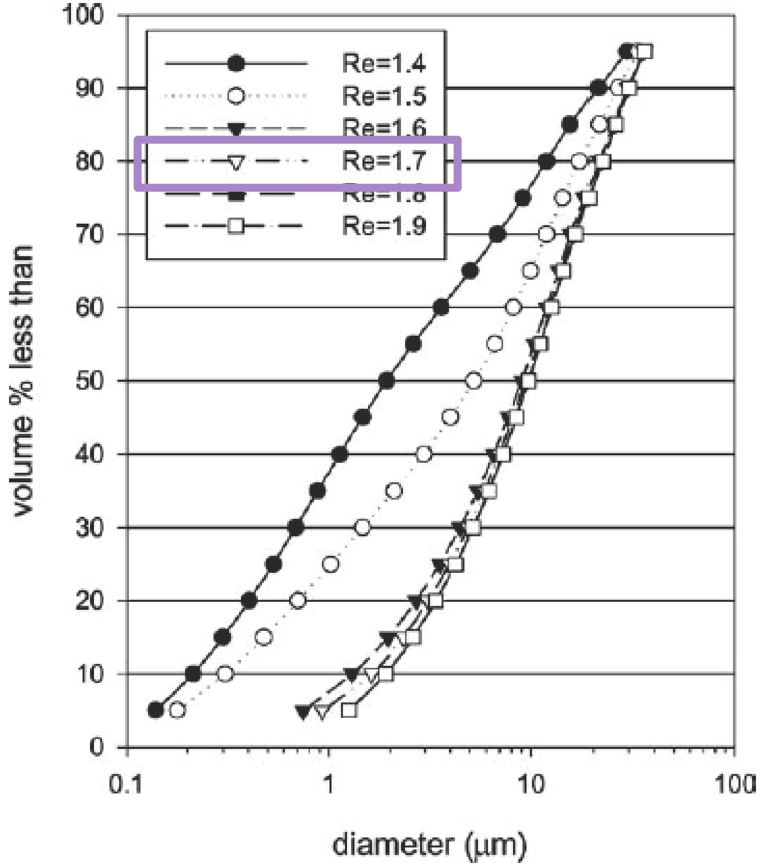
In these last two cases, the KERNEL Functions represent the following:

KERNEL 160-000rri is <u>REAL Index = 1.60</u> and <u>IMAGINARY Index = 0.00</u> or

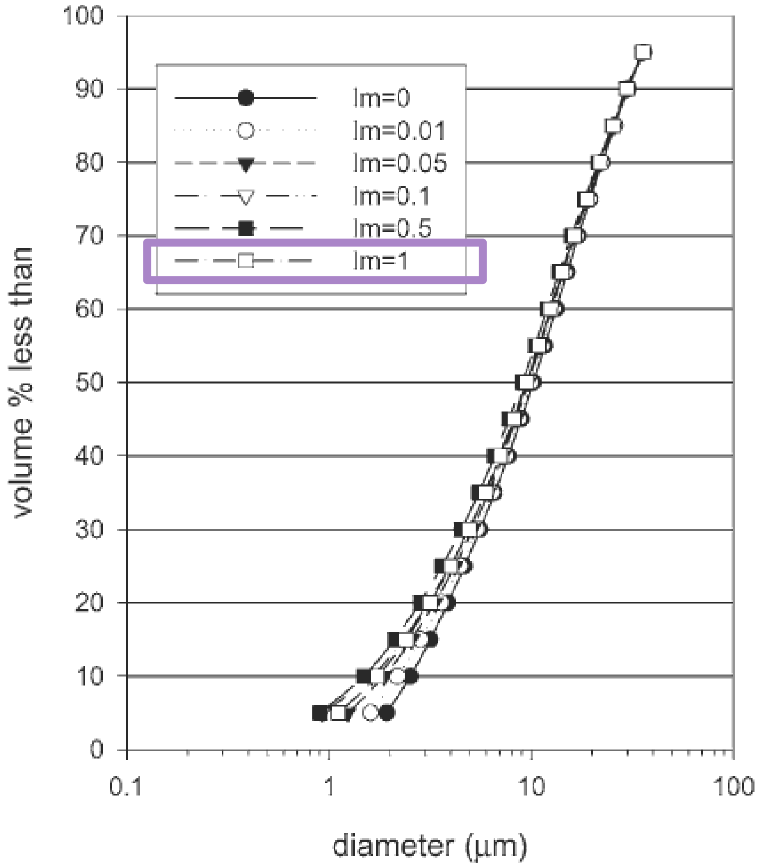
KERNEL 160-020rri is <u>REAL Index = 1.60</u> and <u>IMAGINARY Index = 0.20</u>

Effect of RI: Cement

For SRM 114q*, NIST uses 1.70 – 1.0i



Fixed absorbance, vary real



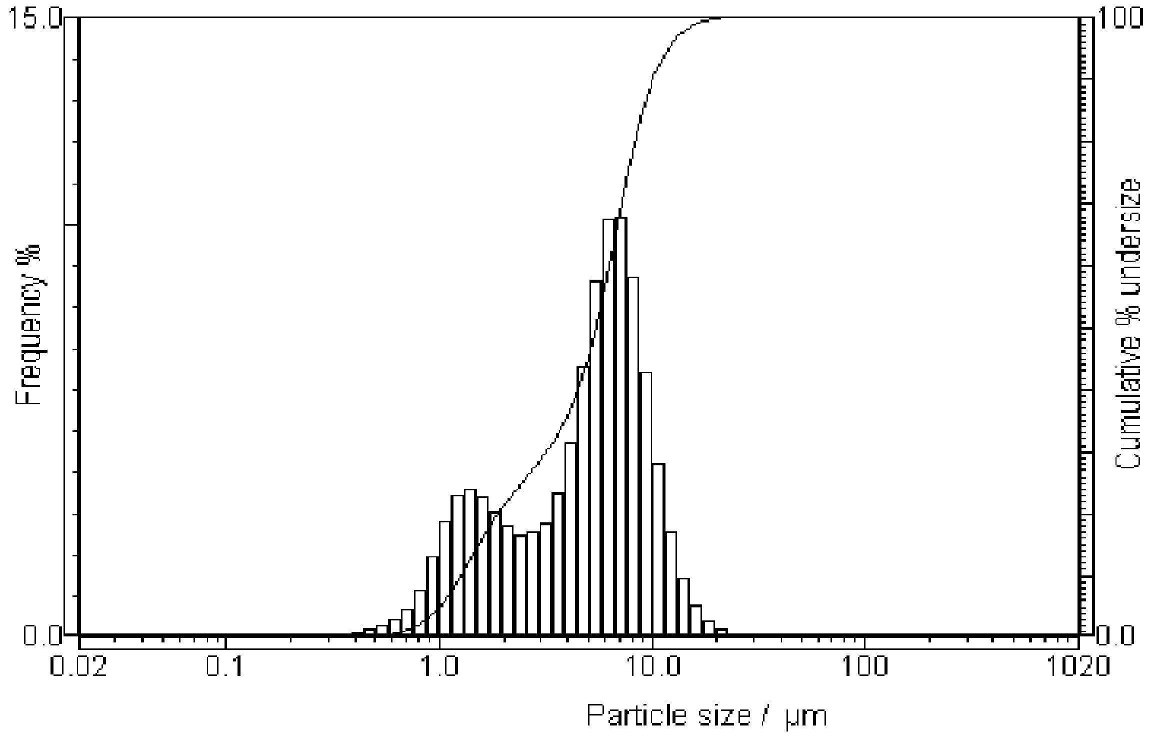
Fixed real, vary absorbance

***NIST Special Publication 260-166, "Certification of SRM 114q: Part II**
https://www.nist.gov/sites/default/files/documents/srm/SP260-166.pdf

Starch Example

STARCH SAMPLE

MODERATE IMAGINARY INDEX



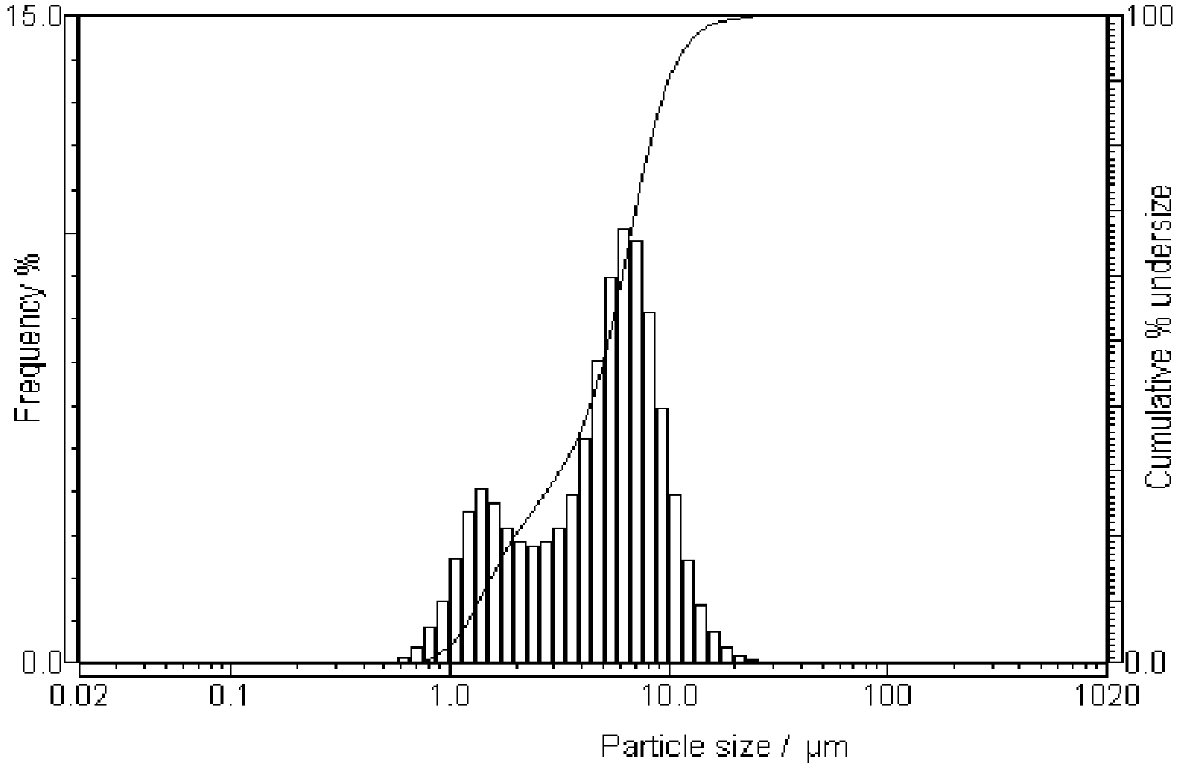
INDEX = 1.22 - 0.1i

(reasonable value for this material)

Starch Example

STARCH SAMPLE

VERY HIGH IMAGINARY INDEX



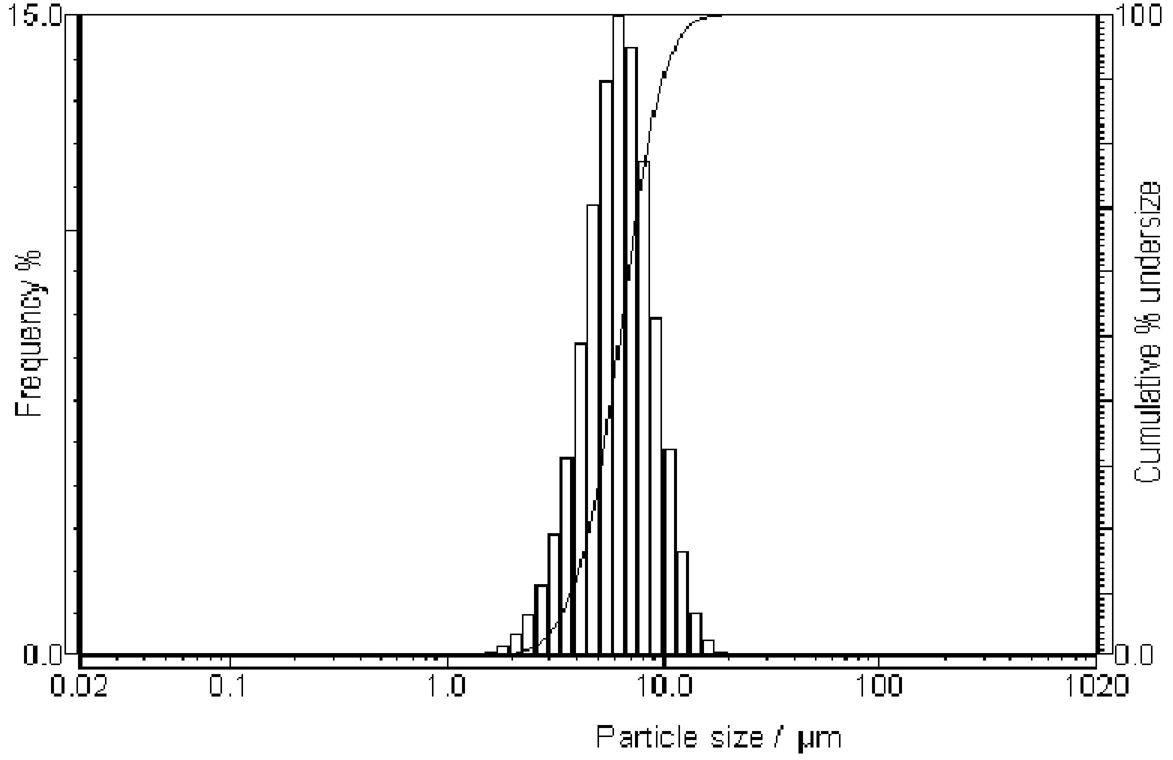
INDEX = 1.23 - 4.13i

(high value for this material)

Starch Example

STARCH SAMPLE

ZERO IMAGINARY INDEX



INDEX = 1.22 - 0.0i

(low value for this material)

Practical Approach to Refractive Index

Check if RI selection matters for your sample

OPAQUE PARTICLES….. If it is NOT transparent, non-zero imaginary component should be inserted.

NON-SPHERICAL PARTICLES…..If material is not perfectly spherical, non-zero imaginary component should be inserted.

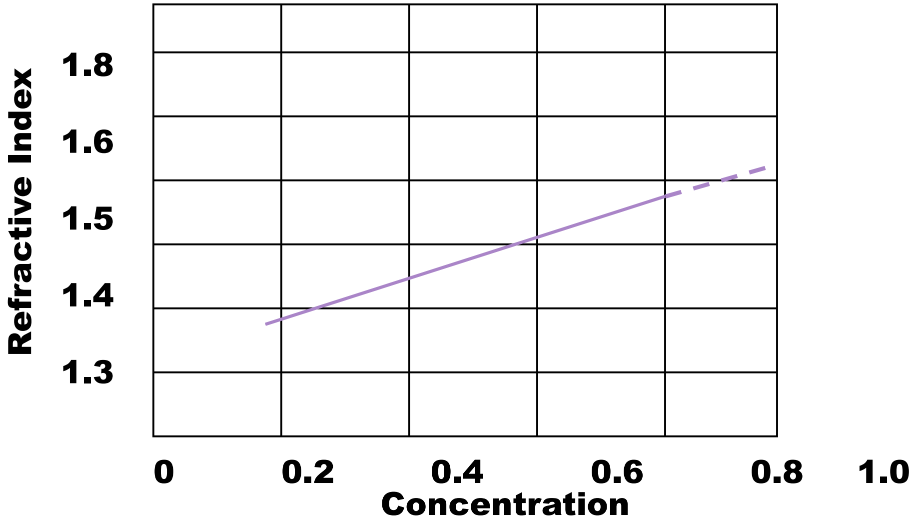
VERY LARGE PARTICLES…..Particles that are larger than ~20 microns are influenced very little by refractive index of material. High, default real index and large imaginary component should be selected.

IMAGINARY VALUE….The imaginary component is the Extinction Coefficient (k) which is a direct function of the absorption coefficient (α). If the particles are completely transparent, the value approaches zero (0). If they are opaque, the value can be very large.

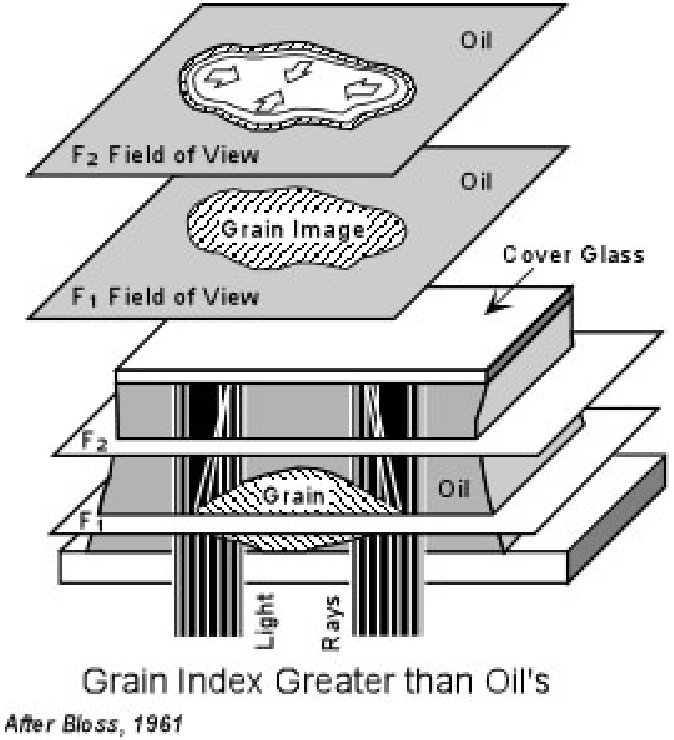
For LA-960 users: determine real component, vary imaginary component to minimize residual R value.

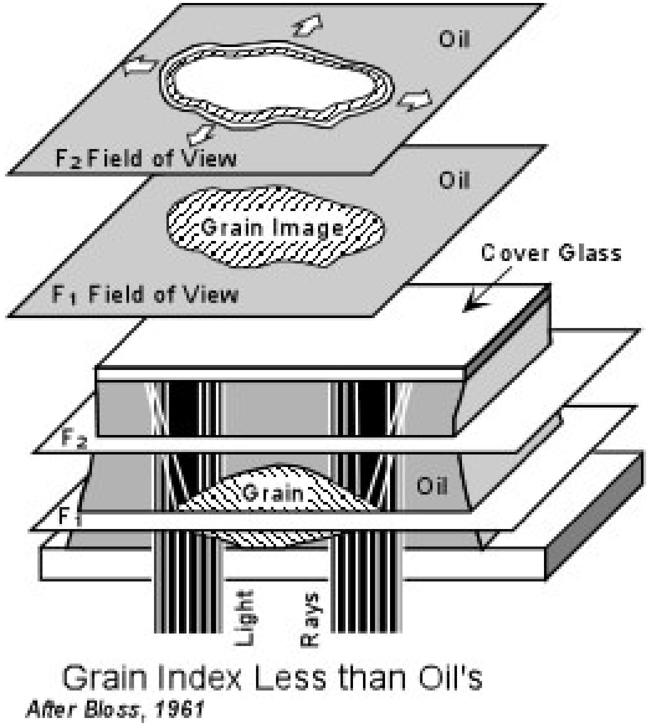
Measurement: Abbe Refractometer

- Dissolve sample at different concentrations
- Plot concentration (partial molar volume) as a function of RI
- Extrapolate to infinite concentration



Measurement: Becke Lines

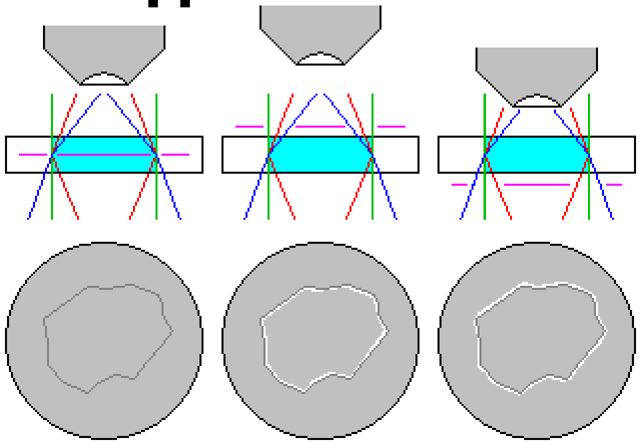




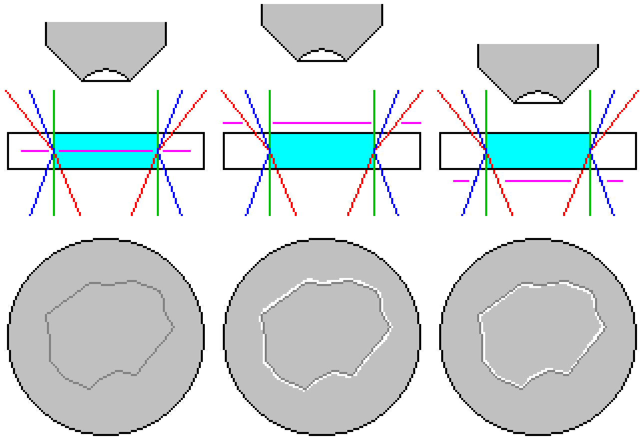
Bright line is called the *Becke line* and will always occur closest to the substance with a higher refractive index

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



A grain 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.

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Info Source: Luxpop.com

Index of Refraction

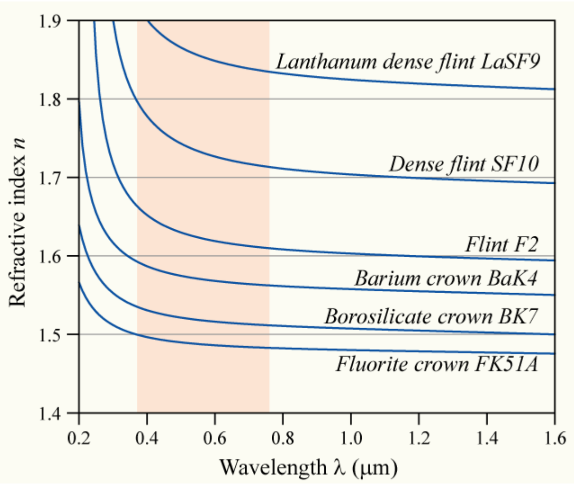
- Return the refractive index of a substance at a given wavelength, λ (nm). Further information in addition to the index of refraction also may be given.
- Luxpop returns the absolute refractive index (i.e. with resp. to vacuum), unless stated otherwise. Click here for more index of refraction terminology.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

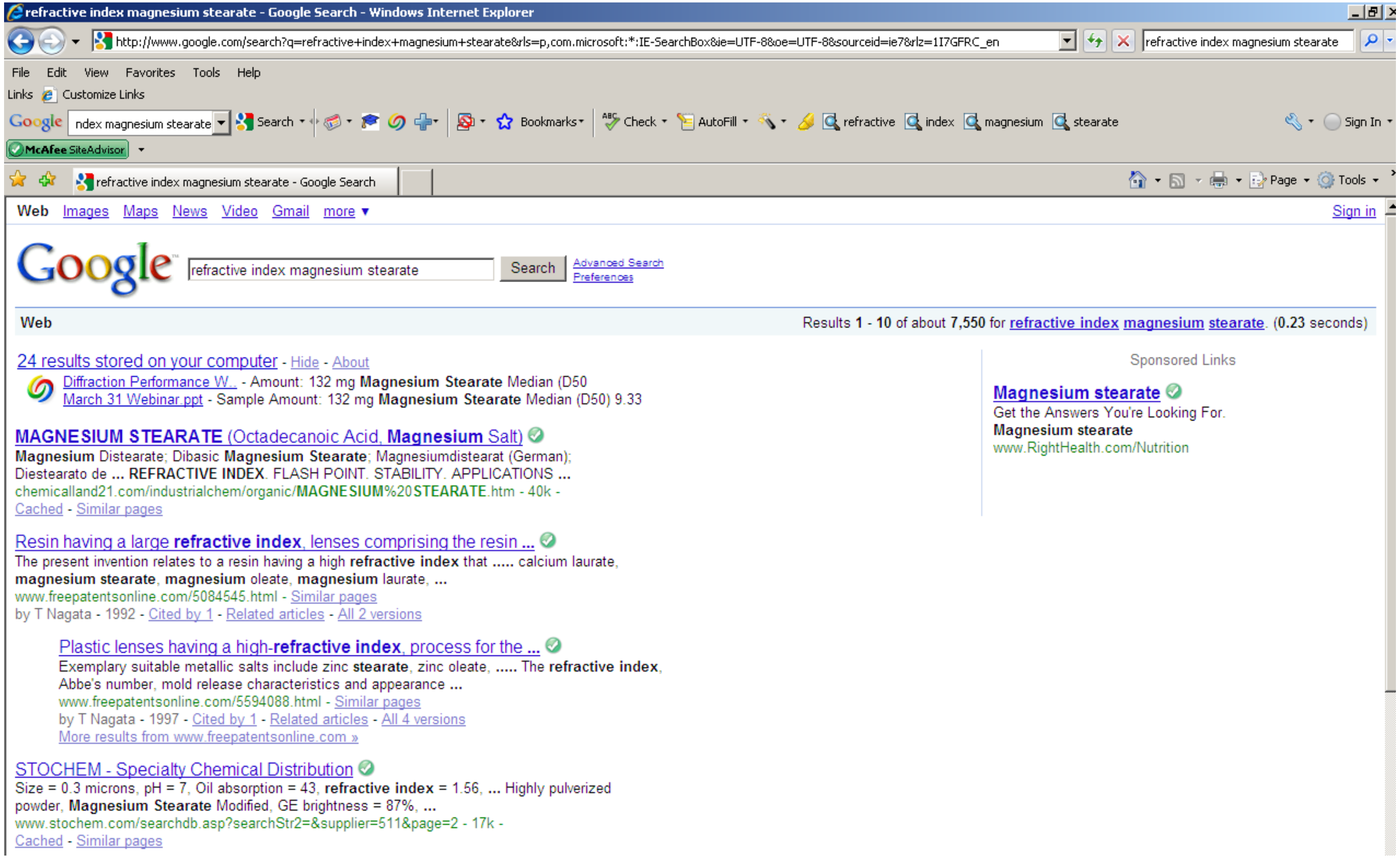
At a wavelength of 650 nm (1.908 eV), the index of refraction of ZnO is
n = 1.98, k = 0.000.

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.



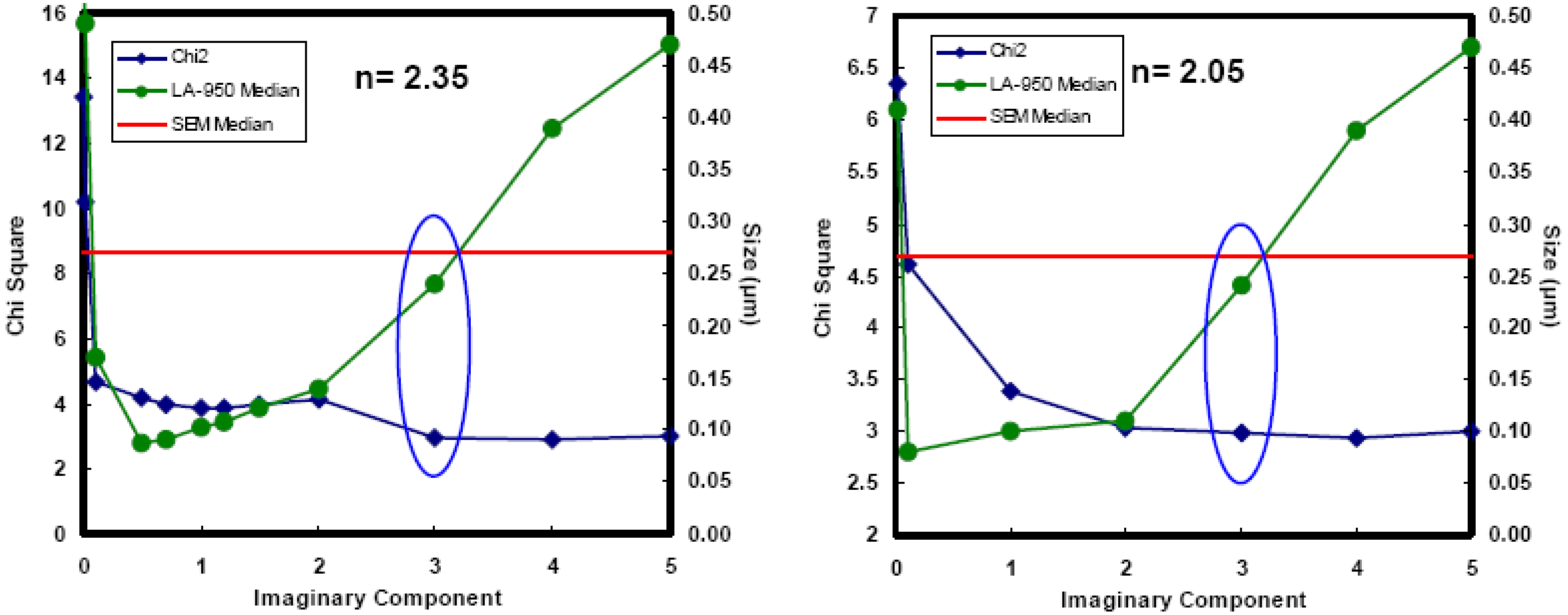
Info Search: Google Search



What about Mixtures?

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

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



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

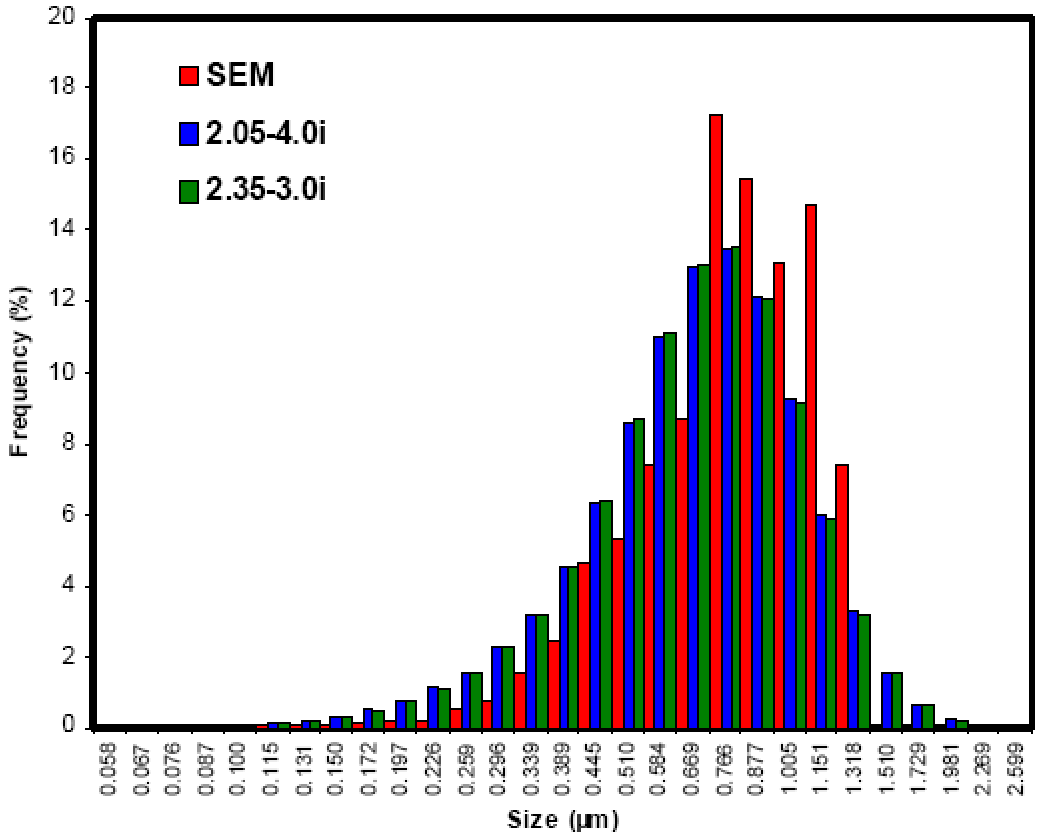


Table 1

	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

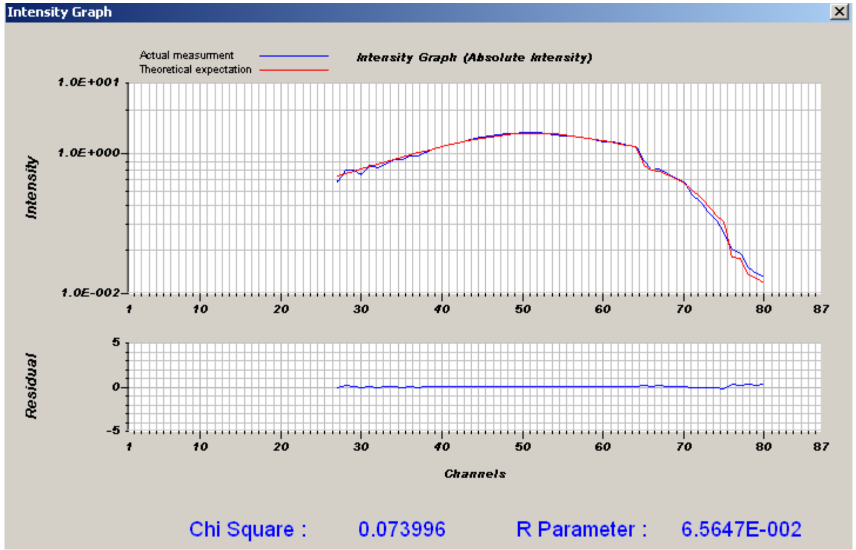
Chi Square and R Parameter

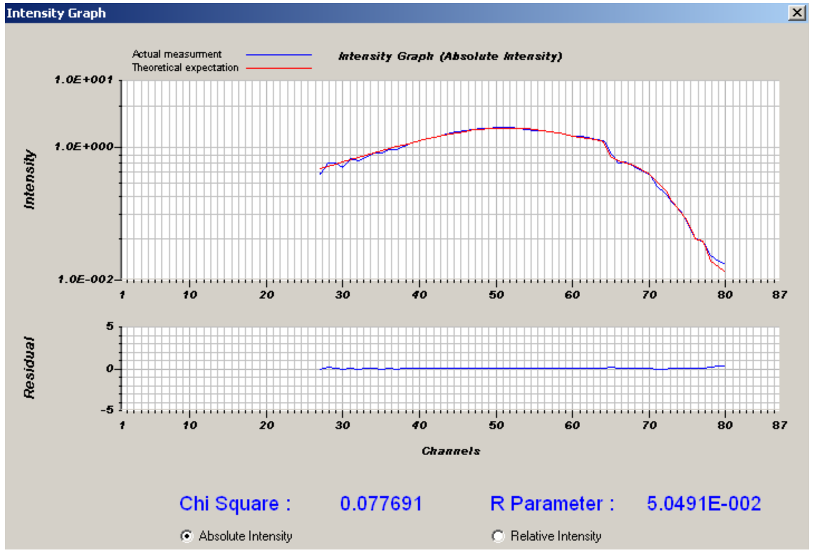
$$\chi^2 = \sum \left\{ \frac{1}{\sigma_i^{\,2}} [y_i - y(x_i)]^2 \right\}$$

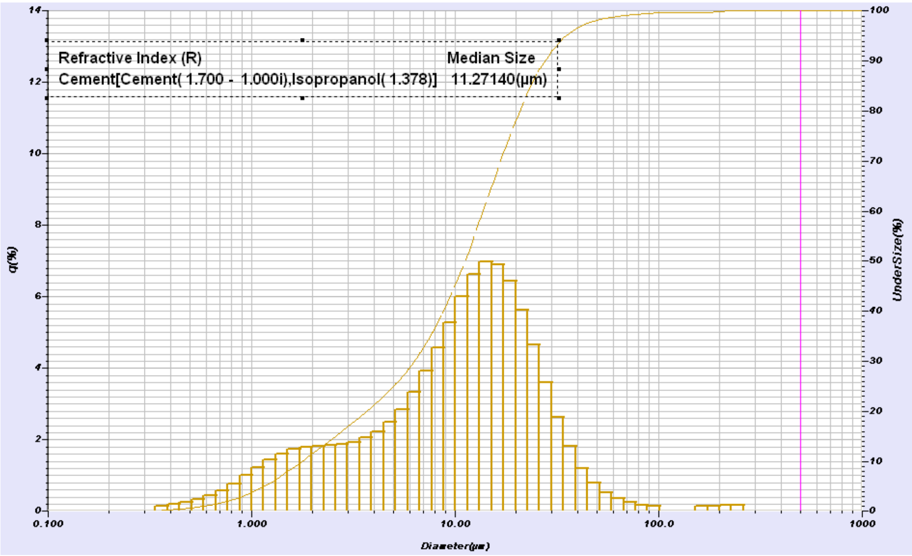
$$R = \frac{1}{N} \sum_{i=1}^{N} \left\{ \frac{1}{y_{(x_i)}} \left| y_i - y(x_i) \right| \right\}$$

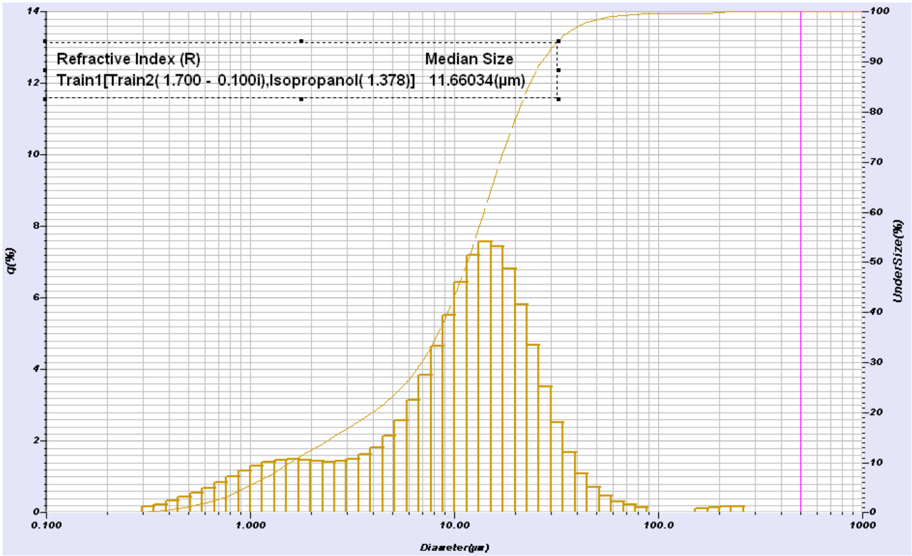
y_i The measured scattered light at each channel (i) of the detector.
$y(x_i)$ The calculated scattered light at each channel (i) of the detector based on the chosen refractive index kernel and reported particle size distribution.
σ_i The standard deviation of the scattered light intensity at each channel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

Using R Value for i



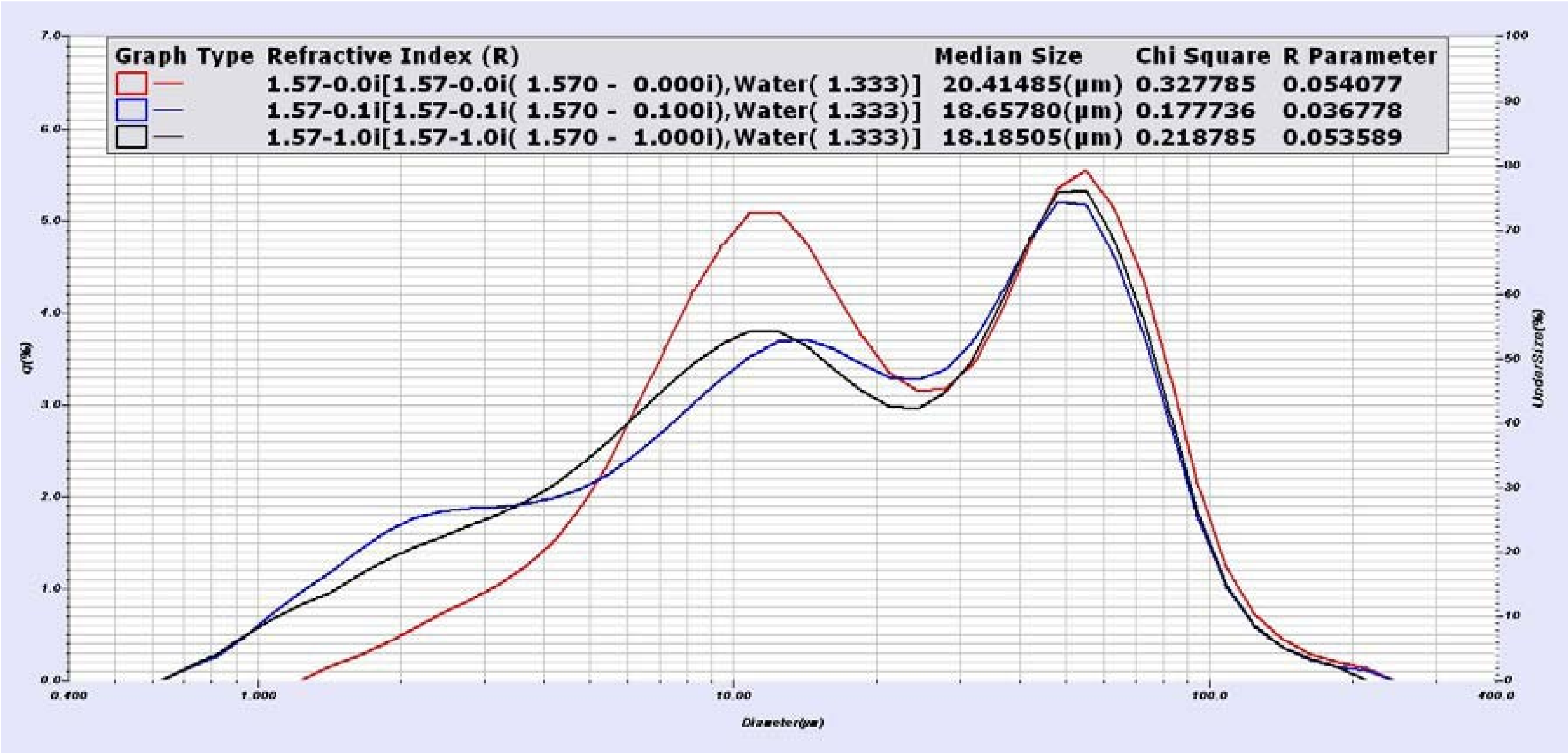






Using R Value for i

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



Automation by Method Expert

Analytical conditions

Circulation Pump Speed

Circulation Pump Speed

Particle Concentration

Particle Concentration

Ultrasonic Treatment

Ultrasonic Treatment

Measurement Duration

Measurement Duration

Calculation conditions

Real Refractive Index Wizard

Real Refractive Index Wizard

Imaginary Refractive Index Wizard

Imaginary Refractive Index Wizard

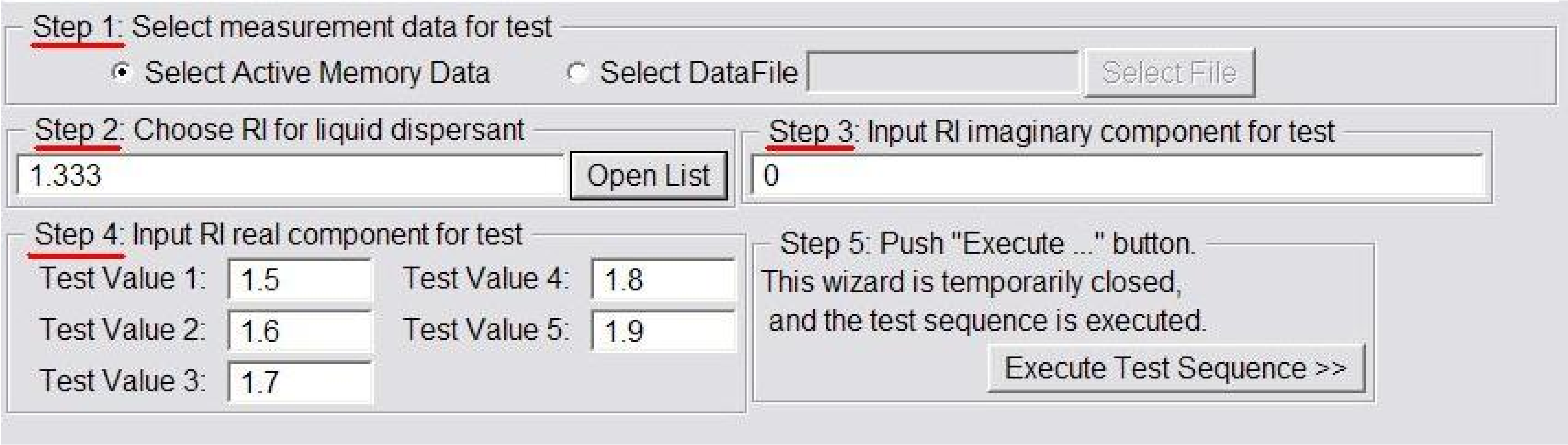
Automated RI Computation

Real part study

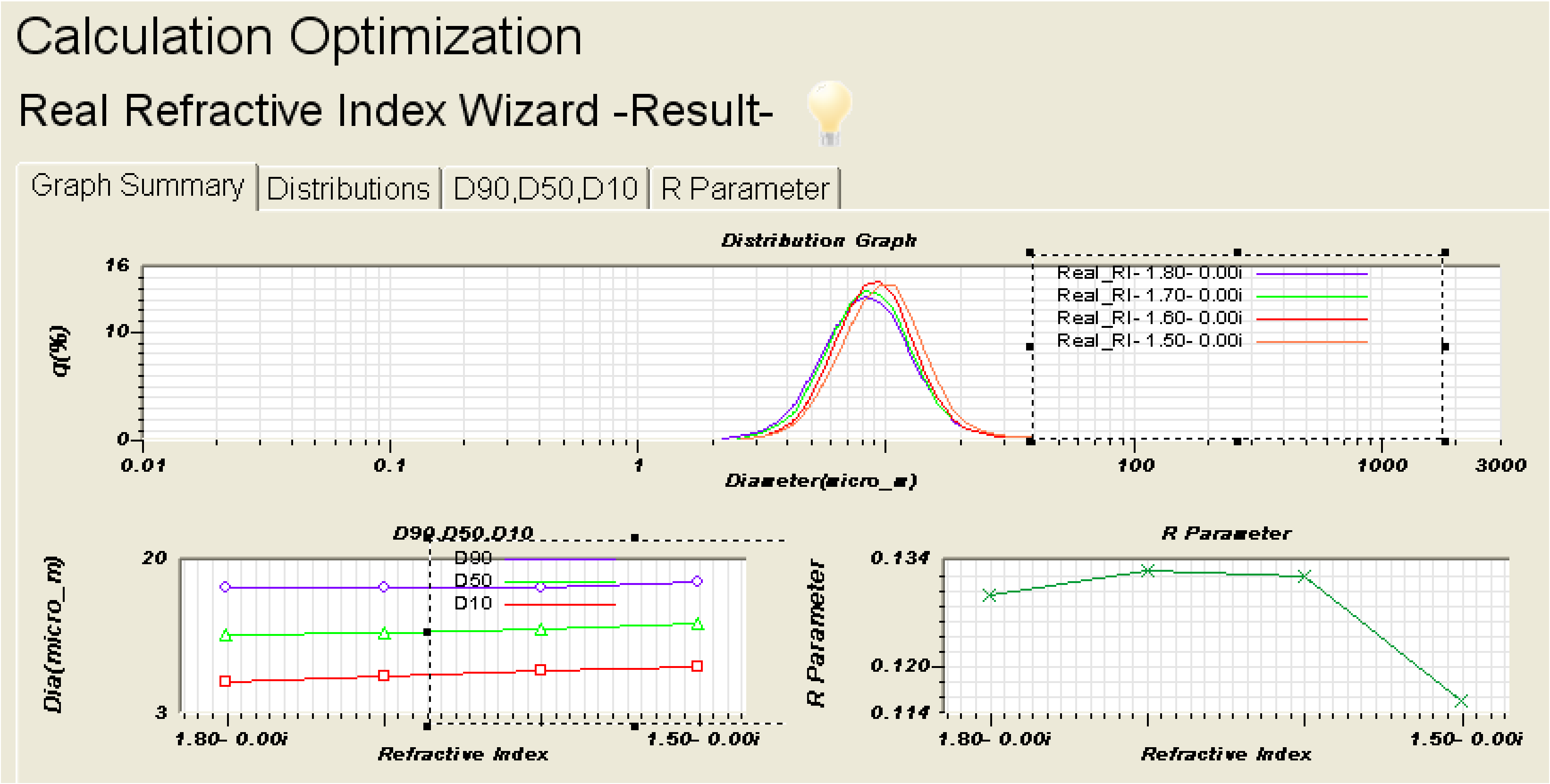
Need to fix imaginary part

Set up to 5 real parts

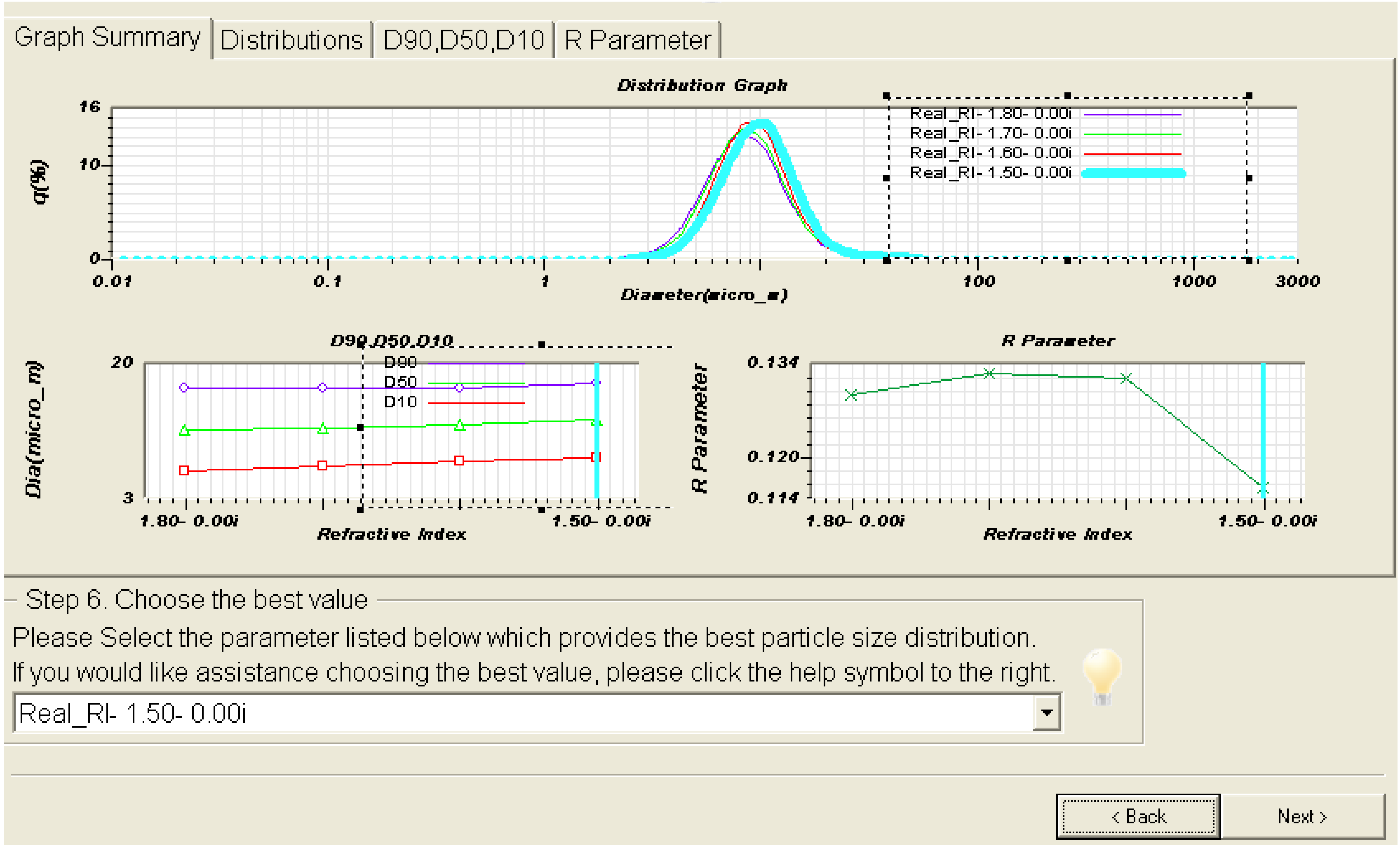
Software will compute all RI and display R parameter variation with RI selection



Automated RI Computation

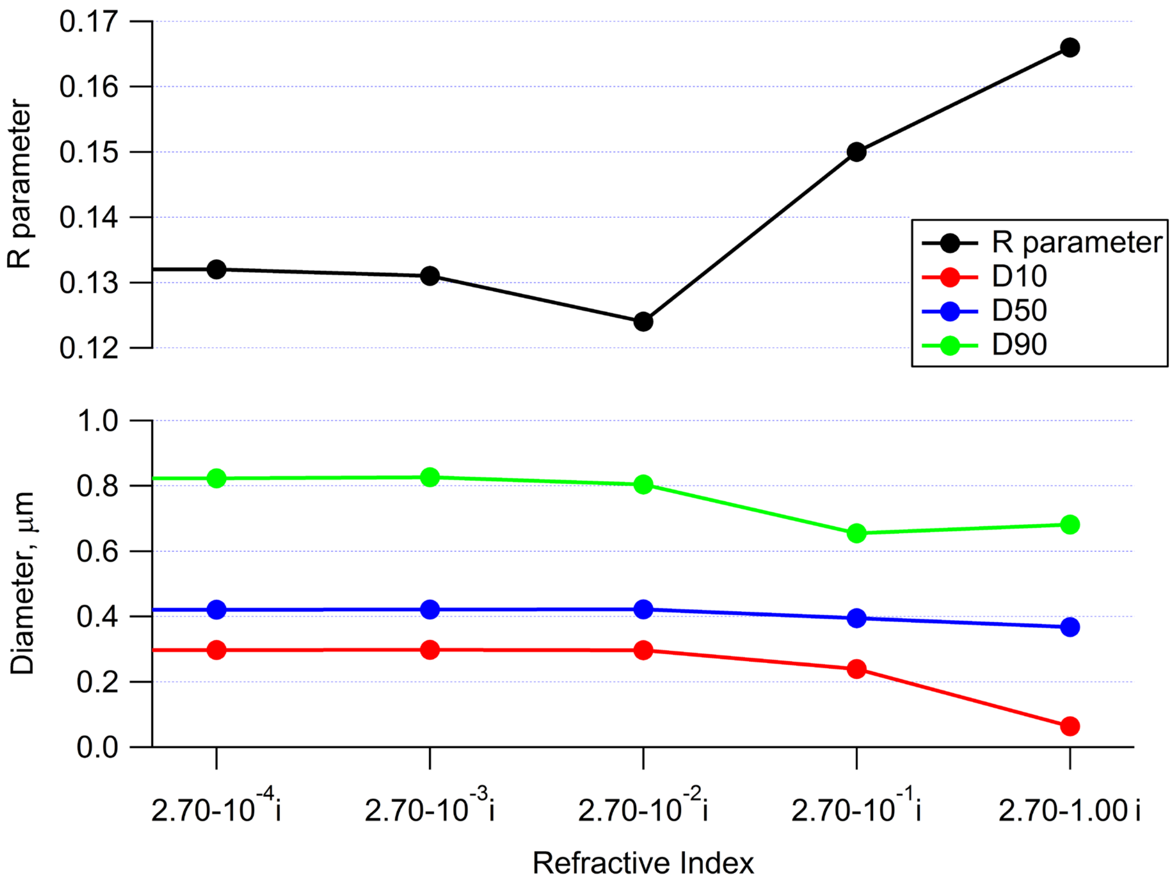


Automated RI Computation

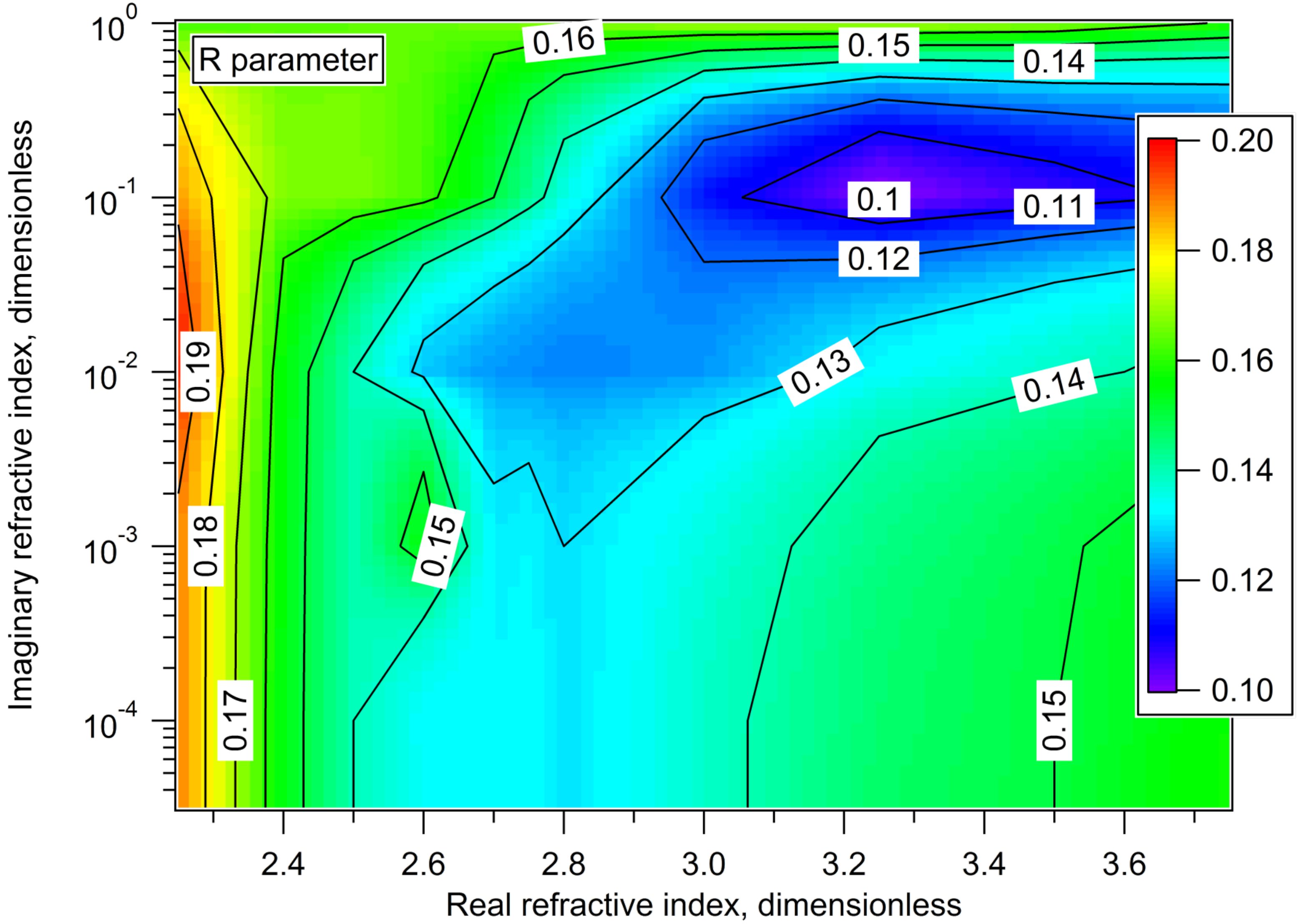


Study on TiO_2

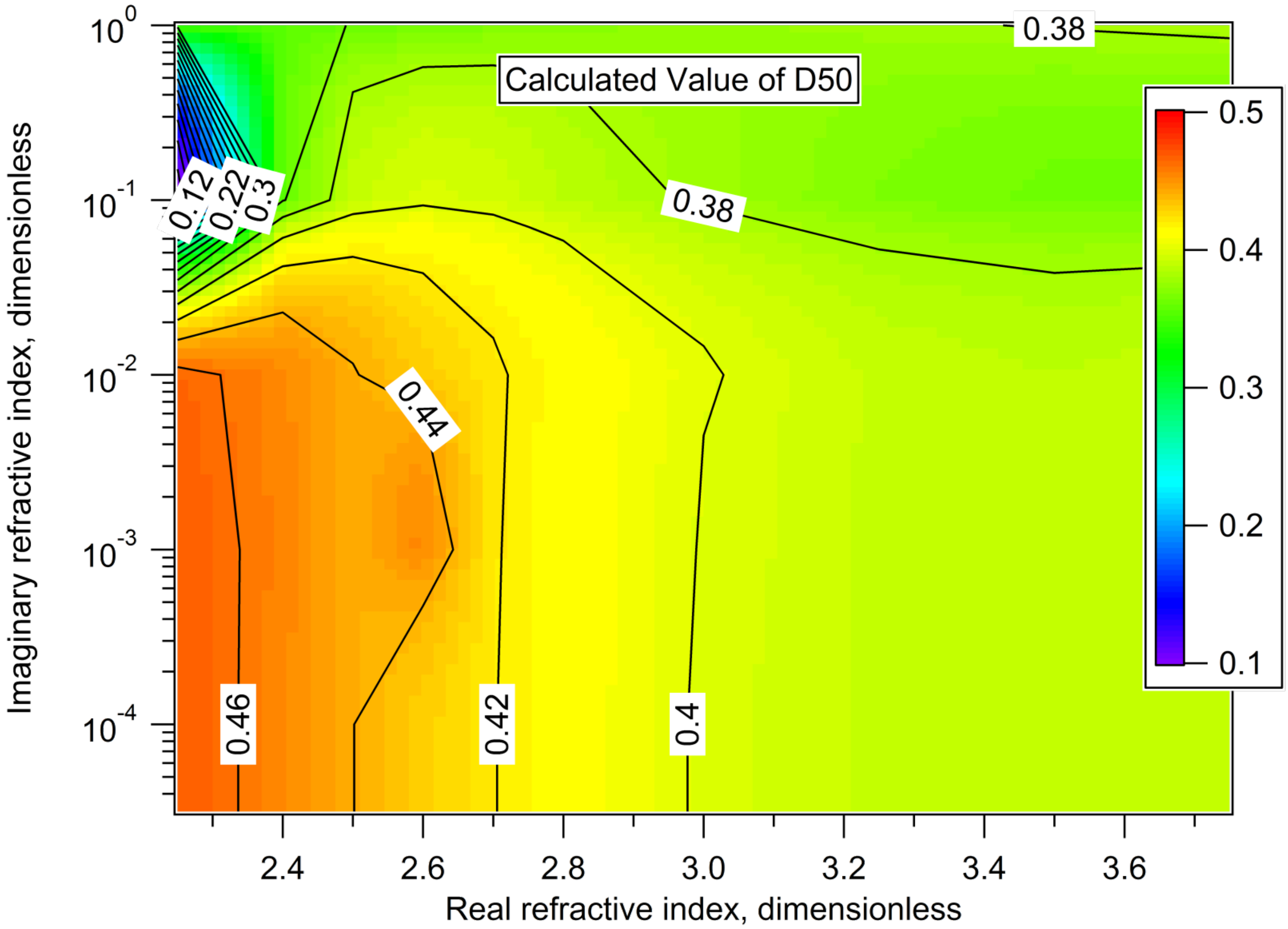
Look up real refractive index, use R parameter to find imaginary.



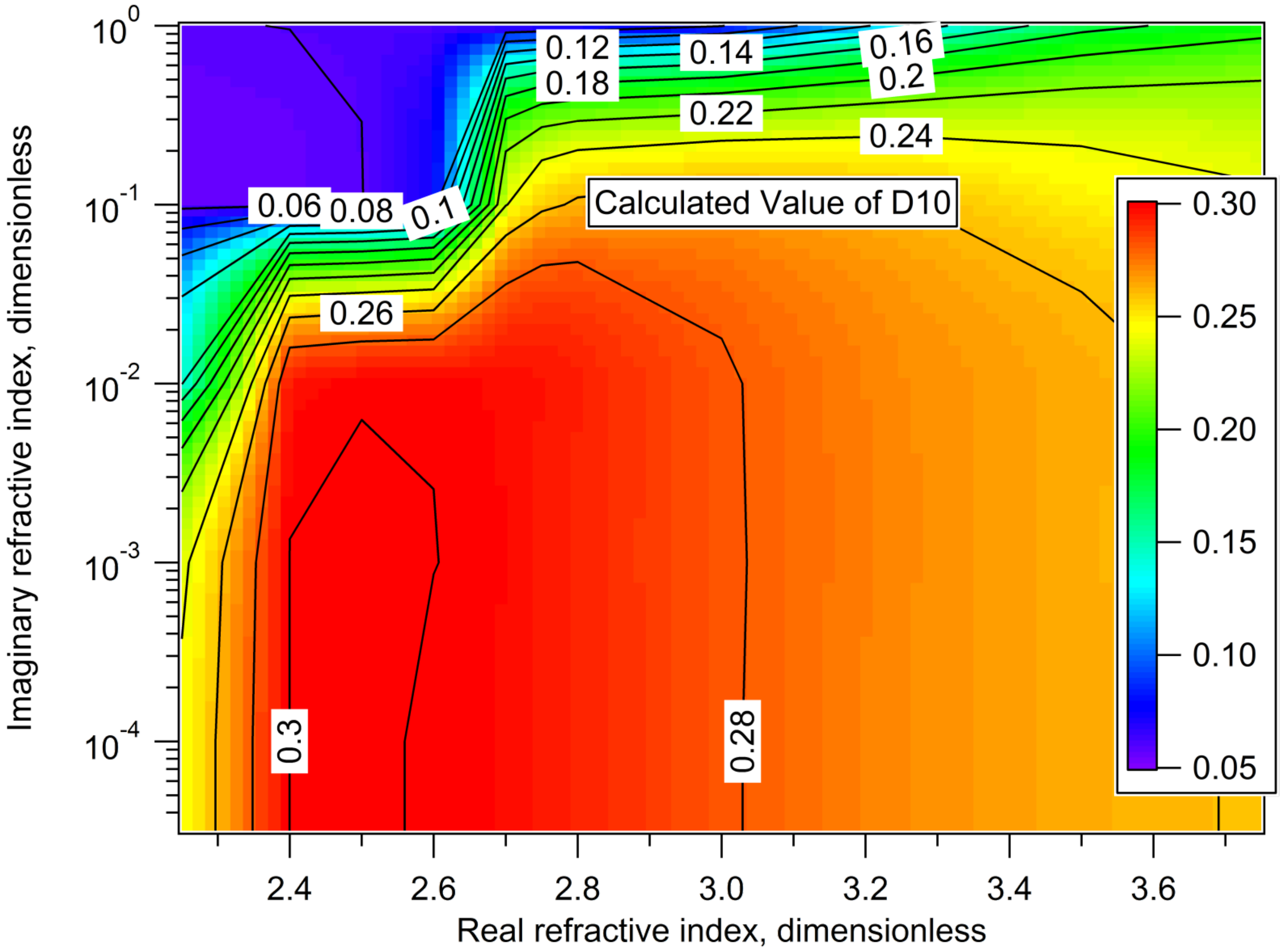
Effect of RI on R parameter



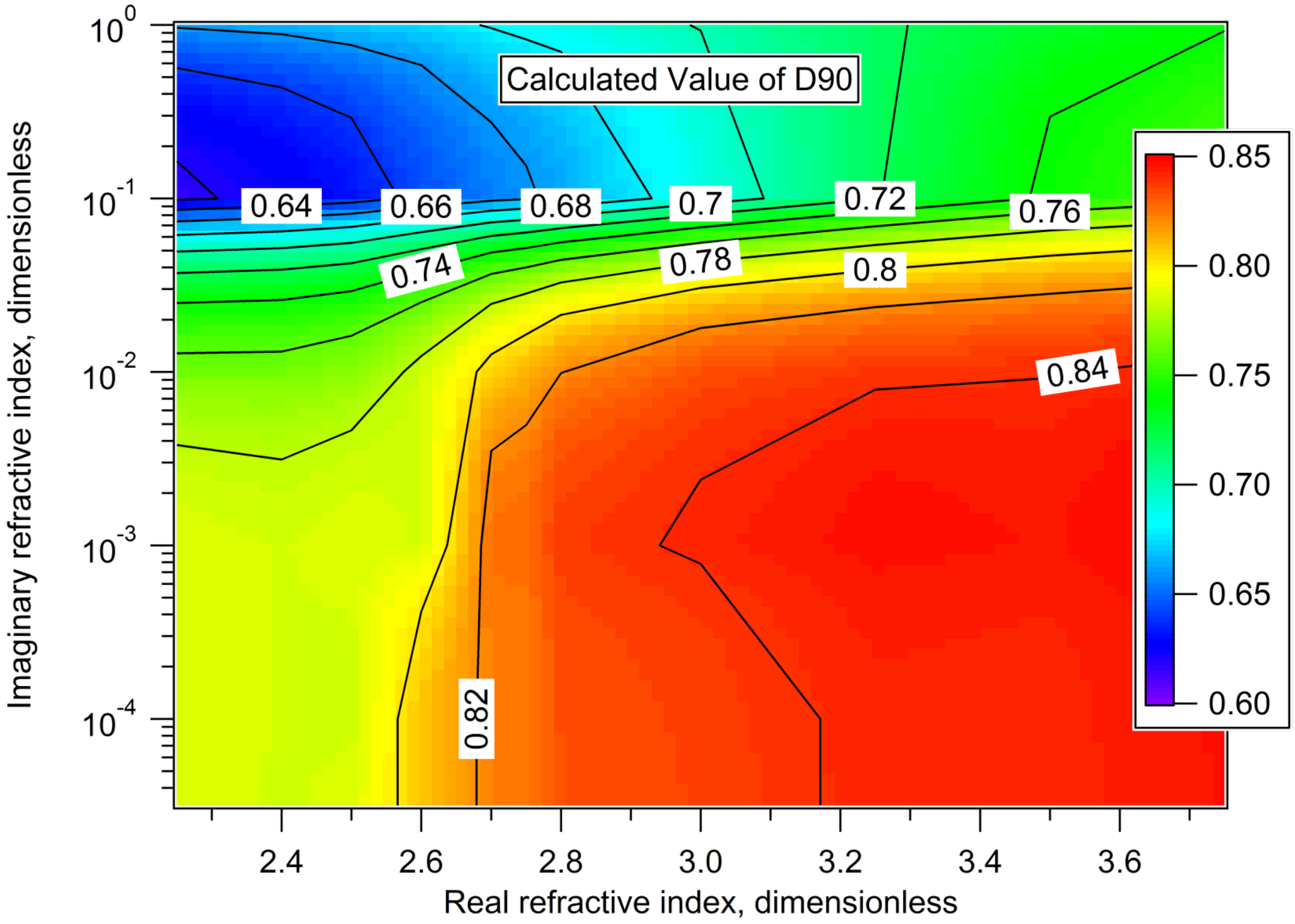
Effect of RI on measured D_{50}



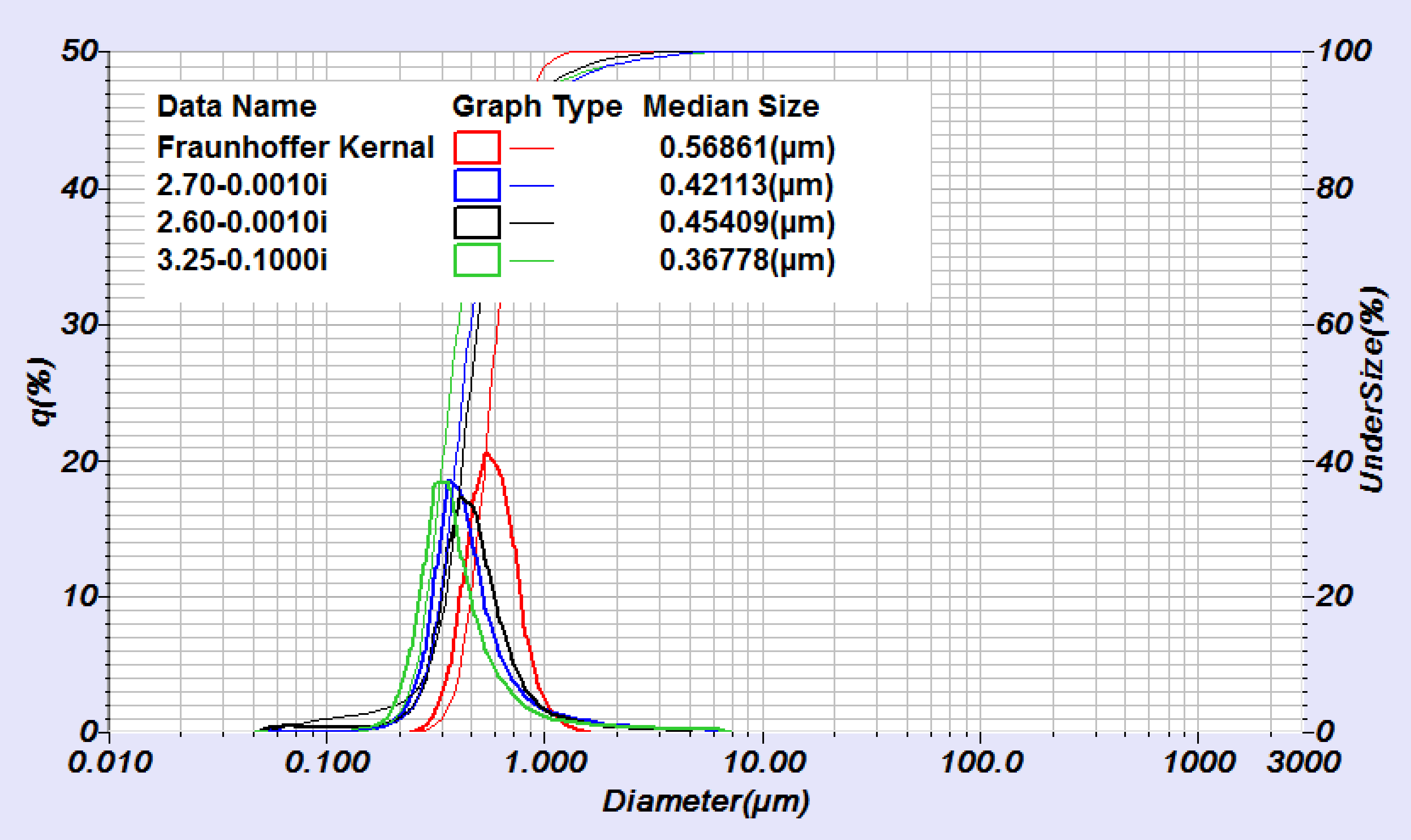
Effect of RI on measured D_{10}



Effect of RI on measured D_{90}



Results

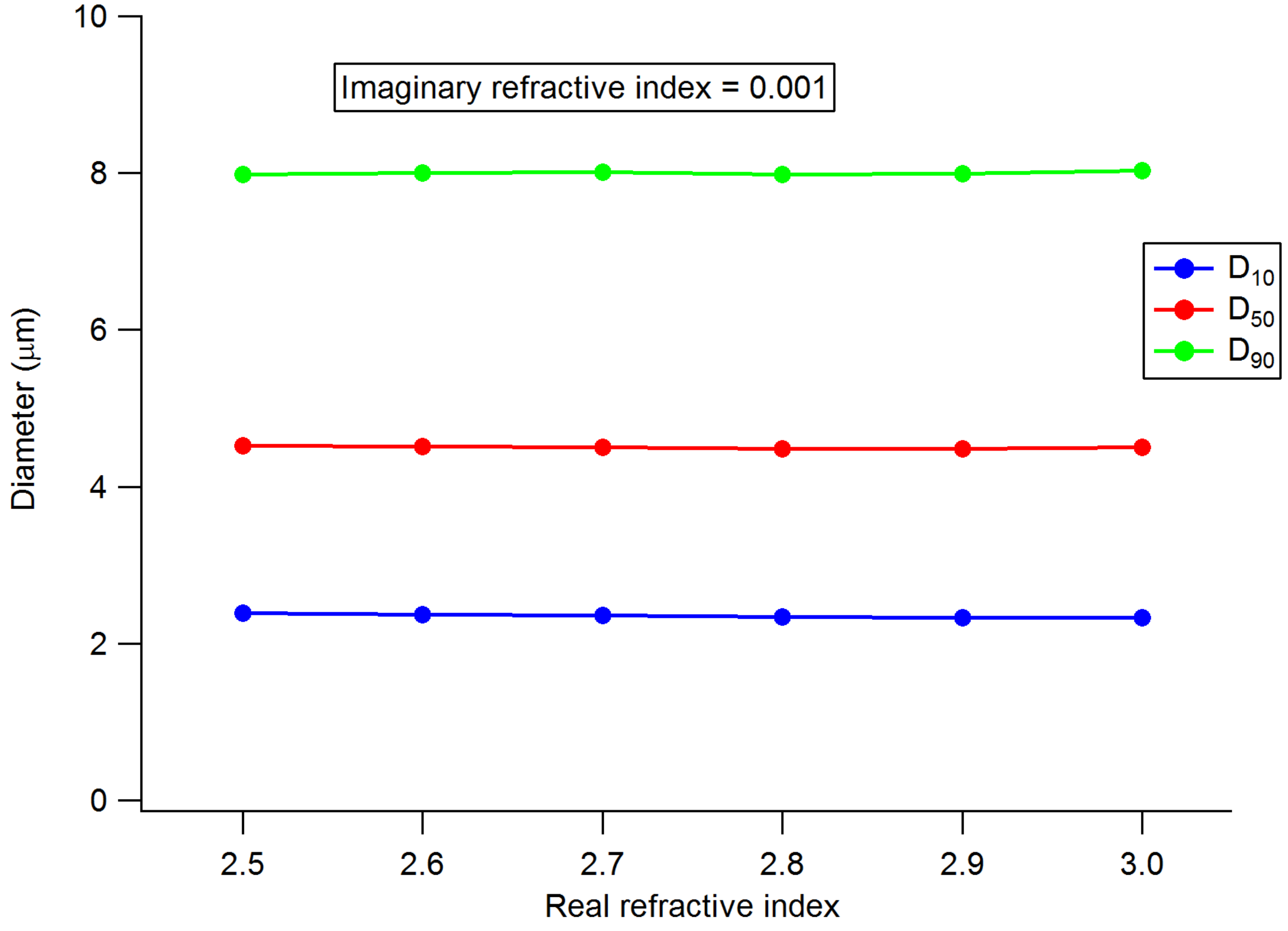


50
40
30
20
10
0
q(%)
100
80
60
40
20
0
UnderSize(%)
0.010
0.100
1.000
10.00
100.0
1000
3000
Diameter(μm)
Data Name
Graph Type
Median Size
Fraunhoffer Kernal
0.56861(μm)
2.70-0.0010i
0.42113(μm)
2.60-0.0010i
0.45409(μm)
3.25-0.1000i
0.36778(μm)

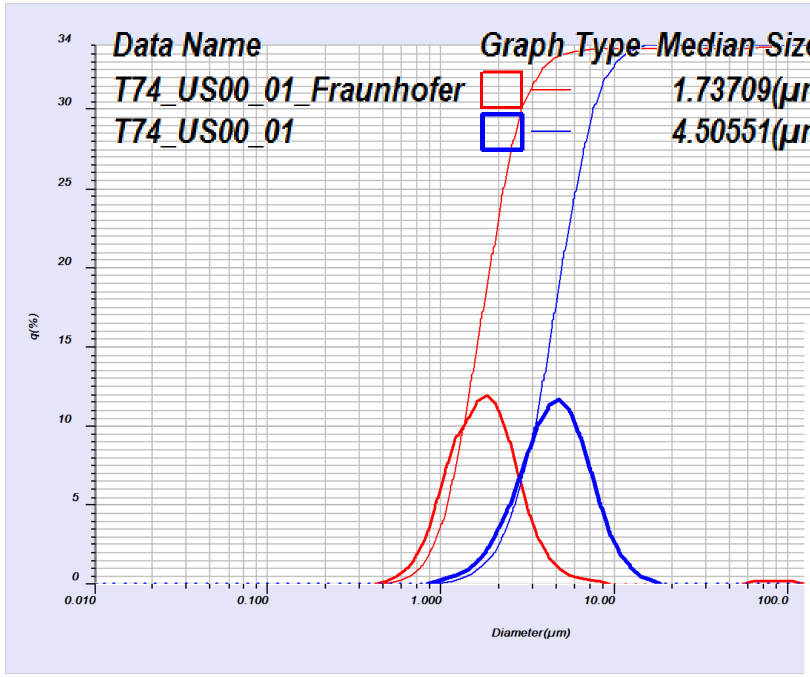
Results

Refractive index calculation approach	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%

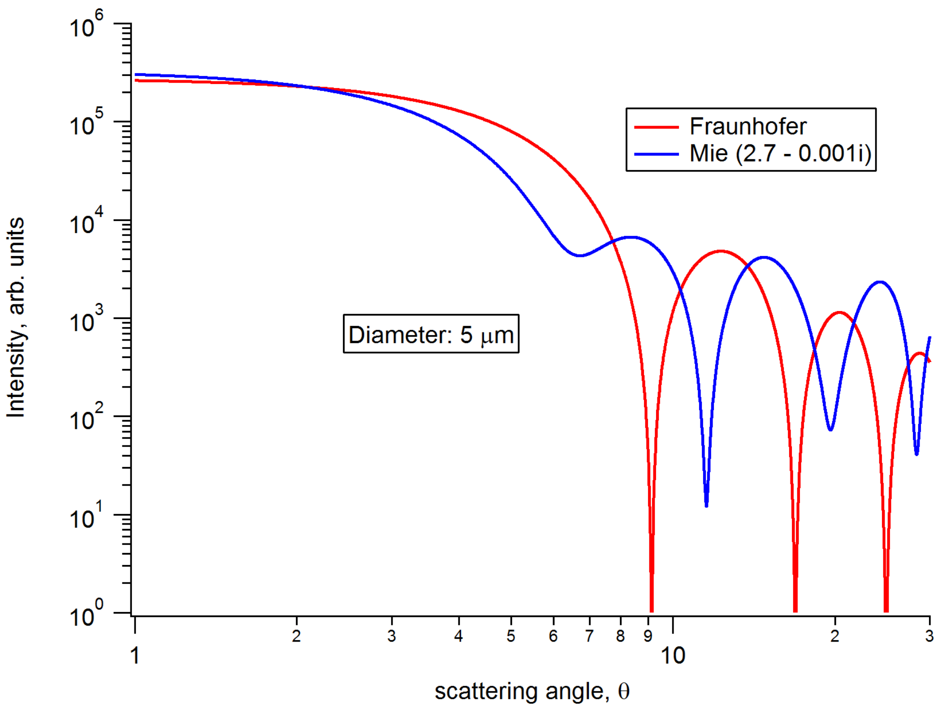
5 micron TiO_2, Effect of RI



Mie and Fraunhofer are different



Calculated Scattering



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.

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

Thank-you

Thank you

Omoshiro-okashiku

Joy and Fun

Thank you

감사합니다

Cảm ơn

ありがとうこざいました

Dziękuję

धन्यवाद

Grazie

Merci

谢谢

நன்றி

ขอบคุณครับ

Obrigado

Σας ευχαριστώ πάρα πολύ.

شُكْرا

Tack ska du ha

Большое спасибо

Danke

Gracias