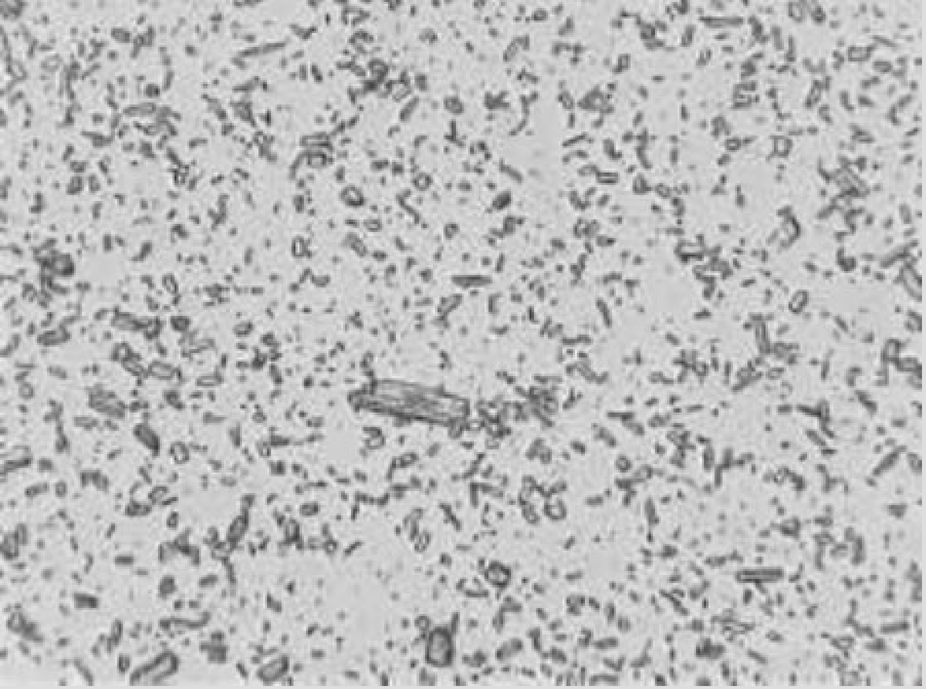
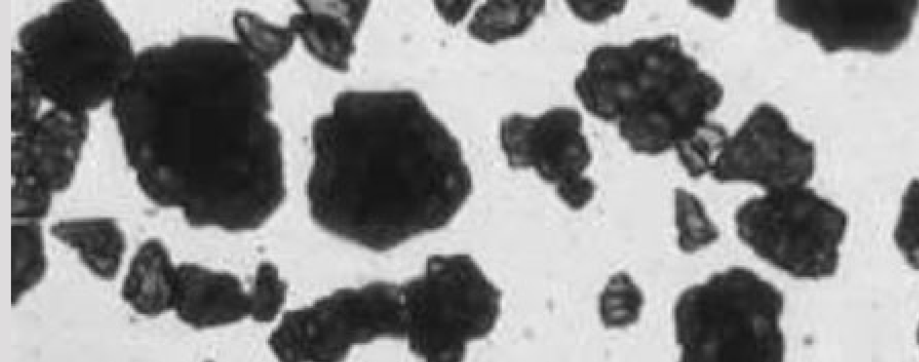
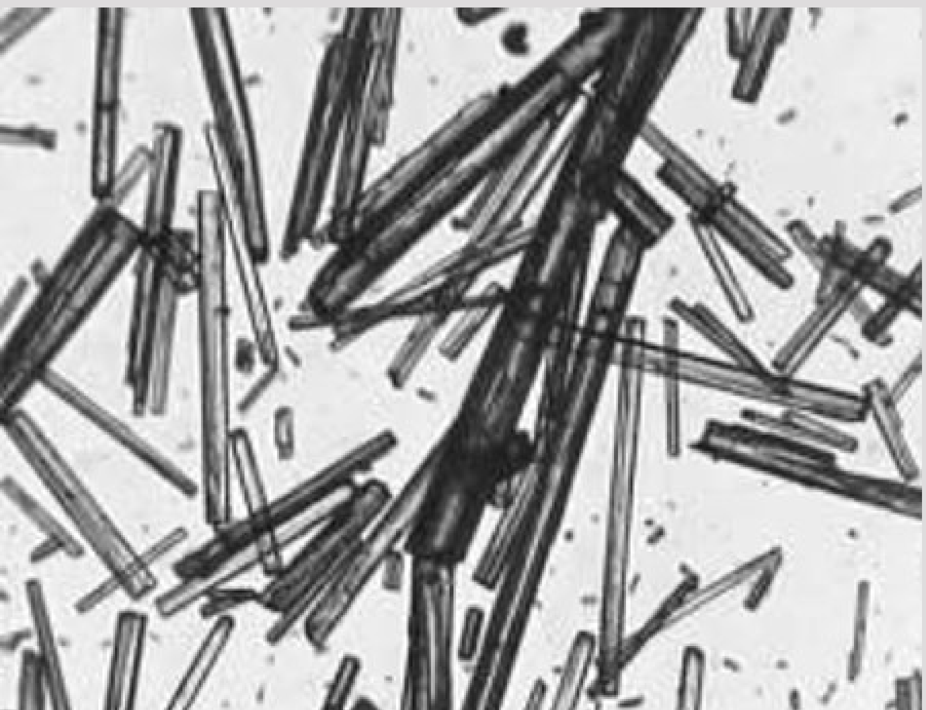
Mastersizer 3000 Customer Training Course

Part 1: Basic Principles and Data Quality



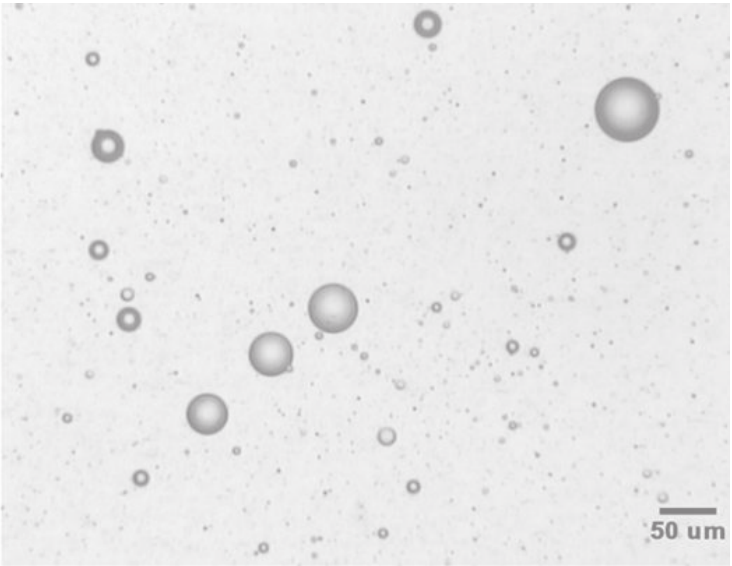


Basic concepts of particle size



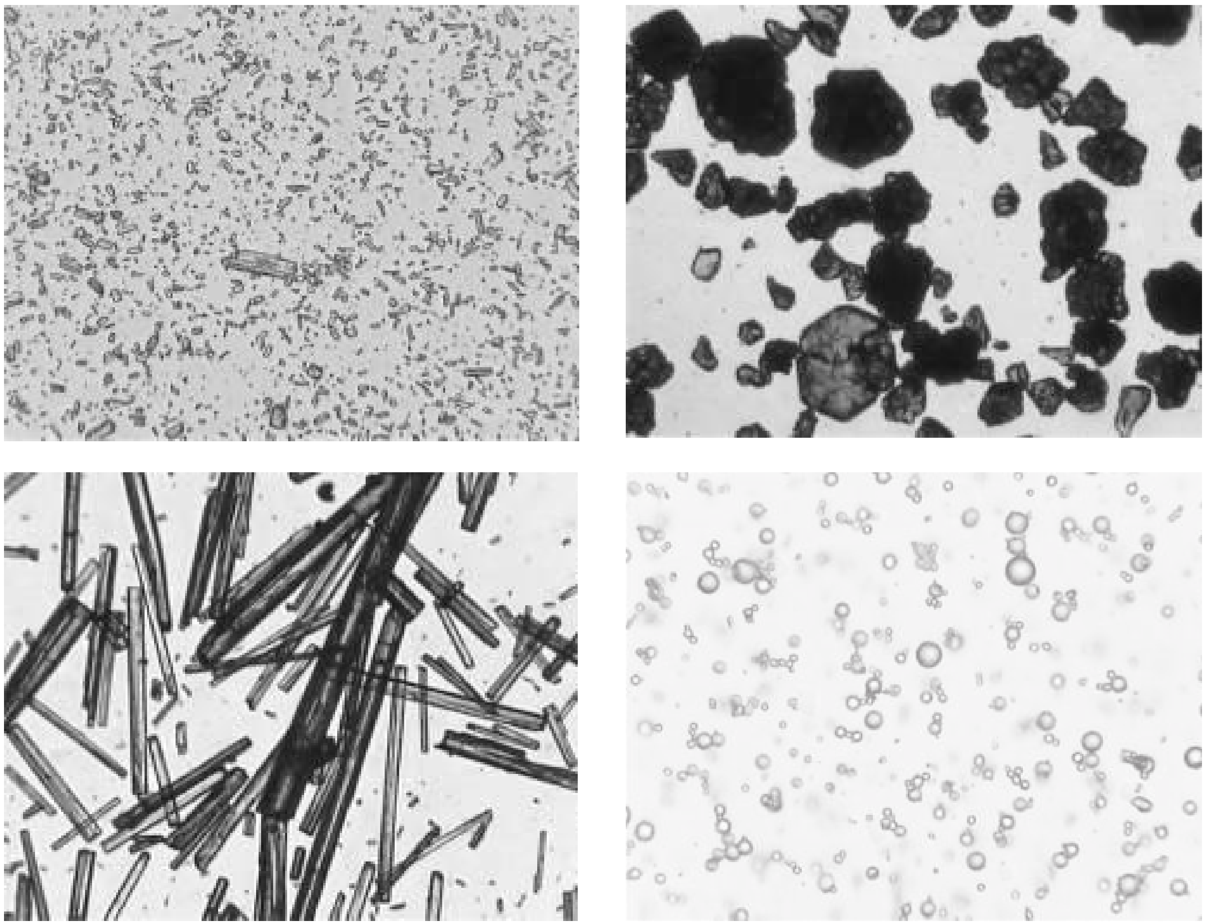
What do we mean by a particle?

- A particle can be described as a discrete sub-portion of a substance, e.g.
  - solid particles
  - gas bubbles
  - or liquid droplets



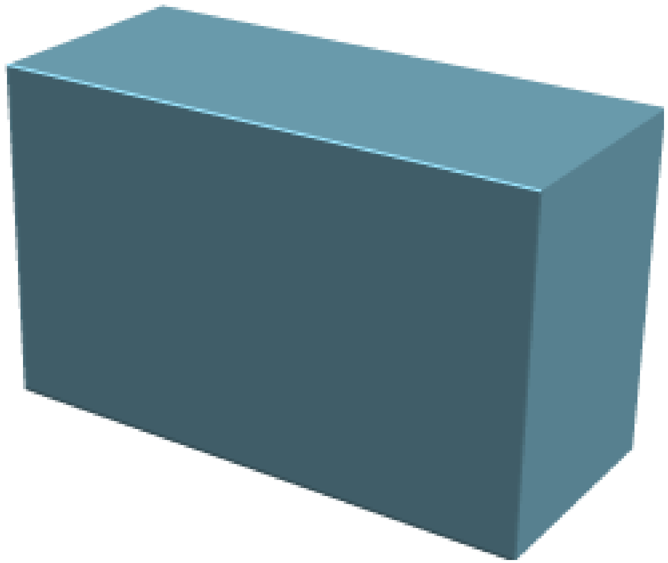
- Laser diffraction measures particles in the size range from nanometres to millimetres

Particles come in many different shapes (as well as sizes)



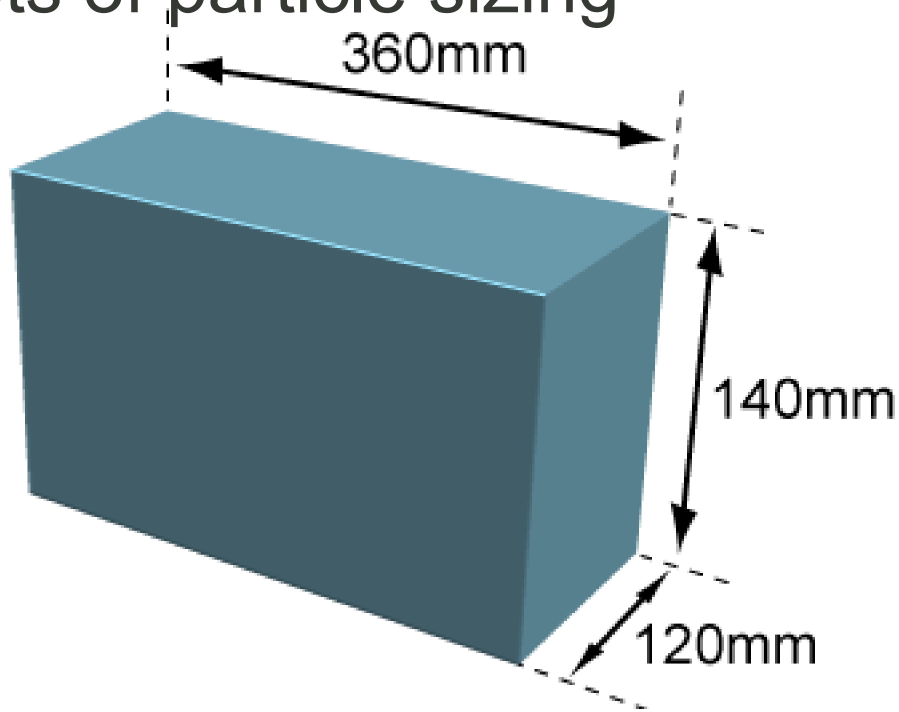
- How do we describe the size of these particles?

Basic concepts of particle sizing



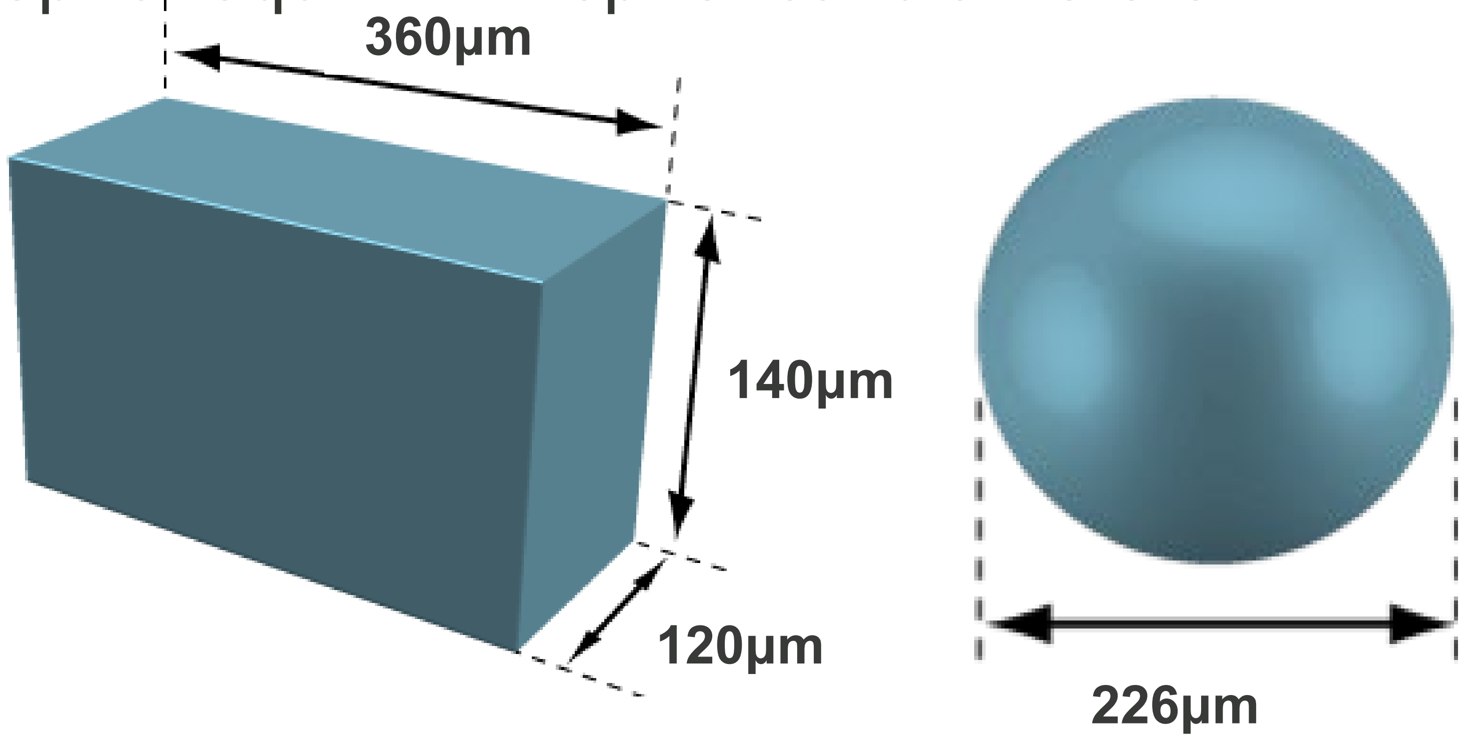
- You are given a regular-shaped object and a ruler and asked to give a one-number indication of its size
- What would your reply be ?

Basic concepts of particle sizing



- You may reply: “360x140x120mm”
  - Which might be correct but it is not **one** number.
  - It is not possible to describe the size of this 3-dimensional object with a single number

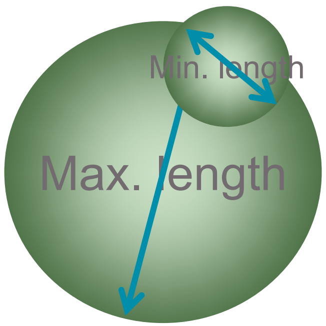
Concept of equivalent spherical diameters

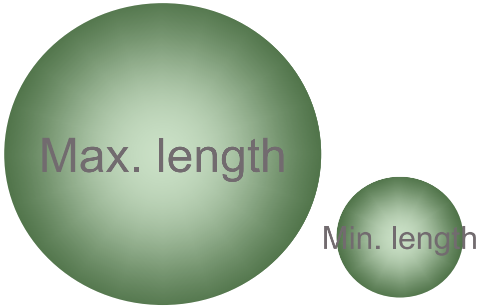


- The rectangular box has the same volume as a sphere of 226µm diameter.
  - The volume equivalent spherical diameter is 226µm

How do we describe the size of these particles

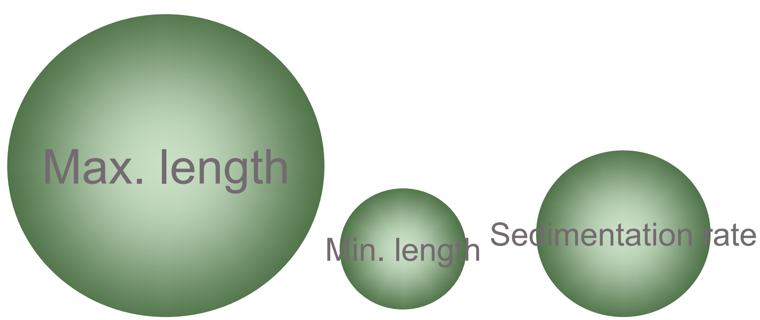
- Equivalent spheres
  - Maximum length
  - Minimum length





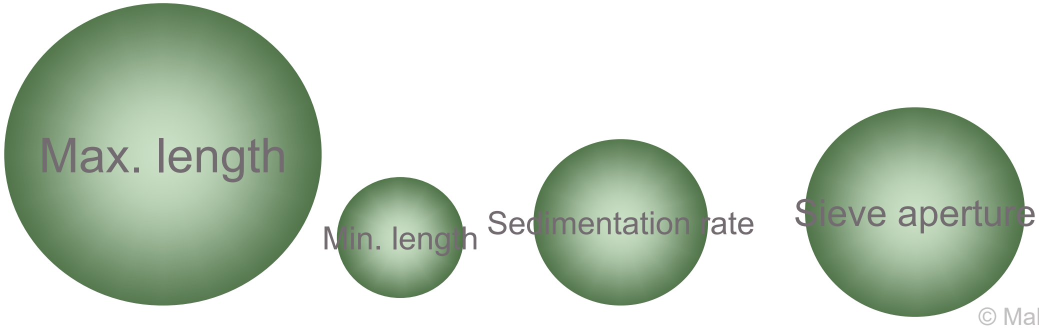
How do we describe the size of these particles

- Equivalent spheres
  - Maximum length
  - Minimum length
  - Sedimentation rate



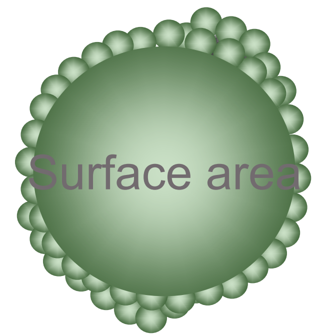
How do we describe the size of these particles

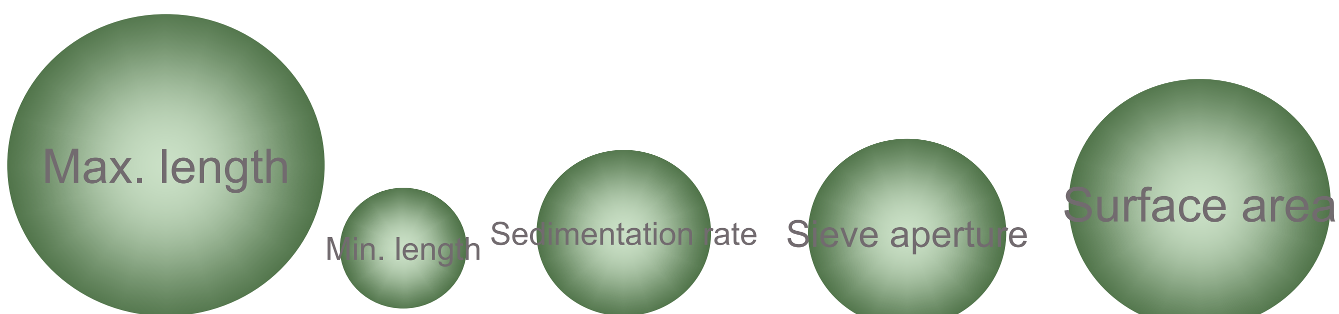
- Equivalent spheres
  - Maximum length
  - Minimum length
  - Sedimentation rate
  - Sieve aperture



How do we describe the size of these particles

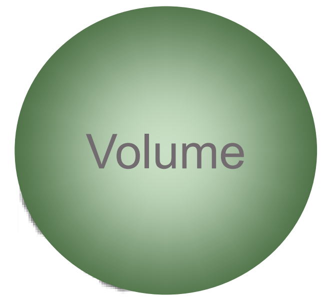
- Equivalent spheres
  - Maximum length
  - Minimum length
  - Sedimentation rate
  - Sieve aperture
  - Surface area

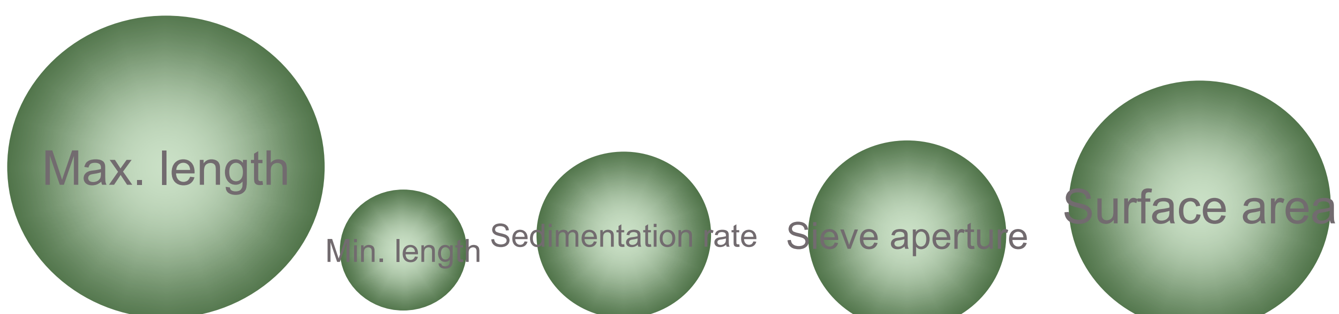




How do we describe the size of these particles

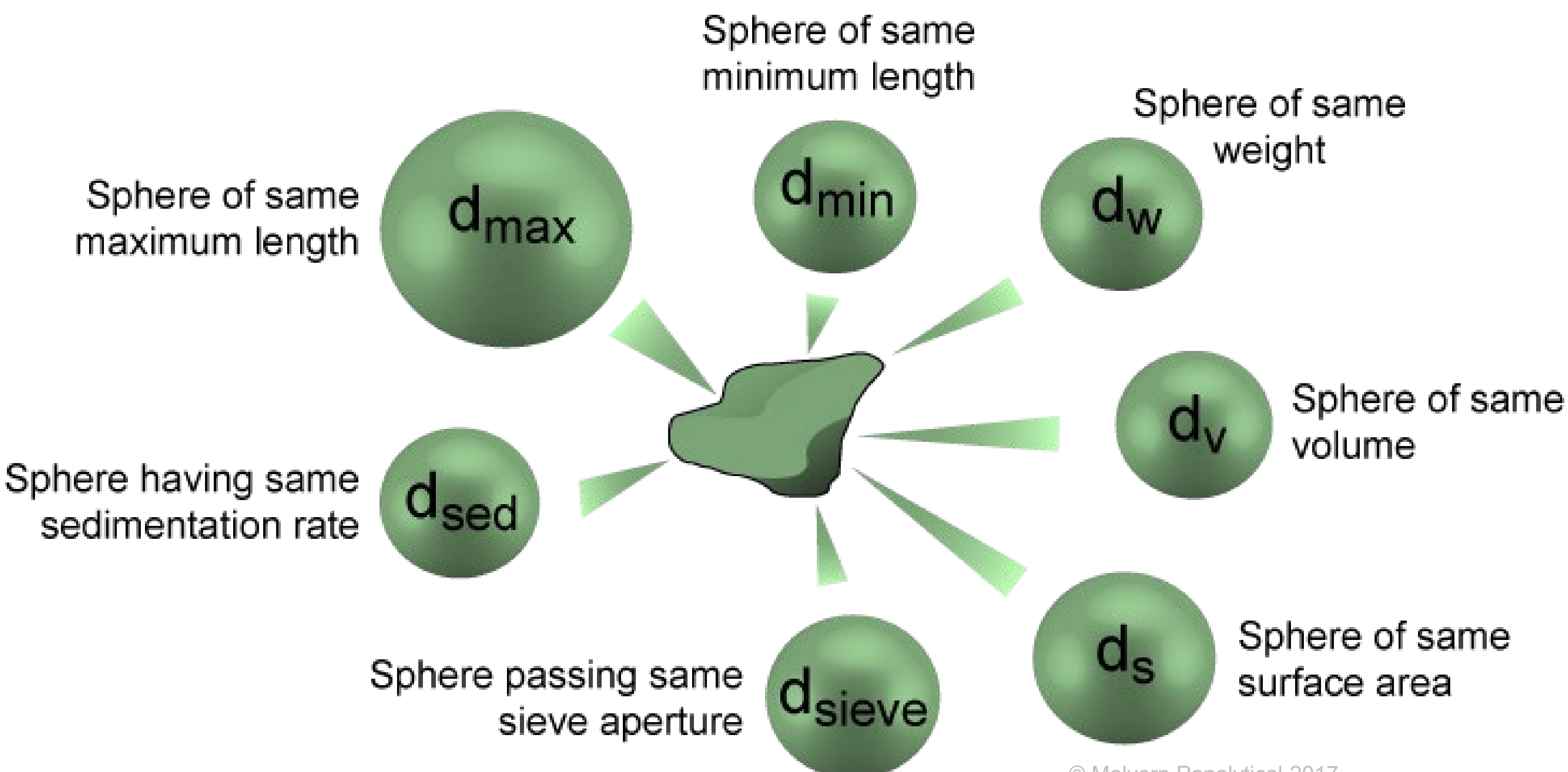
- Equivalent spheres
  - Maximum length
  - Minimum length
  - Sedimentation rate
  - Sieve aperture
  - Surface area
  - Volume

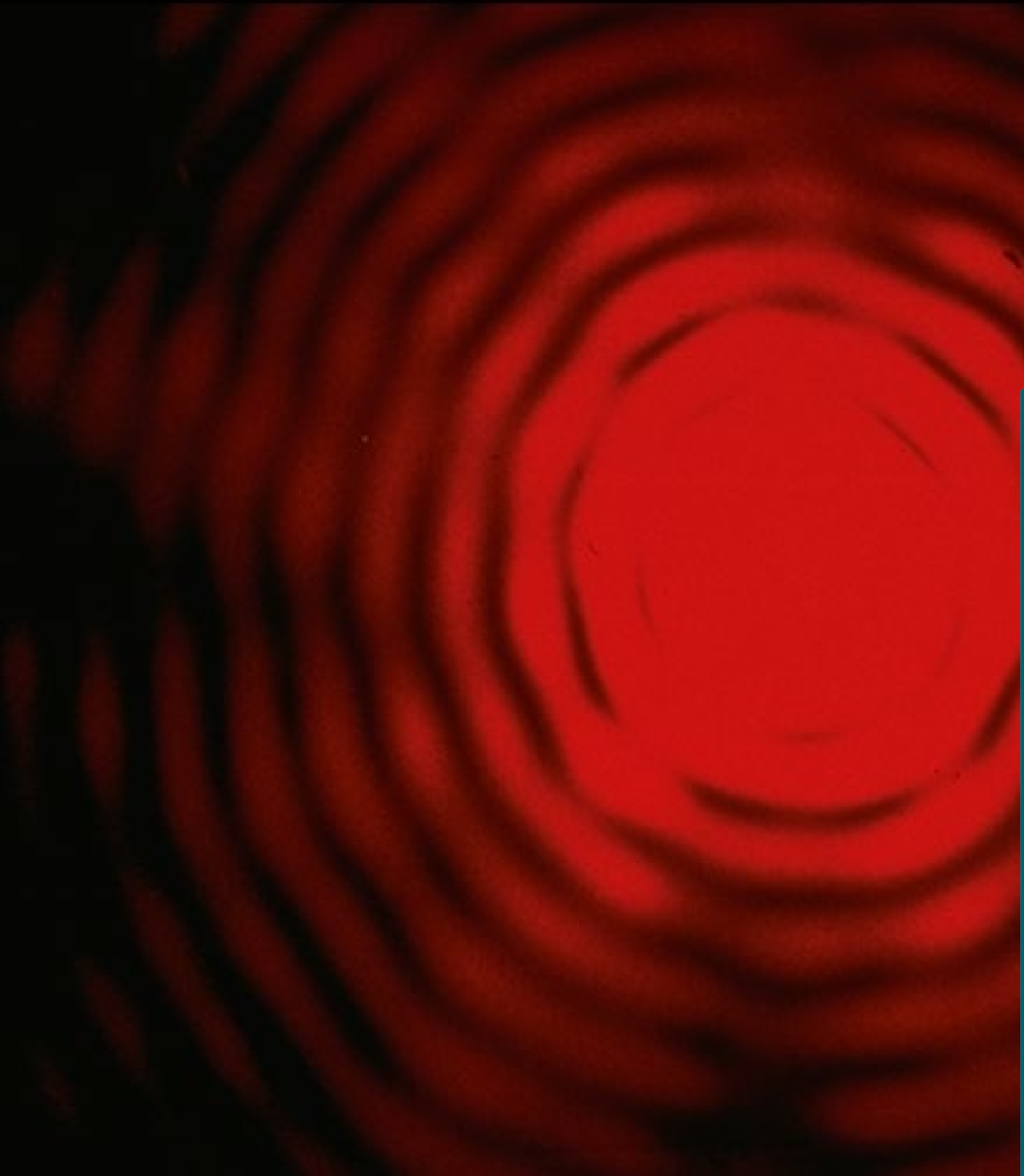




Concept of equivalent spherical diameters

- Different particle sizing techniques report different equivalent spherical diameters
  - Dependent on the physical property that is measured

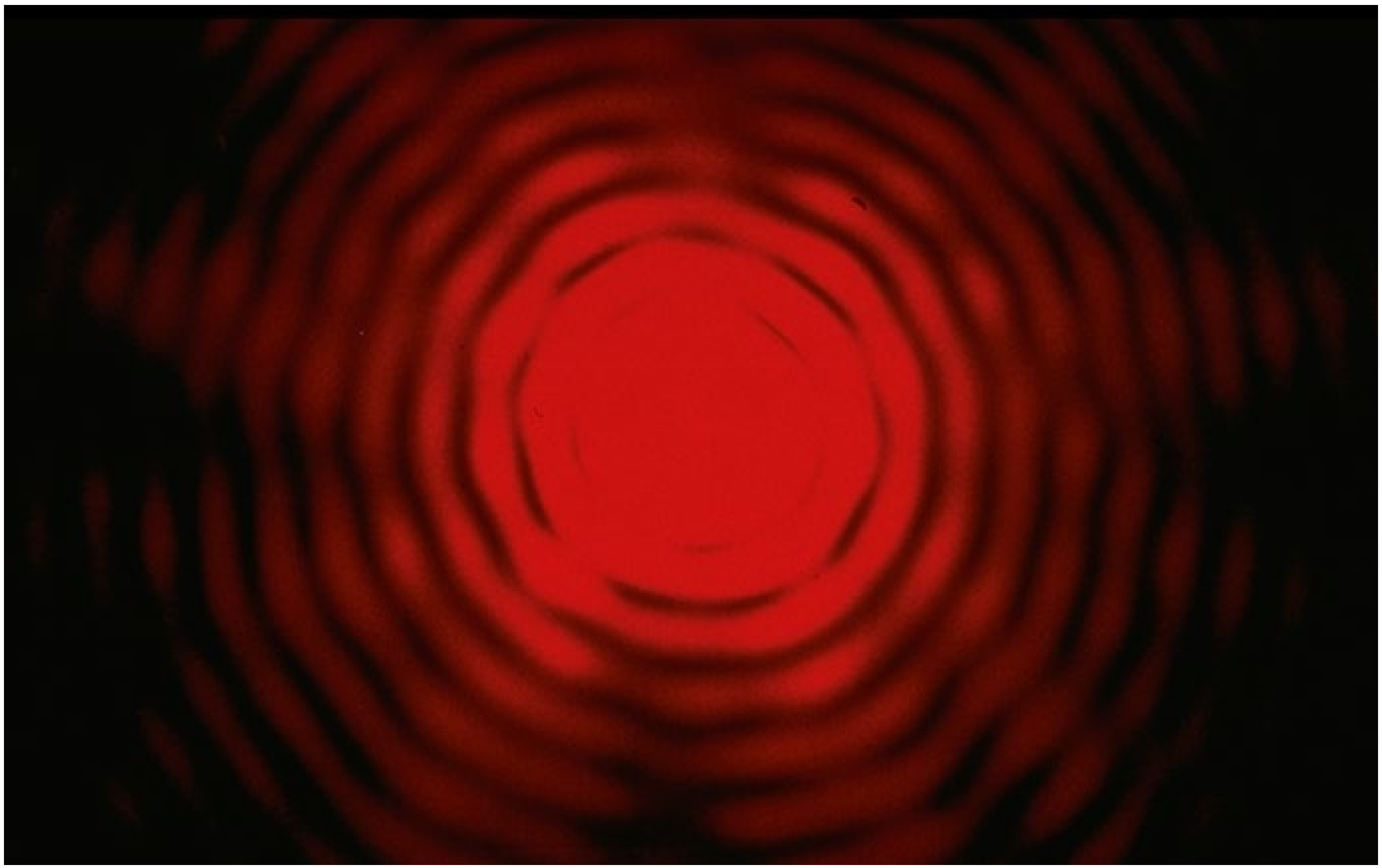




How does laser diffraction work?

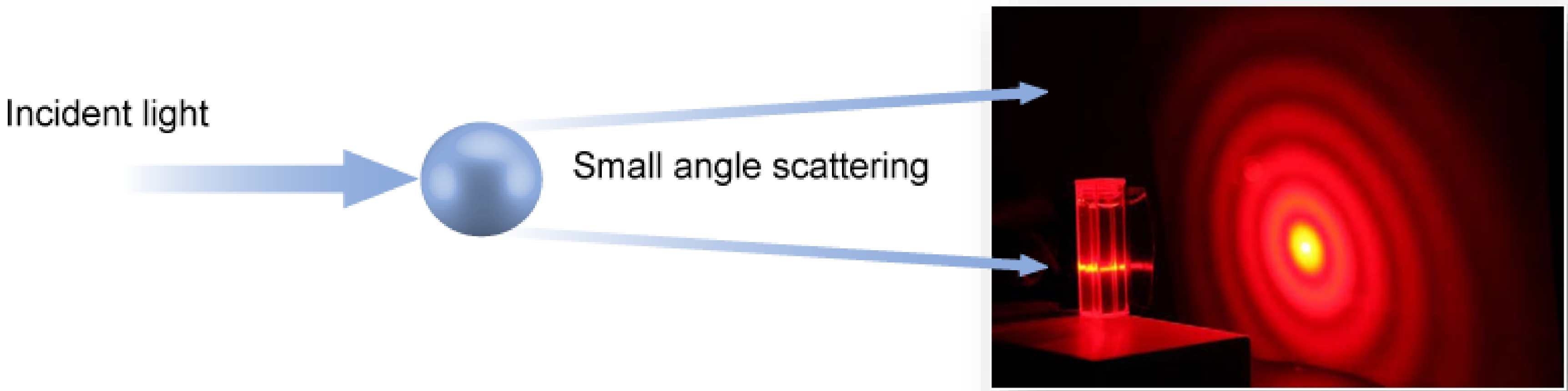
Malvern Panalytical

Laser Diffraction – The light scattering pattern from a group of particles



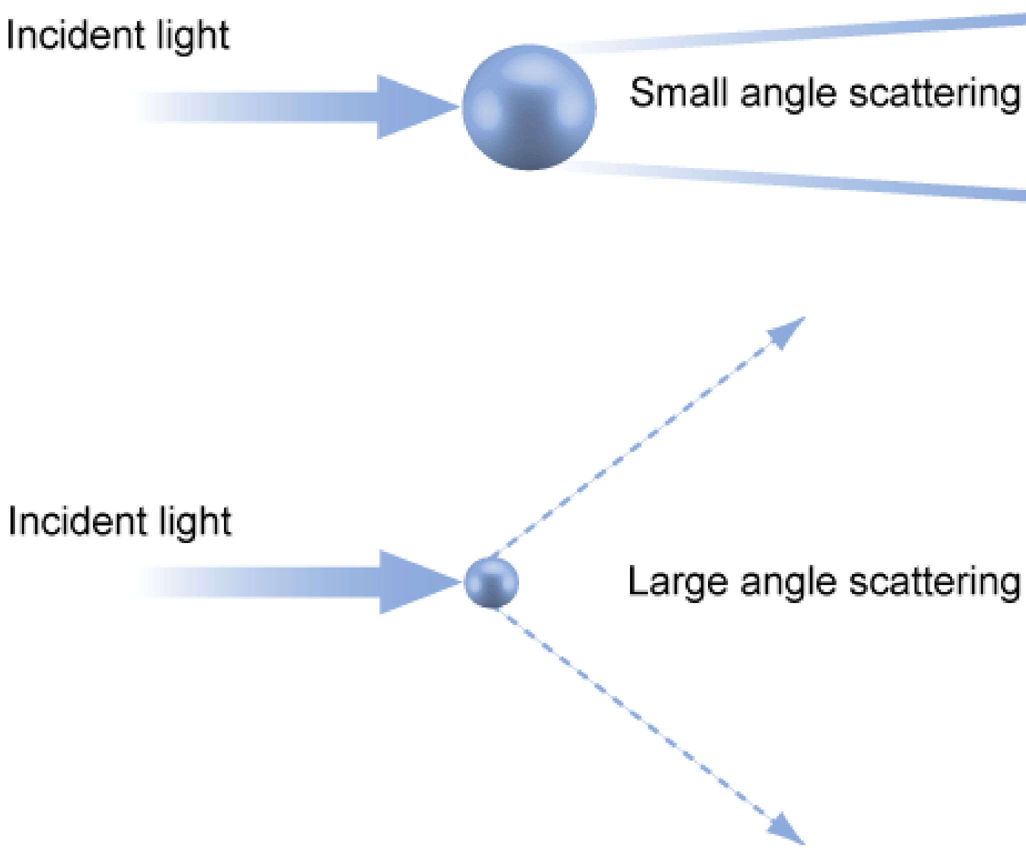
Laser diffraction: light scattering

Large particles

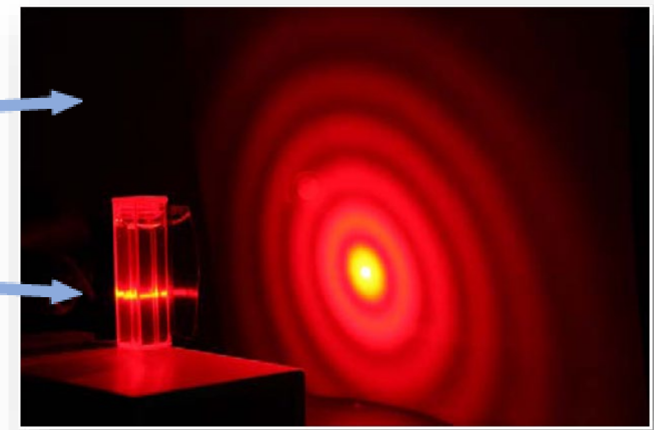


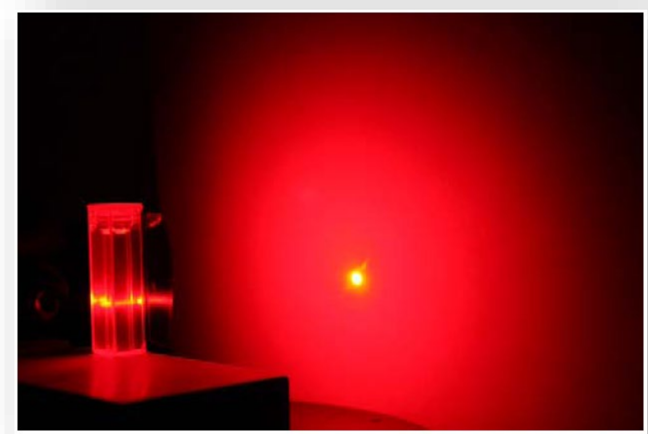
Dr Kevin Powers, PERC, University of Florida

Laser diffraction: light scattering



Large particles

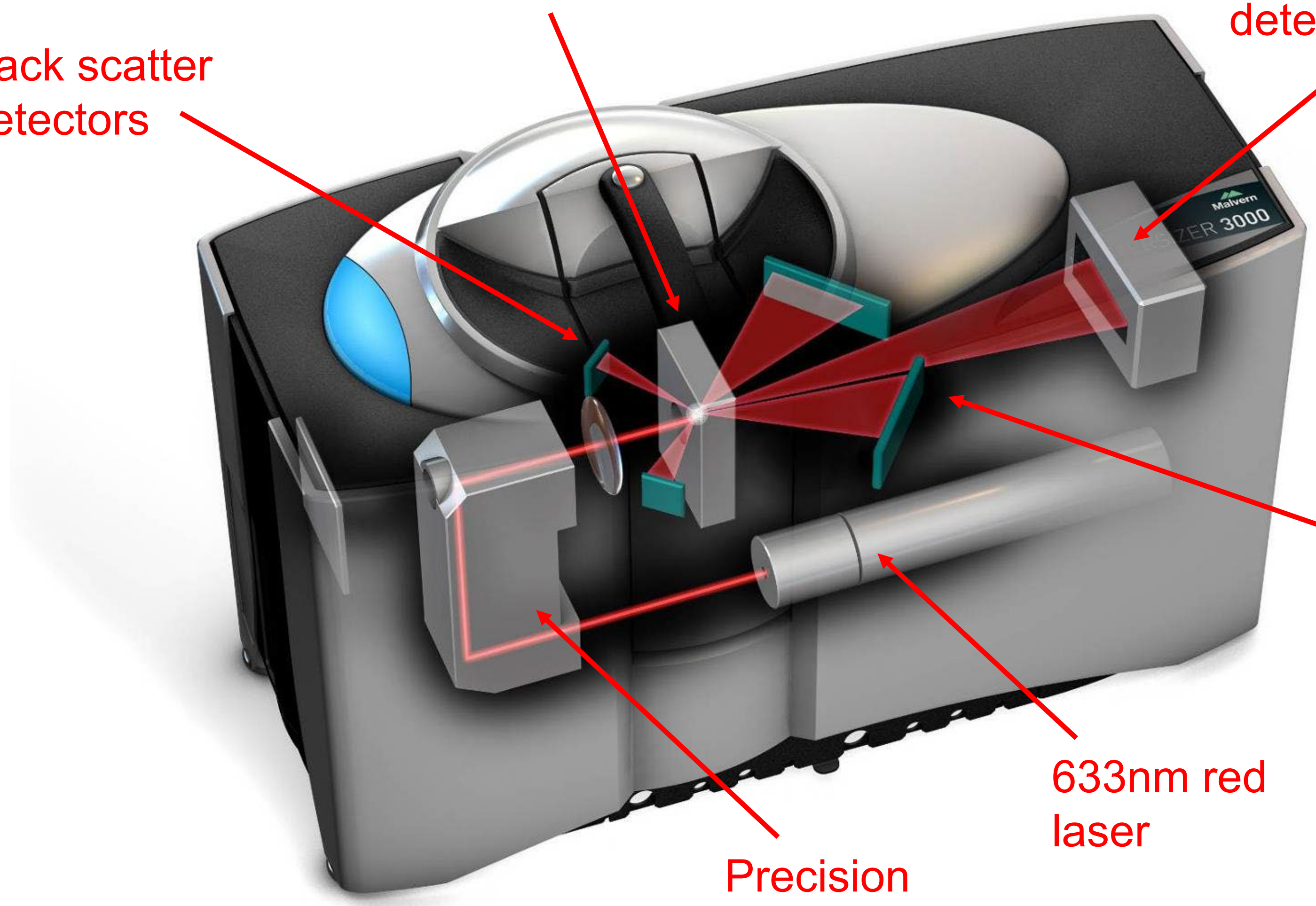




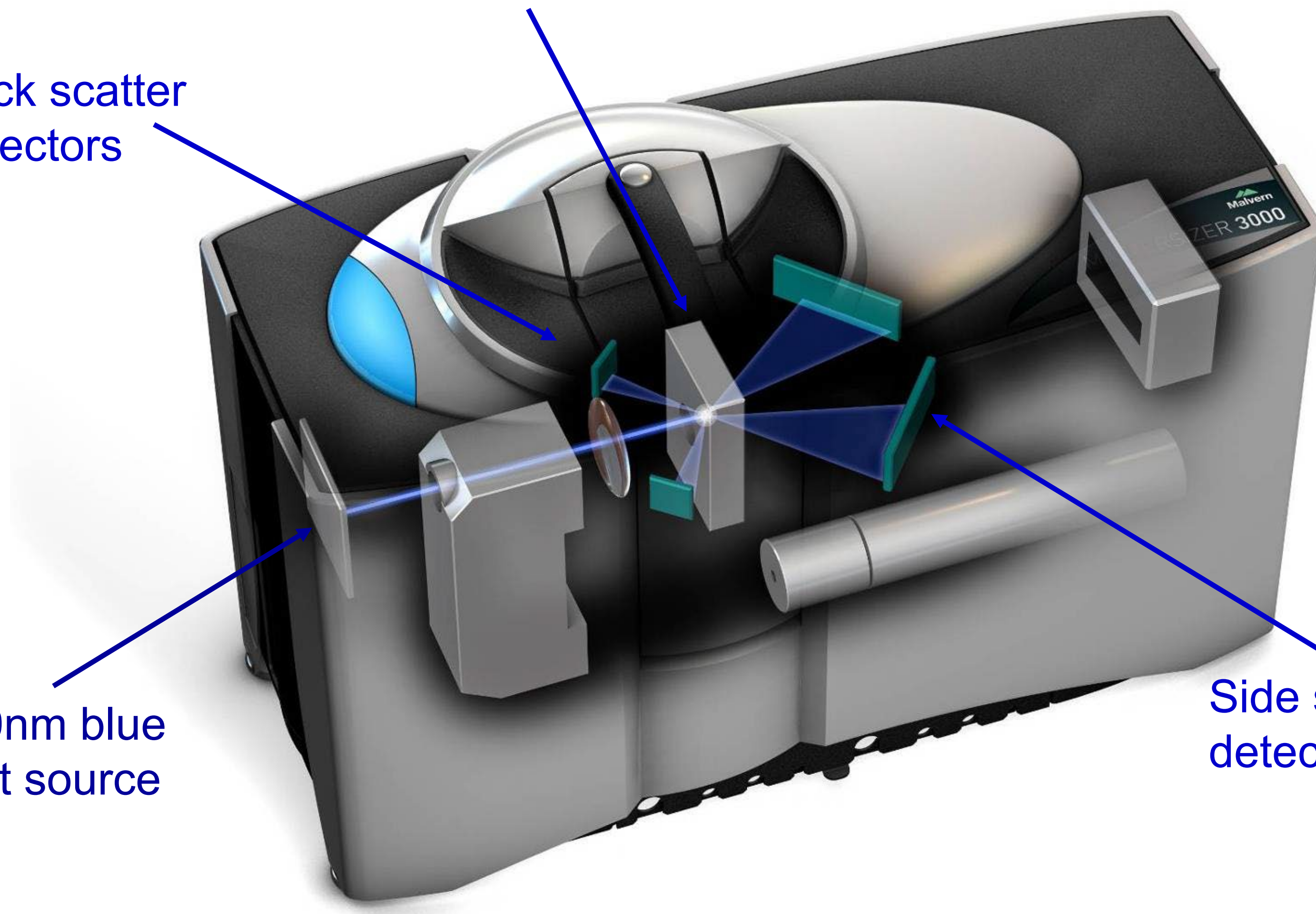
Submicron particles

Dr Kevin Powers, PERC, University of Florida

Mastersizer 3000 optics: red light measurements



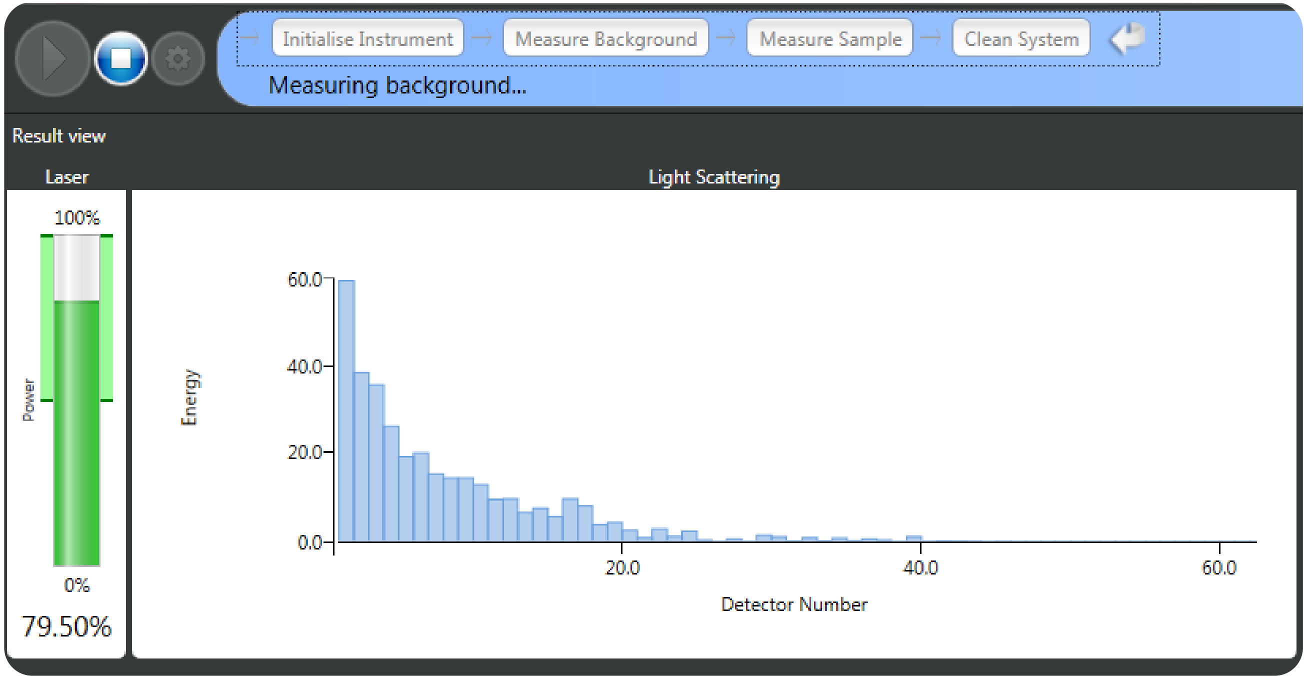
Mastersizer 3000 optics: blue light measurements



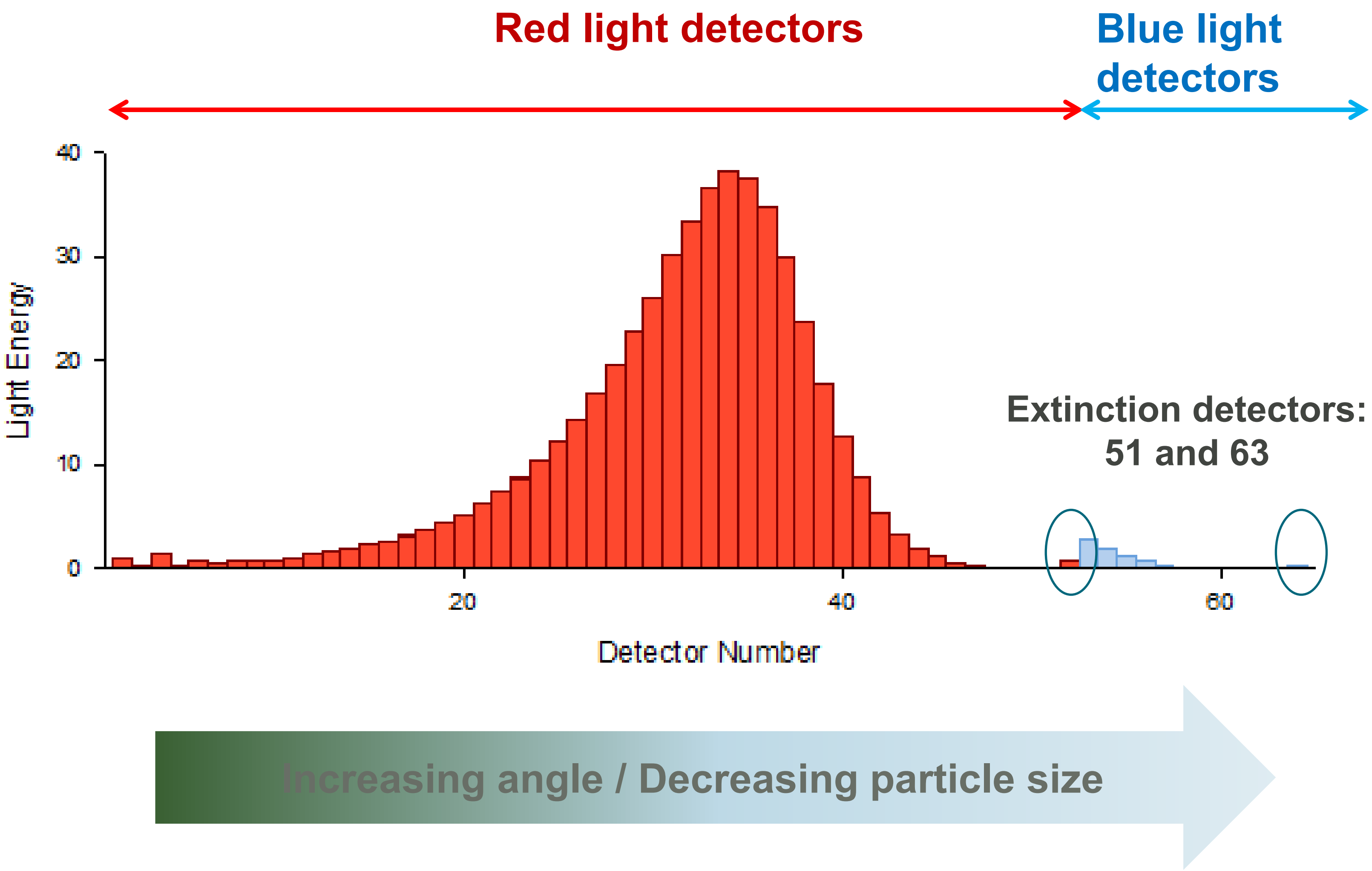
Shorter wavelengths resolve smaller particles.

Measuring the scattering data

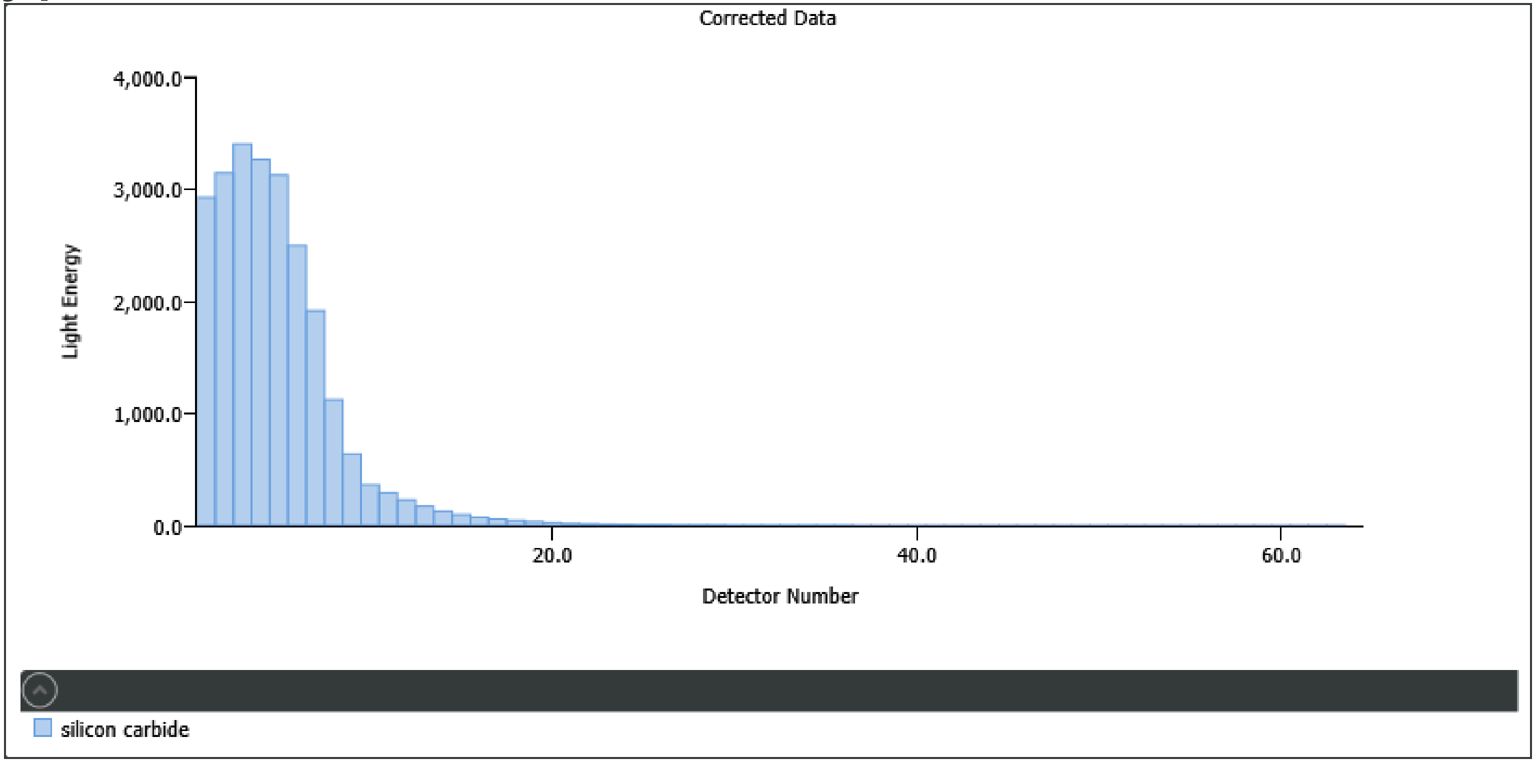
- Angular scattering data is presented in real-time in the measurement manager
- Increasing detector numbers represent increasing angle



The measured scattering data

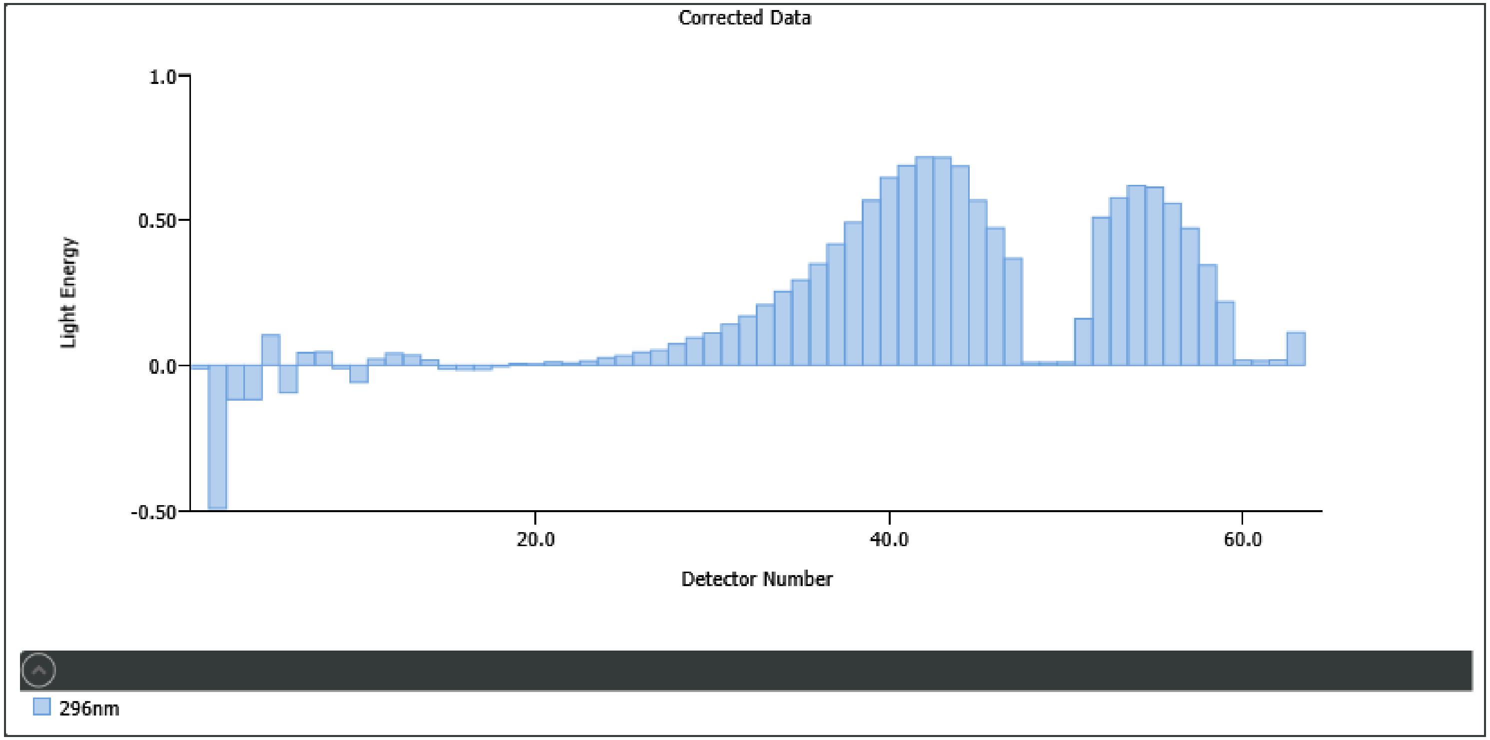


The Mastersizer 3000
Typical Data Set – Coarse Particles

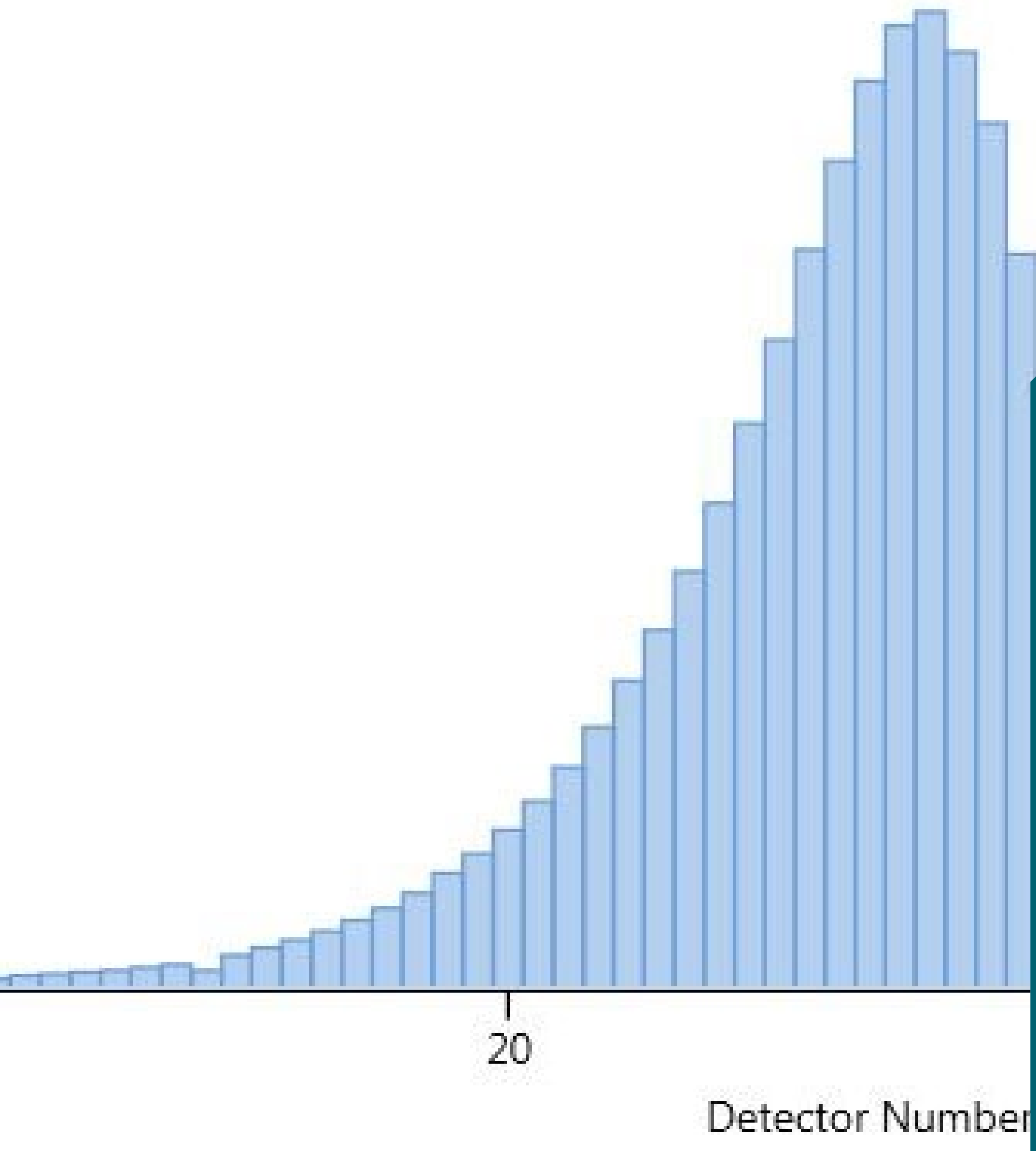


Large particle scattering is concentrated in the low angle region which corresponds to low detector numbers.

The Mastersizer 3000
Typical Data Set – Sub-Micron Particles



Small particles scatter light at high angles which produces data in the high detector number region.



Data quality

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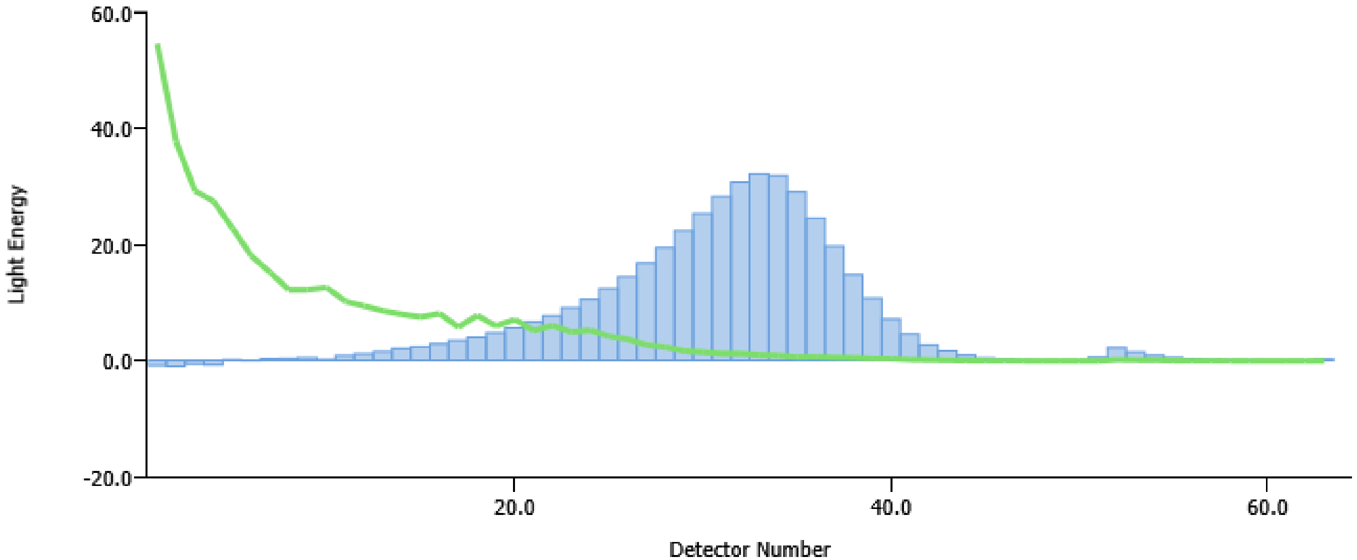
Data quality - introduction

- Data is the fundamental light scattering caused by the sample

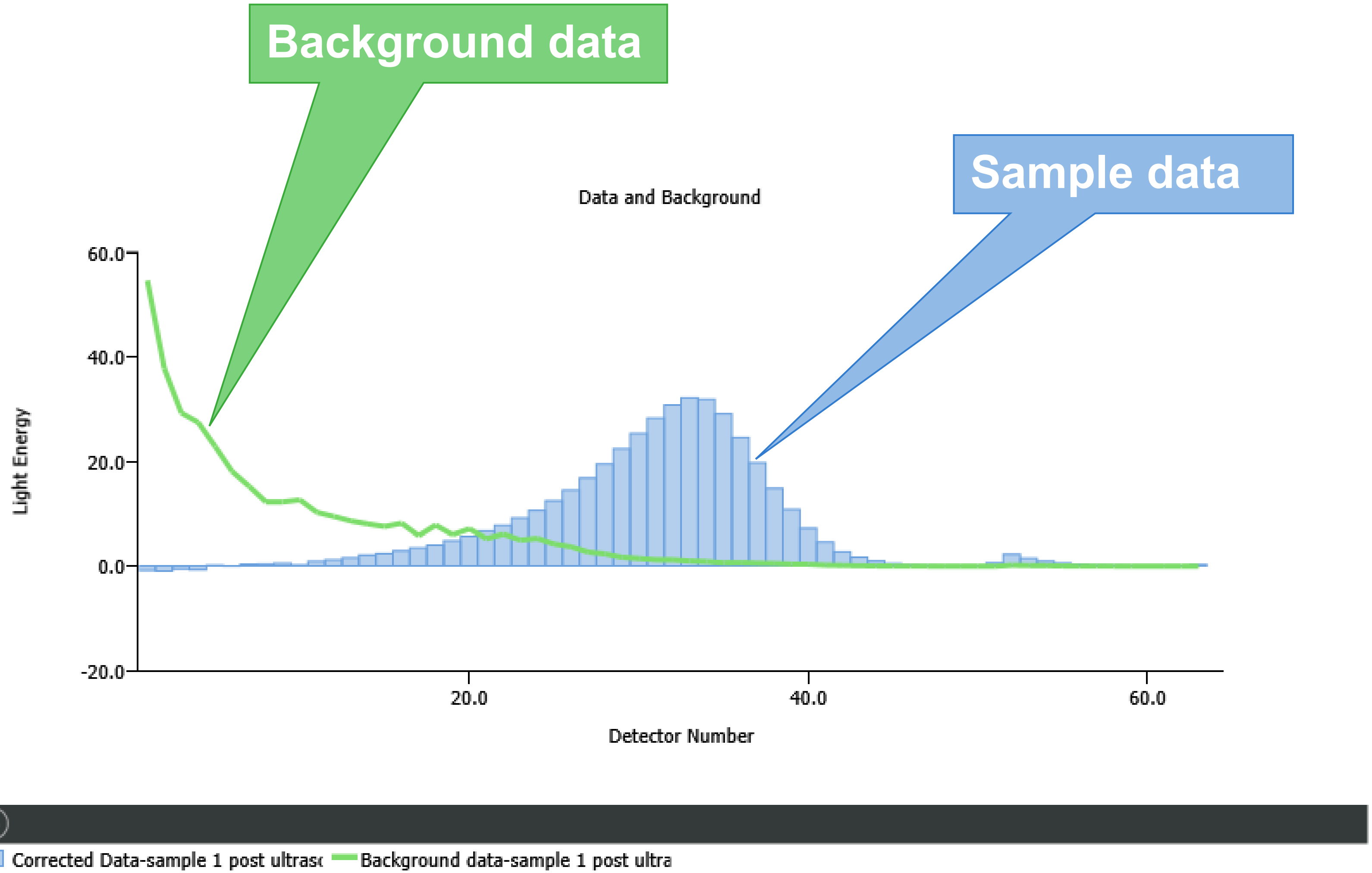


- Data is not the particle size result (.pdf)
- Data is independent of the optical model
- A stable result requires stable data

What is good quality data?

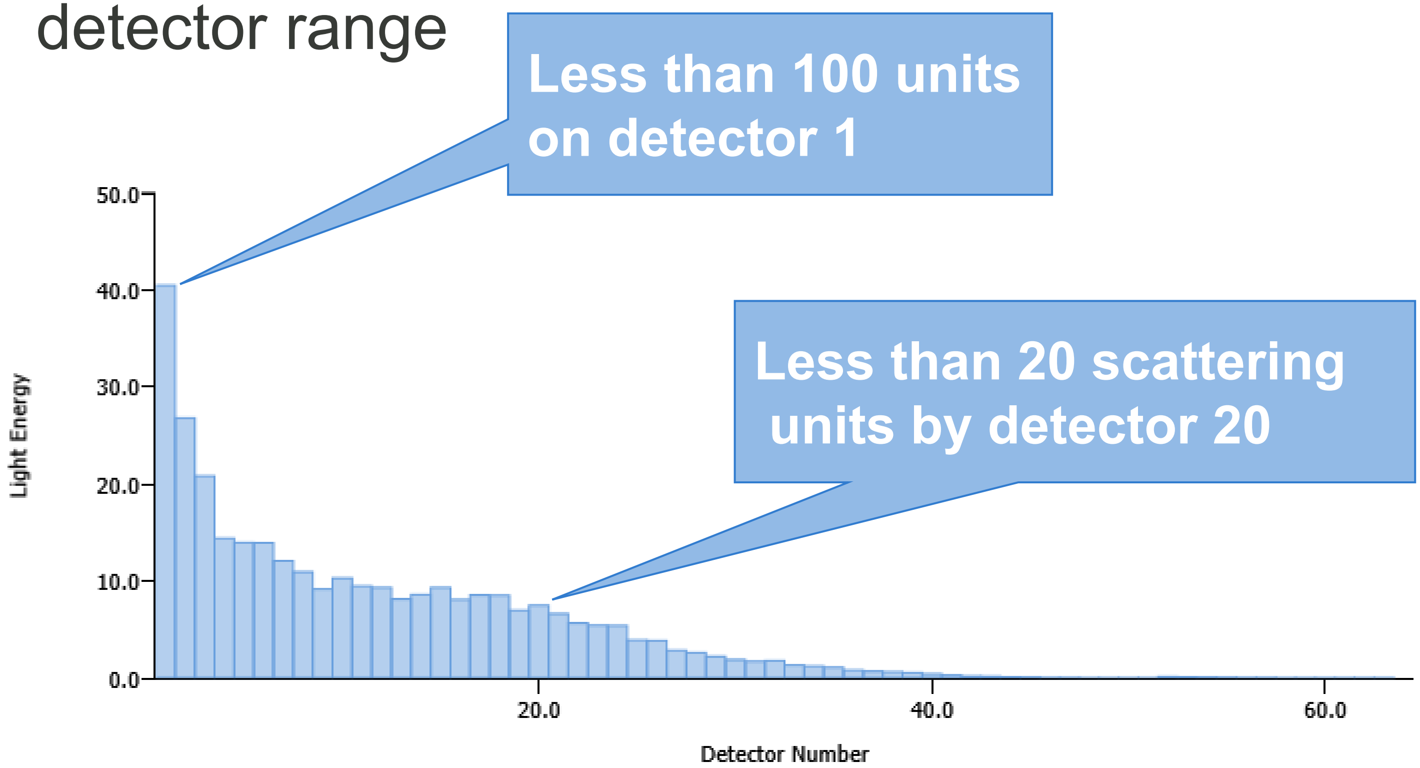
- A good background measurement shows:
  - Clean cell windows and dispersant
  - Good alignment of the system
  - Stability of the dispersant
- Good sample measurement should have:
  - Sufficient signal to noise ratio
  - Limited negative data
  - No multiple scattering
  - No beam steering

Data components - types of data



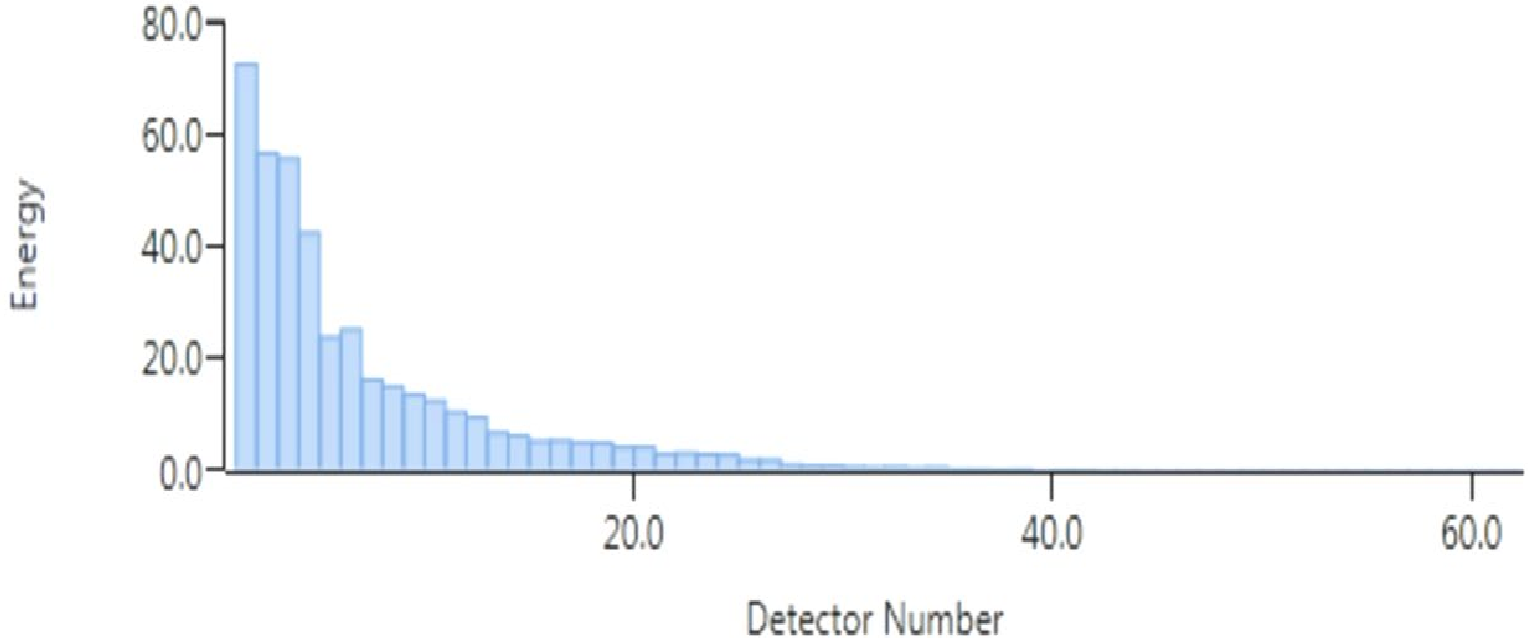
Background data and system cleanliness

- A good measurement requires a clean, stable background
- This should show progressive decrease across the detector range



A clean background – wet system

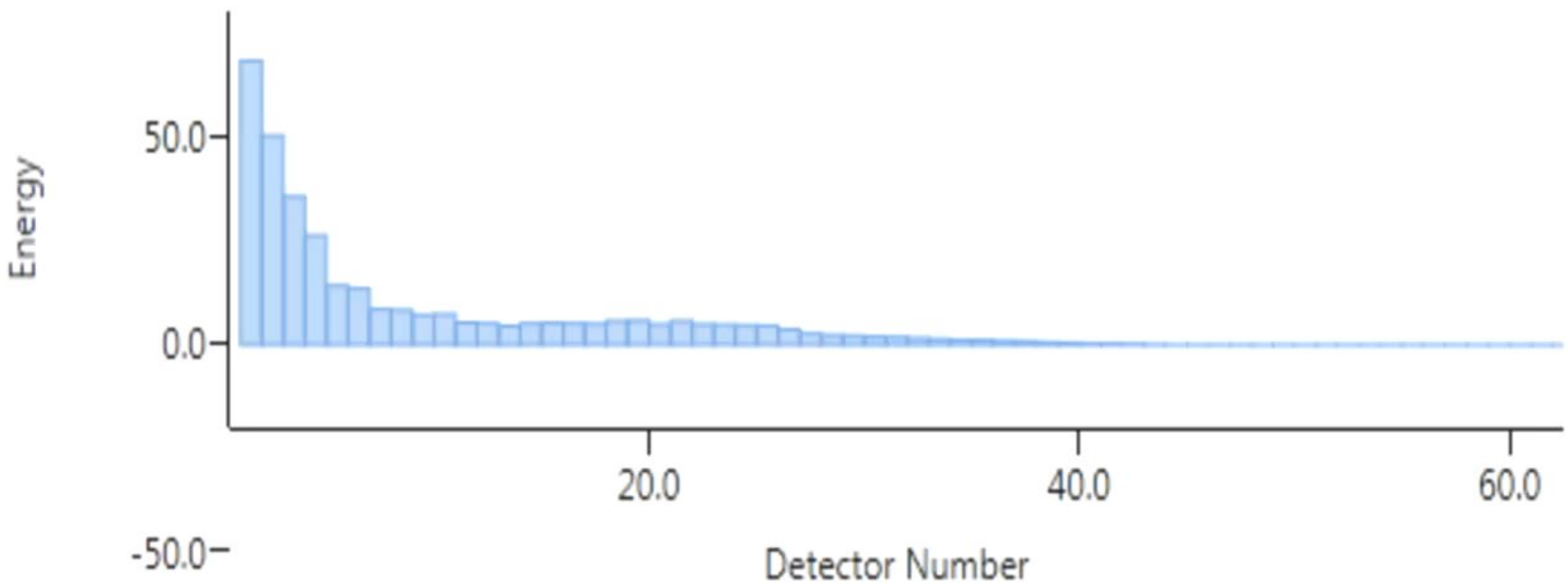
- A good clean background on a wet system should look very similar to this...



- Less than 100 on detector 1
- Less than 20 on detector 20
- Decreasing curve
- Limited fluctuations

A clean background – dry system

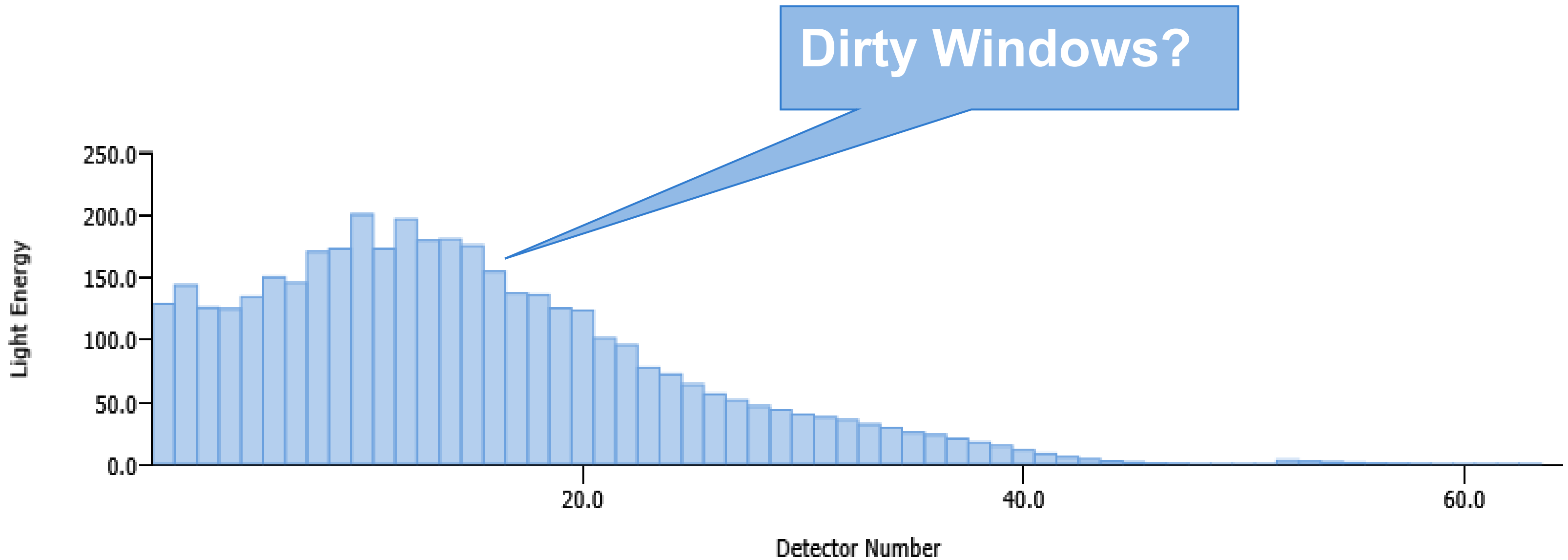
- The air flow causes larger fluctuations in the background than in a wet measurement.
- The same rules apply!



- Less than 100 on detector 1
- Less than 20 on detector 20
- Decreasing curve
- Limited fluctuations

Poor background - material stuck to the windows

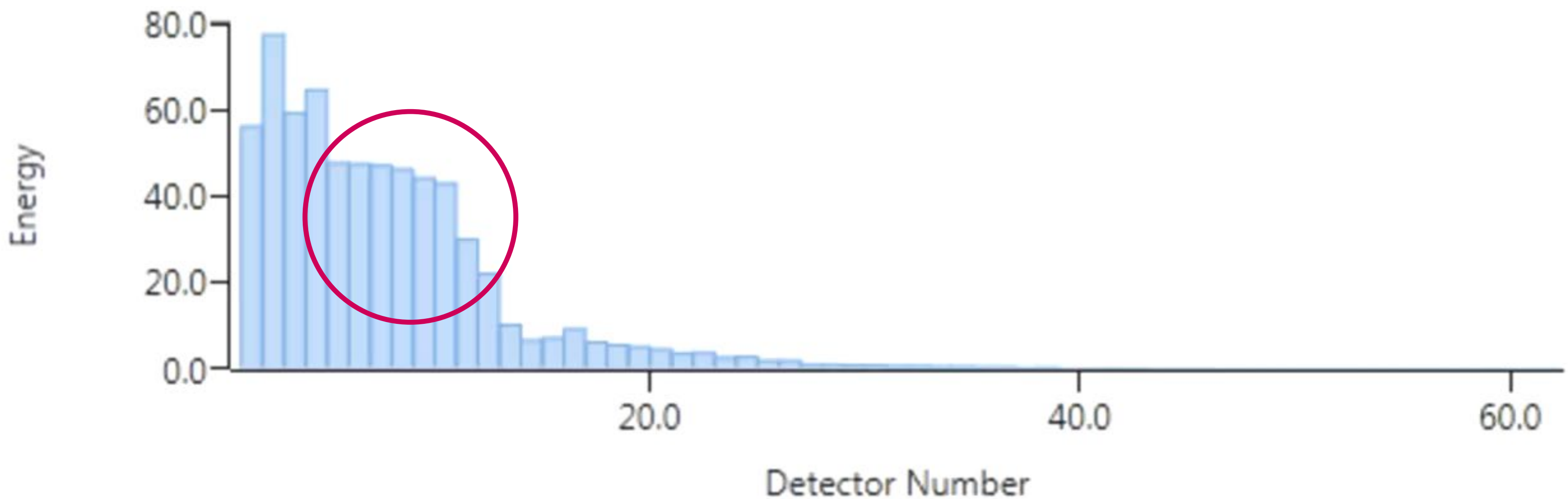
- A 'hump' in the data is often an indication of material stuck to the cell windows



- All scattered light is included in the measurement

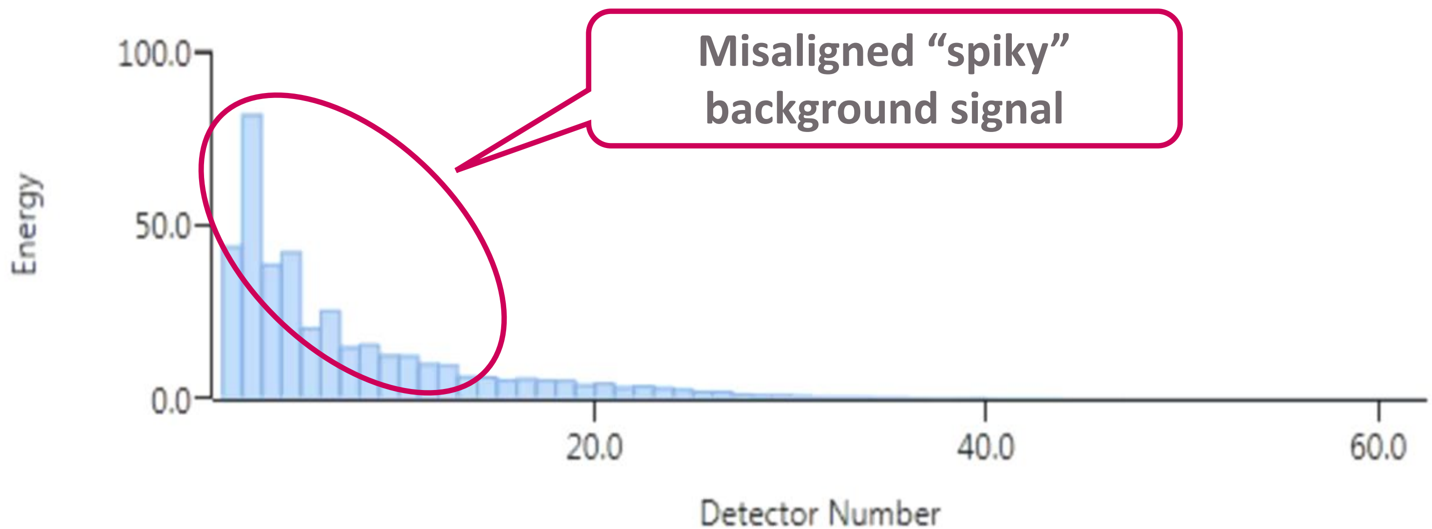
Poor background – contaminated dispersant

- Intermittent peaks in the background may be caused by contaminants in the dispersant
  - Particulates (rinse the dispersion unit)
  - Bubbles (degas dispersant, stop-start pump)



Poor background – misaligned system.

- A spiky background signal indicates misalignment
  - Detectors are arranged on opposite sides of the pinhole
- Misalignment can be caused by
  - Contamination on the cell windows
  - A change in the refractive index of the dispersant

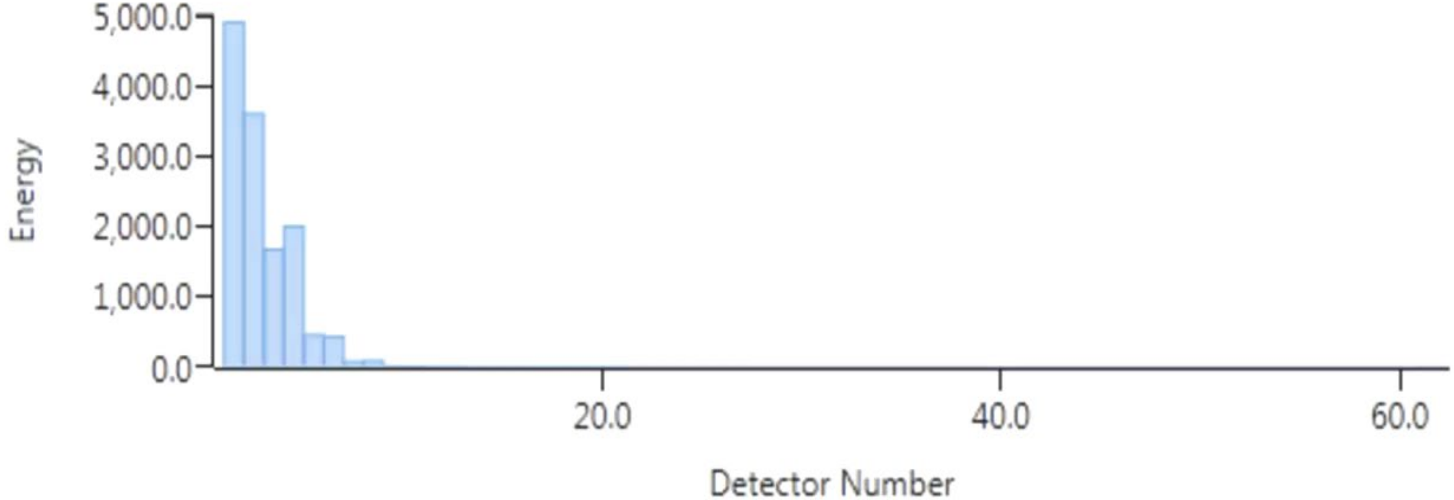


Poor background: instability due to thermal gradients

- The dispersion unit may be warmer than the dispersant
- This temperature difference causes thermal gradients in the dispersant
  - And high backgrounds and possible alignment problems

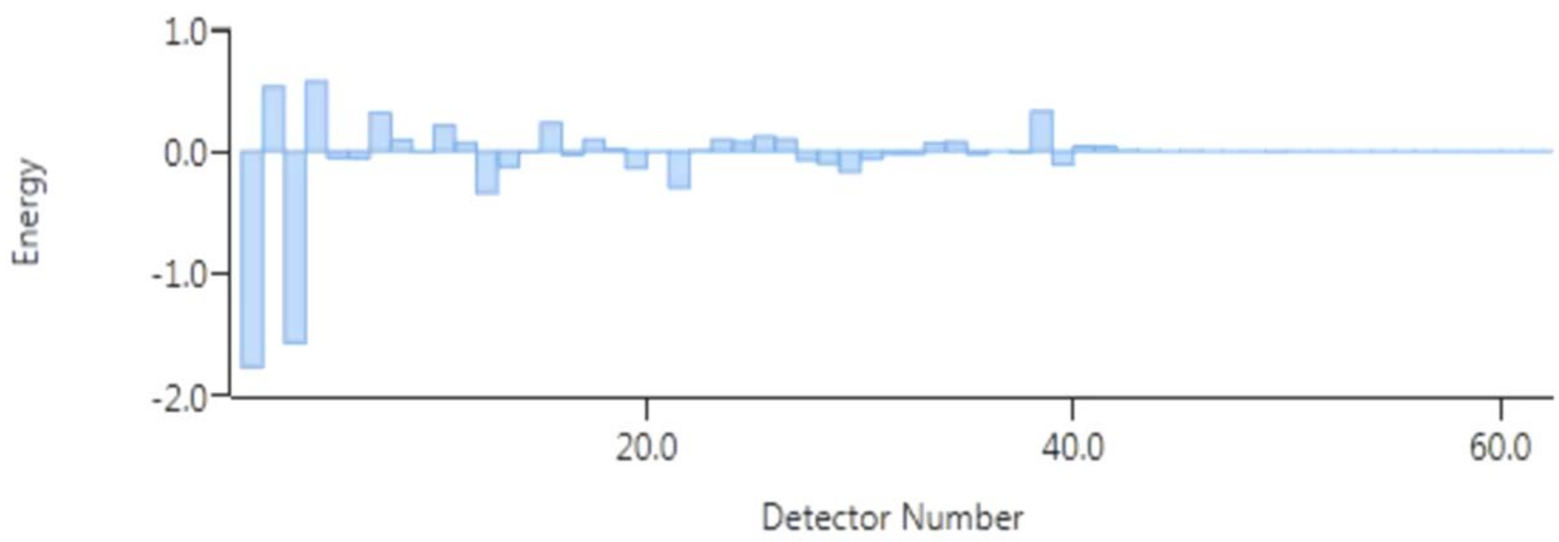
How will I recognise thermal gradients?

- Thermal gradients cause high background signals, and large fluctuations
  - The background signal decreases as the temperature stabilises and refractive index gradients disappear
  - This will take longer for more volatile dispersants



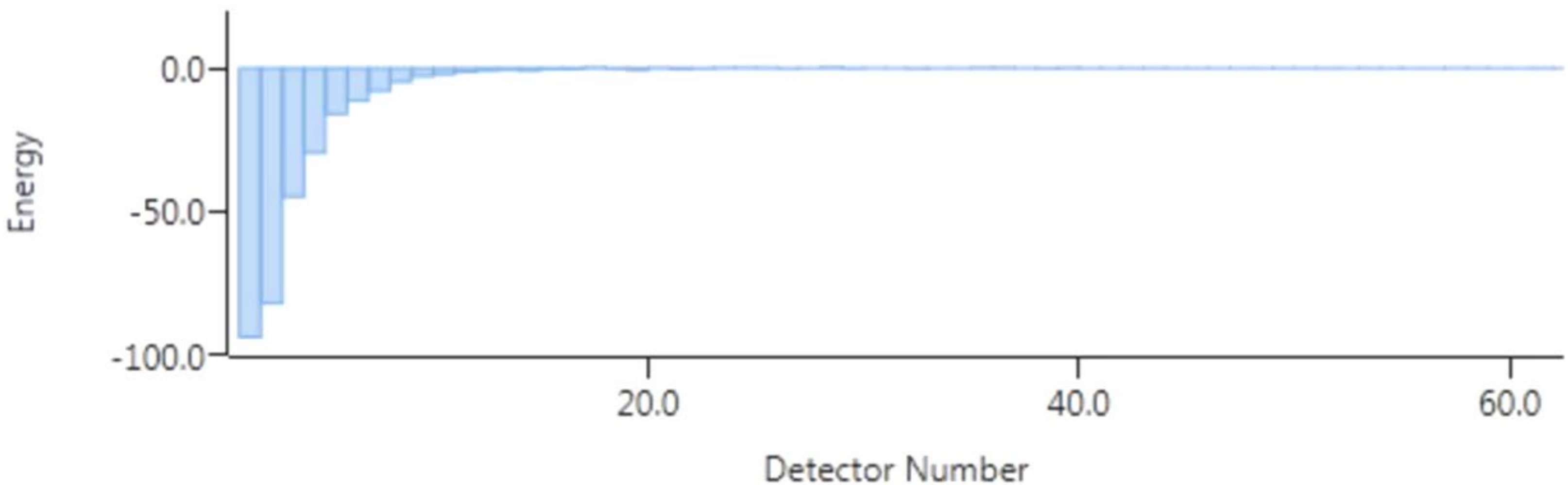
The Add Sample stage

- The background signal as been subtracted
- The live data should then show random fluctuations around zero
- Any ‘blocks’ of scattering will indicate dispersant contamination



The Add Sample stage – negative data

- The background signal has been subtracted
- The live data should then show random fluctuations around zero
  - Significant negative data suggest that the background had not stabilised before it was measured
  - If you see this signal, re-measure the background



Sample addition

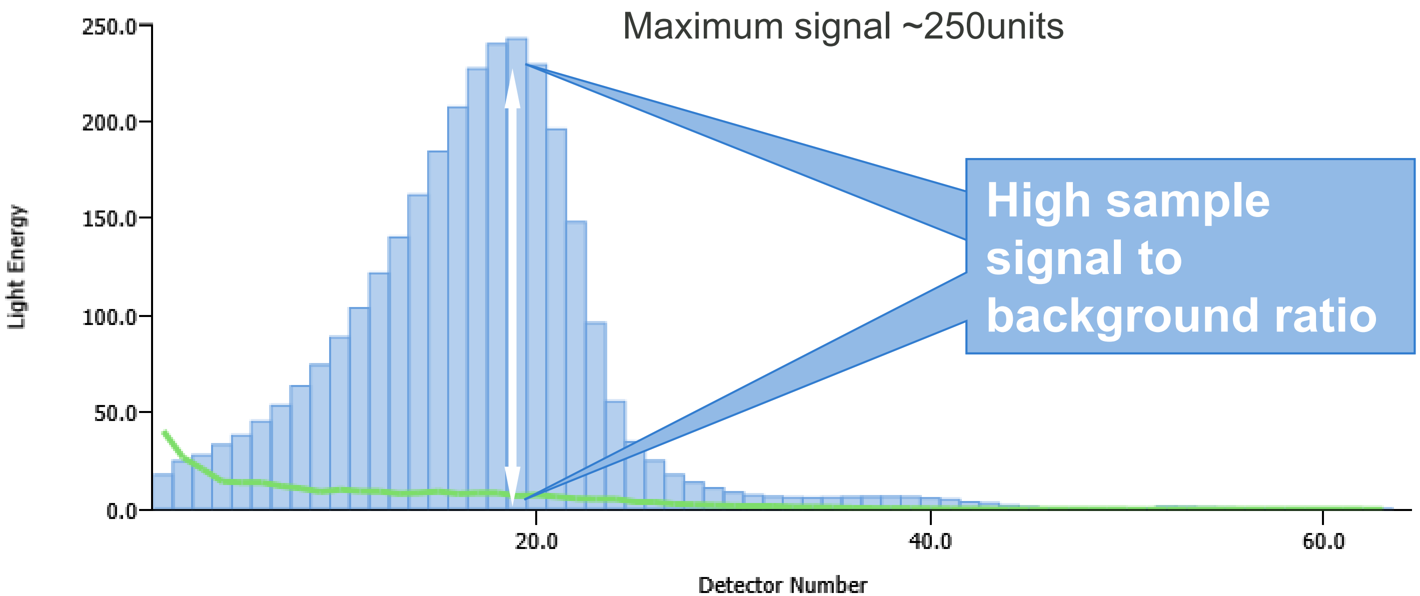
- How much sample should be added to the dispersion unit?
  - **Too little**:
    - Signal to noise ratio may be poor, or
    - Not enough sample may have been added to be representative of the bulk – particularly if the sample is very polydisperse
  - **Too much:**
    - Multiple scattering may affect the reported particle size distribution – particularly if the material is small (typically < 10 microns)

- What is the *correct* obscuration range?

Obscuration = amount of laser light blocked and/or scattered by the sample, a guide to concentration

Low obscuration limit: signal to noise ratio

(42.58 micron glass beads measured at an obscuration of **only 7%**)

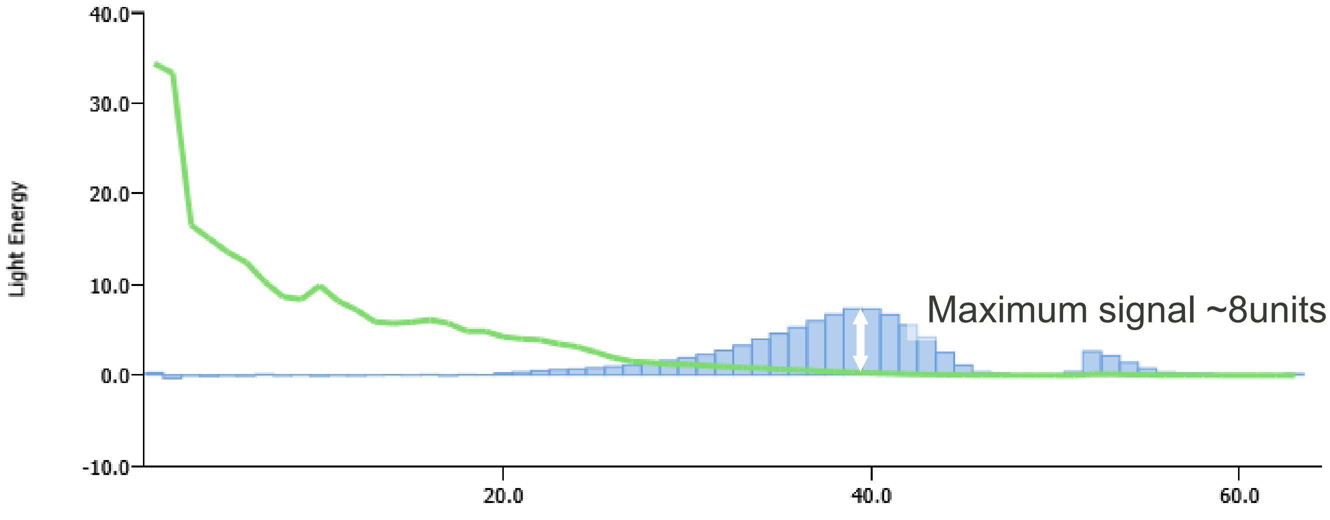


Note: the signal to noise ratio is usually high for large particles because these scatter light more strongly.

Consequently, signal-to-noise ratio is less of an issue for large particles.

Low obscuration limit: signal to noise ratio

(1 micron Latex measured at an obscuration of 5%)



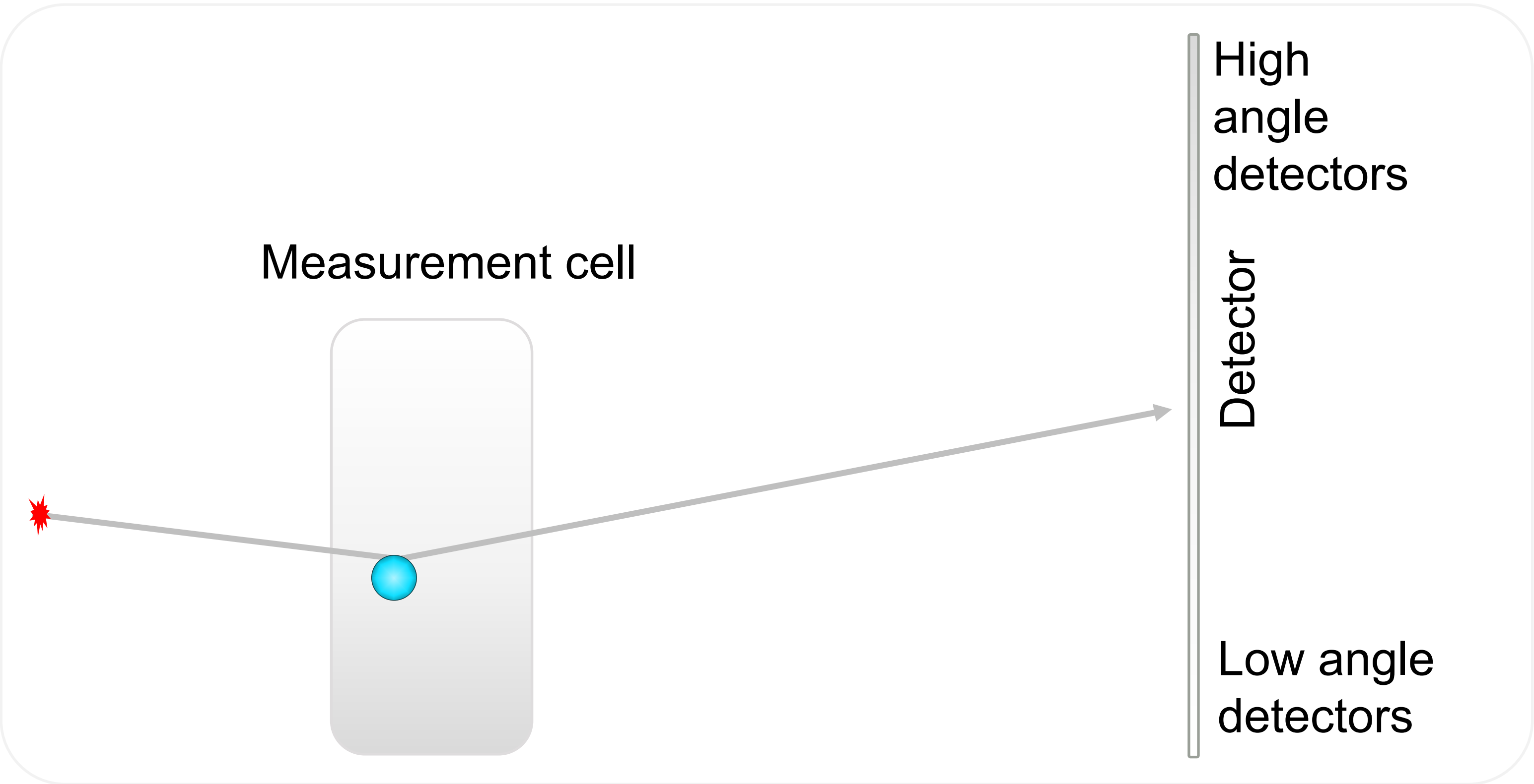
The signal-to-noise ratio is the amount of sample data relative to the background data.

Because small particles scatter light weakly, it is important that the background does not swamp the data signal.

However, in this graph, the data is good since it falls where there is little or no overlap between the sample data and the background data.

What defines the upper obscuration limit?

- If we add too much sample the results may be affected by multiple scattering
  - This generally affects samples smaller than 10µm



What defines the upper obscuration limit?

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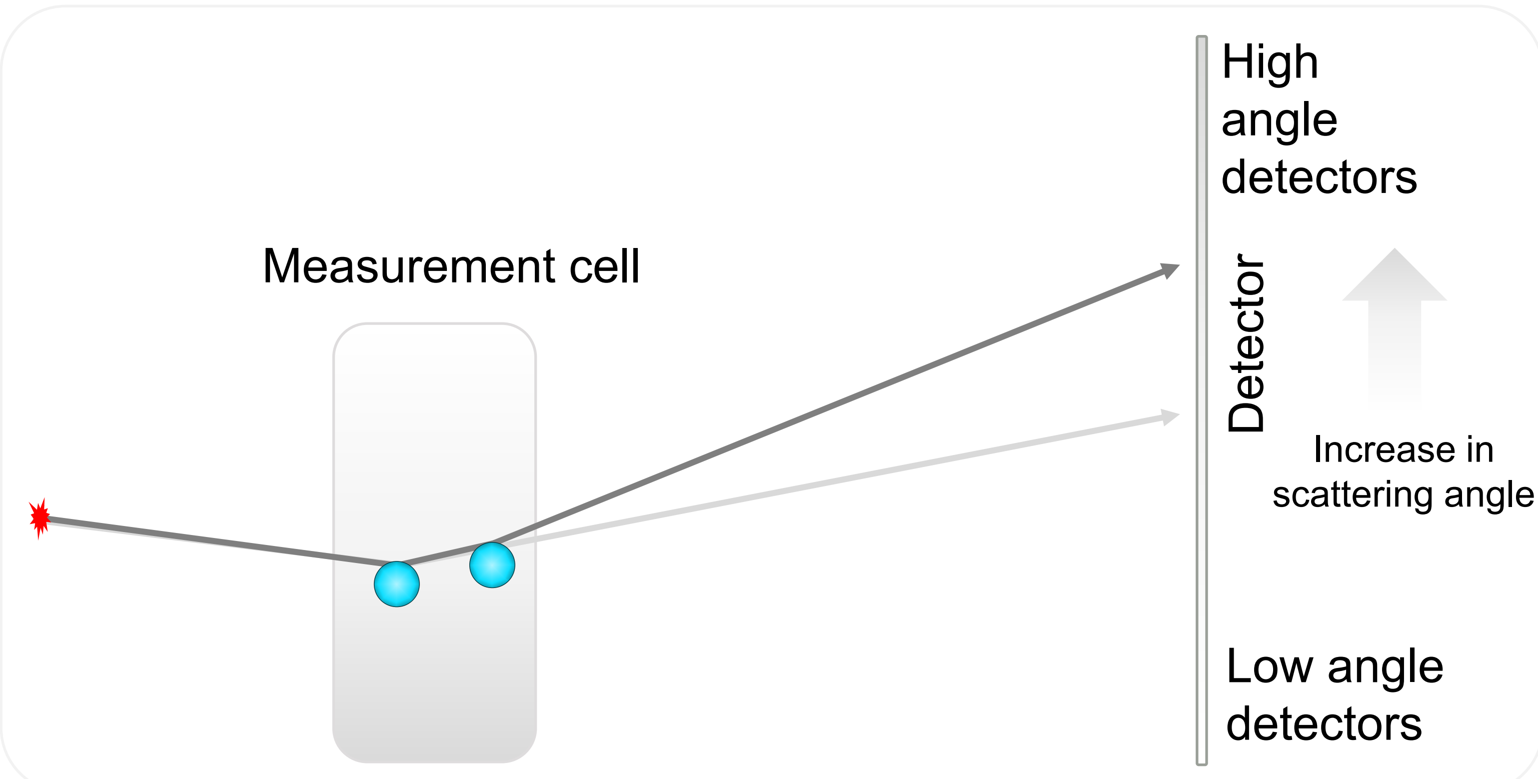
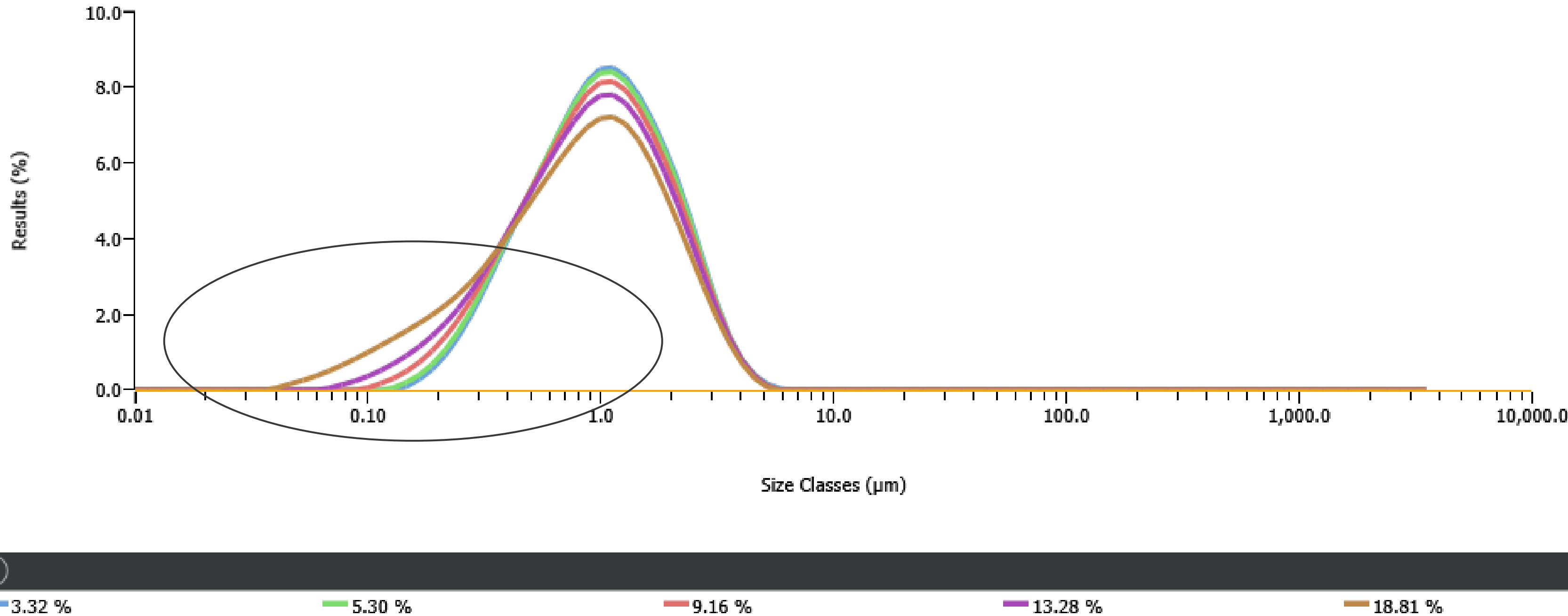


Wet analysis - multiple scattering

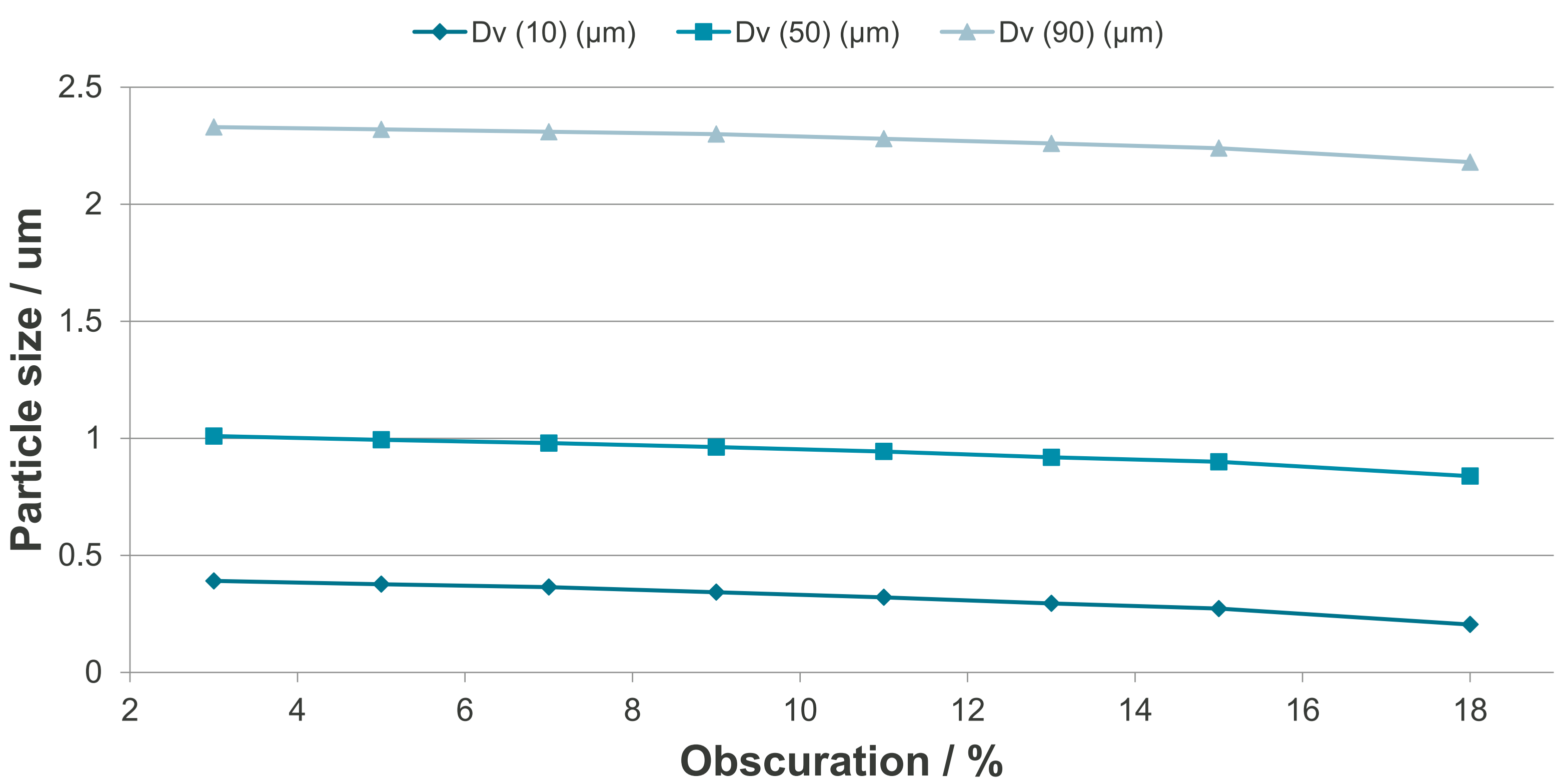
….leading to exaggerated fines being interpreted



- If in doubt, carry out an obscuration titration to determine the effect of measuring at increasing obscurations on the particle size distribution.

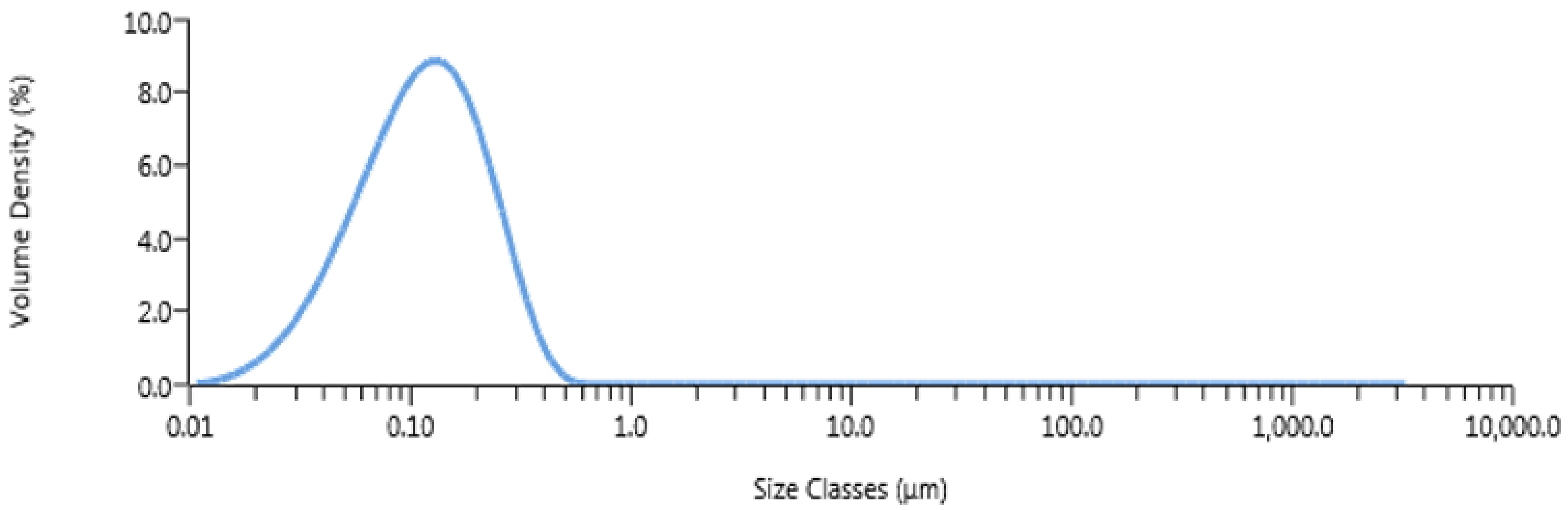
High obscuration limit: multiple scattering

- The upper limit of the obscuration range depends on multiple scattering:
  - Sample should be measured in the range where size is stable with obscuration.



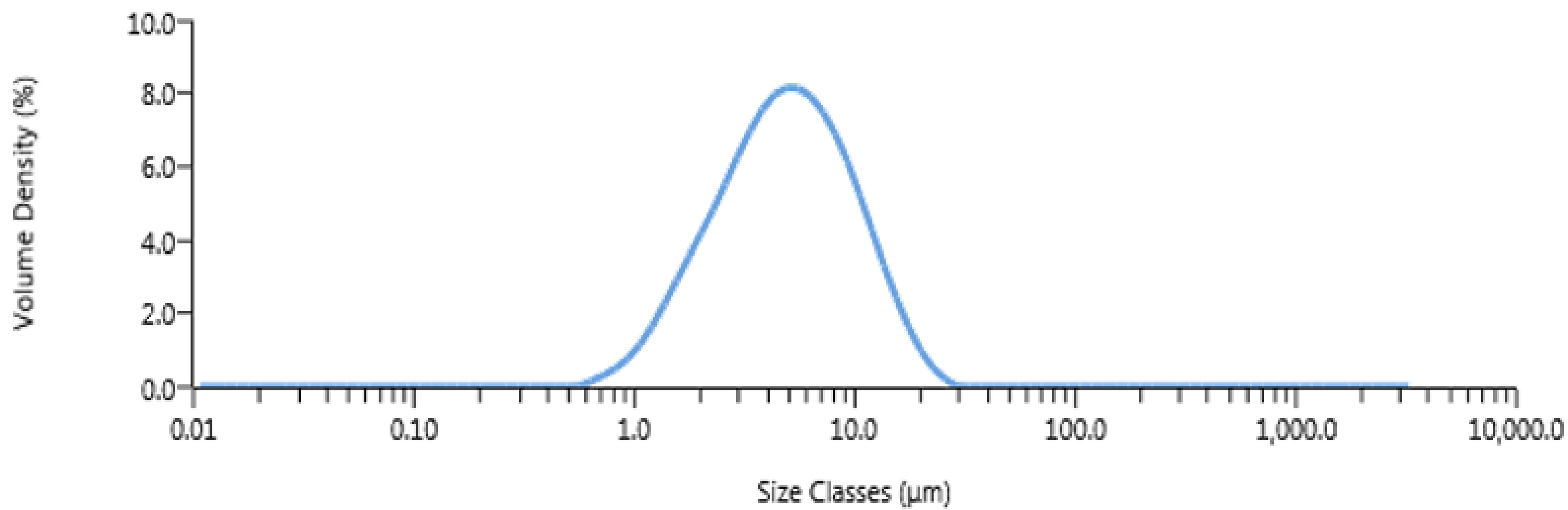
Target obscuration ranges: Wet measurements

- Very fine particles
- <1um
- <5% obscuration



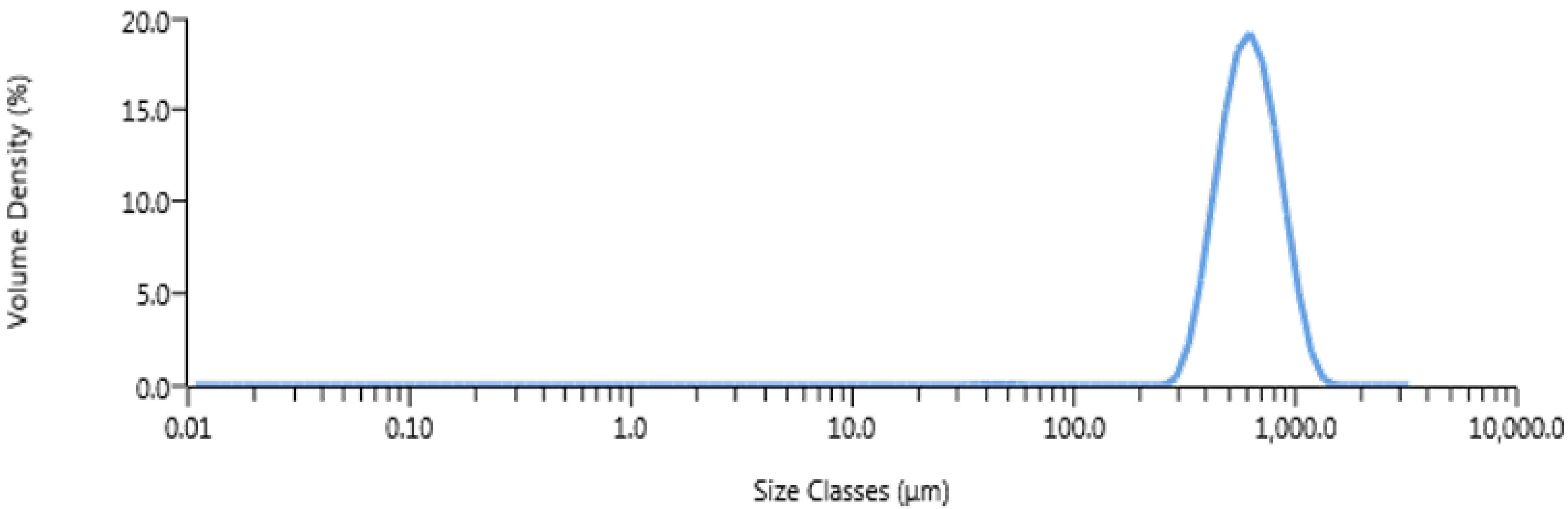
Target obscuration ranges: Wet measurements

- Fine particles
- 1-100um
- 5-10% obscuration



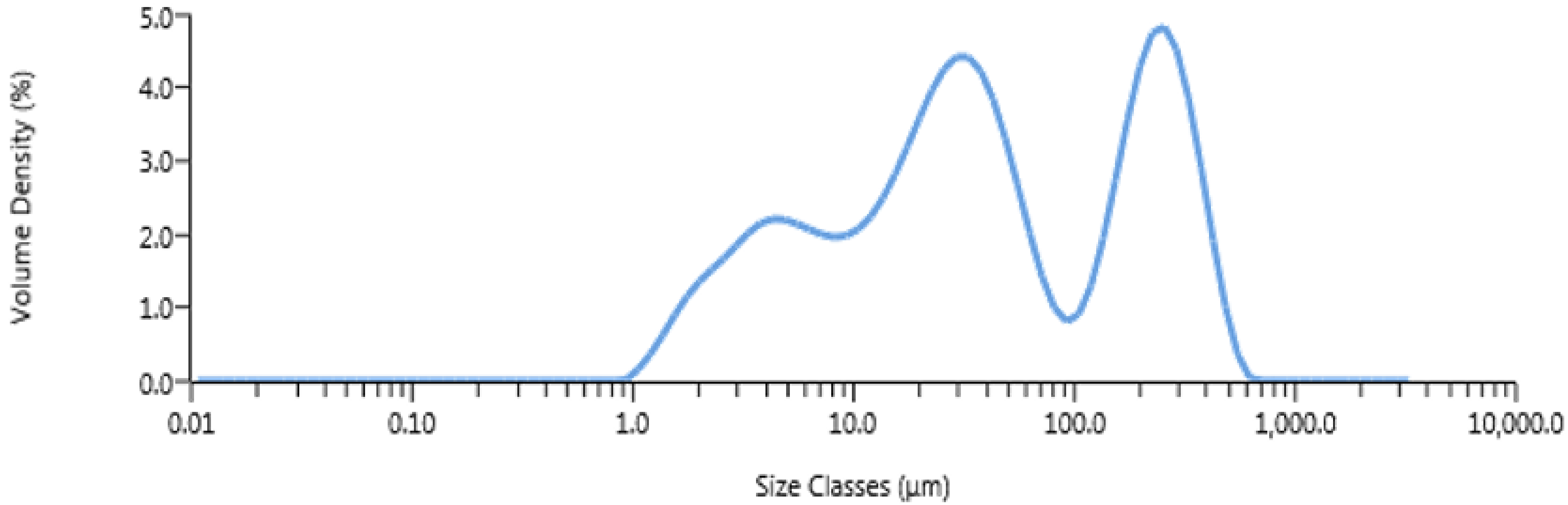
Target obscuration ranges: Wet measurements

- Coarse particles
- >100um
- 10-20% obscuration



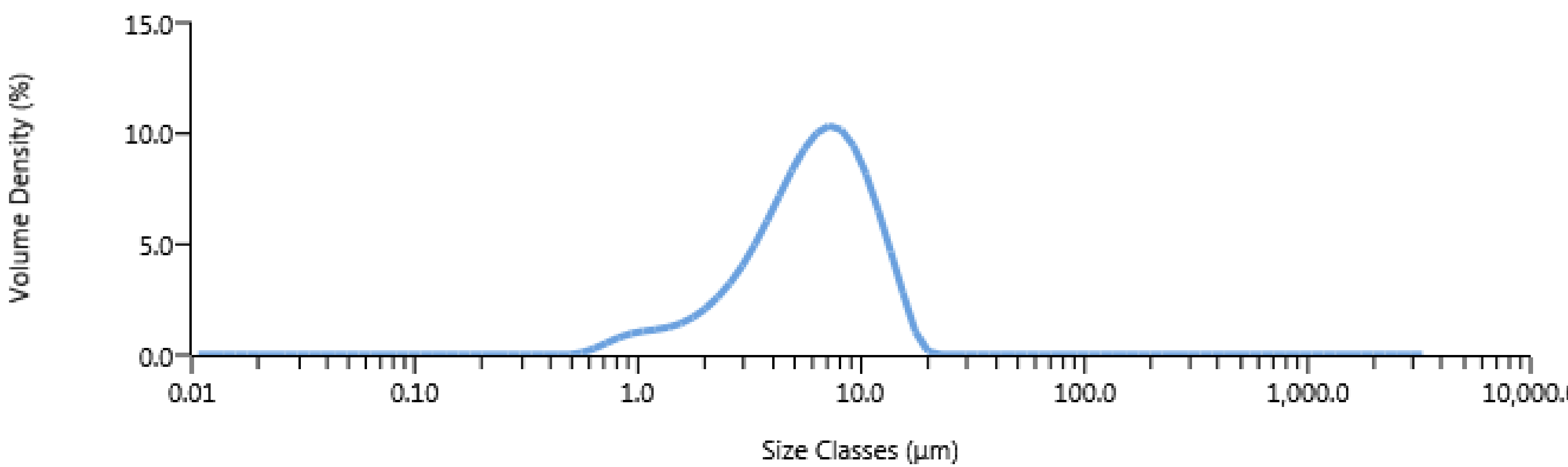
Target obscuration ranges: Wet measurements

- Polydisperse samples
- eg 1-500um in one sample
- 10-20% obscuration



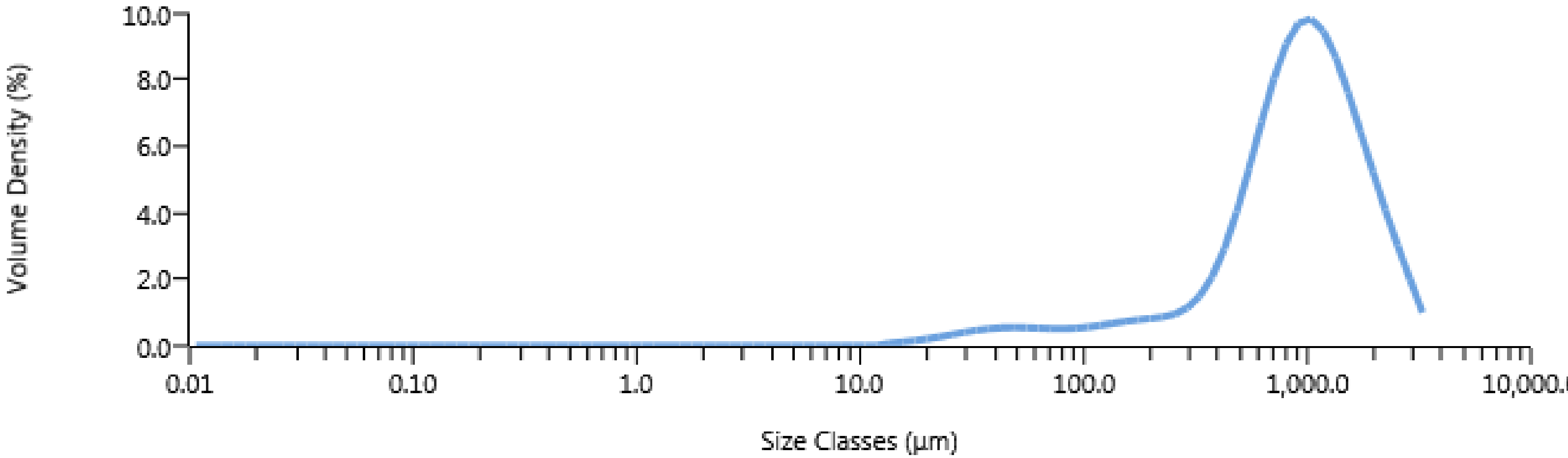
Target obscuration ranges: Dry measurements

- Fine and cohesive powders
- 0.5 to 3-5% obscuration
- Obscuration filtering ensures that only detector scans within the set obscuration range are included in the results



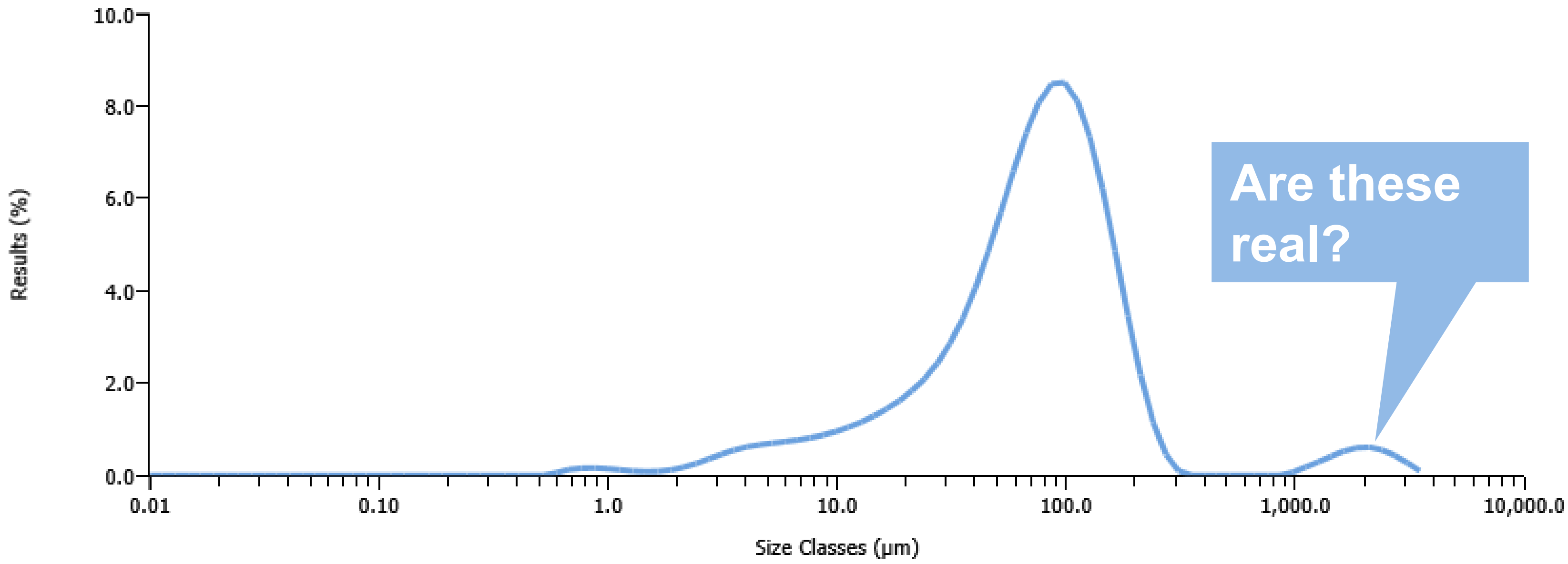
Target obscuration ranges: Dry measurements

- Coarse and free-flowing powders
- 0.1 to 6-8% obscuration
- Obscuration filtering ensures that only detector scans within the set obscuration range are included in the results



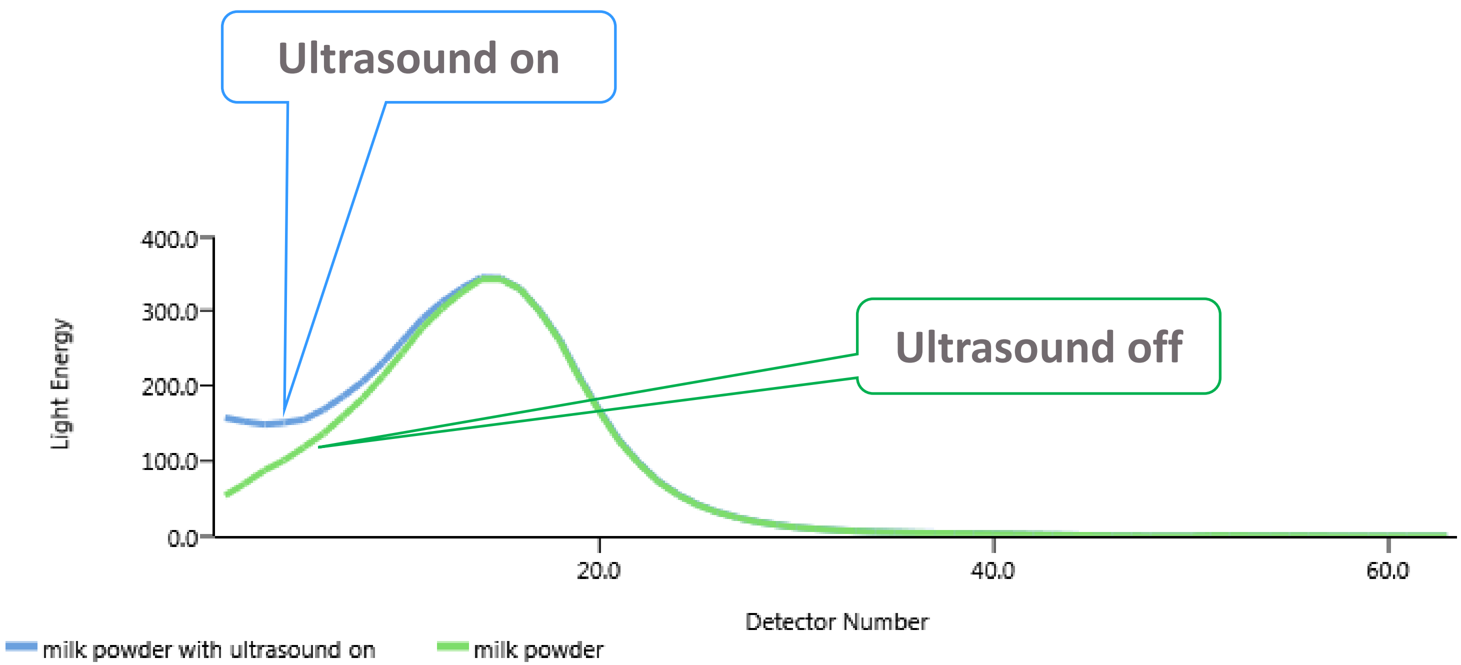
Beam Steering

- The peak on the right of this graph suggests the presence of large particles.
- However this could be caused by Beam Steering, resulting from:
  - Thermal instability following the use of ultrasound in solvents
  - Partial dissolution of the sample in the dispersant - changing its refractive index
- Or real large particles?



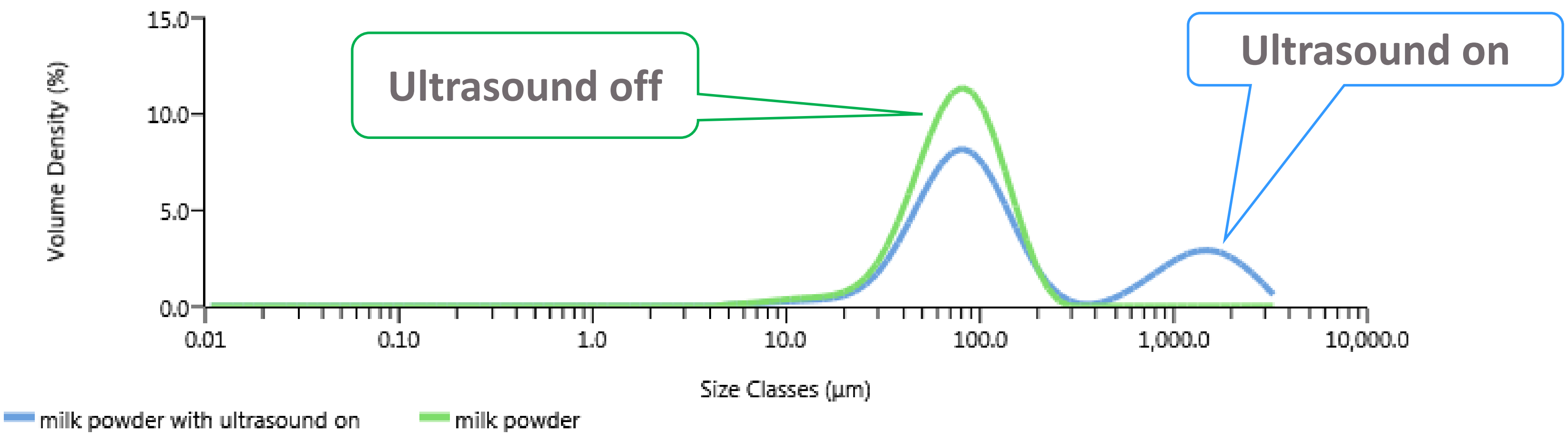
Unexpected large particles: Beam steering

- Ultrasound generates heat in the dispersant
  - Causing scattering signal on low angle detectors
  - Particularly in more volatile dispersants



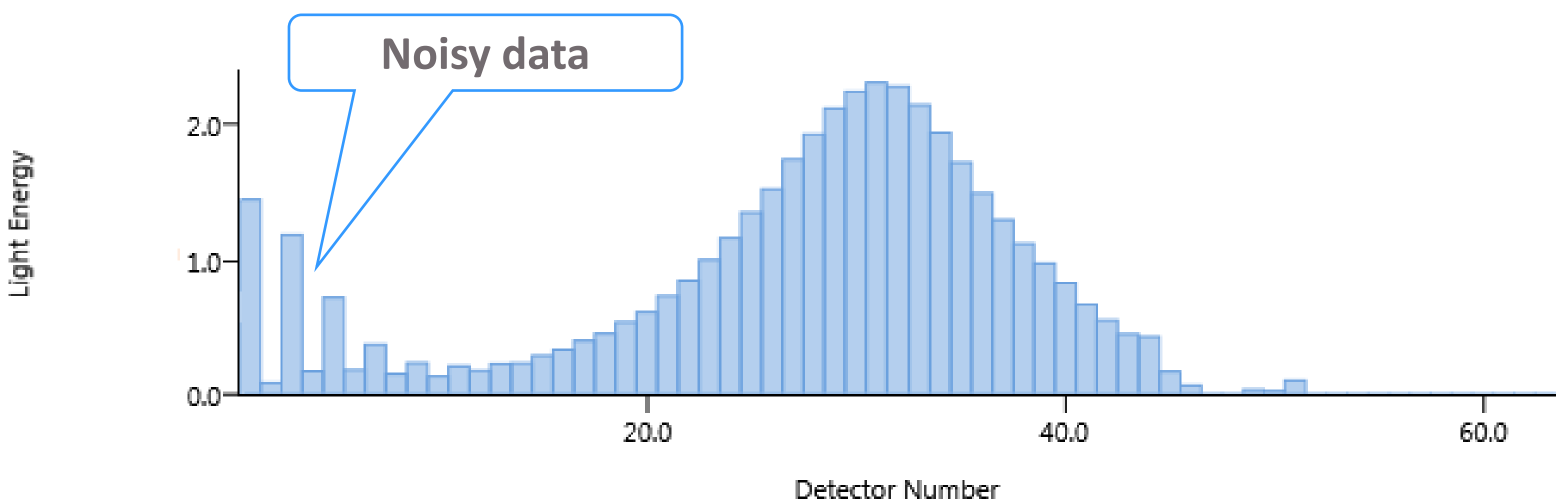
Unexpected large particles: Beam steering

- Ultrasound generates heat in the dispersant
  - Causing scattering signal on low angle detectors
  - Particularly in more volatile dispersants
  - This low angle scattering is interpreted as large particles
- Use a pre-measurement delay after ultrasound
  - Allows thermal gradients to dissipate



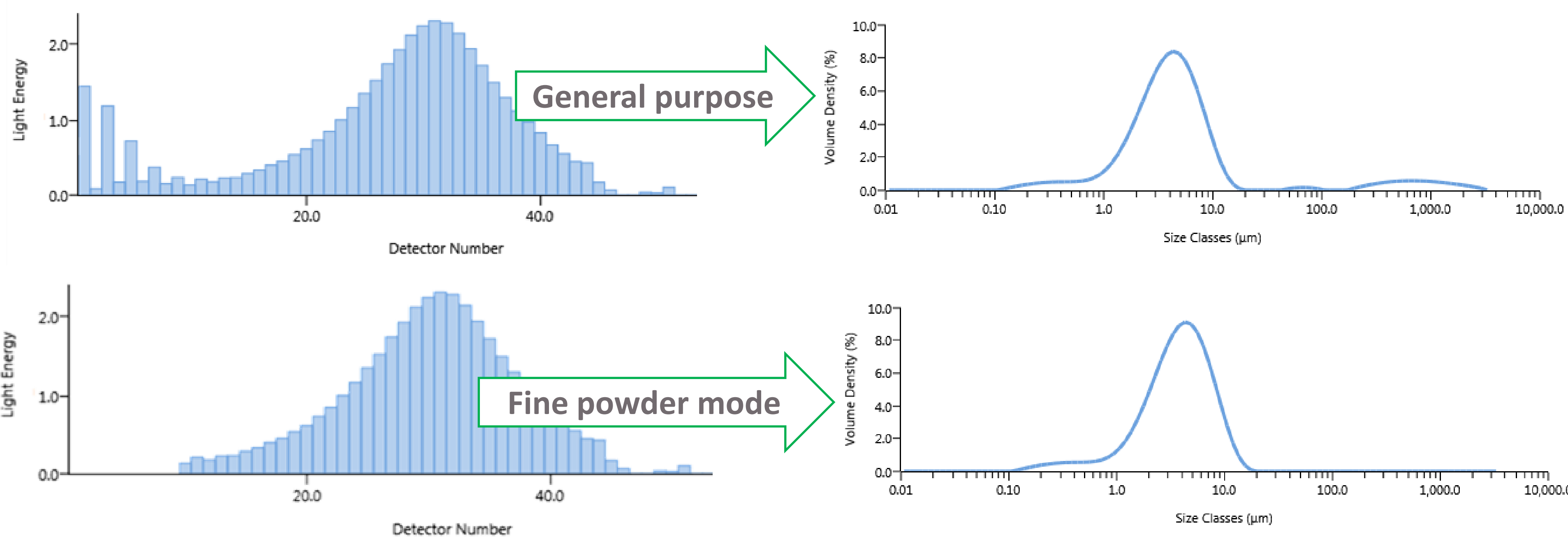
Unexpected large particles: Dry measurements

- Noise on the low angle detectors (1 to 10) can be significant when measuring fine particles dry
  - The noise is caused by thermal fluctuations in the air
  - This noise can be interpreted as large particles
- Measuring a longer background may help
  - Otherwise use the fine powder analysis mode.



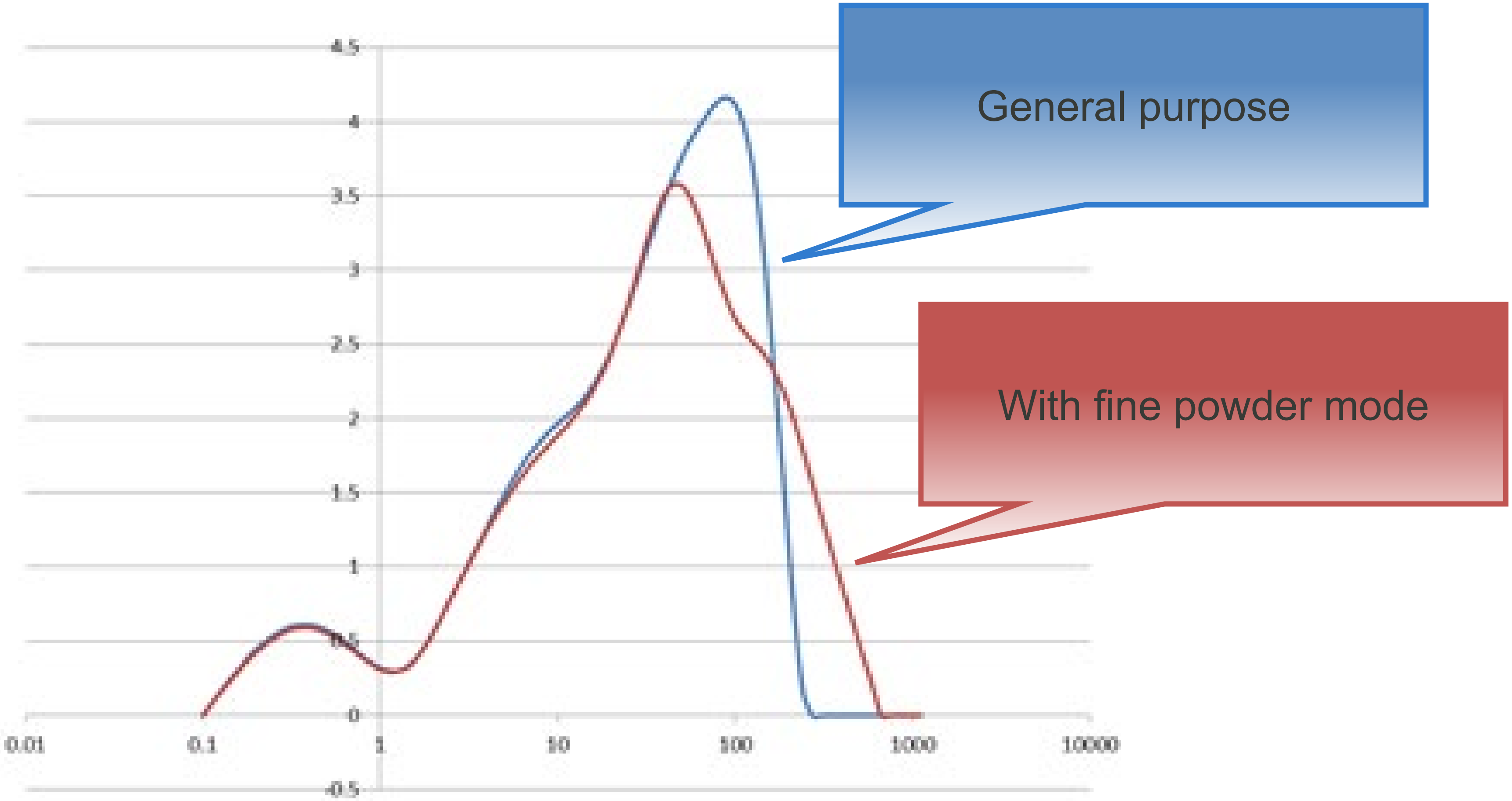
Dry measurements: Fine powder mode

- Fine powder mode removes the first 9 detectors
  - Eliminating the noise which may affect measurement of samples smaller than 10 micron
    - And removing the large modes that it produces
  - Limits the top end of the dynamic range to 600 micron



And when fine powder mode is not appropriate…

- … strange results can be generated.



Further considerations for dry measurements:

- Check:
  - Are the cell windows clean?
  - Is the air pressure correct?
  - Does the air filter need changing?
    - Is there oil droplet contamination or moisture in the air supply?
  - Is the feeder earthed against static electricity ?
  - Is the vacuum bag full?

- Is the sample flow even?
  - if the sample obscuration is high, try lowering the feed rate or adjusting the hopper height
  - try changing the height of the hopper, different basket, ball bearing
  - try a different feed tray: often one tray design will deliver a more even sample flow for a particular material

- Use Fine Powder Mode when material less than 10 microns is present

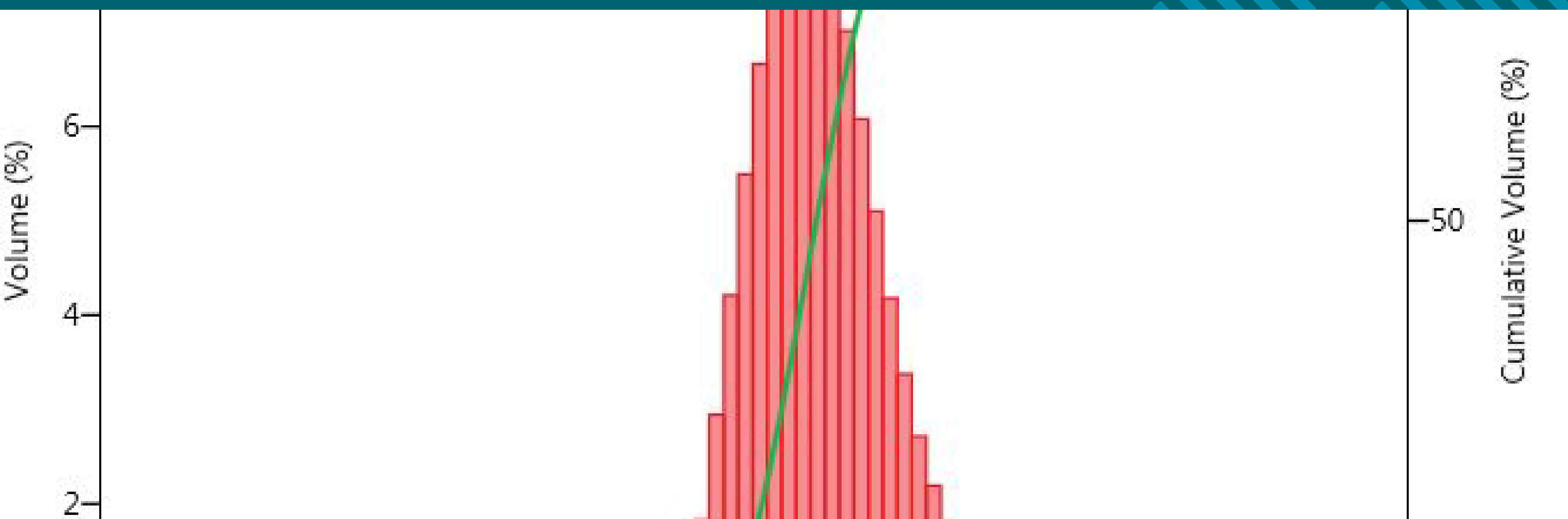
Summary - data quality

- Background data
  - Make sure that:
    - Material is not stuck to the cell windows
    - There is no dispersant contamination
    - There are no thermal gradients
    - That the system has been properly aligned

- Sample data
  - Check that
    - There are reasonable signal to noise levels
    - There is no multiple scattering
    - There is no negative data
    - There is no noisy data
    - The inner detector data is free from castellation
    - There is no beam steering

Mastersizer 3000 Part 2:

Obtaining and Understanding the Size Distribution

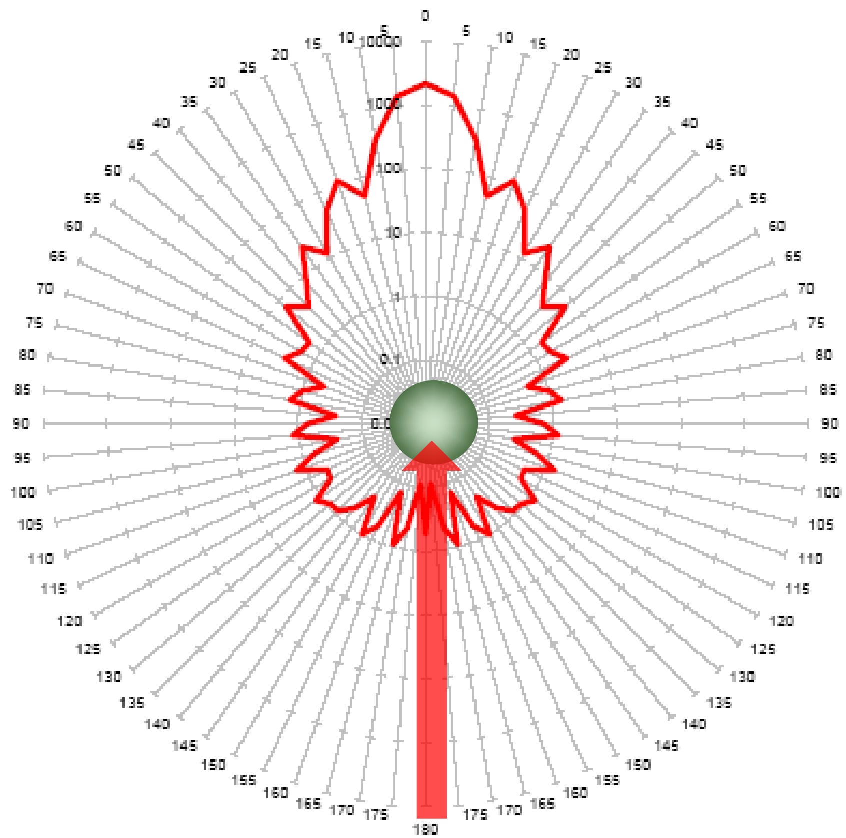


What does laser diffraction measure?

- Laser diffraction systems measure the scattering pattern produced by an ensemble of particles suspended in a laser beam

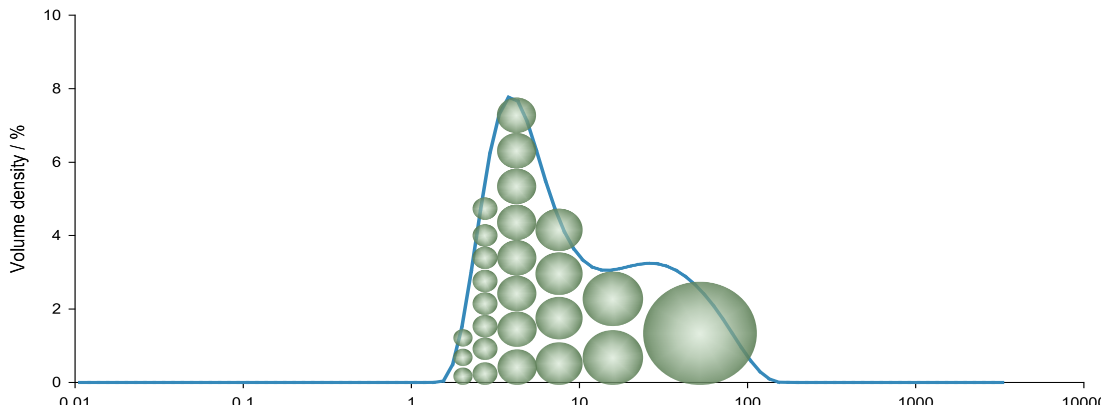
What does an optical model do?

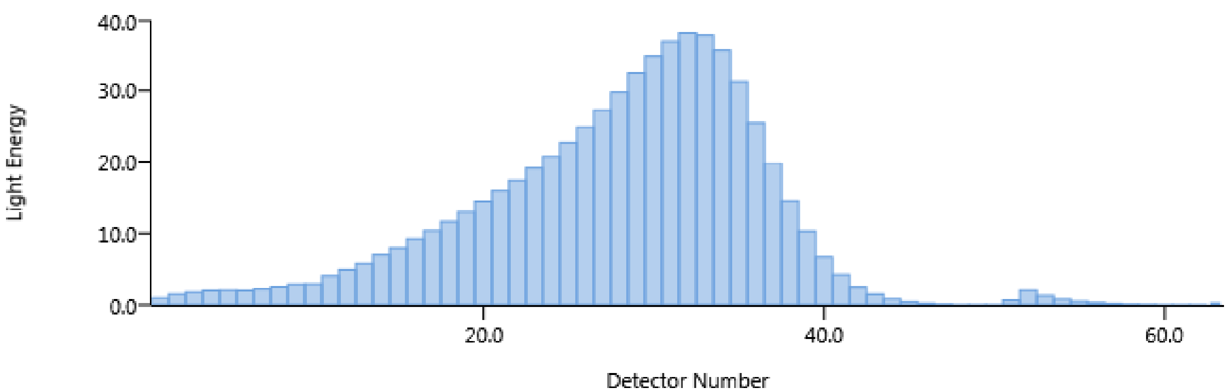
- An optical model predicts the scattering pattern produced by a particle



What does an optical model do?

- And can therefore predict the scattering pattern produced by many particles





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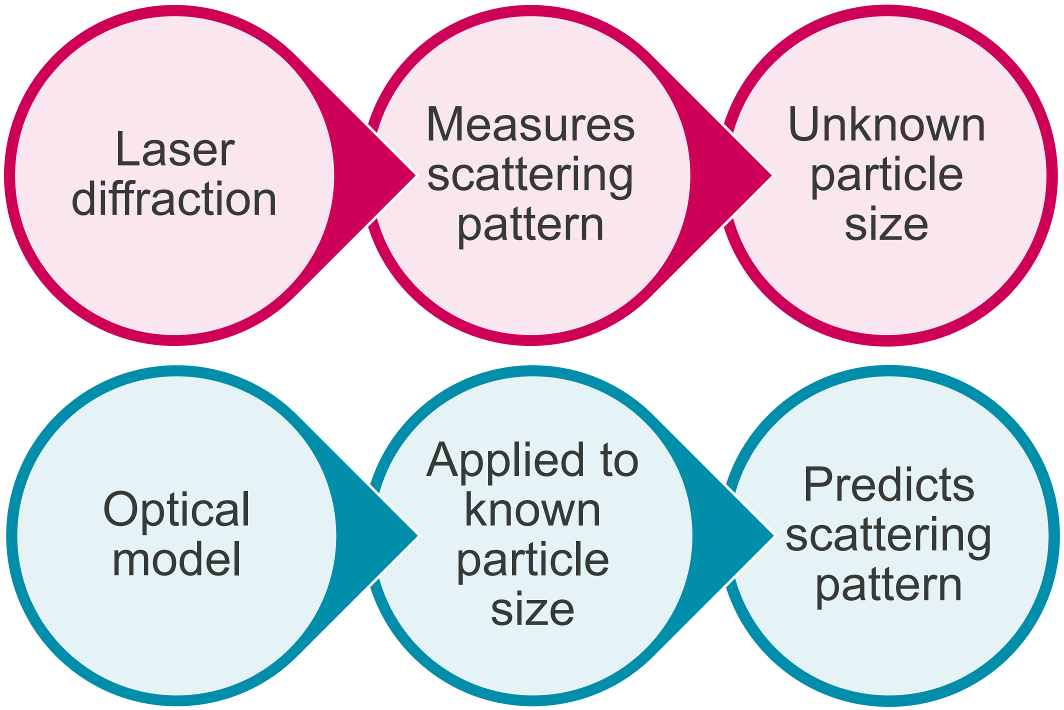
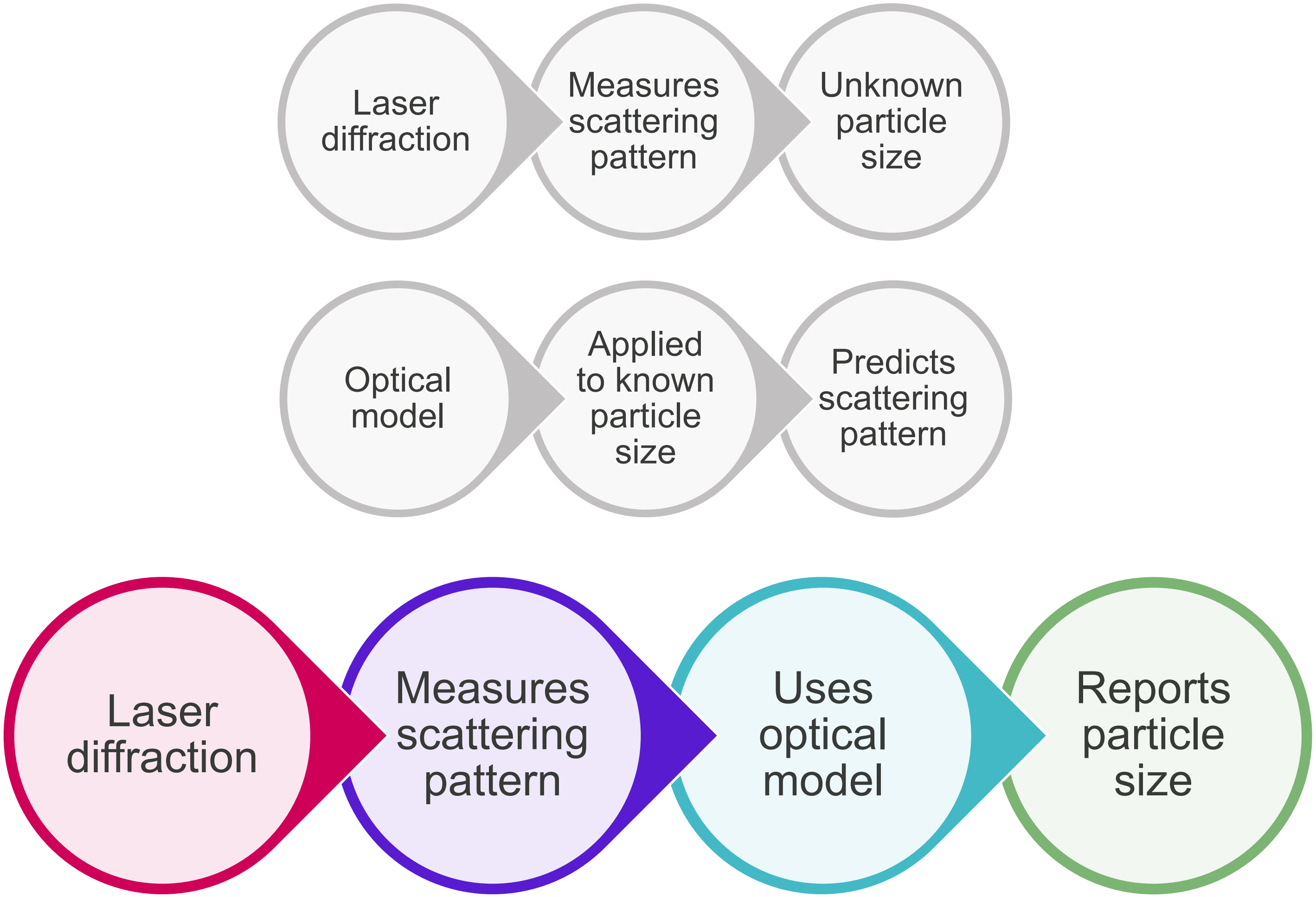
How do we use the optical model?



How do we use the optical model?

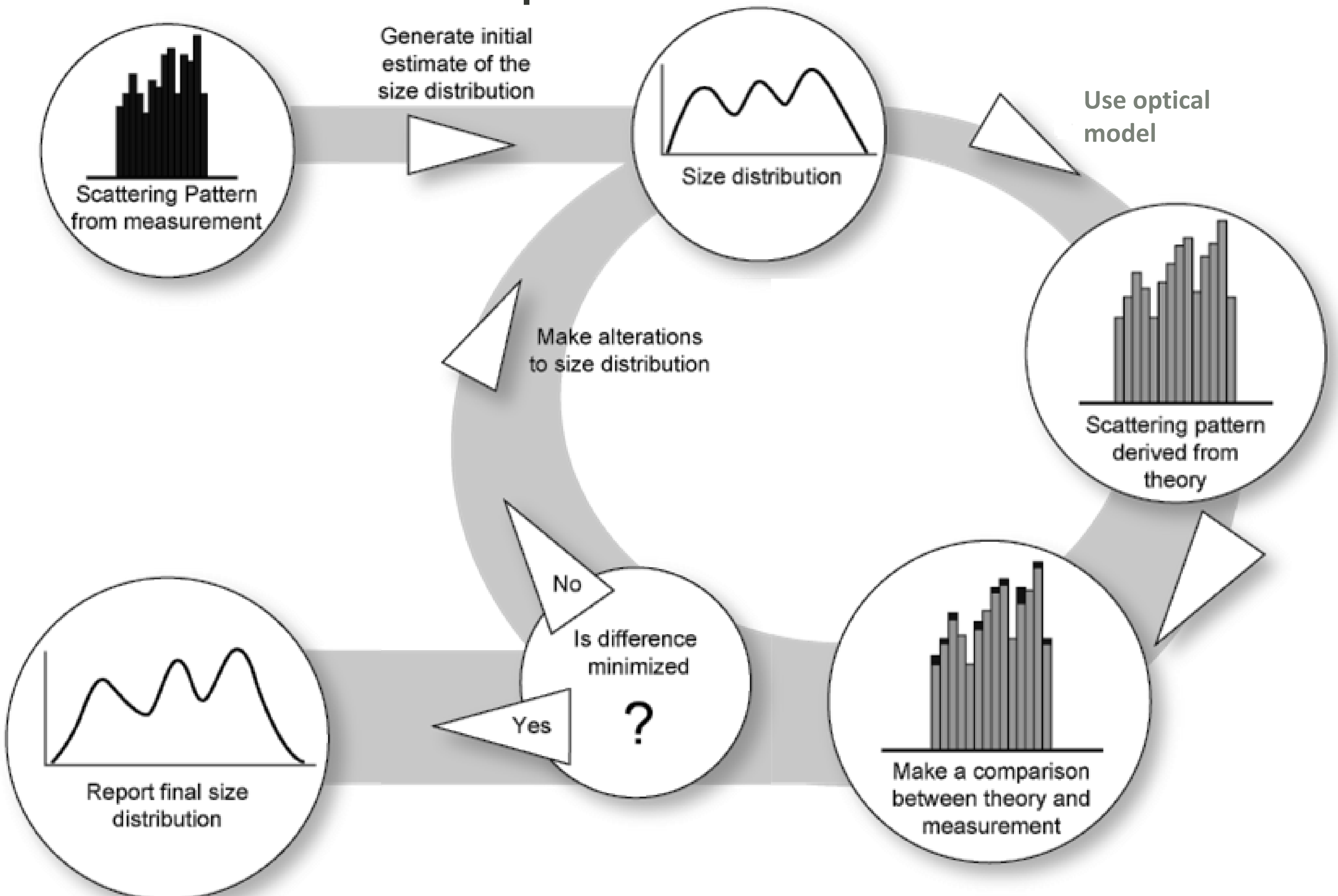


Understanding the data inversion process

Consider the following example:

- What is the answer to 6 x 7 ?
  - The answer to this is easy, it's 42!
  - Working this way through the problem gives one answer
- But what is 42?
  - 21 x 2
  - 40 + 2
  - 126 ÷ 3
  - $\sqrt{1764}$
  - We see that working backwards yields many possible solutions

How do we use the optical model?



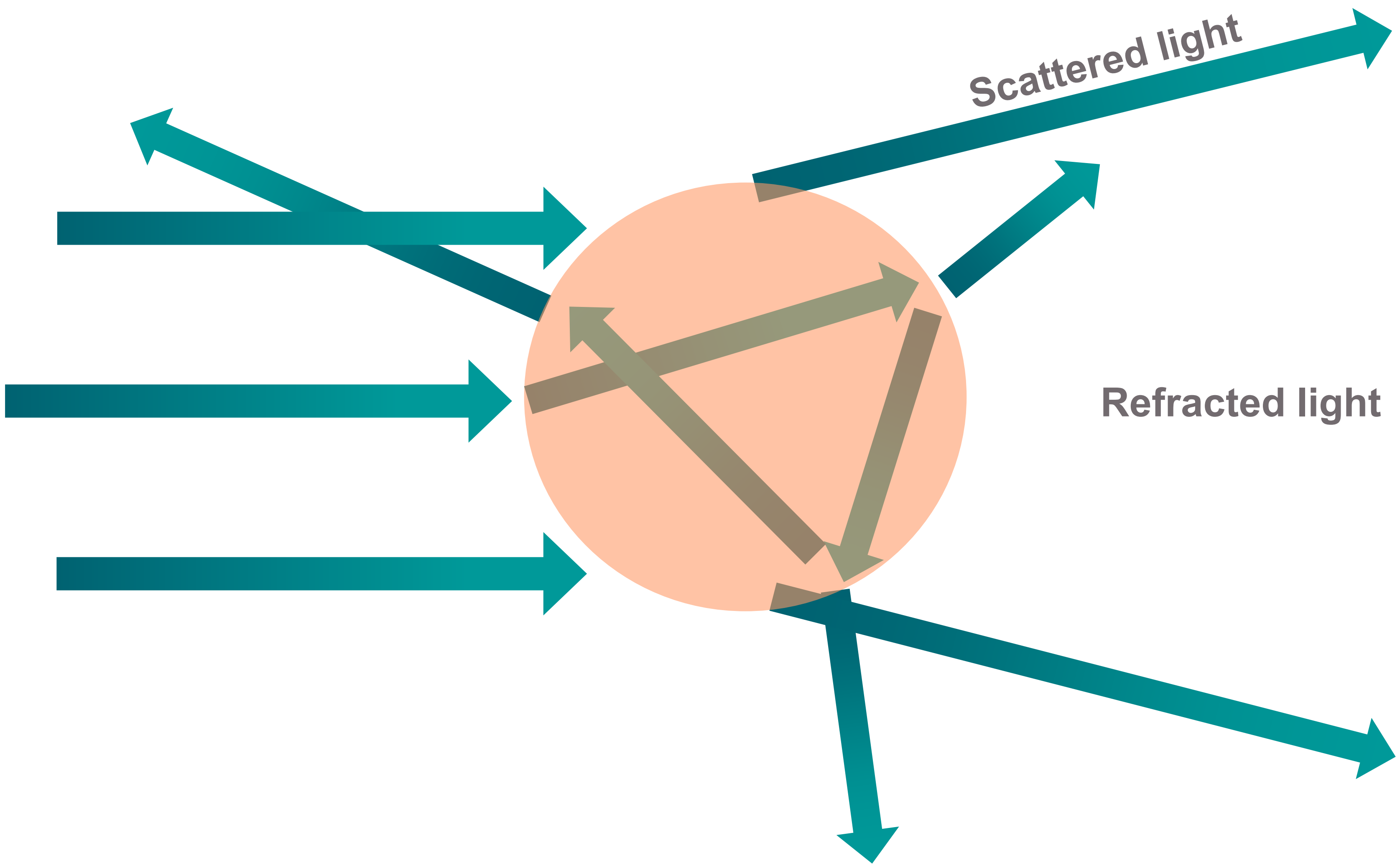
Scattering models: Mie Theory

- Models the interaction of light with matter
  - Assuming that the particles are spherical
  - Assuming that it is a two phase system
- Valid for all wavelengths of light and all particle sizes
- Predicts the dependence of scattering intensity on particle size
- Predicts that secondary scattering is observed for small particles

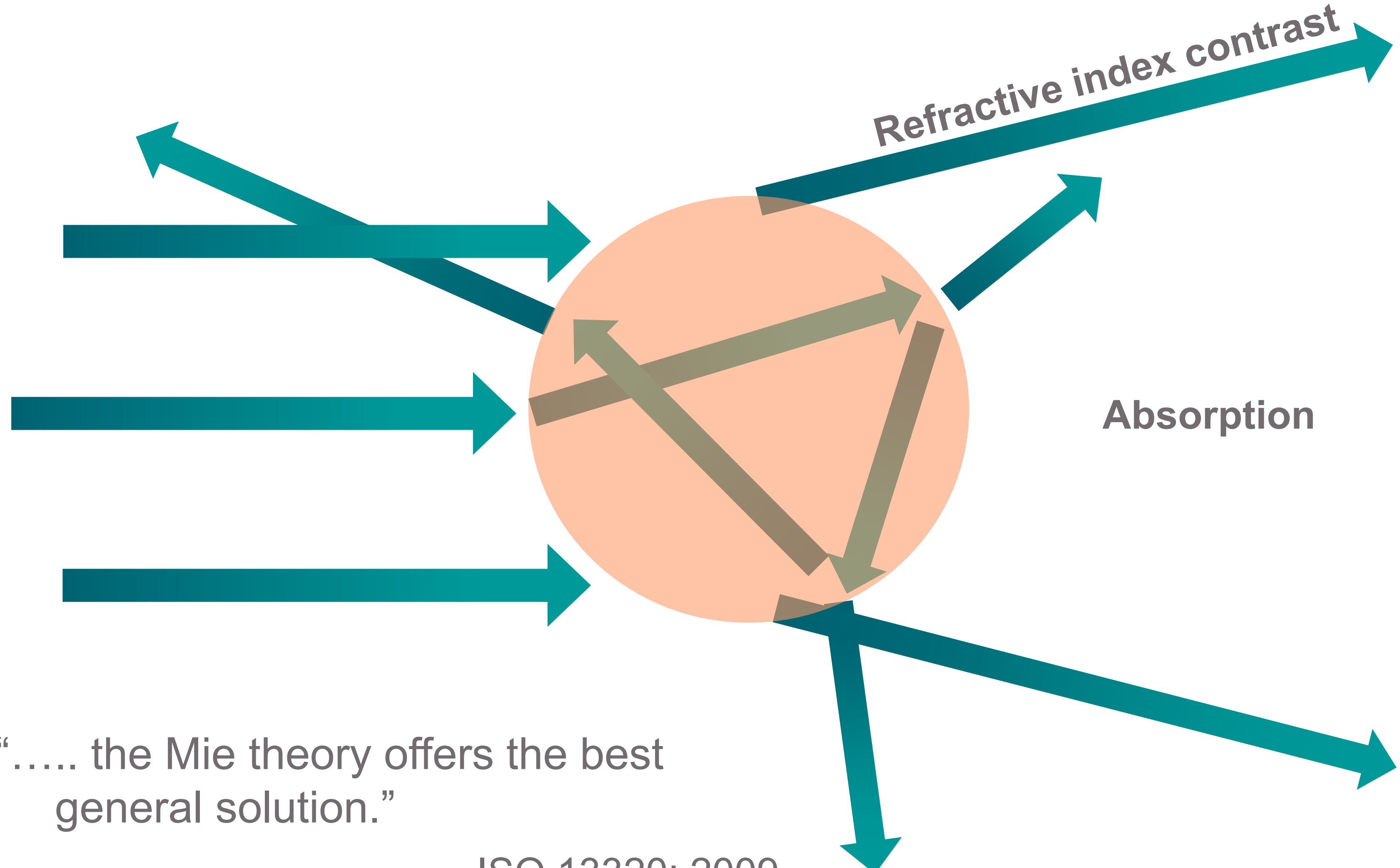
'For particles smaller than about 50µm Mie theory offers the best general solution'

ISO13320

Mie Theory: Predicted scattering



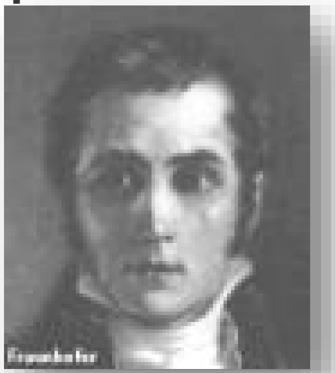
Mie Theory: Optical properties



"….. the Mie theory offers the best general solution."

ISO 13320: 2009

Scattering models: Fraunhofer Approximation

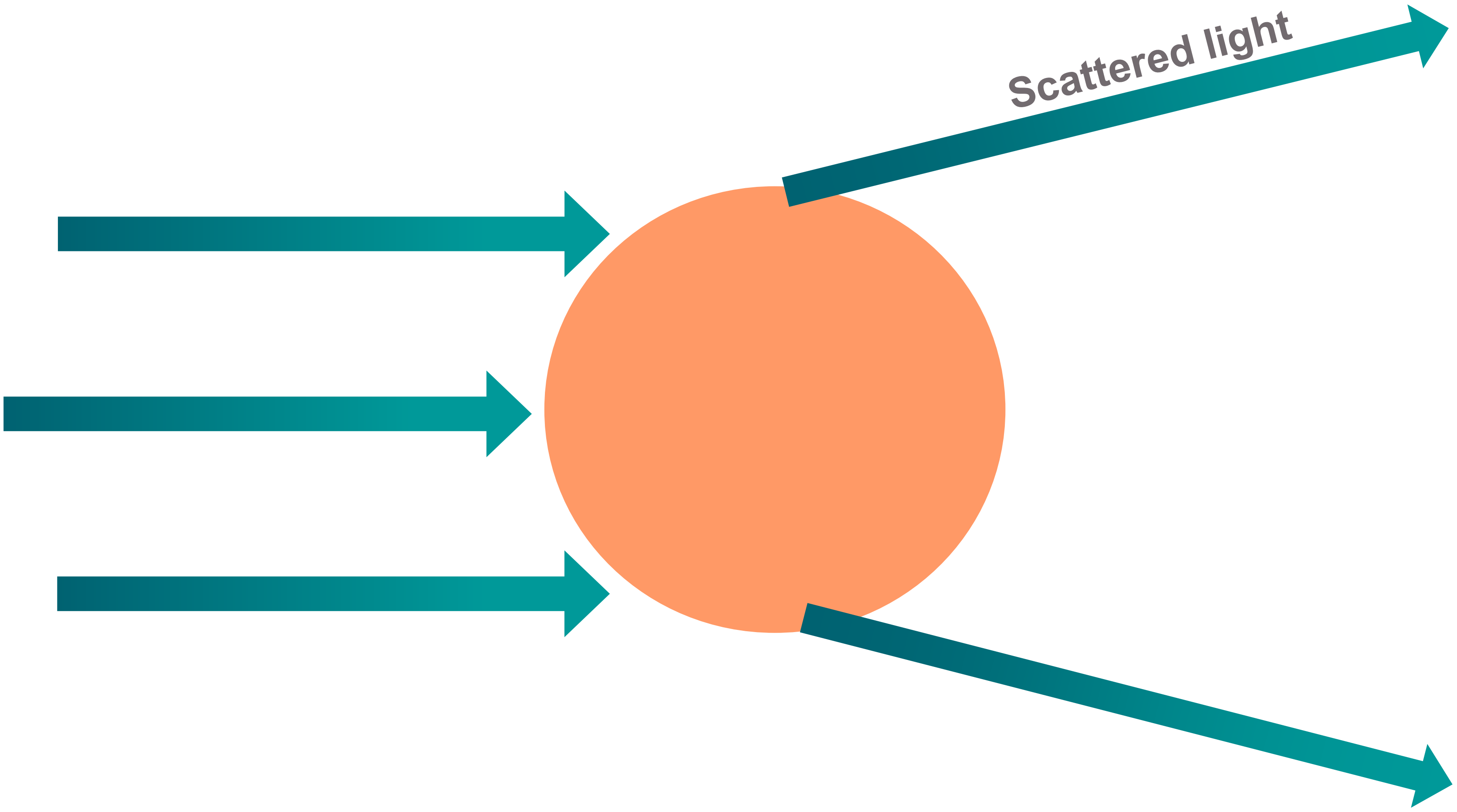


- Same basic assumptions as Mie Theory
  - Assuming that the particles are discs
  - Assuming that it is a two phase system
- Plus the additional assumptions that
  - The refractive index contrast is high (RRI > 1.73)
  - The particles are opaque
  - The wavelength of the light is much shorter than the particle size
  - The angle of refracted light is small
- In the MS3000 software the Fraunhofer approximation is available as a particle type.

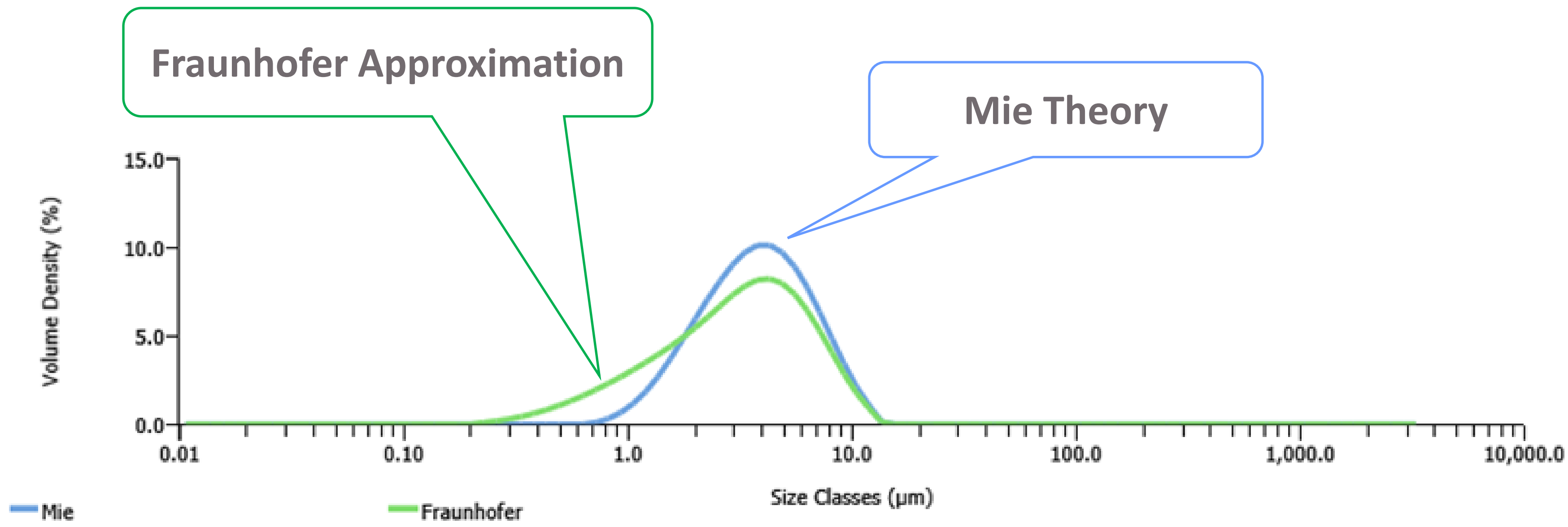
'The advantage of this equation is that it is relatively simple and quick to calculate'. 'The Fraunhofer approximation does not make use of any knowledge of the optical properties of the material'.

ISO13320

Fraunhofer Approximation: Predicted scattering



Comparing the results of the scattering models



'If the Fraunhofer approximation is applied for samples containing an appreciable amount of small, transparent particles, a significantly larger amount of small particles may be calculated.'

ISO13320

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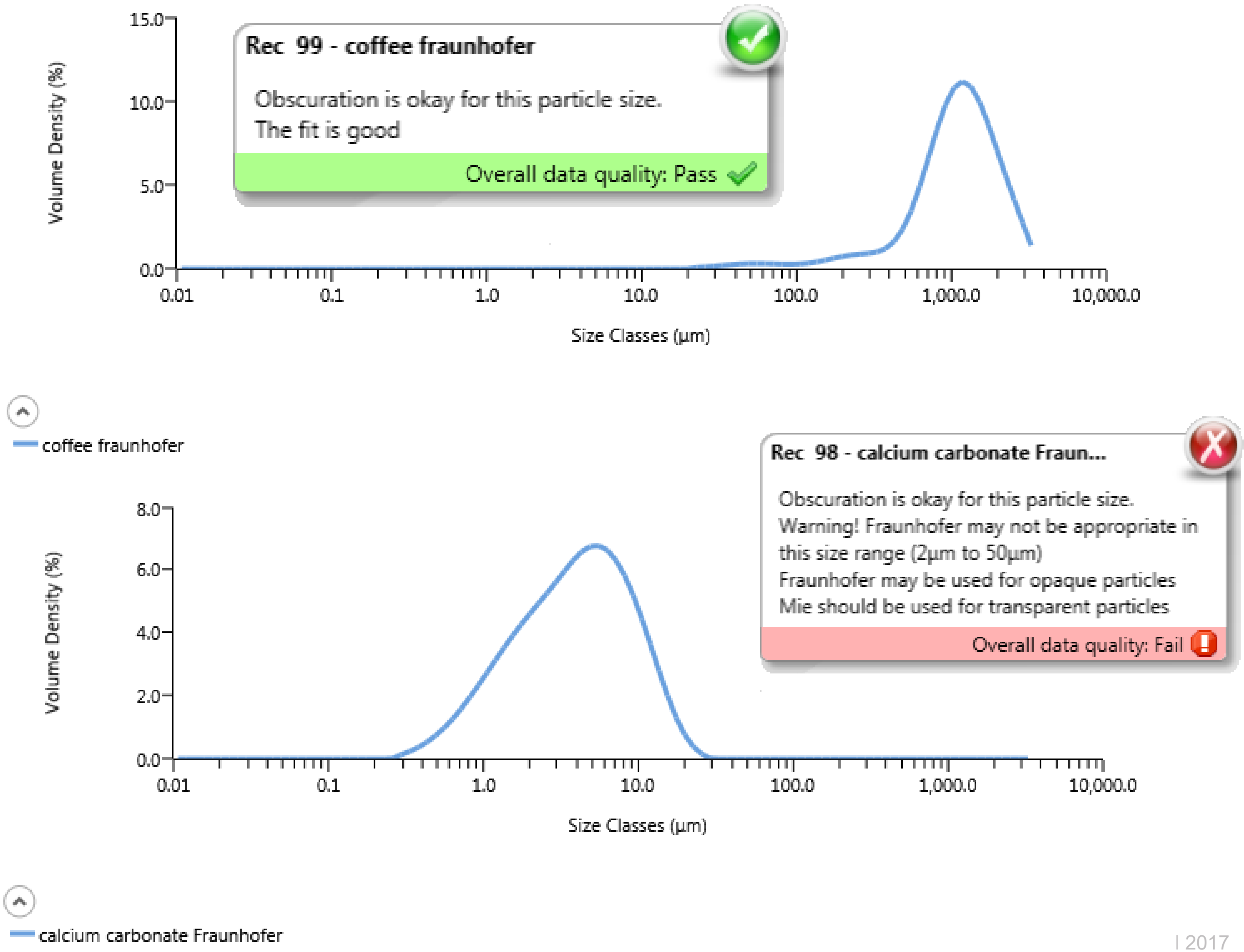
Scattering models - Fraunhofer Approximation

- **Disadvantages**

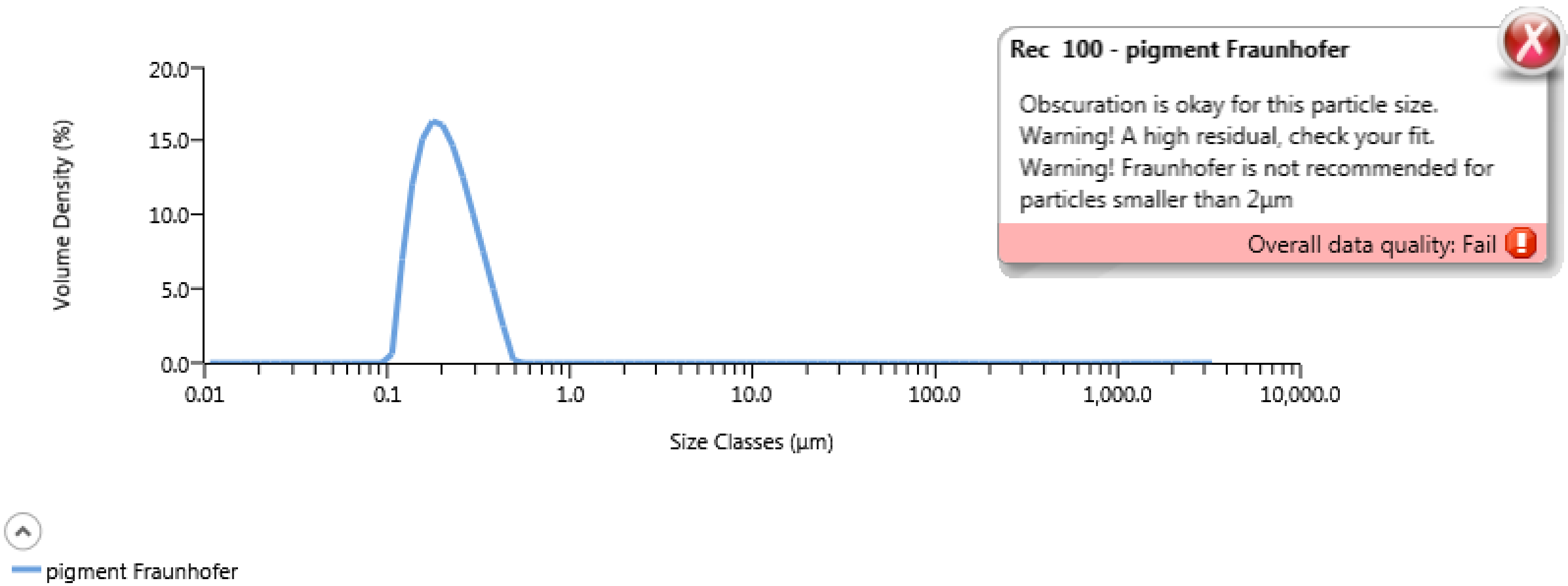
  Will produce incorrect answers when…
  - Particles are <50µm
  - The angle of scatter becomes large and secondary scattering occurs.
  - The relative refractive index is small (<1.3) - this equates to a particle refractive index of 1.73 in water.

- **Claimed Advantage**
  - "No need to know the *optical properties* of your material."

Mie vs Fraunhofer: Data quality advice



Mie vs Fraunhofer: Data Quality advice



Which optical properties do we need?

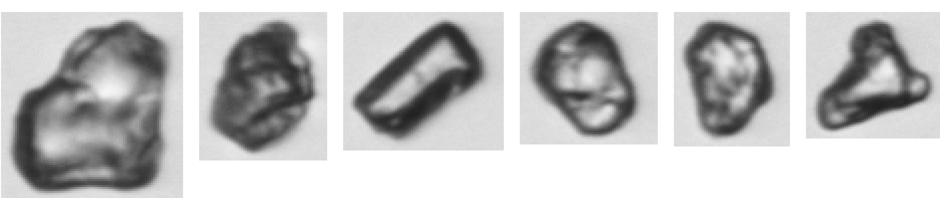
- To use Mie theory correctly we need to know three optical properties:
  - The refractive index of the dispersant
  - The refractive index of the sample material
  - The imaginary part of the refractive index of the sample material
    - Often referred to as the absorption

‘Good understanding of the influence of the complex refractive index in the light scattering from particles is strongly advised in order to apply the Mie theory or the Fraunhofer approximation appropriately.’

ISO13320

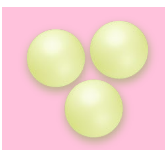
The imaginary refractive index (or absorption)

- The absorption can be determined by looking at the dispersed sample under a microscope and observing its
  - Shape
  - Transparency
  - Internal structure
- Absorption is generally required to a factor of 10
  - E.g. 0.1 or 0.01 (not 0.023)



Images of some calcium carbonate particles, an absorption of 0.01 would be used for these particles.

Estimating absorption from particle appearance

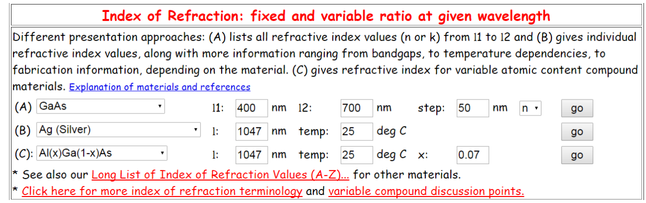
Appearance	Absorption	Example
	0	Latices
	0.001	Emulsions
	0.01	Crystalline milled powders
	0.1	Slightly colored powders
	1.0+	Highly colored (complementary) and metal powders

Methods for determining the refractive index

- Four main routes to refractive index information
  - Reference books and the internet
    - Appendix of ISO 13320
    - Malvern materials database
    - CRC handbook
    - Manufacturers label (for dispersants)
    - Online info
  - Refractometer measurements
  - Microscope observations
  - Empirical/semi-empirical models

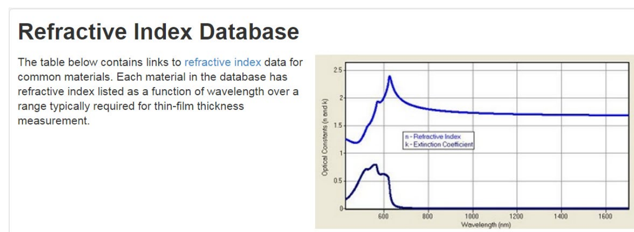
Online sources for refractive index information

- www.Luxpop.com



- RefractiveIndex.info

- www.Filmetrics.com/refractive-index-database



- Google Scholar

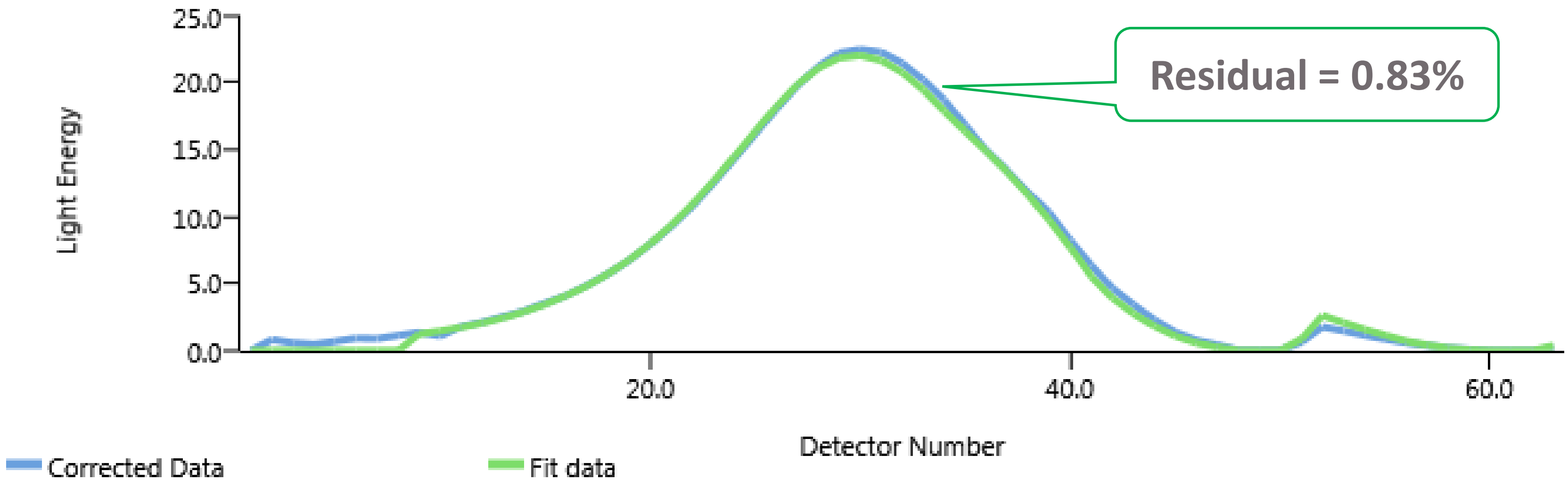
- Remember to look for a wavelength of 633nm for the red light and 470nm for the blue light.

Choosing the refractive index

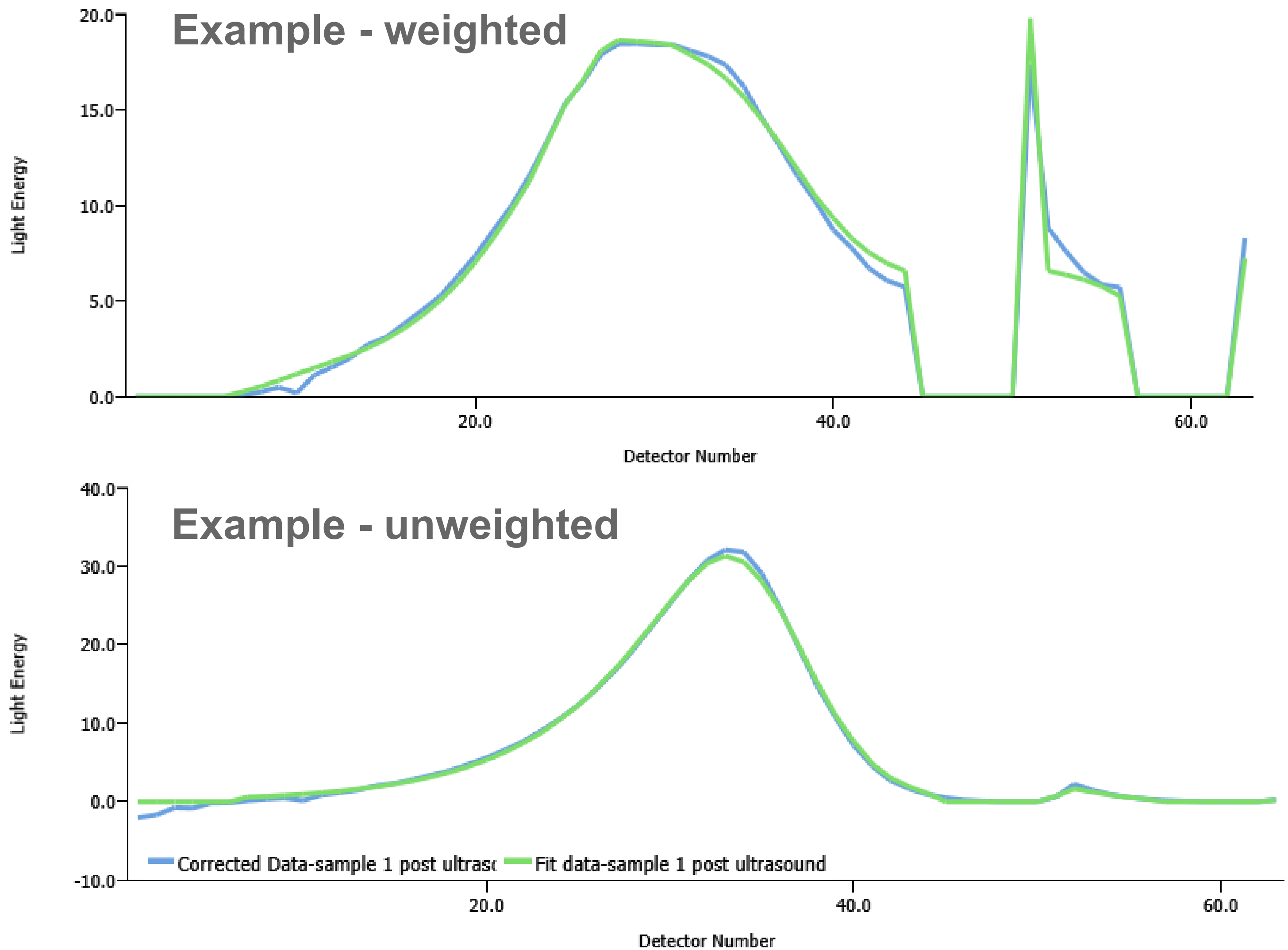
- You can estimate the optical properties based on typical values of similar materials.
  - A Refractive Index is generally only required to 2 decimal places e.g. 1.42 not 1.4234
- Some families of similar materials are:
  - Plastics and elastomers = 1.38 - 1.57
  - Organic compounds = 1.4 - 1.7
  - Inorganic salts = 1.52 - 1.8
  - Metal Oxides = 1.6 - 2.5
- Use the estimated refractive index as a starting point and examine the fit to confirm the suitability of the value chosen.

Assessing the data fit

- The fit report shows the measured and calculated scattering data
- How well these overlay is known as the data fit
- The residual quantifies how good the fit is
  - Residual = area between the two curves

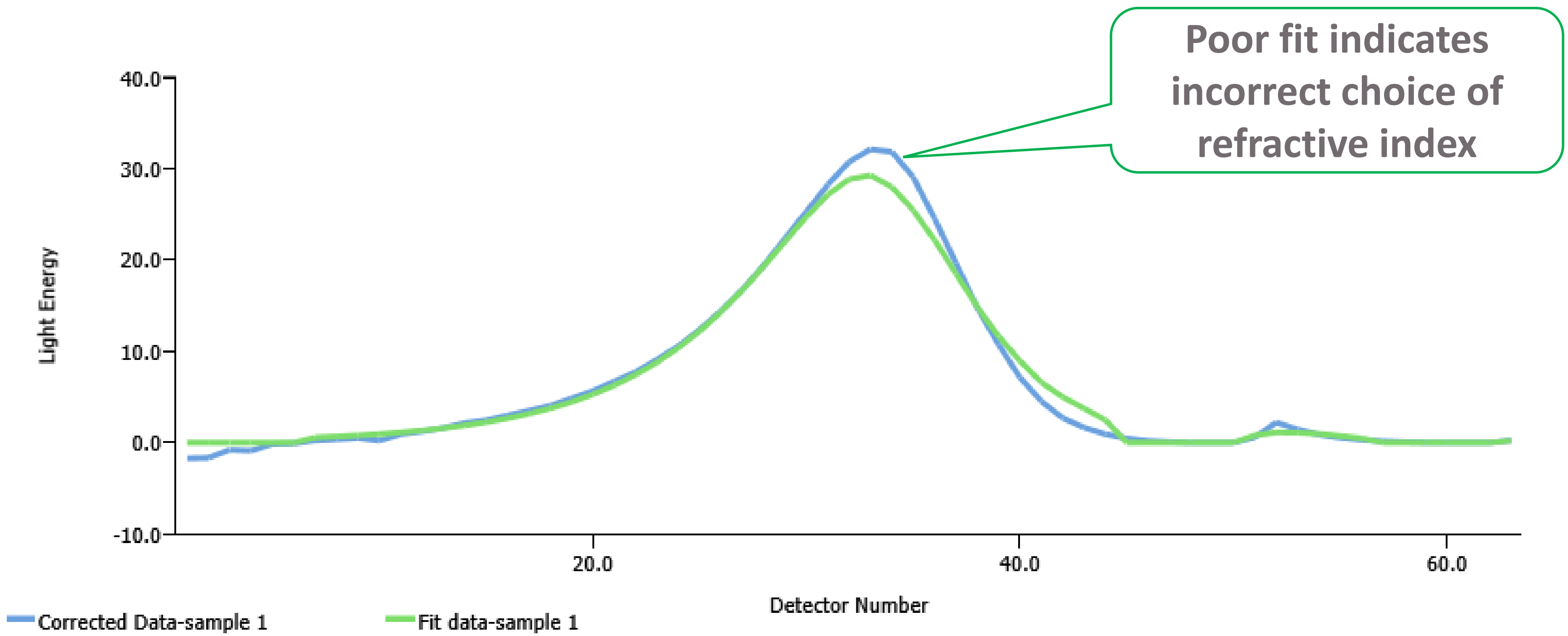


Weighted and un-weighted data fits



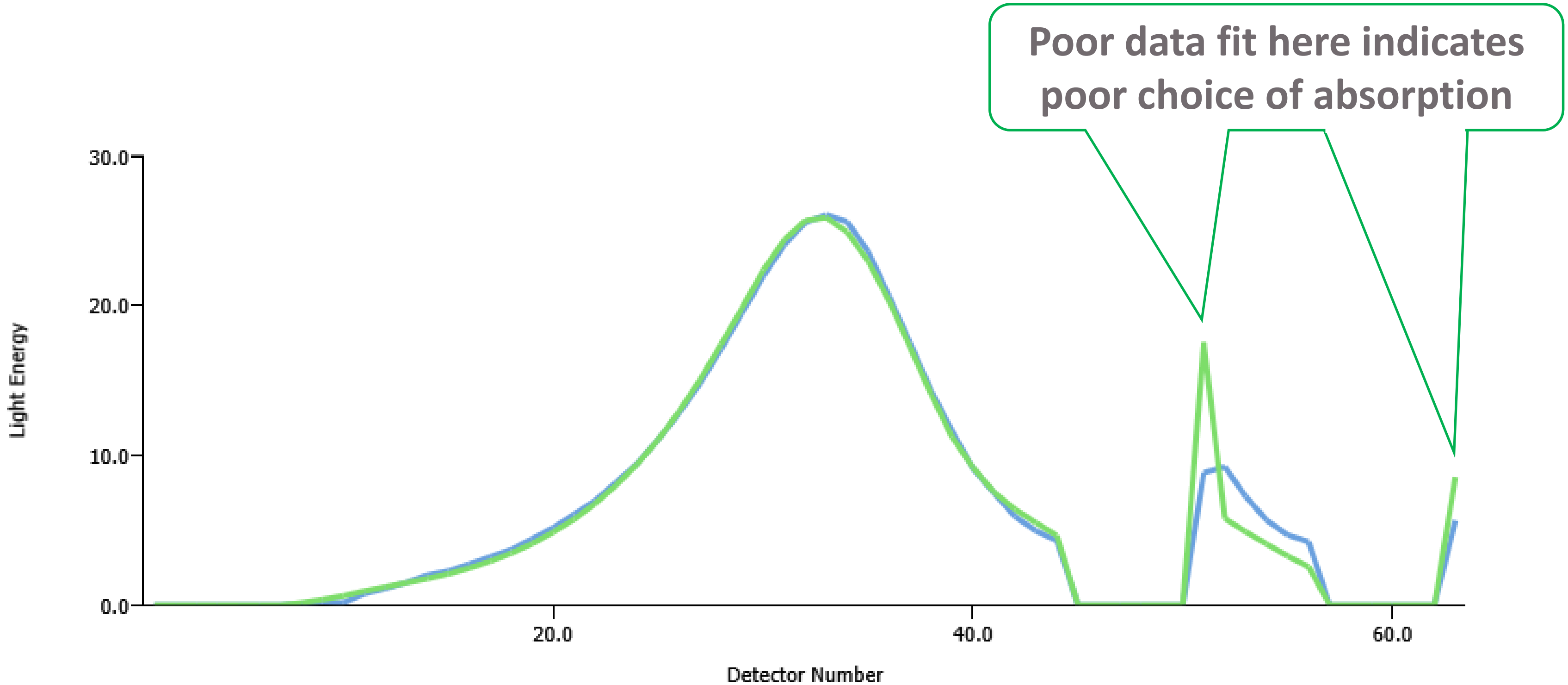
Inspecting the data fit: refractive index

- A poor fit to the focal plane detectors (< 40) suggests an incorrect choice of refractive index



Inspecting the data fit: absorption index

- Misfits to the extinction detectors indicate an incorrect absorption value
  - 51 in the red light
  - 63 in the blue light



Residuals - good "rule of thumb"

- For most size distributions, the residual should typically be less than 1%
- For a **good** fit, the weighted and unweighted residuals should be of similar orders of magnitude
- A low residual is good, but the distribution should be believable

Poor agreement

Record View

Measurement file 4

Drag column header here to group by that column

Record Number	Sample Name	Particle Refractive Index	Particle Absorption Index	Residual(%)	Weighted Residual(%)	Dv 10(µm)
17	Black pigment	1.680	0.100	4.51	2.14	0.0172
16	Black pigment	2.400	1.000	1.00	1.04	0.0147

Good agreement

Residuals for very narrow distributions

- Residuals less than 1.0 are not always achievable.
- Narrow distributions can give higher residuals than expected

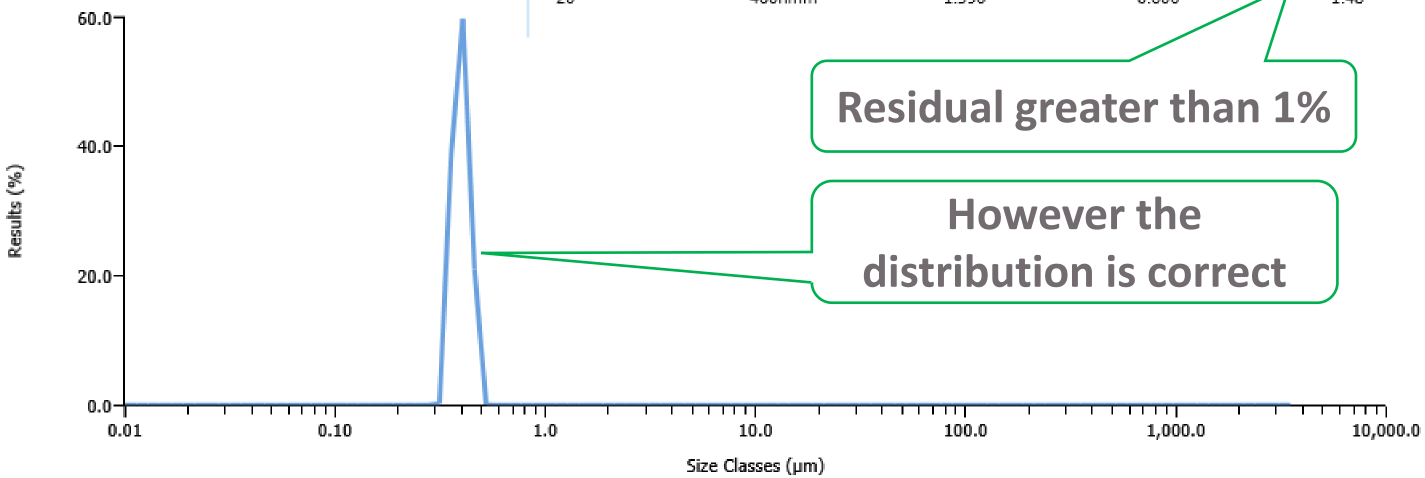
Record View

*Measurement file 4

Drag column header here to group by that column

Record Number	Sample Name	Particle Refractive Index	Particle Absorption In...	Residual(%)	Weighted Residual(%)	Dv 10(µm)
17	Black pigment	1.680	0.100	4.51	2.14	0.0172
18	400nmm	1.590	0.000	2.56	1.03	0.364
19	400nmm	1.590	0.000	3.17	1.04	0.364
20	400nmm	1.590	0.000	1.48	0.99	0.364

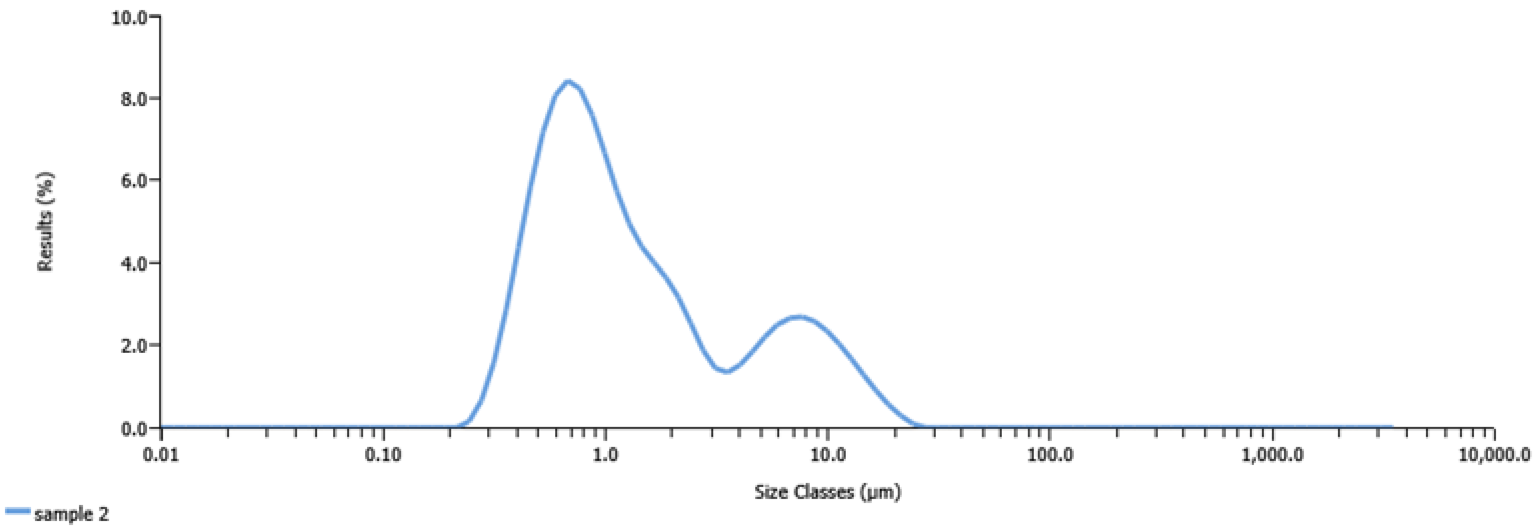
Residual greater than 1%



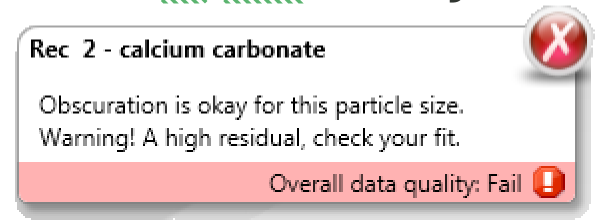
However the distribution is correct

Assessing the data fit: Example

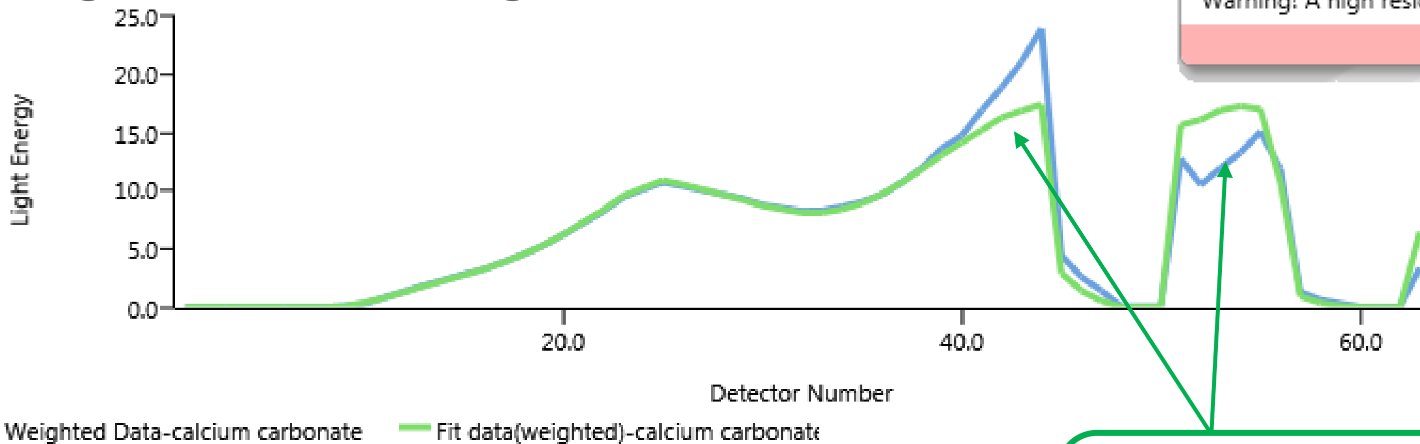
- The user is seeing an "unexpected" mode of small material.
- The optical properties used were:
  - RI:1.4, Absorption: 0.01



Assessing the fit using 1.4/0.01

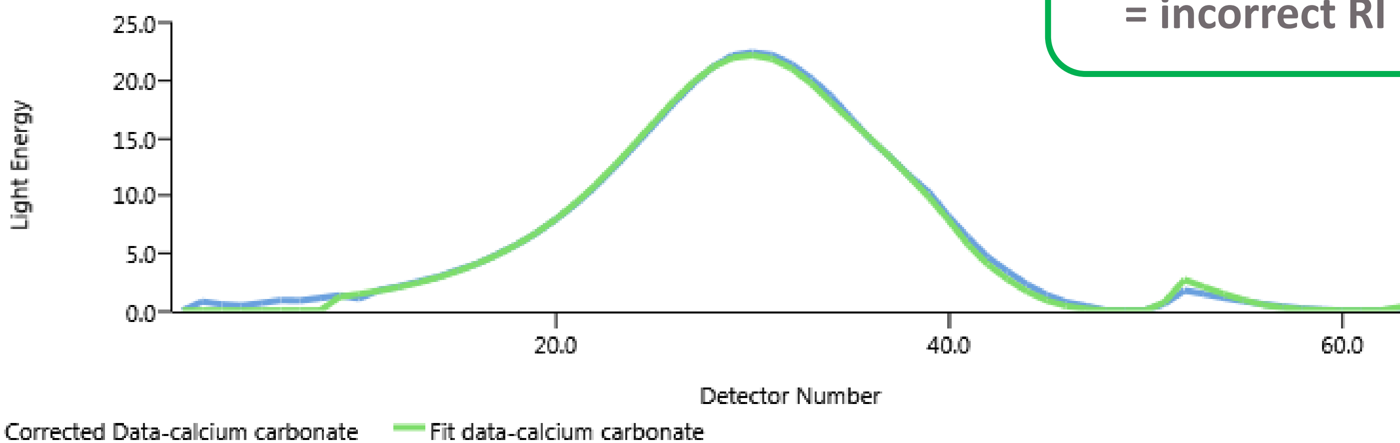


Weighted fit   Weighted Residual = 3.26



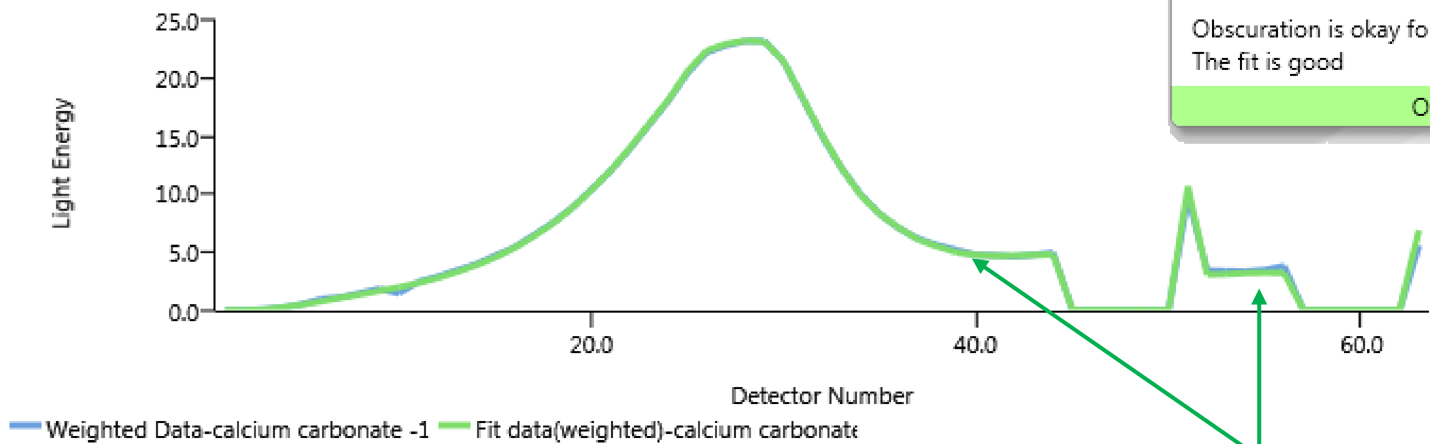
Poor fit
= incorrect RI

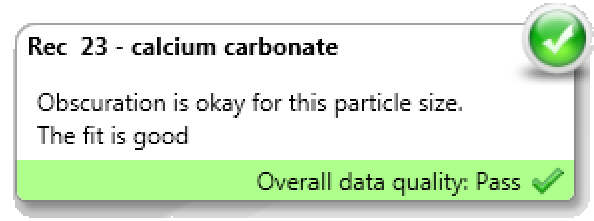
Un-Weighted fit   Residual = 0.82



Assessing the fit using 1.54/0.01

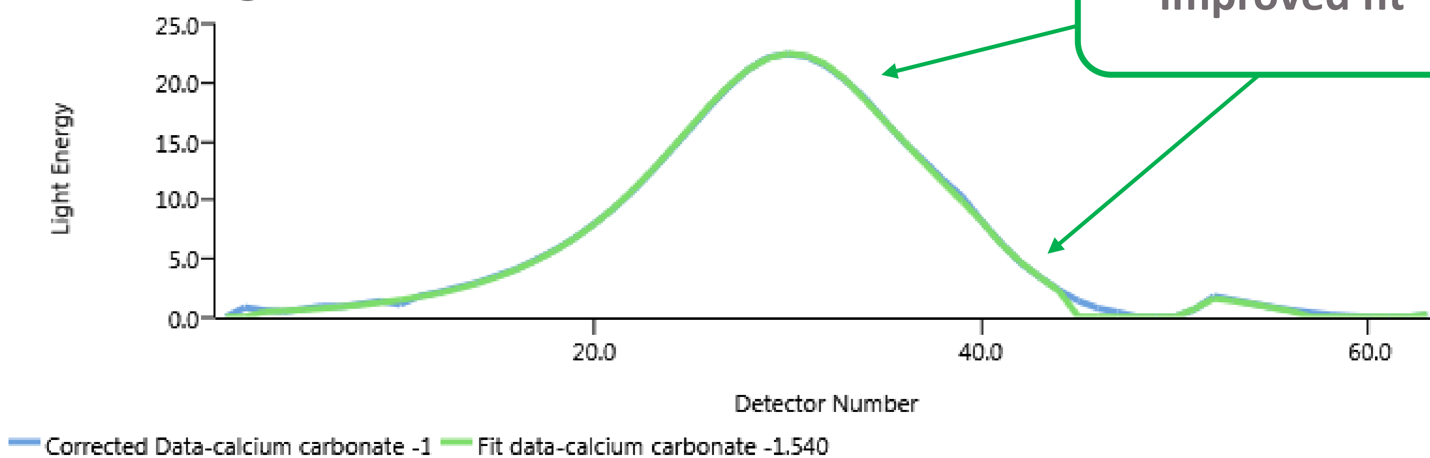
Weighted fit **Weighted residual = 0.48**



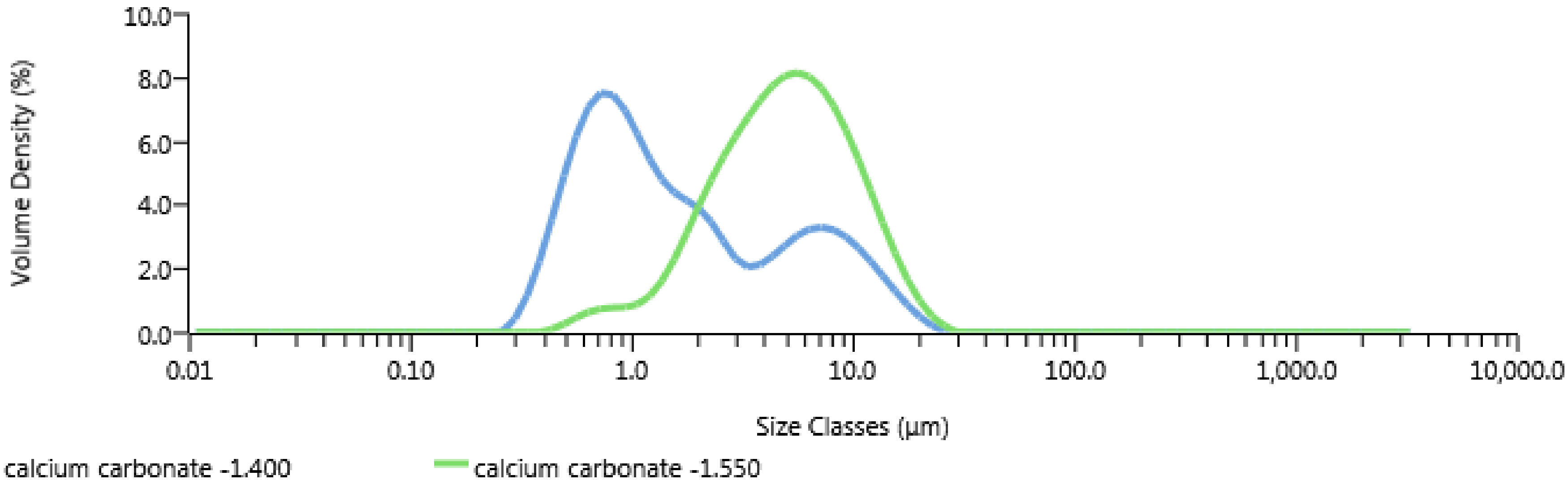


Improved fit

Un-Weighted fit **Residual = 0.57**



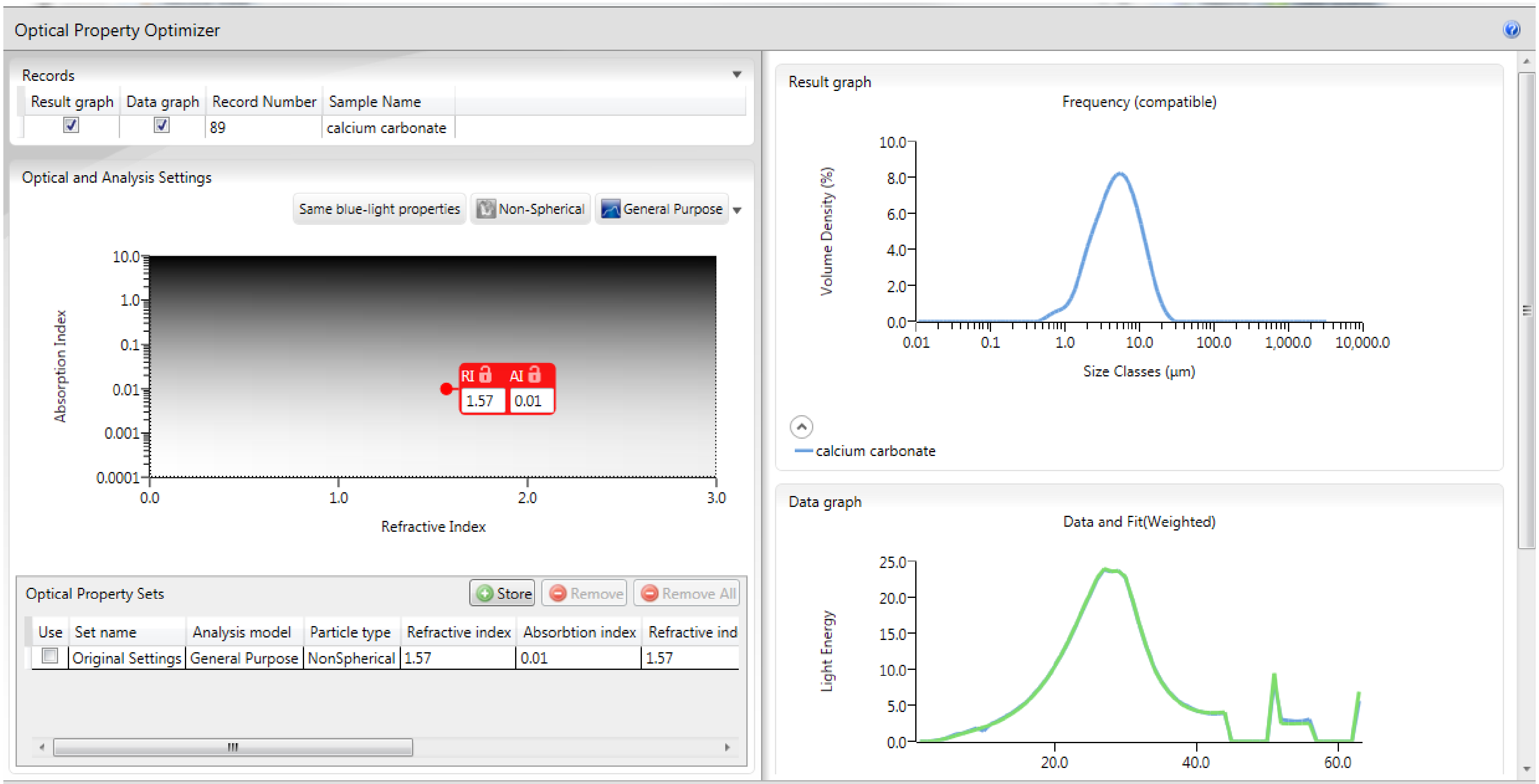
Looking at the results



- Sample is calcium carbonate
  - Reference RI is between 1.53 and 1.63

The optical property optimiser (OPO)

- Offers a quick way to adjust optical properties and assess the fit and result



Setting optical properties of mixtures

- Sensitivity to optical properties increases as particle size decreases.

Option 1 Consider the smallest

- Set the optical properties to suit the finest particles.

Option 2 Consider the average

- Calculate the volume-weighted average optical properties.
- Accept there may be errors in the fines.

Option 3 Consider using Fraunhofer

- Use the Fraunhofer Approximation.
- Accept there may be errors in the fines.

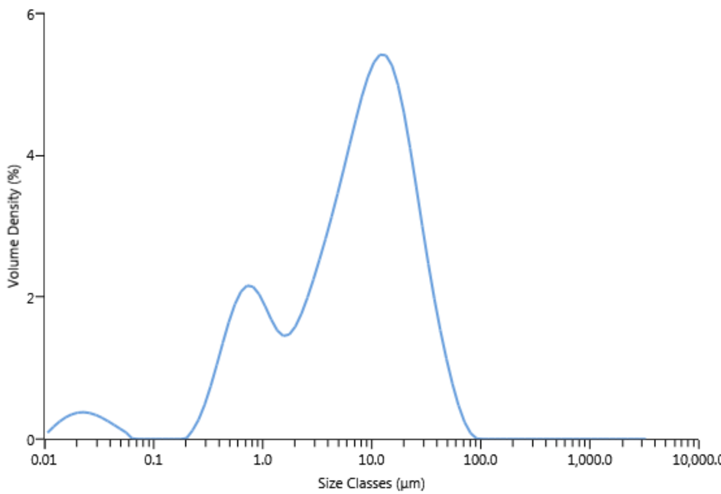
Plastisol – a real life example

- Plastisol uses include:
  - Slush moulding
  - Textile ink
  - Binder in Electric Solid Propellant (rocket fuel)
- Plastisol is a suspension of PVC particles in a liquid plasticizer:

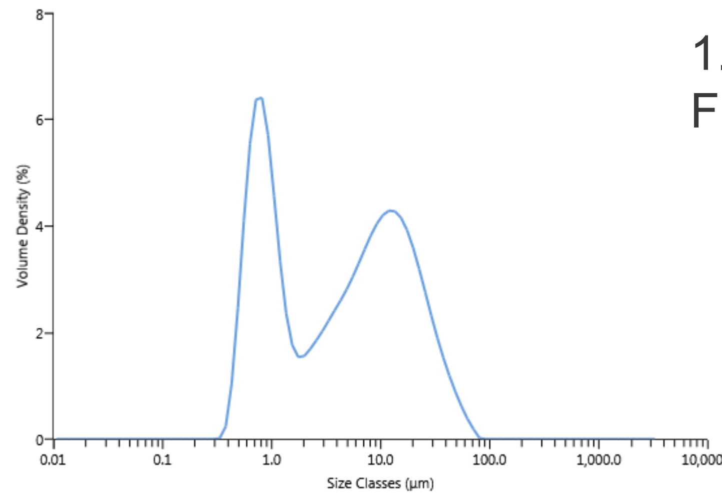
	Refractive index	Absorption
Blowing Agent	1.76	0.1
Filler	1.59	0.1
Pigment	2.51	0.01
Polyvinyl chloride	1.54	0.01

Plastisol – by optical properties

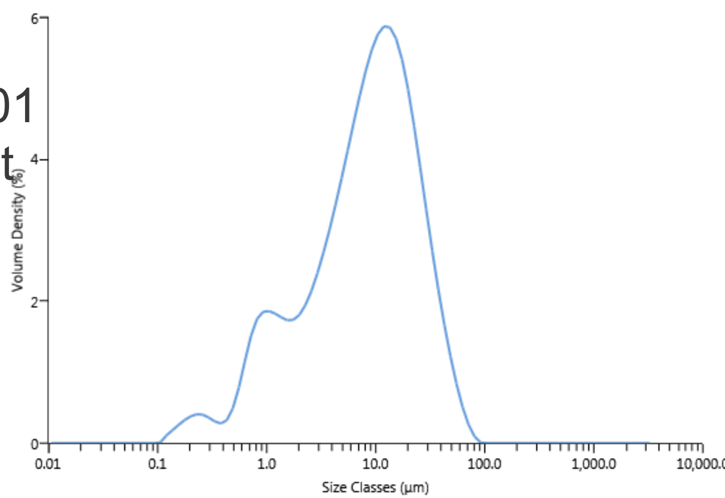
1.76/0.1
Blowing agent



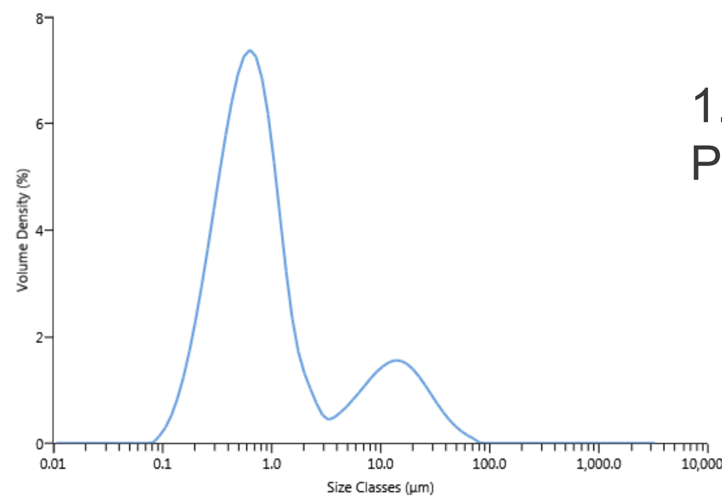
1.59/0.1
Filler



2.51/0.01
Pigment

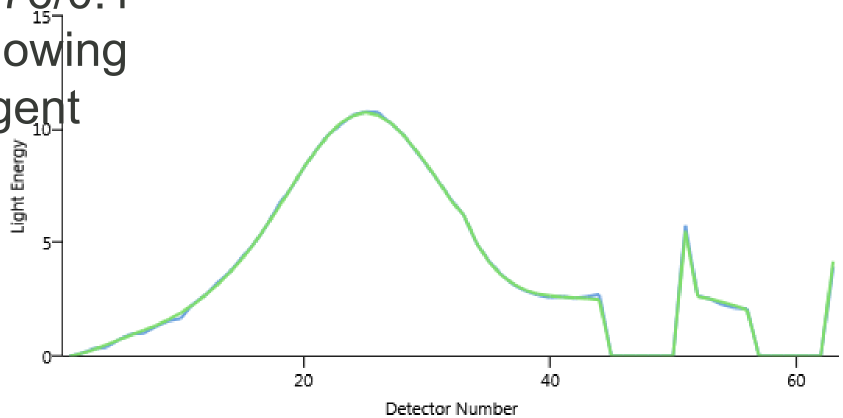


1.54/0.01
PVC

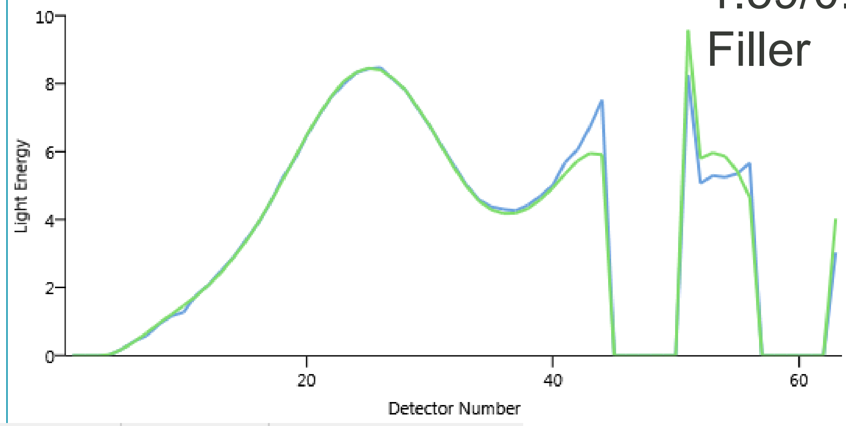


Plastisol – by fit and residual

1.76/0.1
Blowing agent

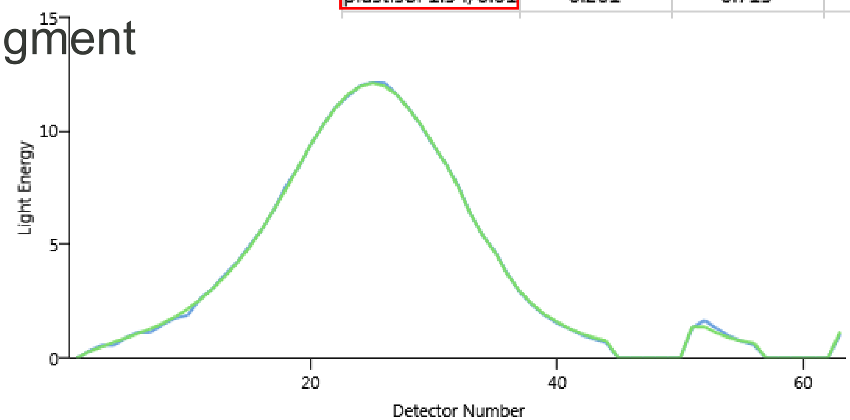


1.59/0.1
Filler

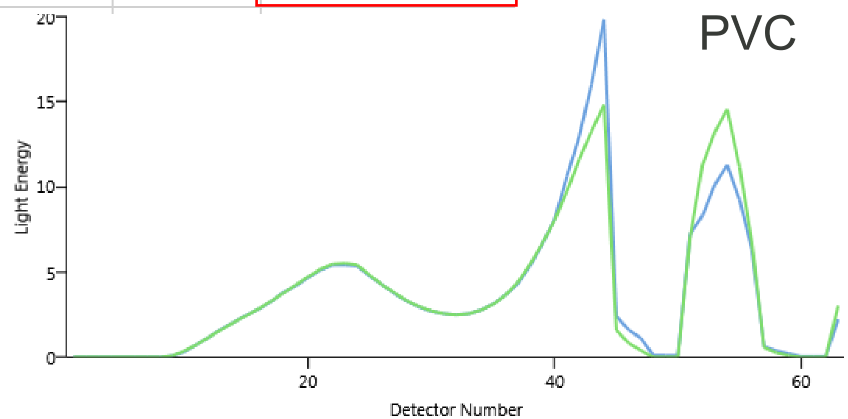


Sample Name	Dx (10) (µm)	Dx (50) (µm)	Dx (90) (µm)	Residual (%)	Weighted Residual (%)
plastisol 1.76/0.1	0.624	7.705	27.053	0.70	0.26
plastisol 1.59/0.1	0.655	4.606	23.874	0.86	1.26
plastisol 2.51/0.01	1.069	8.740	28.163	0.72	0.26
plastisol 1.54/0.01	0.261	0.713	12.492	1.21	3.61

2.51/0.01
Pigment



1.54/0.01
PVC



Plastisol – which optical properties to chose?

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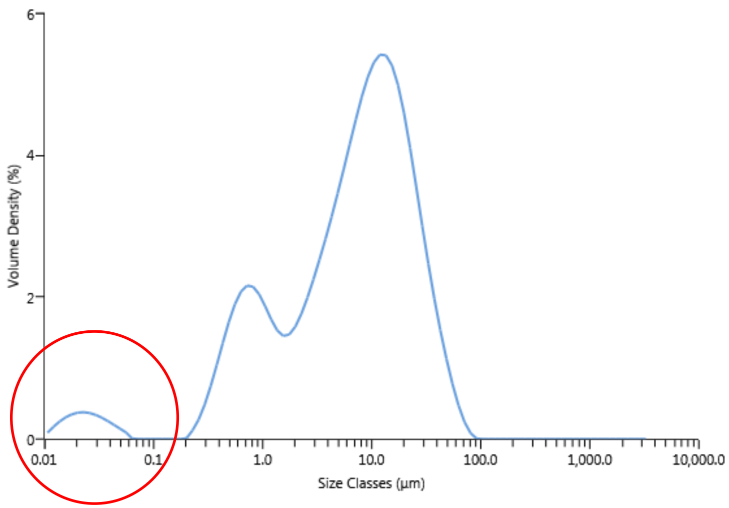
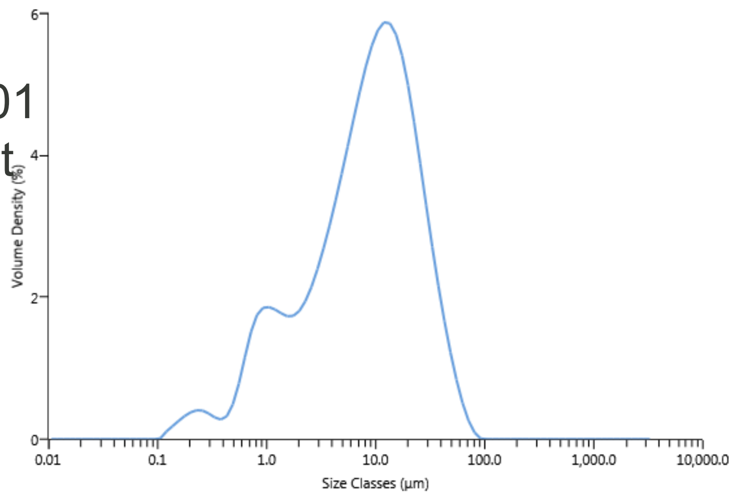
1.76/0.1
Blowing agent

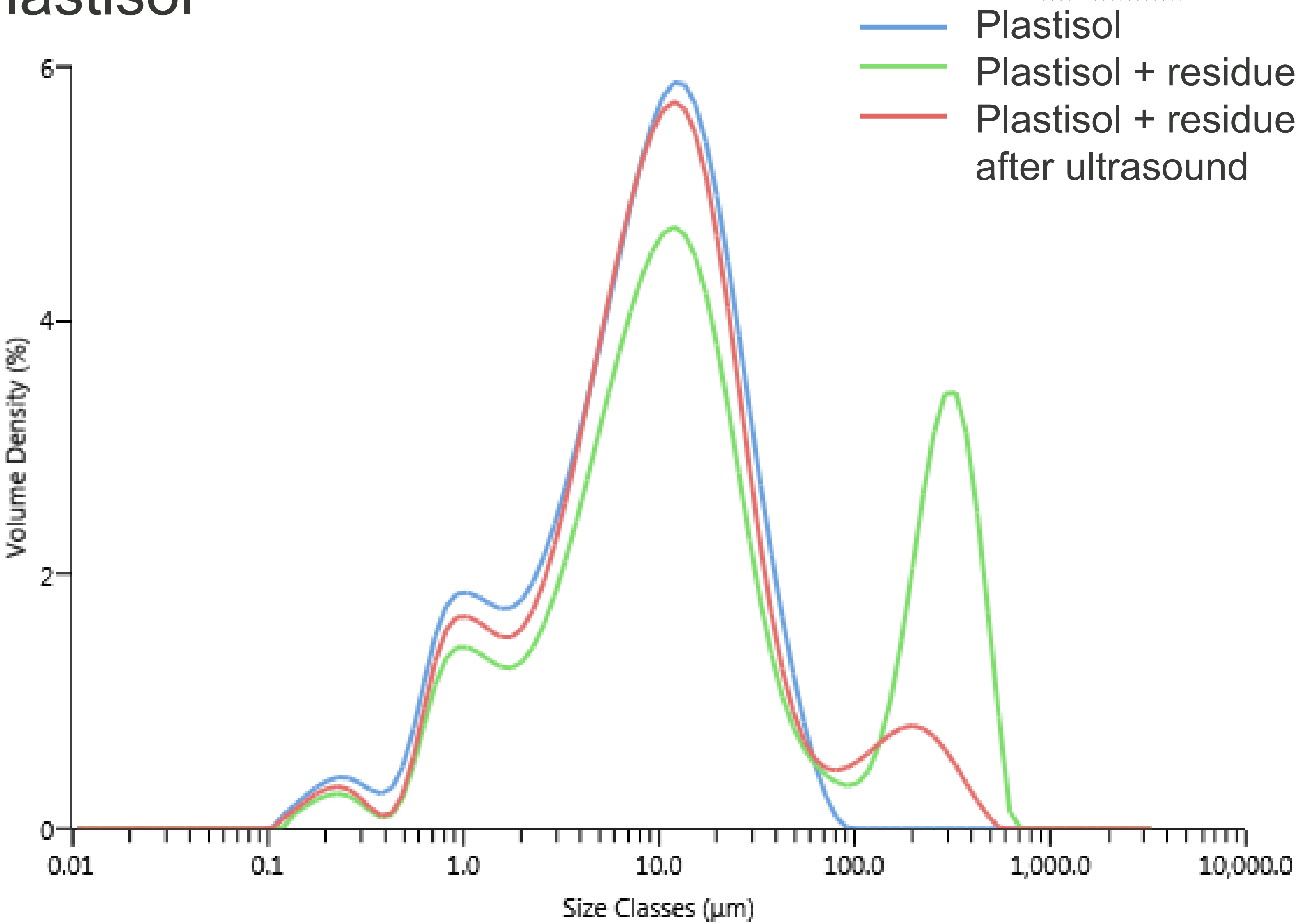


2.51/0.01
Pigment



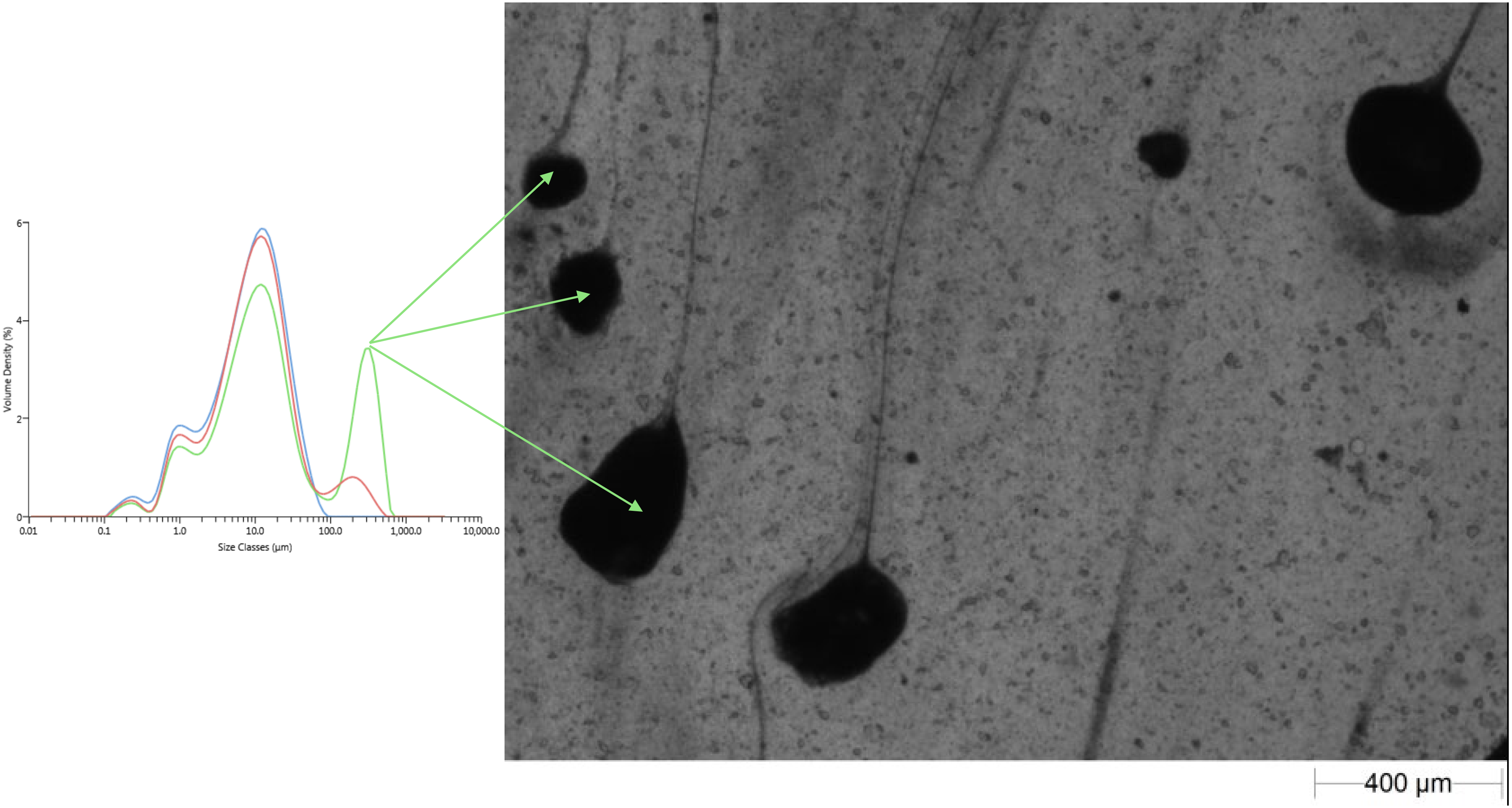
- Similar residuals
- Unresolved peak in 1.76/0.1
- Sample knowledge:
  - Blowing agent >10μm
  - Pigment <1μm
- Laser diffraction knowledge:
  - Sensitivity to optical properties increases as size decreases
- Select 2.51/0.01

Plastisol



Plastisol
Plastisol + residue
Plastisol + residue after ultrasound
Volume Density (%)
0
2
4
6
0.01
0.1
1.0
10.0
100.0
1,000.0
10,000.0
Size Classes (μm)

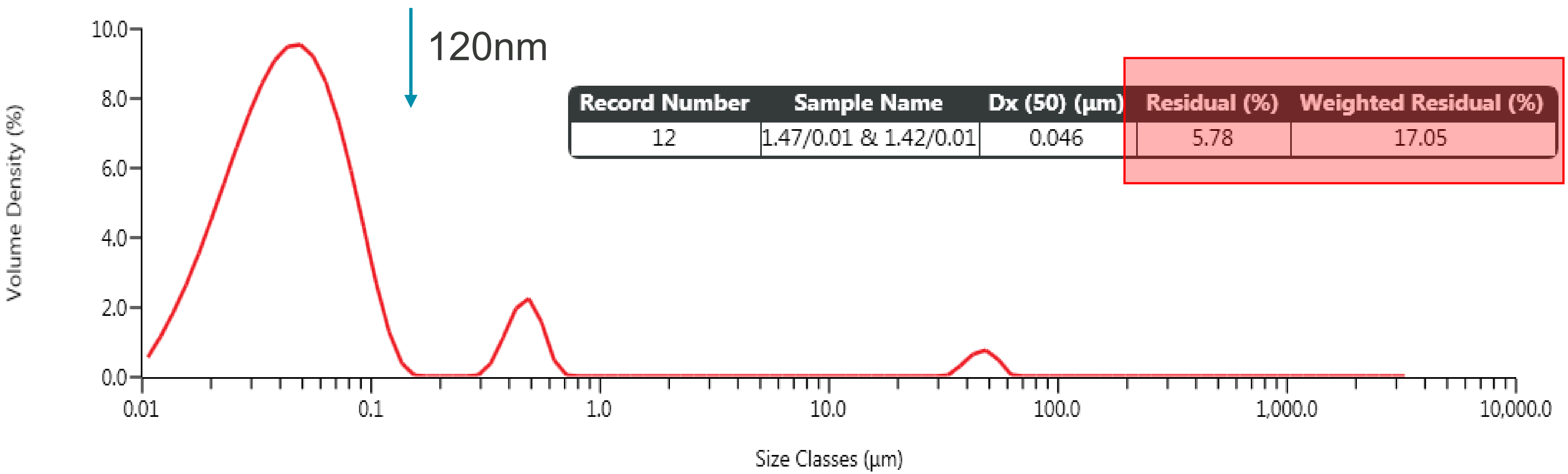
Plastisol



Volume Density (%)
Size Classes (µm)
0.01
0.1
1.0
10.0
100.0
1,000.0
10,000.0
0
2
4
6
400 µm

Pigment – a real life example of using the OPO

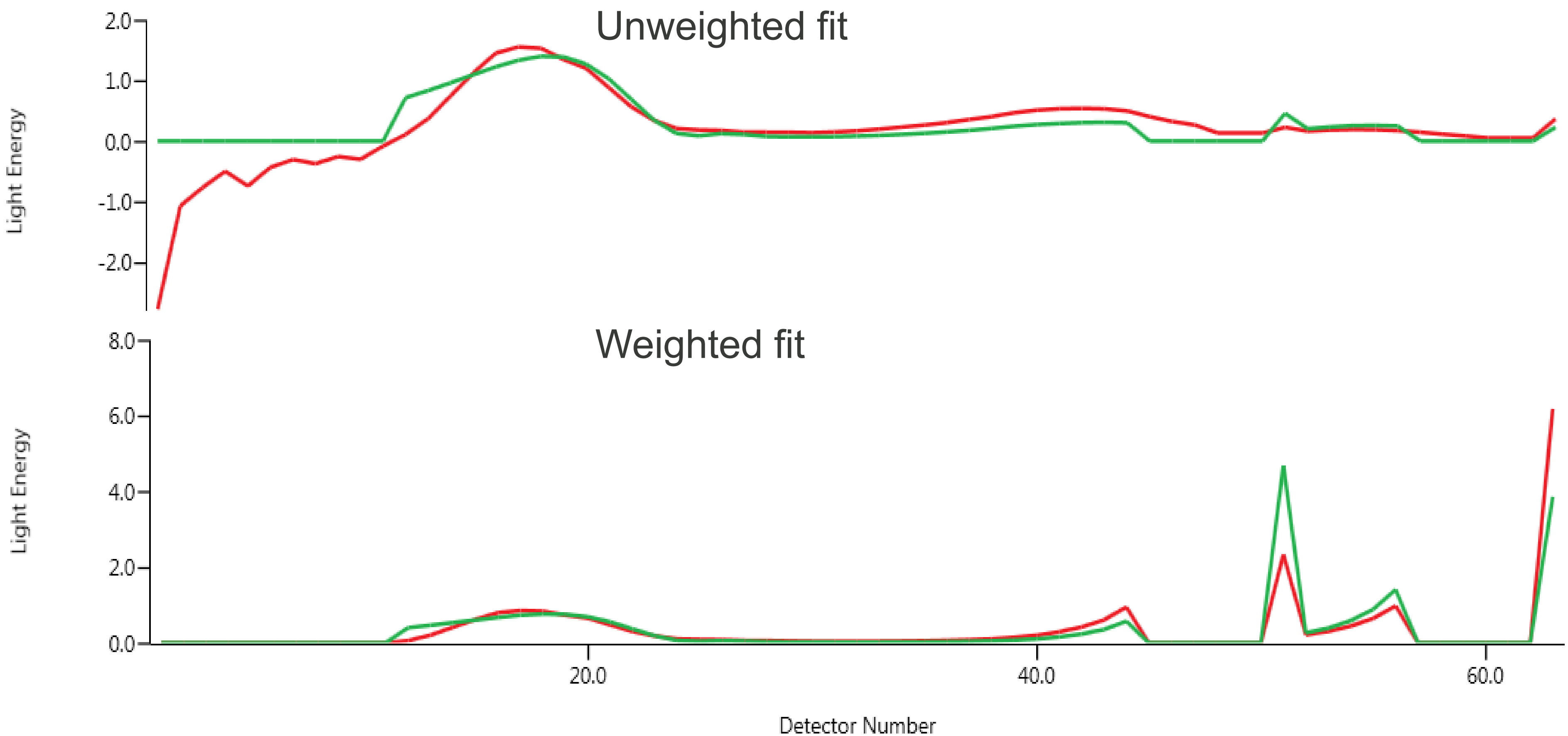
- Red ink
- Expected Dv50 120nm
- Red 1.47/0.01 & Blue 1.42/0.01 (reference)



Record Number	Sample Name	Dx (50) (µm)	Residual (%)	Weighted Residual (%)
12	1.47/0.01 & 1.42/0.01	0.046	5.78	17.05

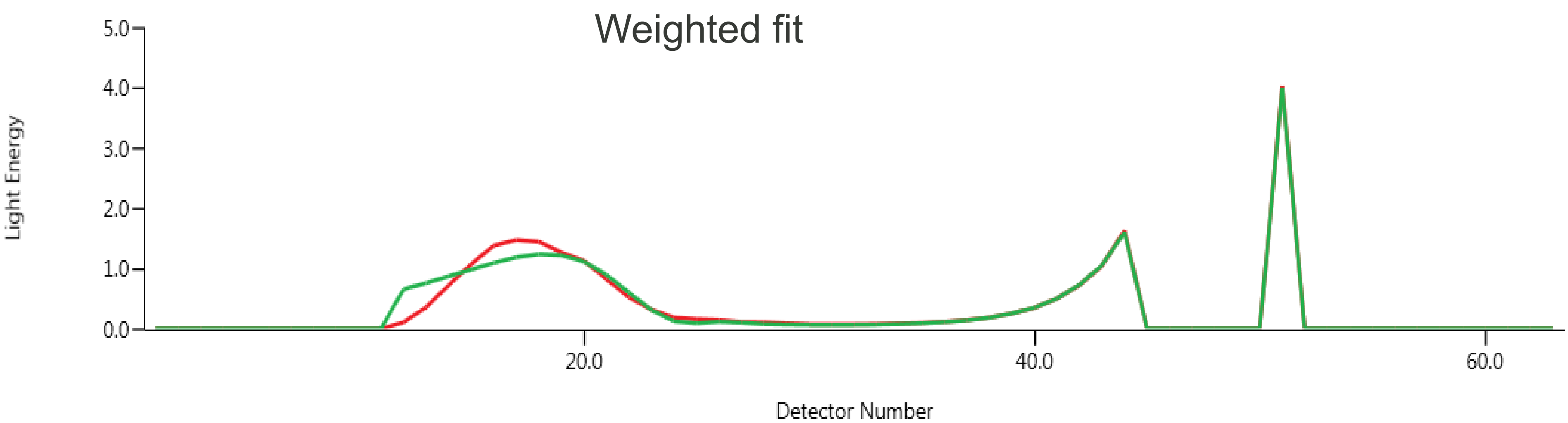
Looking at the fit report for the red ink

- Check fit report



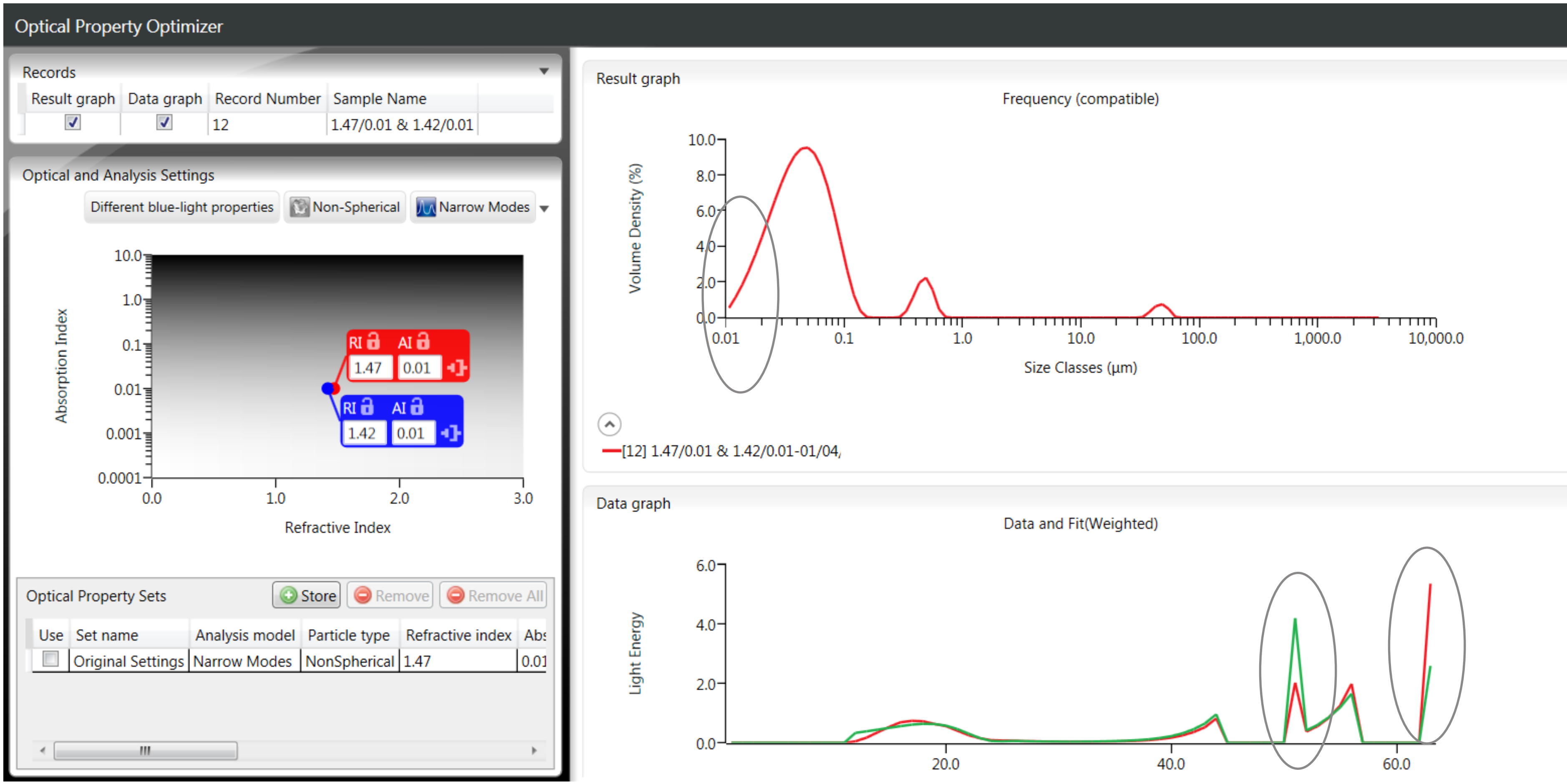
Red ink

- Check fit – **red** light only



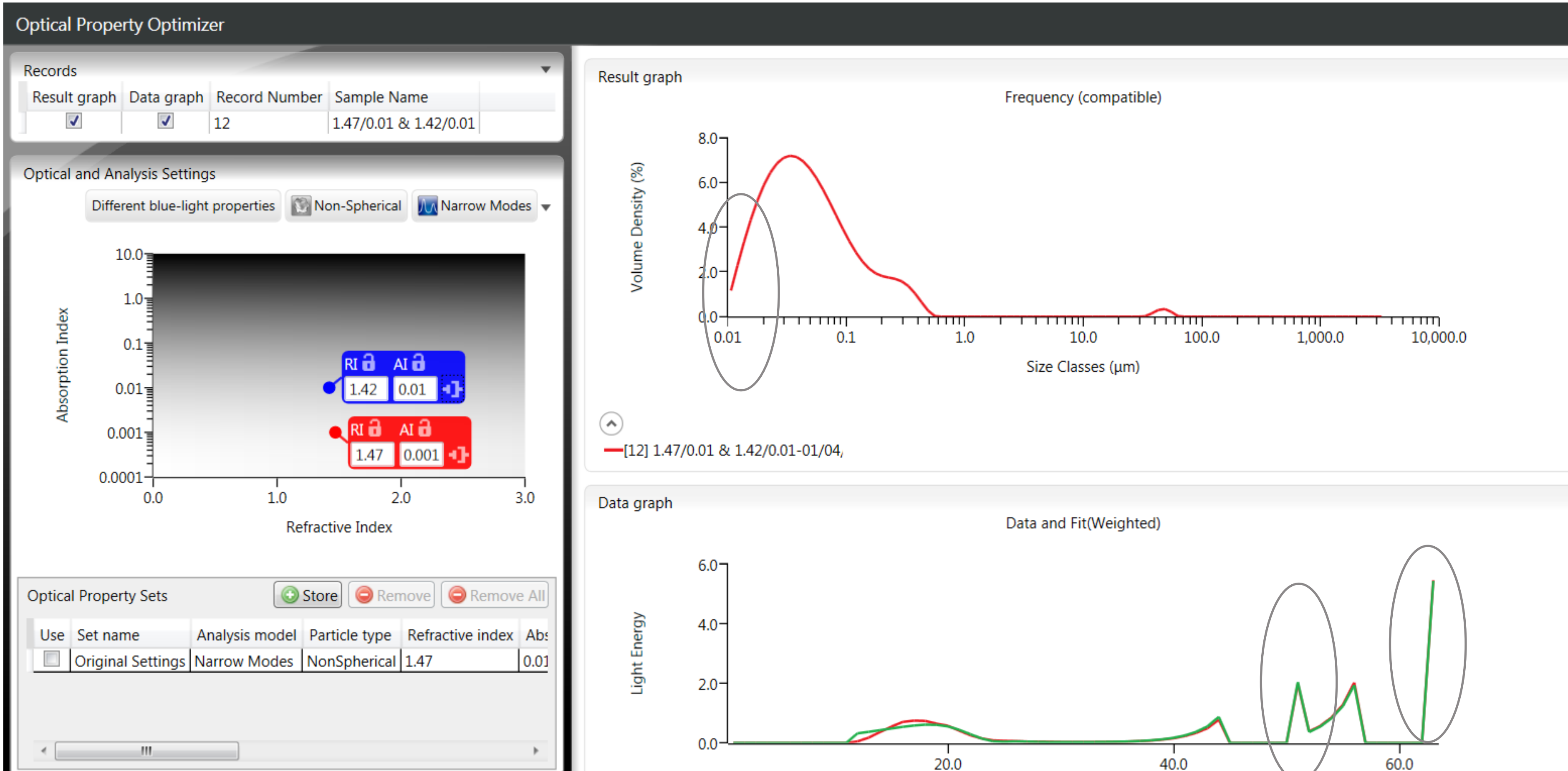
Record Number	Sample Name	Dx (50) (µm)	Residual (%)	Weighted Residual (%)
3	Red ink	0.179	5.80	4.09

OPO – red ink



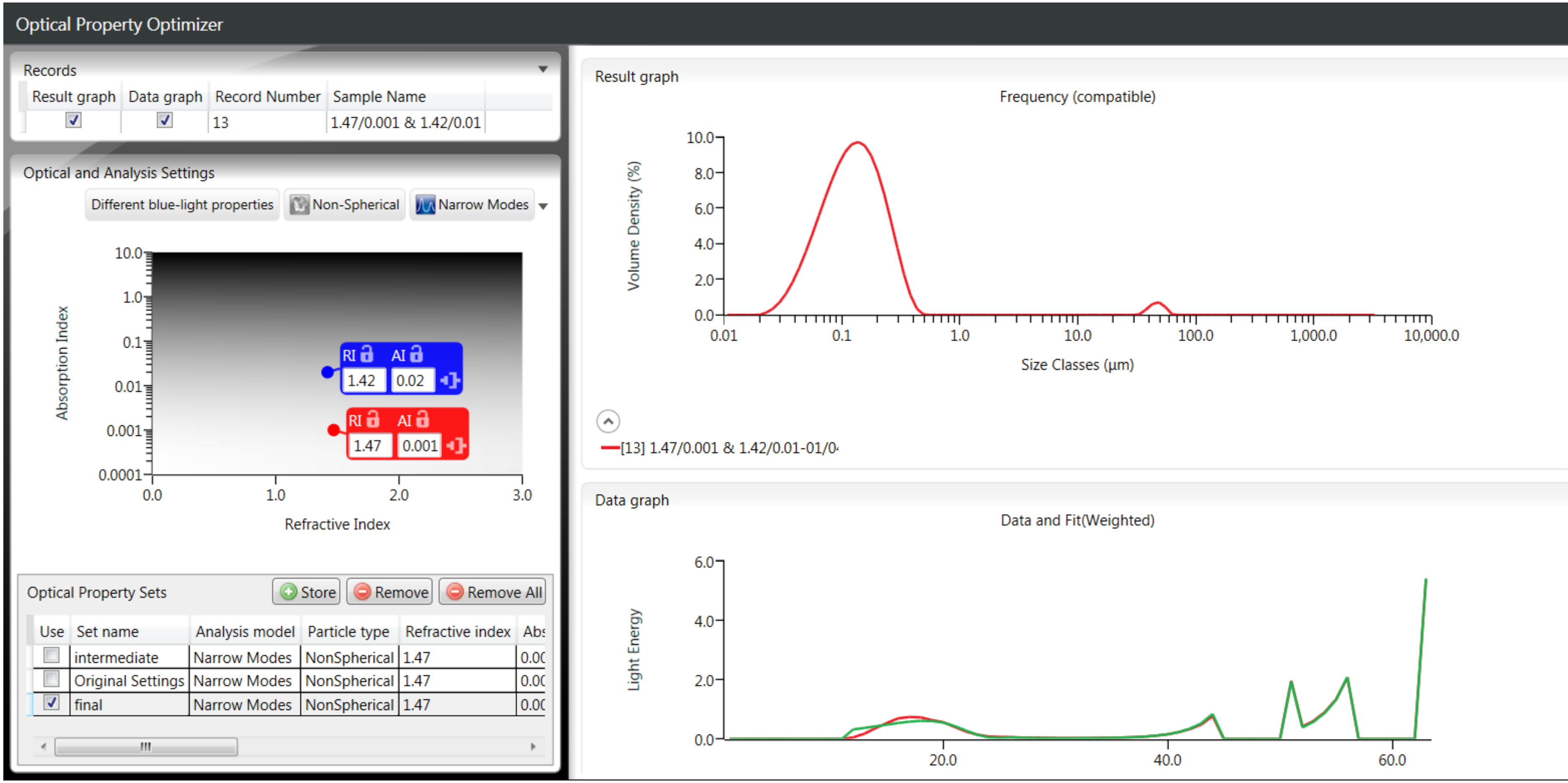
Record Number	Sample Name	Dx (50) (μm)	Residual (%)	Weighted Residual (%)
12	1.47/0.01 & 1.42/0.01	0.046	5.78	17.05

OPO – red ink



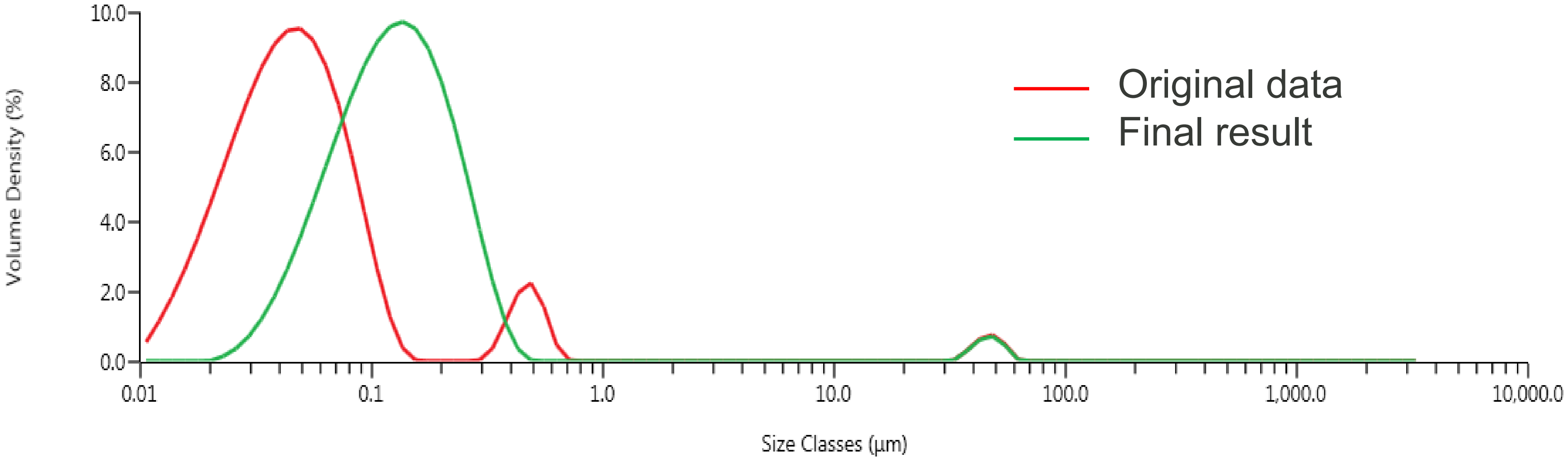
Record Number	Sample Name	Dx (50) (µm)	Residual (%)	Weighted Residual (%)
13	1.47/0.001 & 1.42/0.01	0.043	5.50	2.26

OPO – red ink



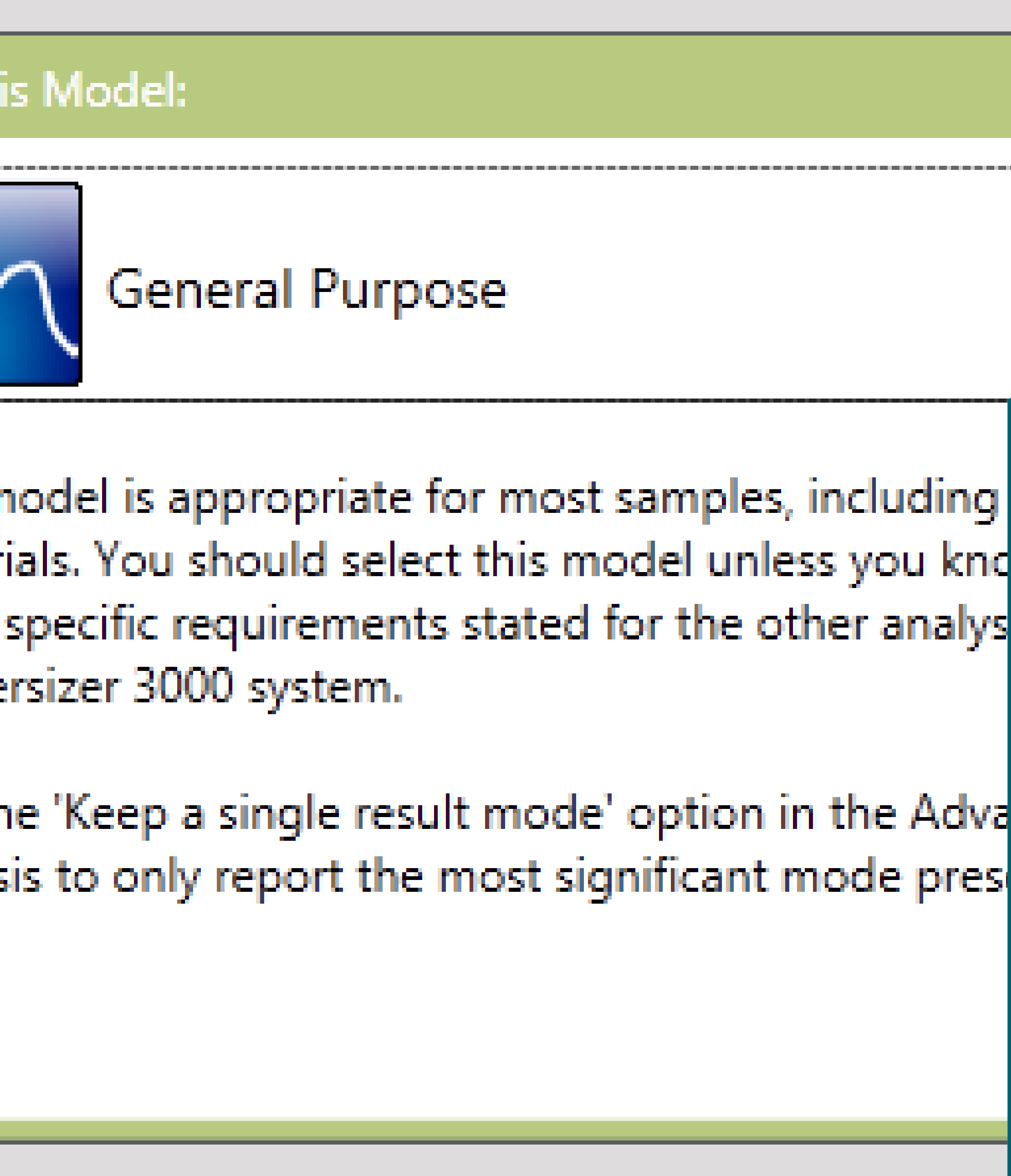
Record Number	Sample Name	Dx (50) (μm)	Residual (%)	Weighted Residual (%)
15	1.47/0.001 & 1.42/0.02	0.125	5.50	2.14

Corrected red ink result



Record Number	Sample Name	Dx (50) (µm)	Residual (%)	Weighted Residual (%)
12	1.47/0.01 & 1.42/0.01	0.046	5.78	17.05
15	1.47/0.001 & 1.42/0.02	0.125	5.50	2.14

- Dv50 now 125nm
- Close to expected value of 120nm



Analysis models

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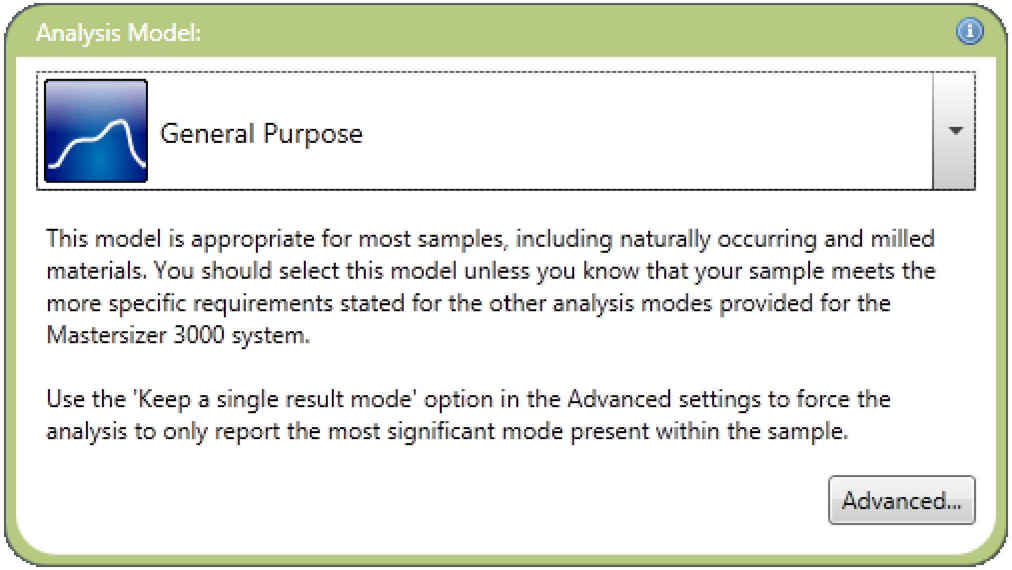
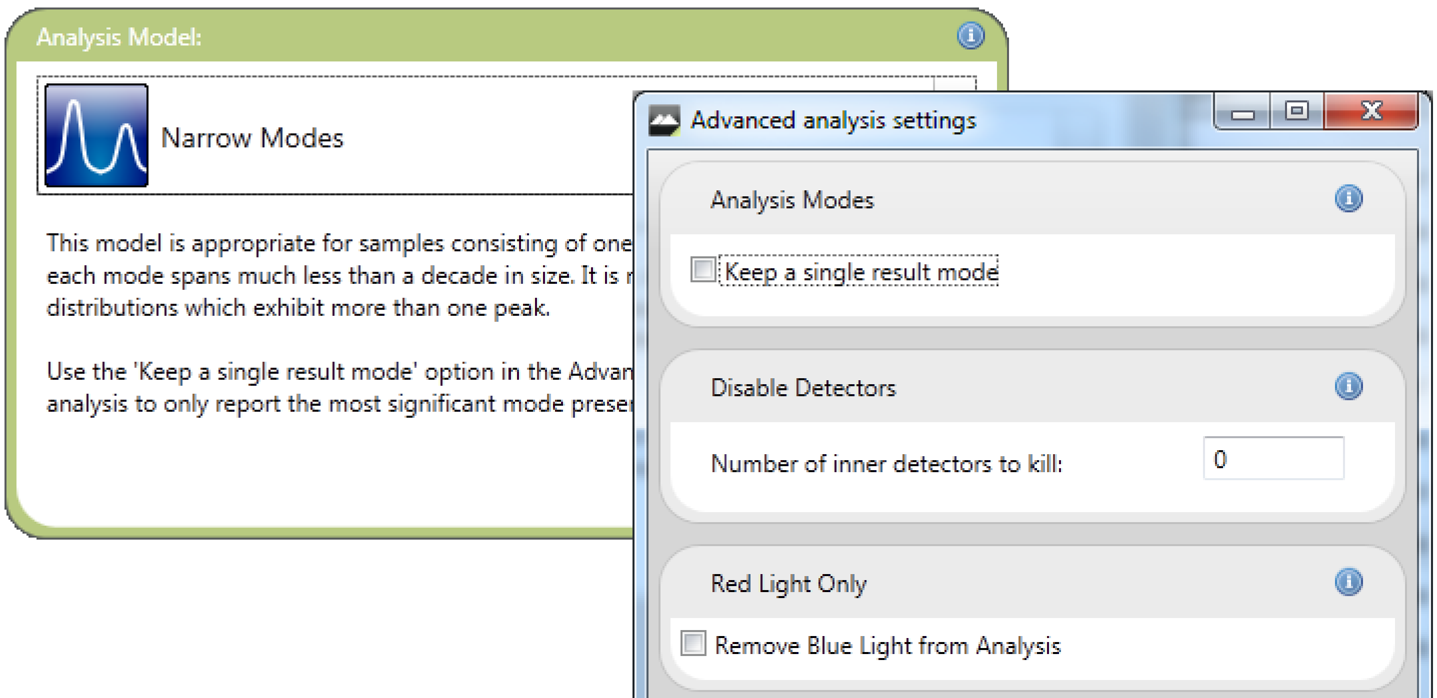
Analysis Models

- Using a particular analysis model enables the software to better interpret the light scattering data.
- General purpose
  - Suitable for the majority of samples



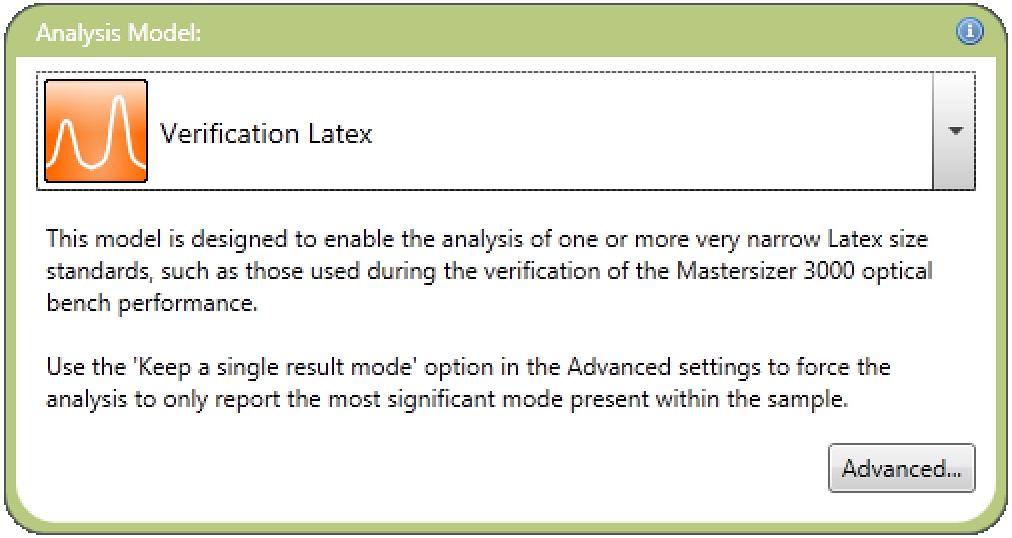
Analysis Models

- Using a particular analysis model enables the software to better interpret the light scattering data.
- Narrow modes
  - Suitable for samples with modes spanning much less than a decade in size



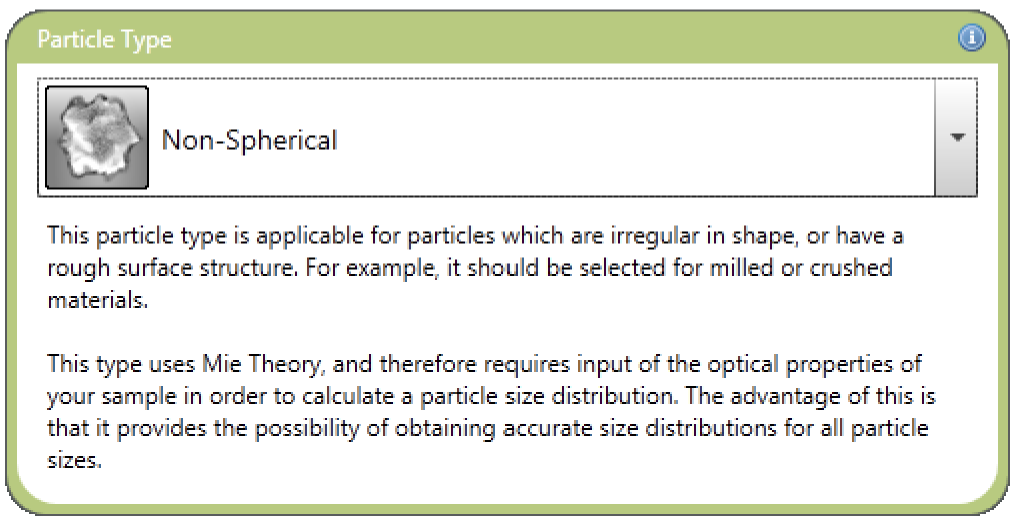
Analysis Models

- Using a particular analysis model enables the software to better interpret the light scattering data.
- Verification latex
  - Suitable for use with very narrow latex size standards



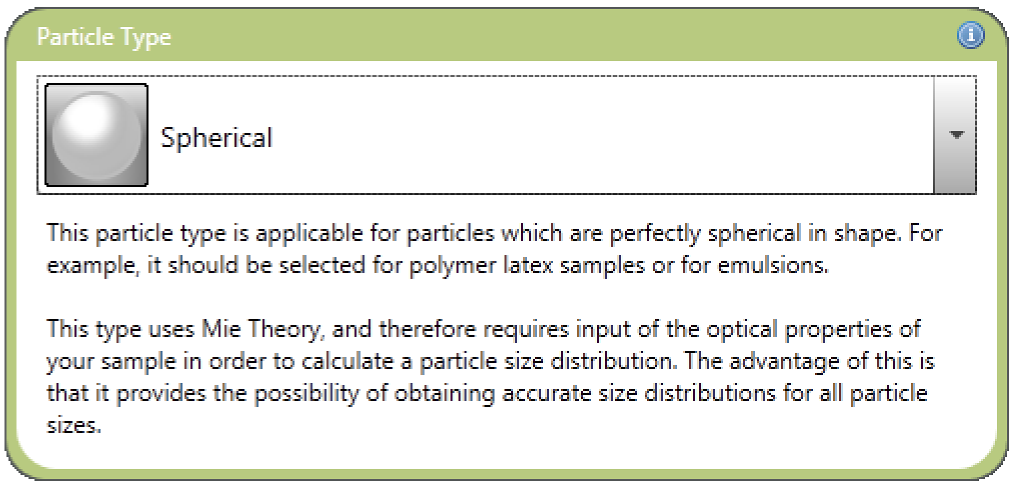
Particle shape, irregular or spherical?

- Irregularly shaped small particles (<1μm) depolarise light more strongly in one direction
- The Non-Spherical option enables this high angle scattering to be correctly interpreted.
- Non-Spherical is the default option as the majority of materials are irregular



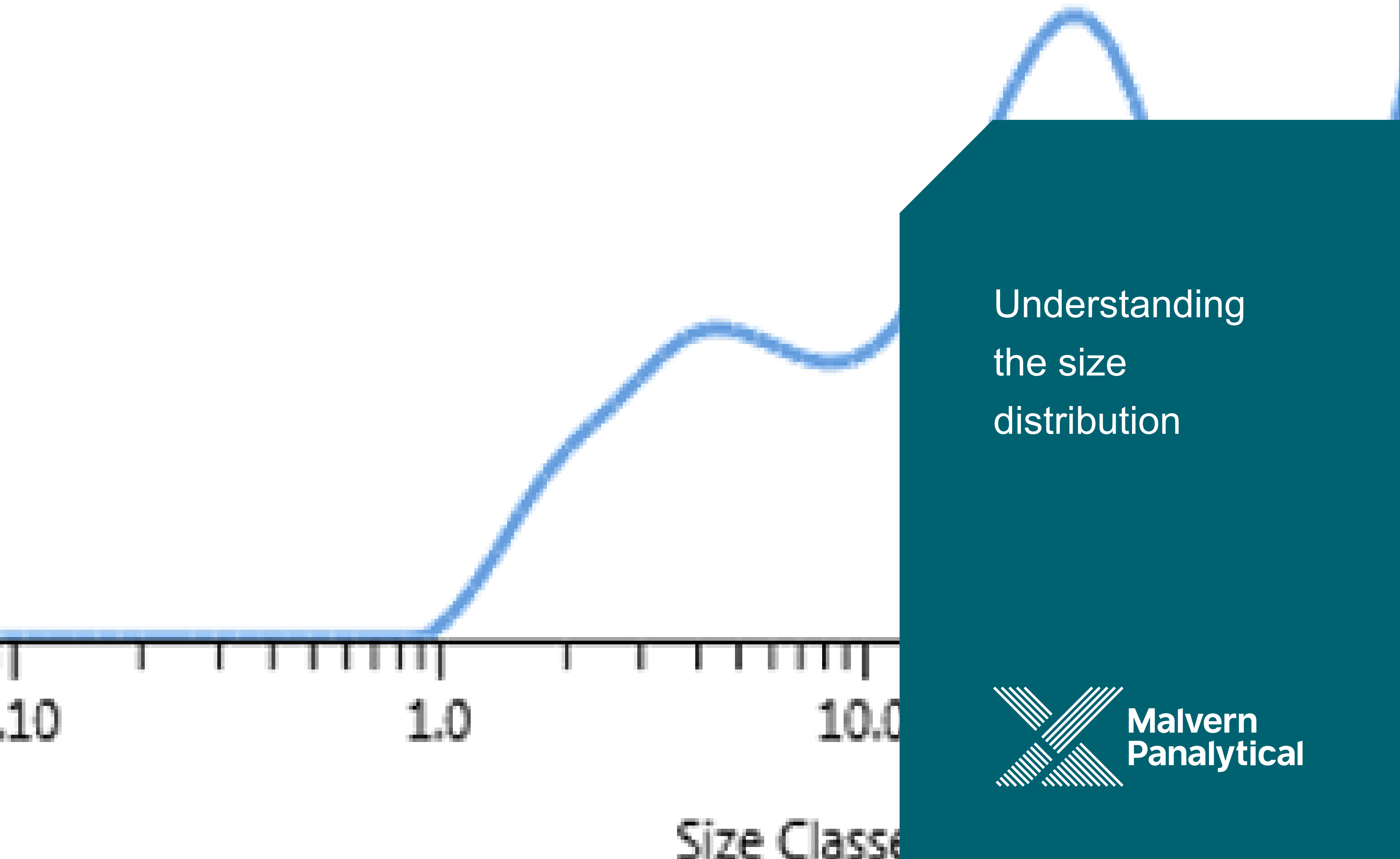
Particle shape, irregular or spherical?

- Spherical samples are rarer but will include glass beads, latex spheres and emulsions.



Fine powder mode

- This removes the noise on the inner detectors caused by temperature gradients in dry powder feeder measurements
  - Or from using ultrasound in organic solvents
- It is only used in measurements of samples which are finer than 600 microns



Understanding the size distribution

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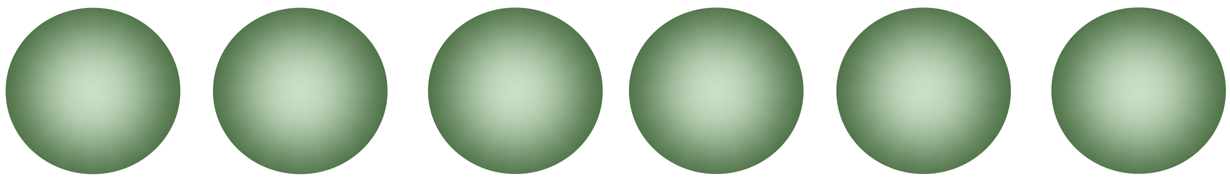
Understanding the size distribution

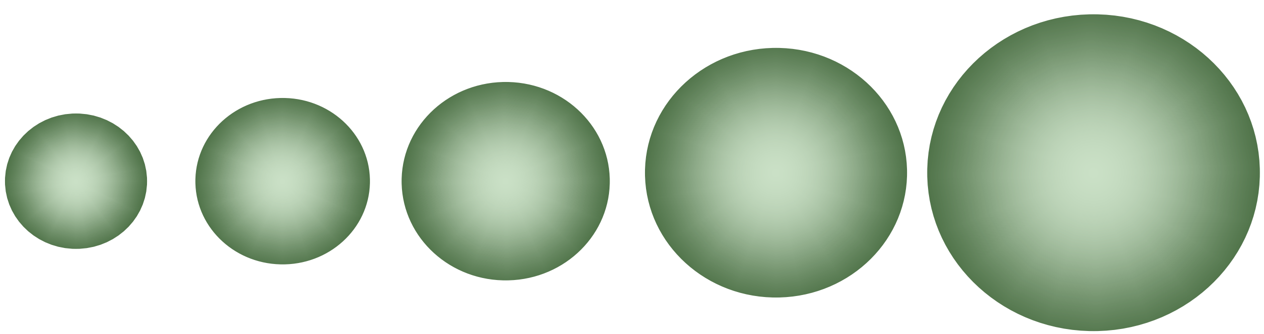
- The Mastersizer 3000 system is designed such that equal volumes of particles of different sizes produce a similar measured scattering intensity.
- The size distribution is reported as a volume distribution as this best reflects the sensitivity of the system.
- What does this mean in practice?

Particle size distributions

- If a sample contains particles that are all the same size it is described as monodisperse

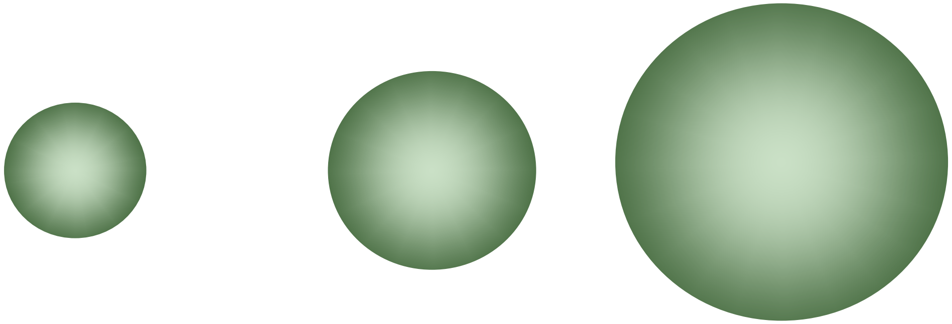


- Most real world samples will contain a distribution of particle sizes and are described as polydisperse



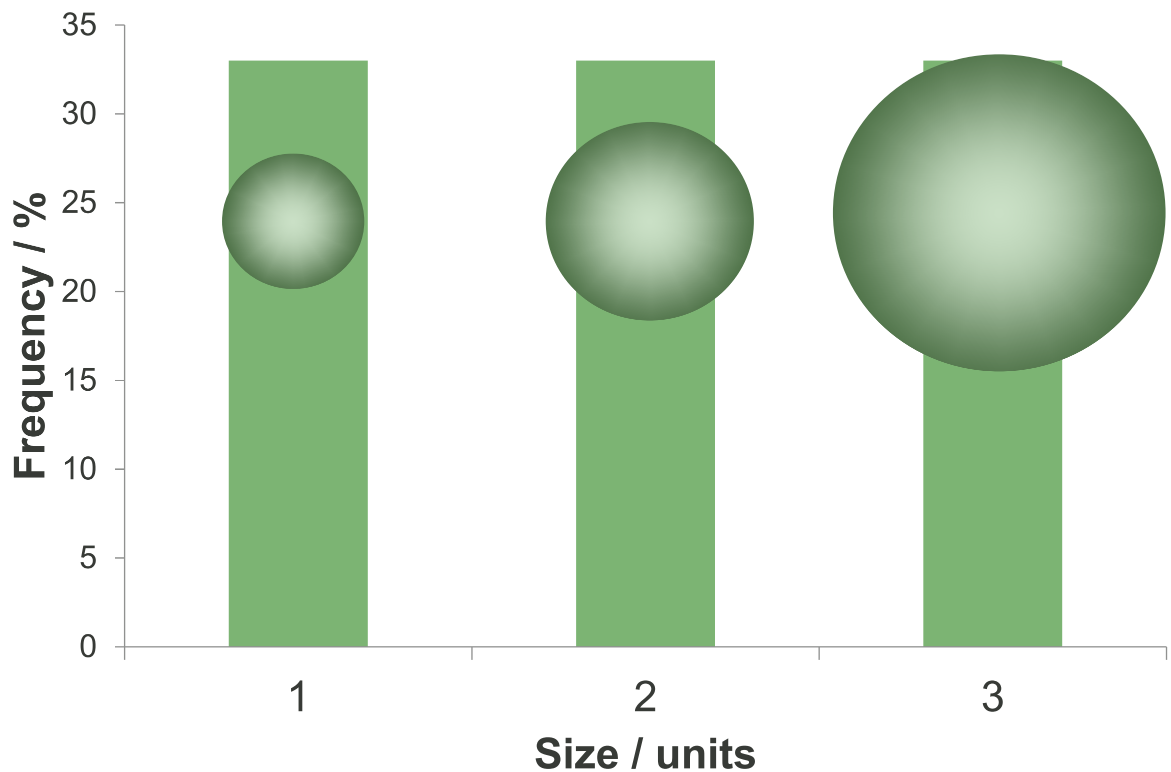
Understanding distribution weighting

- If we have a sample made up of 3 particles
  - With diameters of 1, 2 and 3 units.



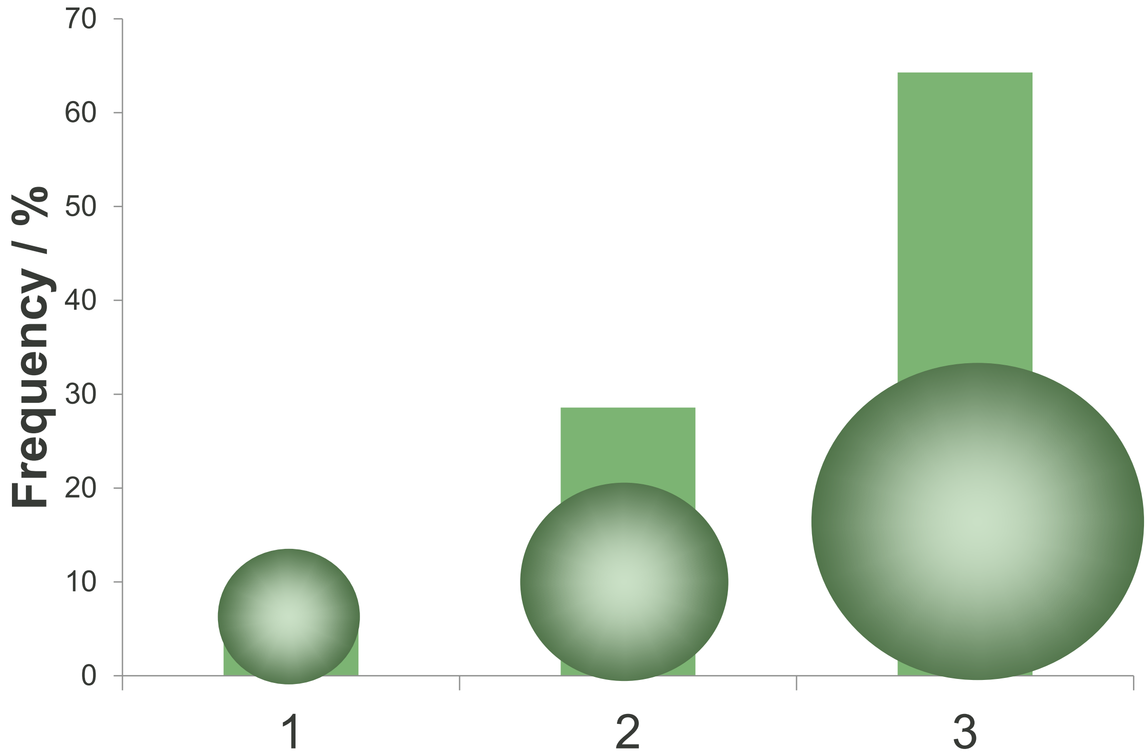
Understanding distribution weighting

- If we measure the sample by a counting technique (such as microscopy) we get a number weighted distribution...
  - And each particle contributes equally

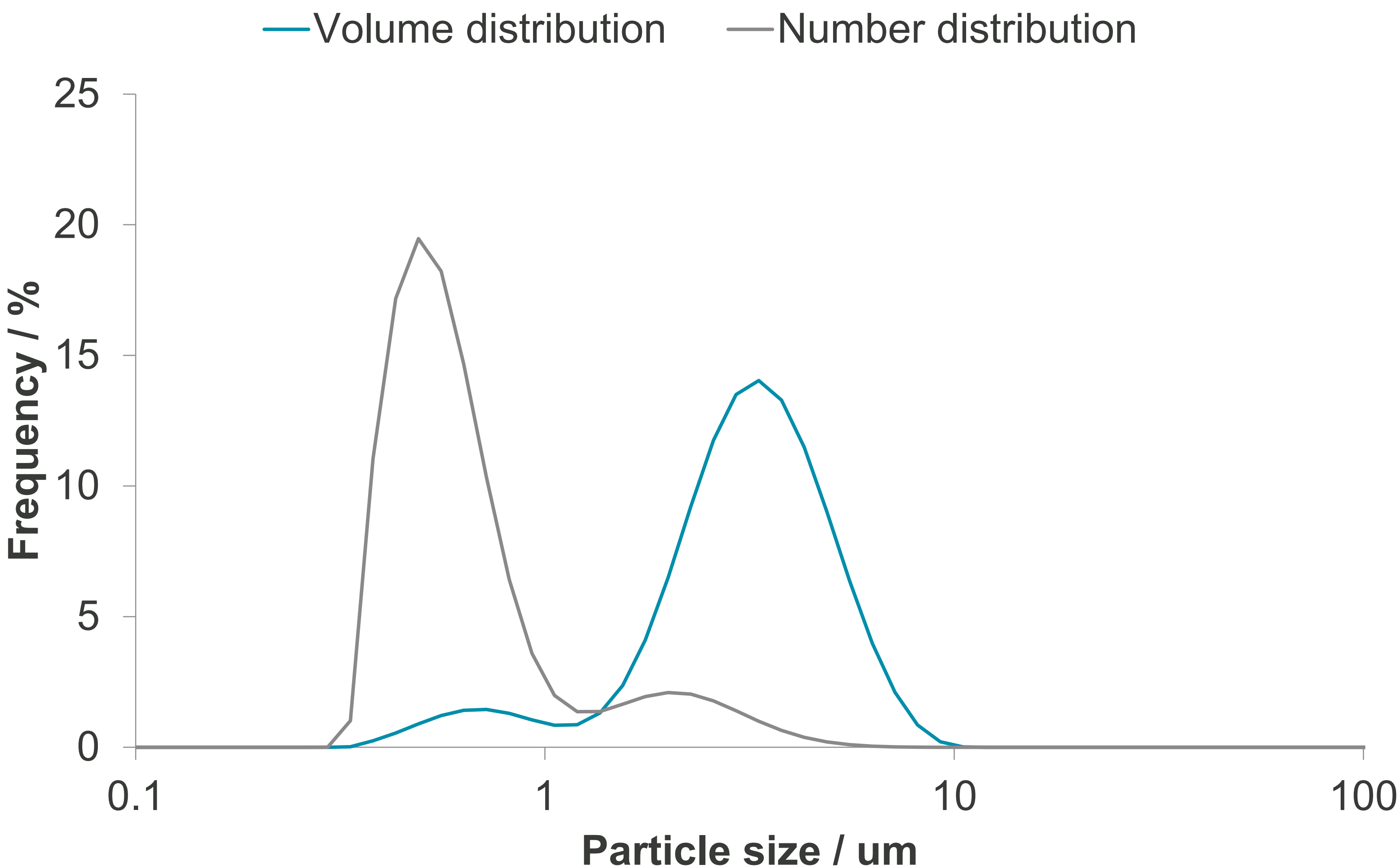


Understanding distribution weighting

- If we measure the sample by laser diffraction we get a distribution weighted by volume
  - And the largest particle features most prominently

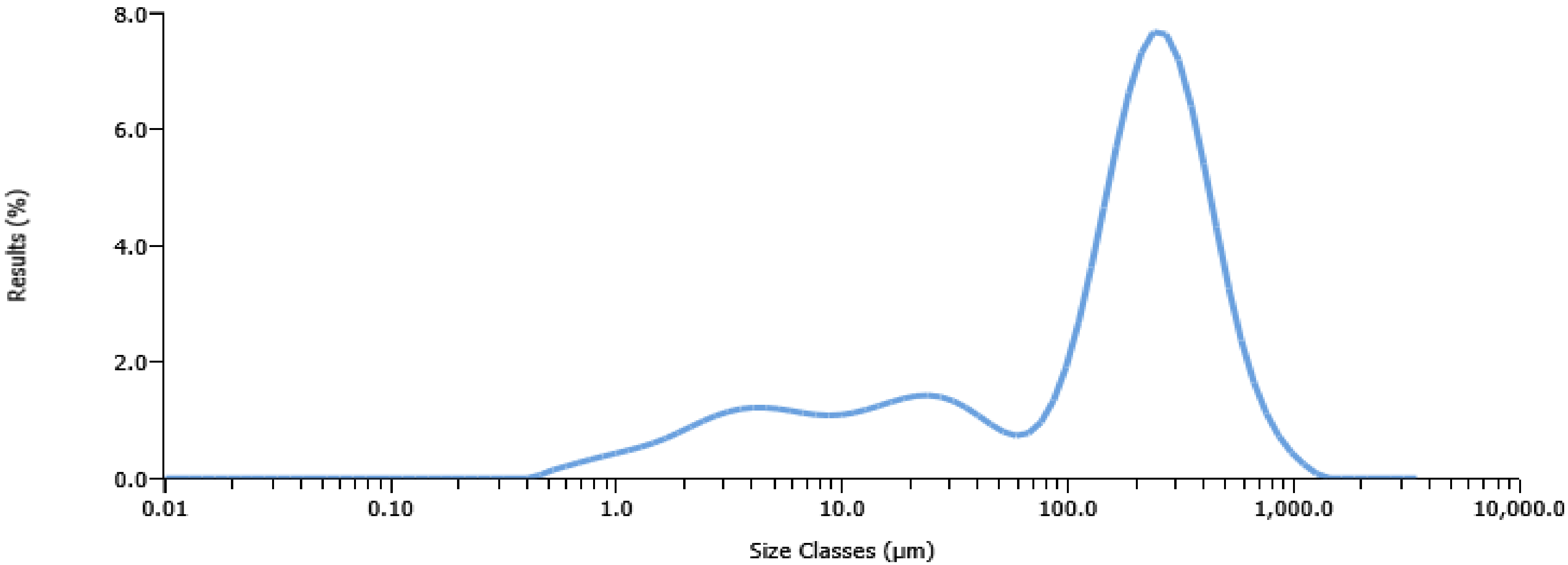


Real example of number and volume distributions



Representing the size distribution

- The particle size distributions are plotted on a logarithmic axis

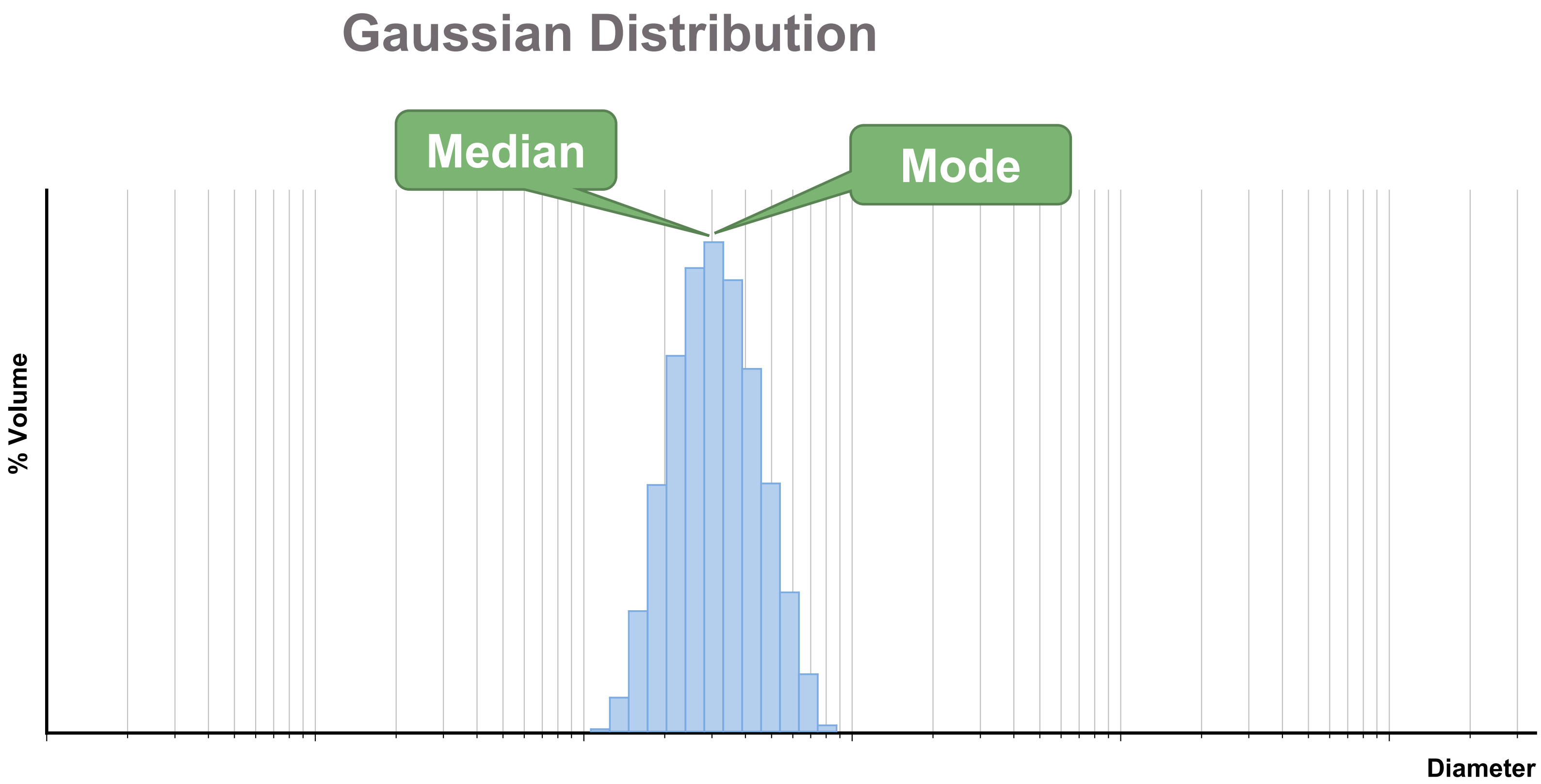


Result

Concentration	0.0834 %	**Span**	0.910
Uniformity	0.277	**Result Units**	Volume
Specific Surface Area	104.6 m^2/kg	**Dv (10)**	38.670 μm
D [3,2]	57.344 μm	**Dv (50)**	61.177 μm
D [4,3]	64.046 μm	**Dv (90)**	94.343 μm

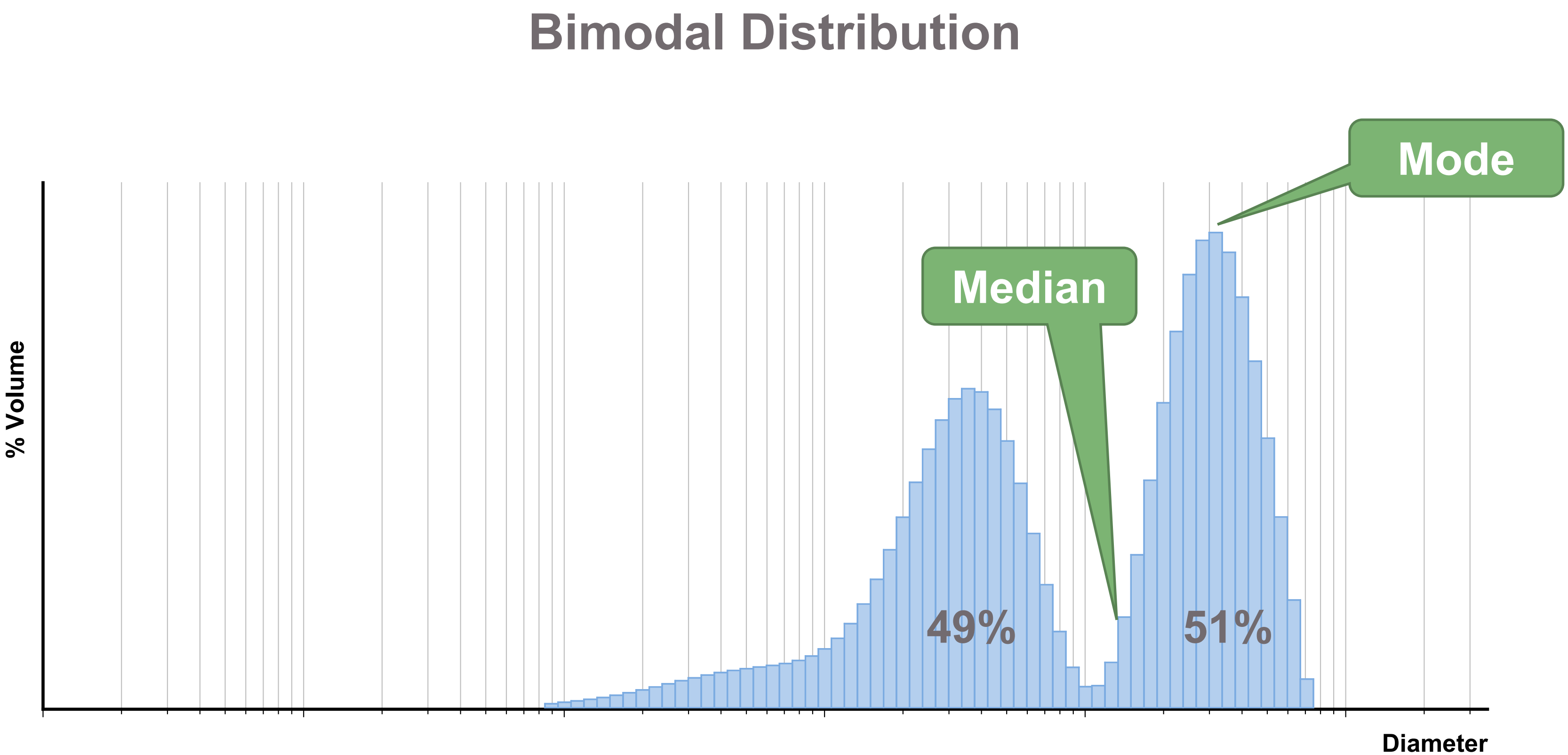
Particle size distribution statistics: Median and Mode

- Median = midpoint of the distribution
- Mode = most commonly occurring size class



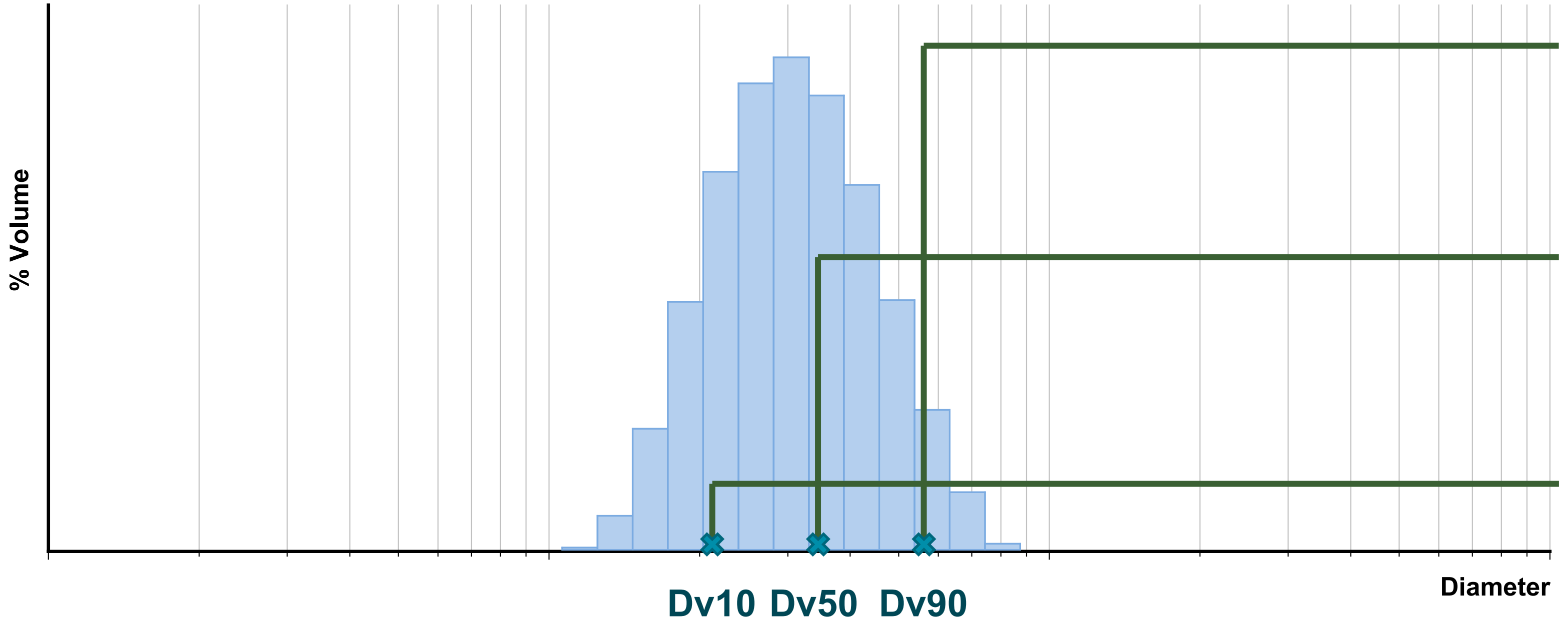
PSD Statistics: Median and Mode

- If the distribution shape is more complex then these parameters will diverge



PSD Statistics: Percentiles

- Percentiles are the size below which there is a certain volume of the sample
- Taken from the cumulative distribution



Record Number	Dx (10) (μm)	Dx (50) (μm)	Dx (90) (μm)
43	2.08	3.32	5.43

PSD Statistics: Percentiles

- Percentiles can be referred to in several ways
  - The 50th percentile
  - Dv50
  - D[v,0.5]
  - $\boldsymbol{x_{0.5}}$ (in the ISO standard)
- The ‘v’ signifies that the percentile is from a volume distribution
  - Dx50 is used when the result may be volume or number
- The Dv10 and Dv90 are also reported by default
- Other percentiles can also be reported

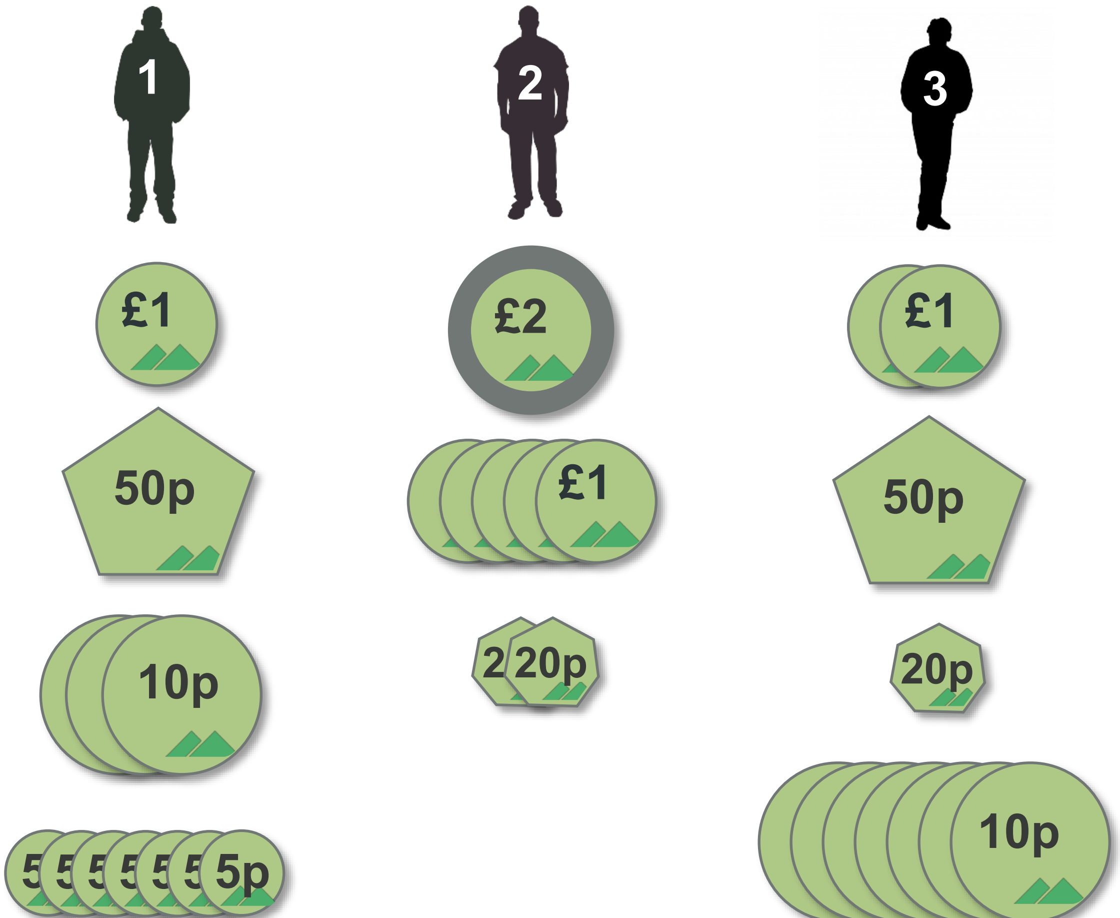
PSD Statistics: Mean particle sizes

- The most familiar mean is the arithmetic mean

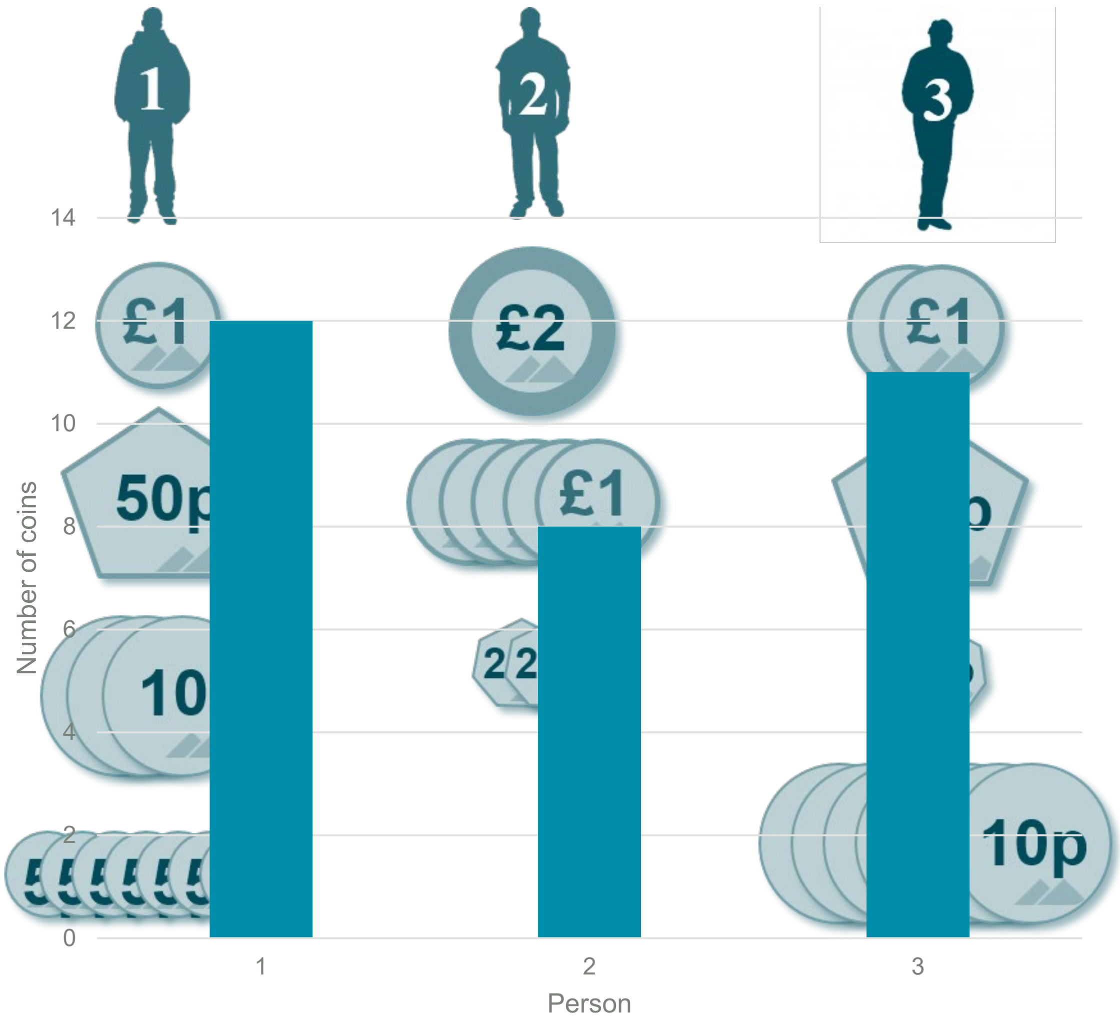
$$X_{nl} = D[1,0] = \frac{1^1 + 2^1 + 3^1}{1^0 + 2^0 + 3^0} = \frac{1 + 2 + 3}{3} = 2$$

- Laser diffraction does not use the arithmetic mean
  - As it measures the volume of particles, not the number
- Laser diffraction reports the volume weighted mean
  - D[4,3]
- And surface area weighted mean
  - D[3,2]

Different types of average

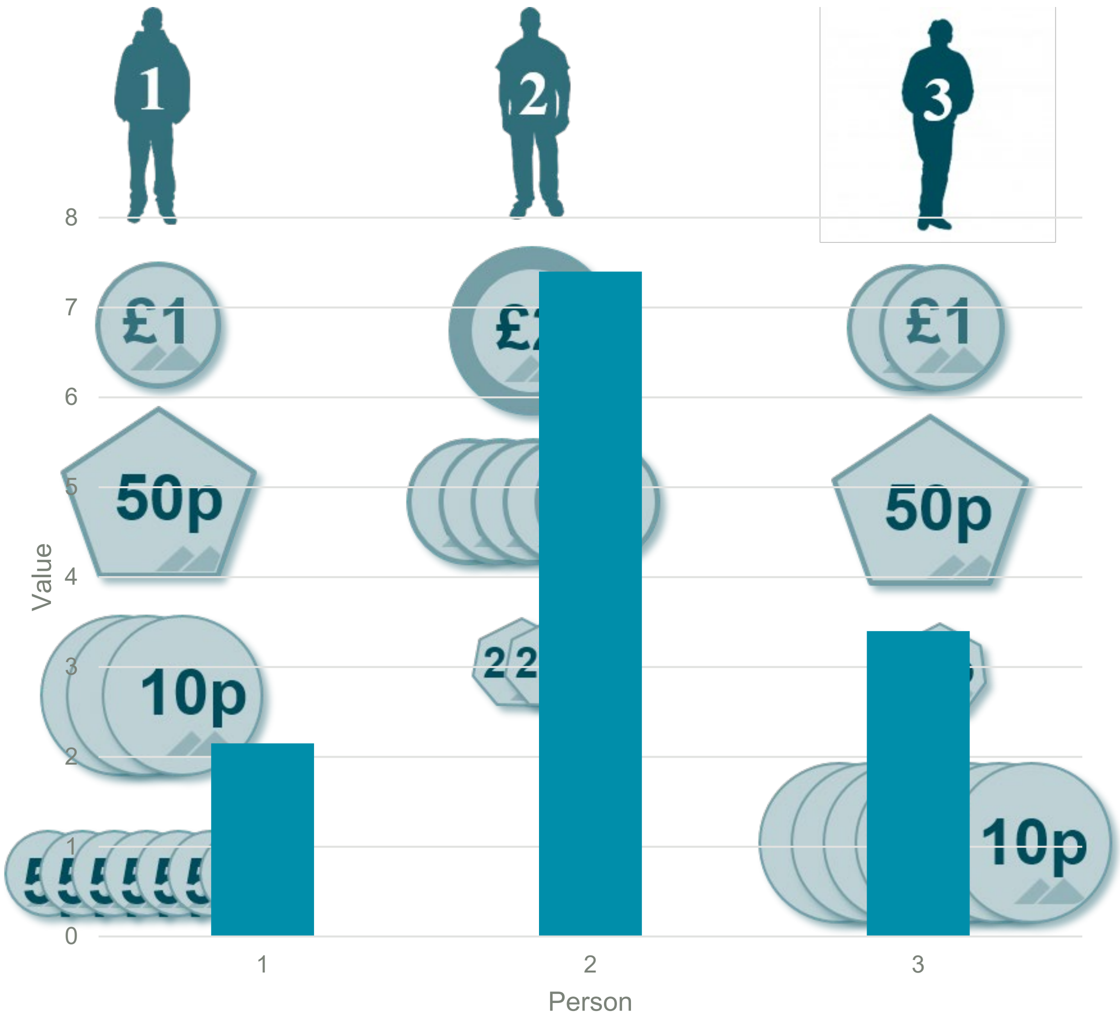


Different types of average



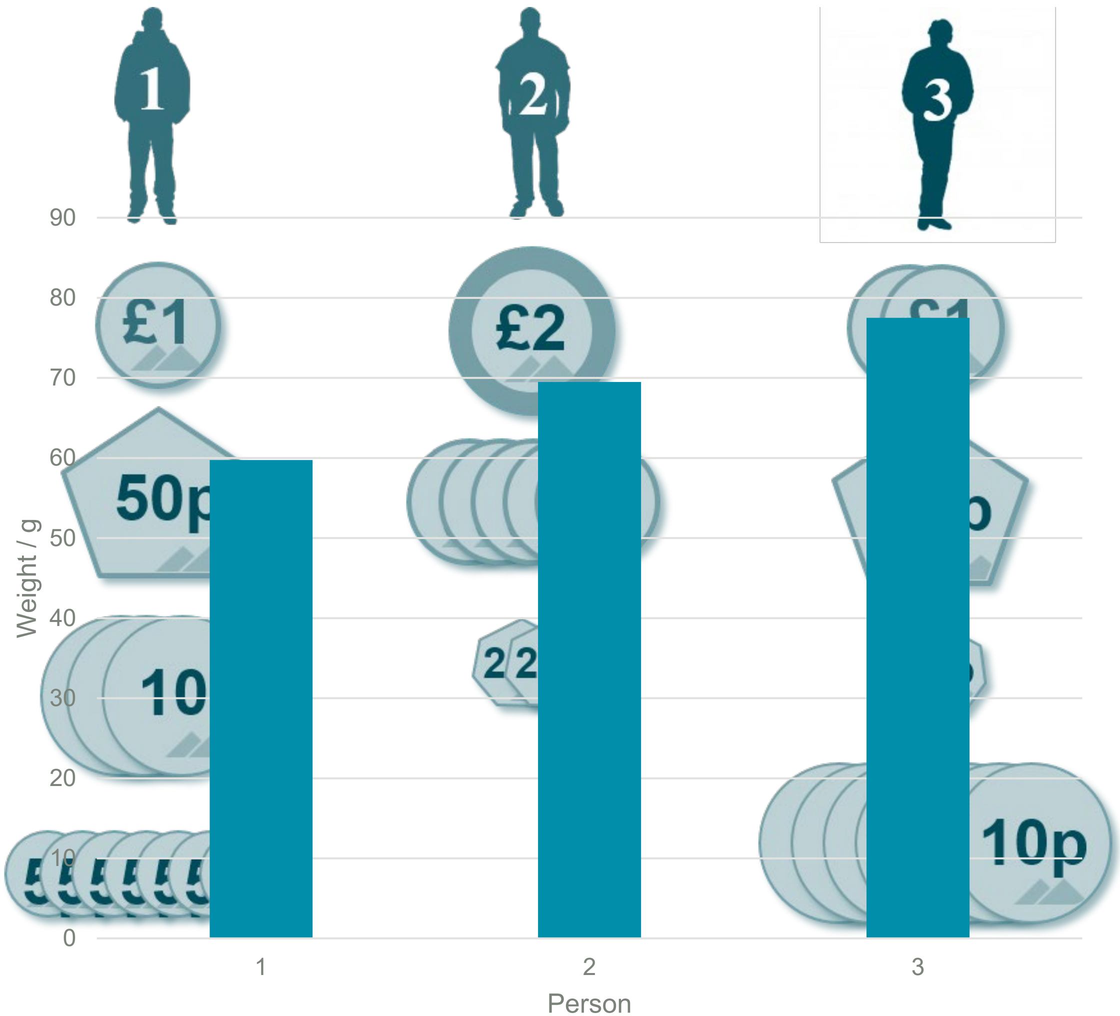
Type	Average
Number	10.33

Different types of average



Type	Average
Number	10.33
Value	4.31

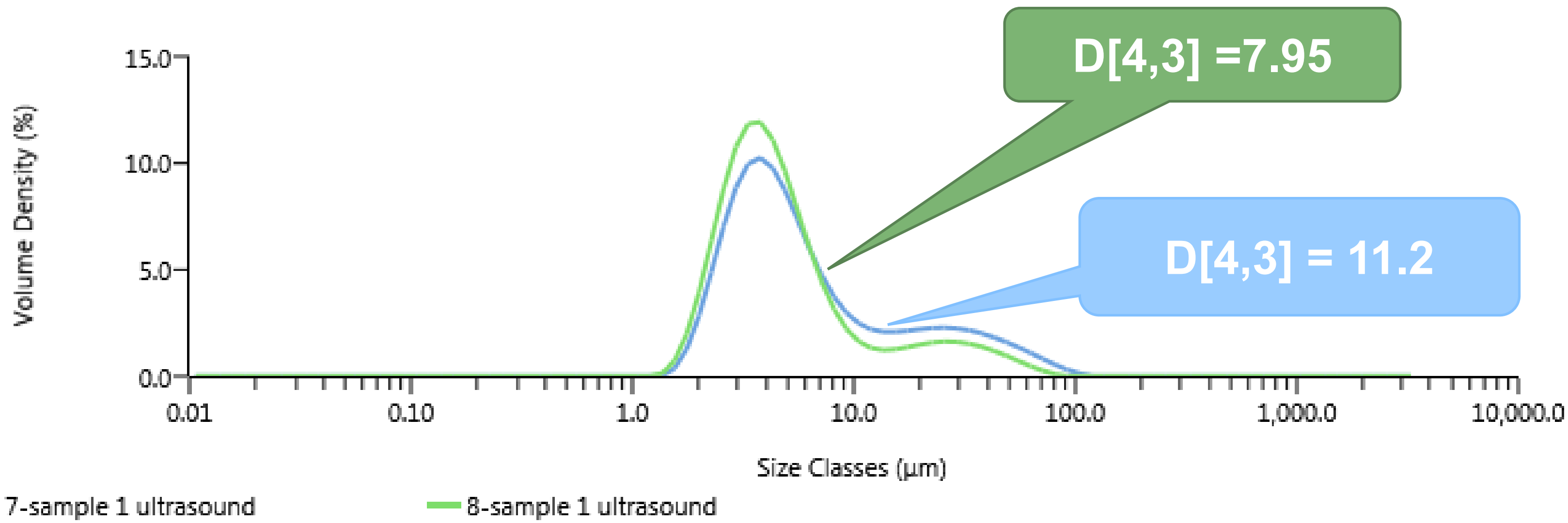
Different types of average



Type	Average
Number	10.33
Value	4.31
Weight	68.9

PSD Statistics: Volume weighted mean

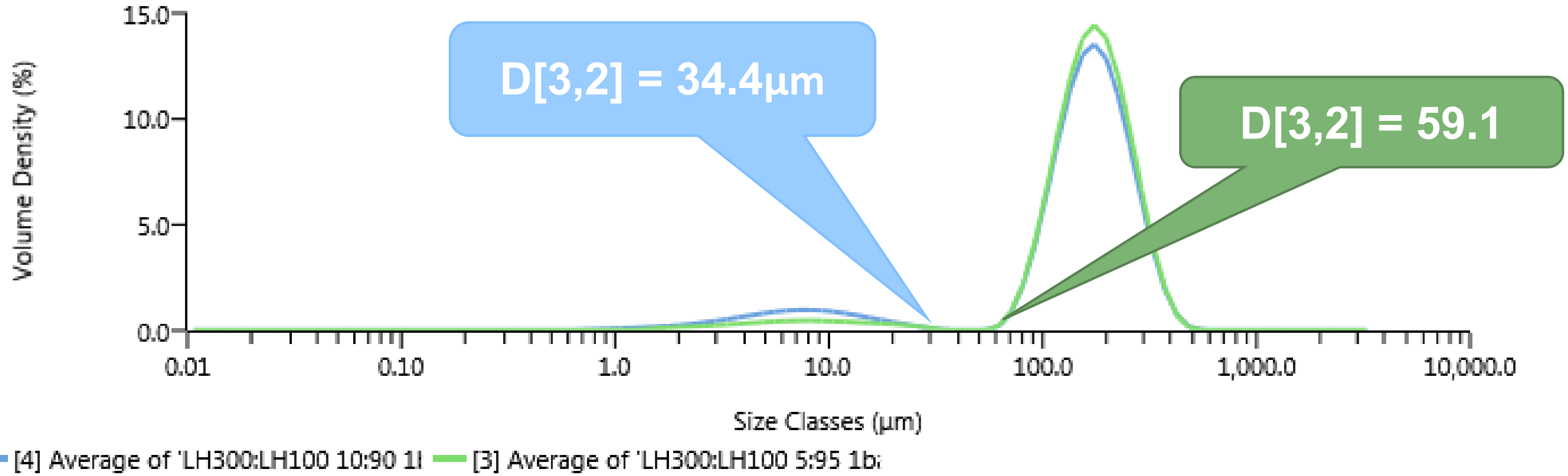
- D[4,3] is sensitive to changes in the coarse particle fraction
  - Useful for monitoring milling or dispersion



Record Number	Sample Name	Dx (10) (μm)	Dx (50) (μm)	Dx (90) (μm)	D [3,2] (μm)	D [4,3] (μm)
7	sample 1 ultrasound	2.55	4.92	30.6	4.78	11.2
8	sample 1 ultrasound	2.38	4.21	20.0	4.11	7.95

PSD Statistics: Surface area weighted mean

- D[3,2] is sensitive to changes in the fine particle fraction
  - Useful when surface area is important

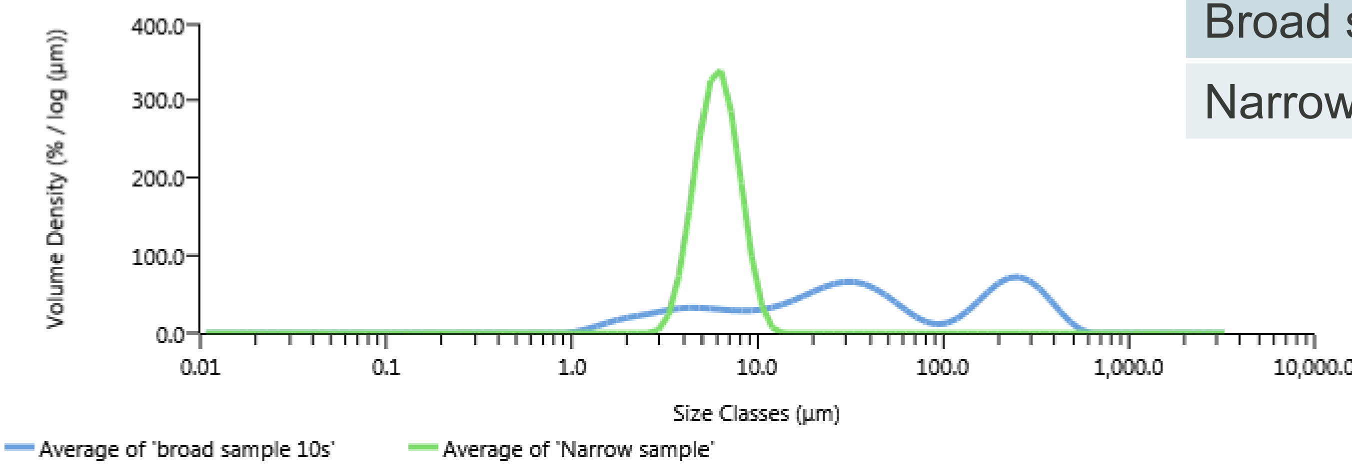


Record Number	Sample Name	Dx (10) (µm)	Dx (50) (µm)	Dx (90) (µm)	D [3,2] (µm)	D [4,3] (µm)
4	Average of 'LH300:LH100 10:90 1bar'	14.9	162	275	34.4	165
3	Average of 'LH300:LH100 5:95 1bar'	90.3	168	279	59.1	175

PSD Statistics: Other parameters

- Span is a measure of distribution width

$$\text{Span} = \frac{(Dv90 - Dv10)}{Dv50}$$



	Span
Broad sample	8.619
Narrow sample	0.695

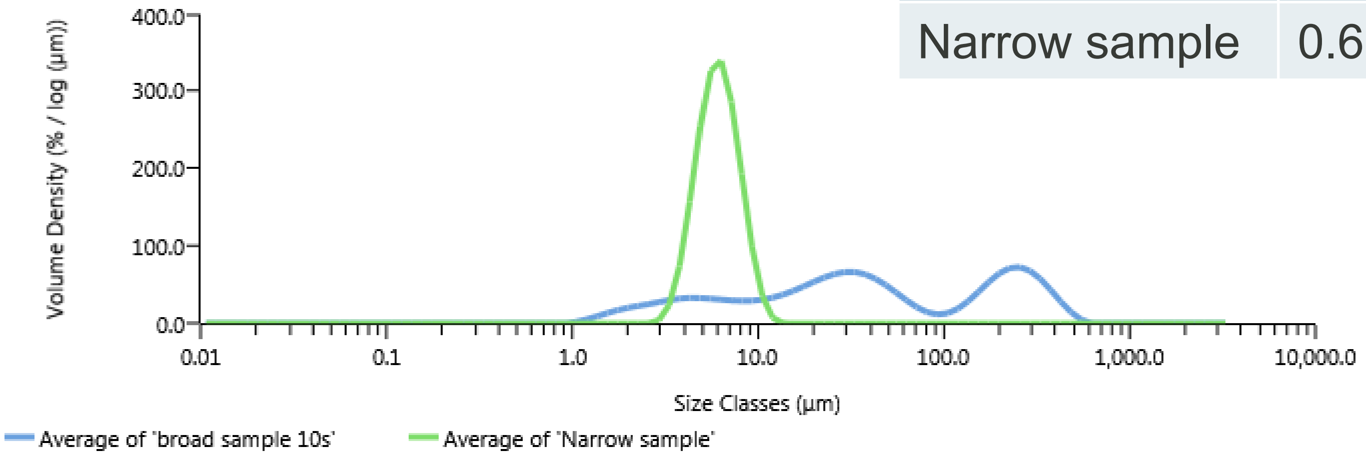
PSD Statistics: Other parameters

- The Uniformity describes distribution spread (has a lower value for narrower distributions)

$$\text{Uniformity} = \frac{\sum V_i |Dv50 - D_i|}{Dv50 \sum V_i}$$

$Dv50 = \text{median}$
$D_i = \text{diameter of size class}$
$V_i = \text{volume in size class}$

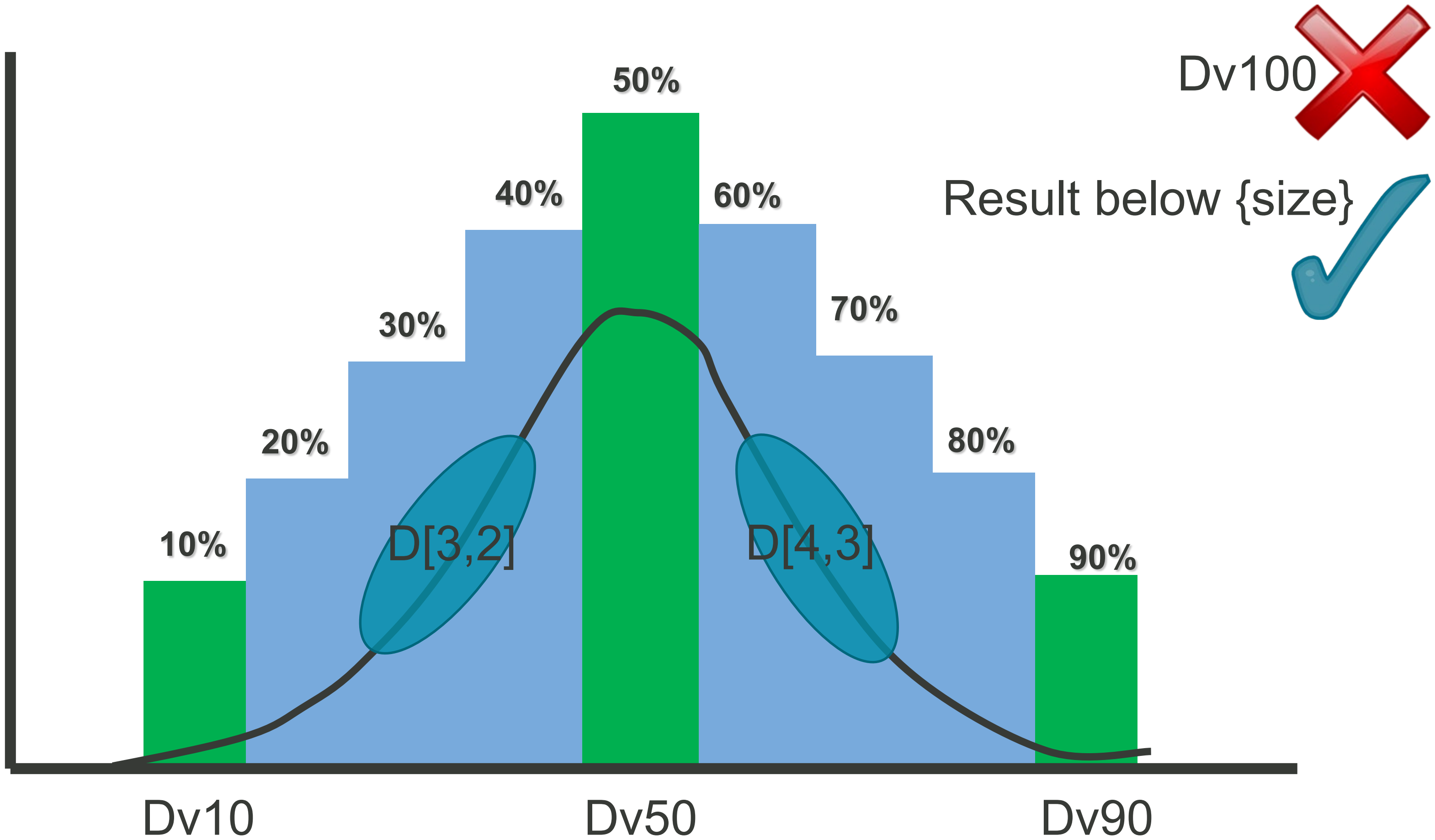
	Span	Uniformity
Broad sample	8.619	2.525
Narrow sample	0.695	0.213



PSD Statistics: Other parameters

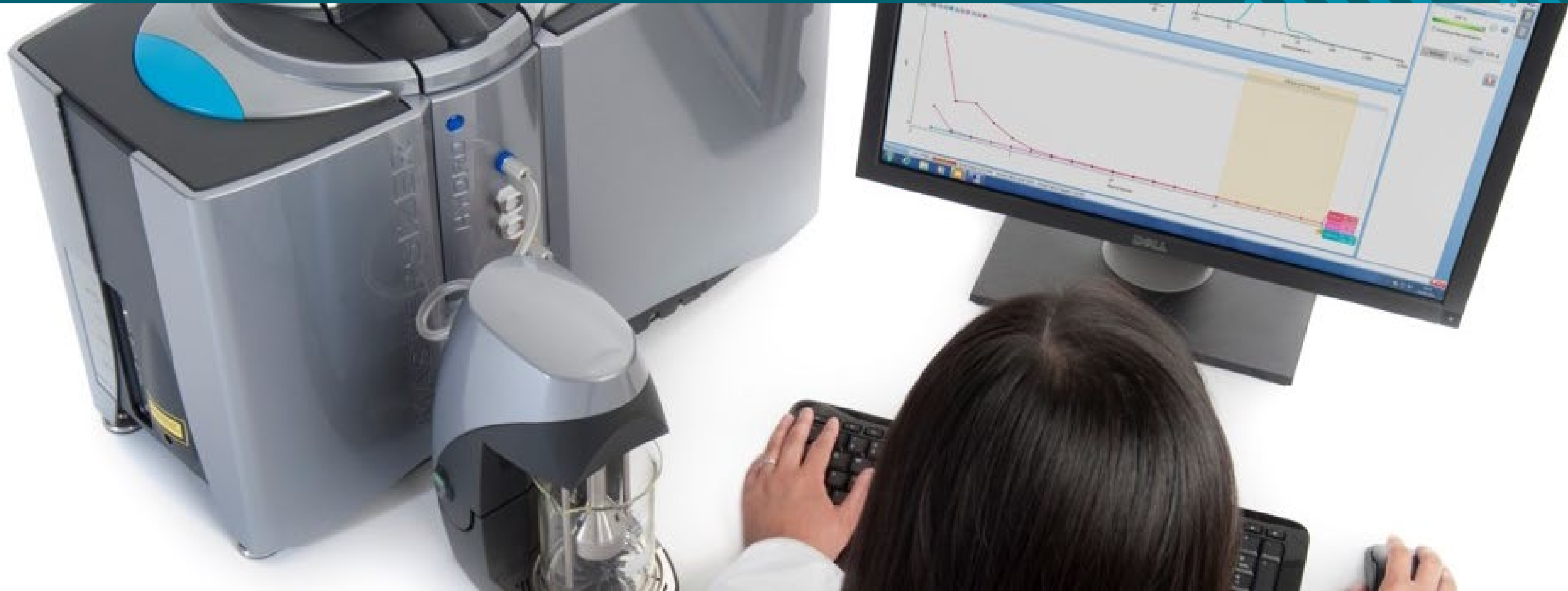
- Specific surface area
  - Total surface area of particles in the sample divided by their total weight
  - Requires the density of the material to be input on the Material page of the SOP/record (default value is 1g/cc)
- Concentration
  - Volume concentration (%) is calculated using the Beer-Lambert law

Chose a parameter that is sensitive to the changes you wish to monitor



Mastersizer 3000 Part 3:

Method development for wet or liquid dispersions



The purpose of method development

- A laser diffraction measurement requires

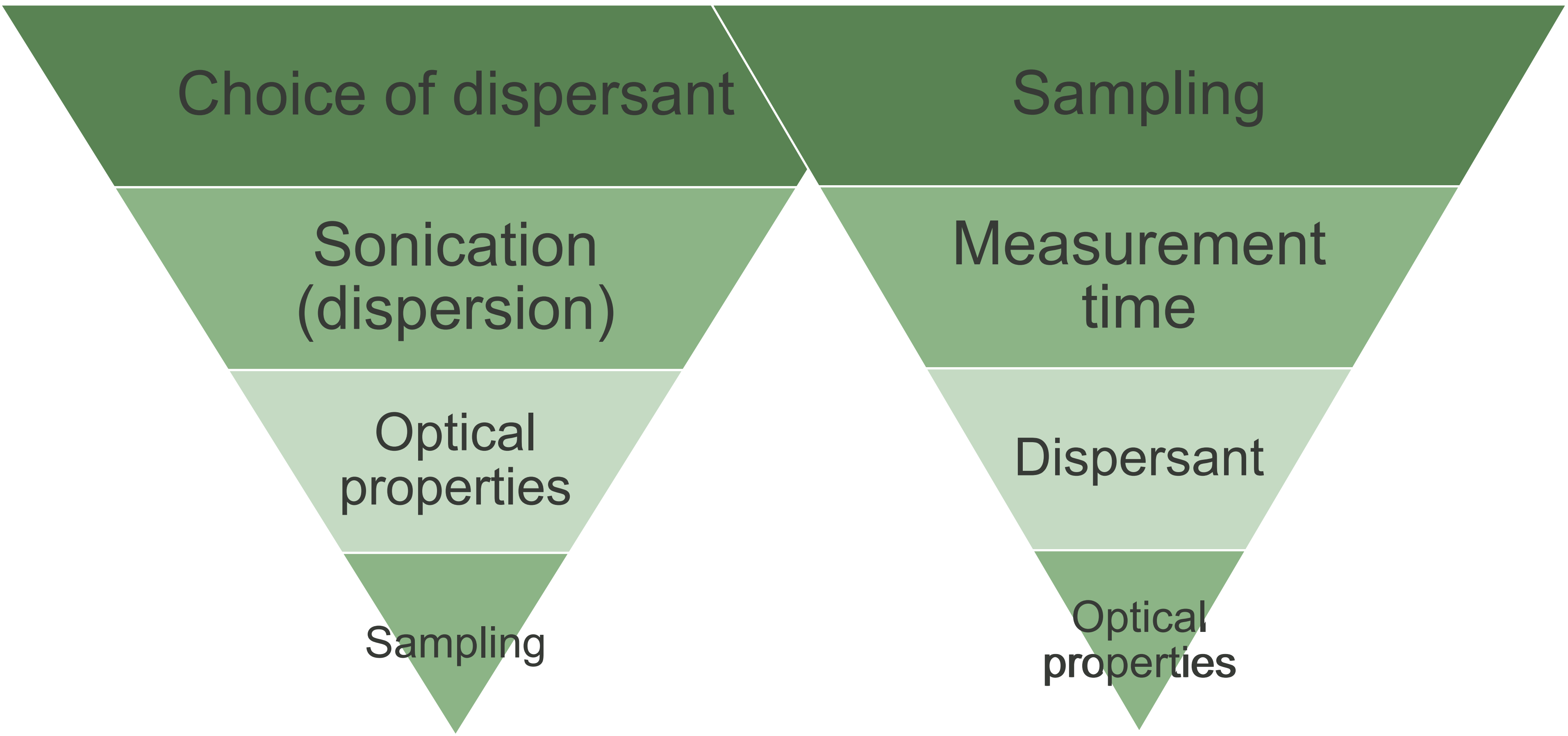
‘a representative sample, dispersed at an adequate concentration in a suitable liquid or gas’

<USP429>

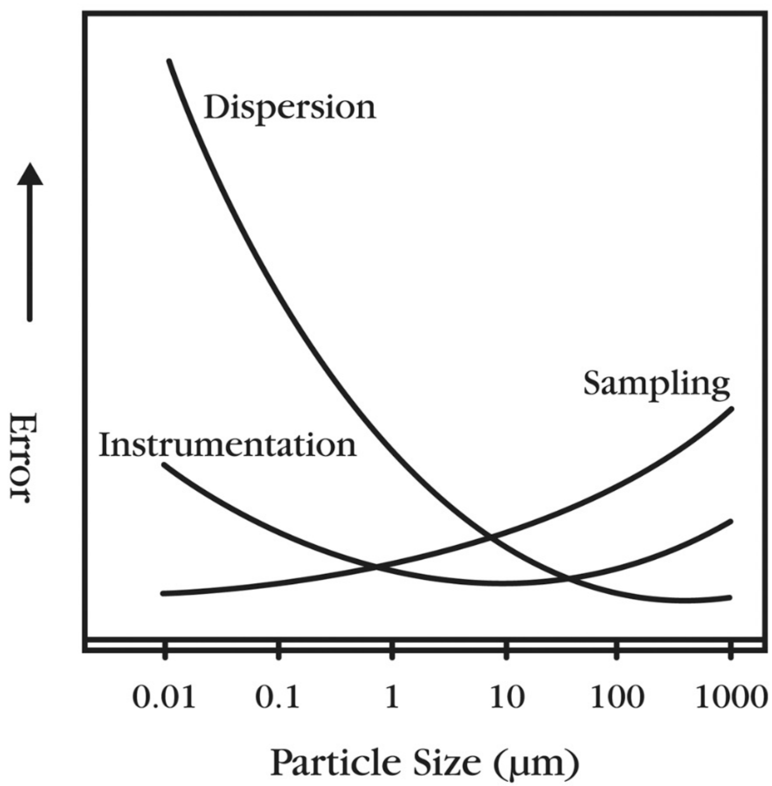
- Method development must define appropriate
  - Sampling
  - Dispersion
  - Measurement conditions

What is the biggest source of error?

Fine particles | **Coarse particles**



What do we need to control when making measurements?

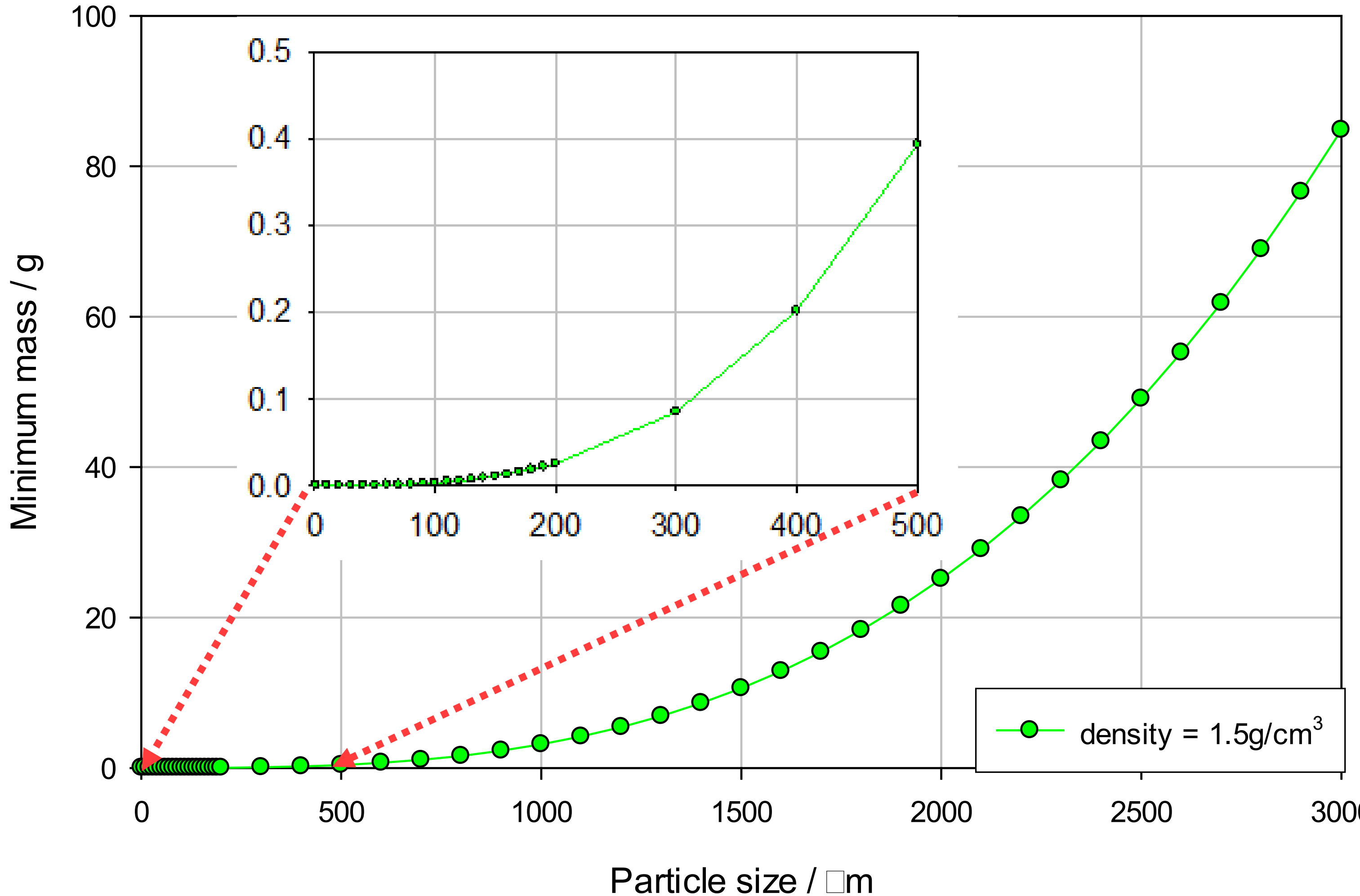


Dr. Henk Merkus, "Quality Assurance in Particle Size Measurement"

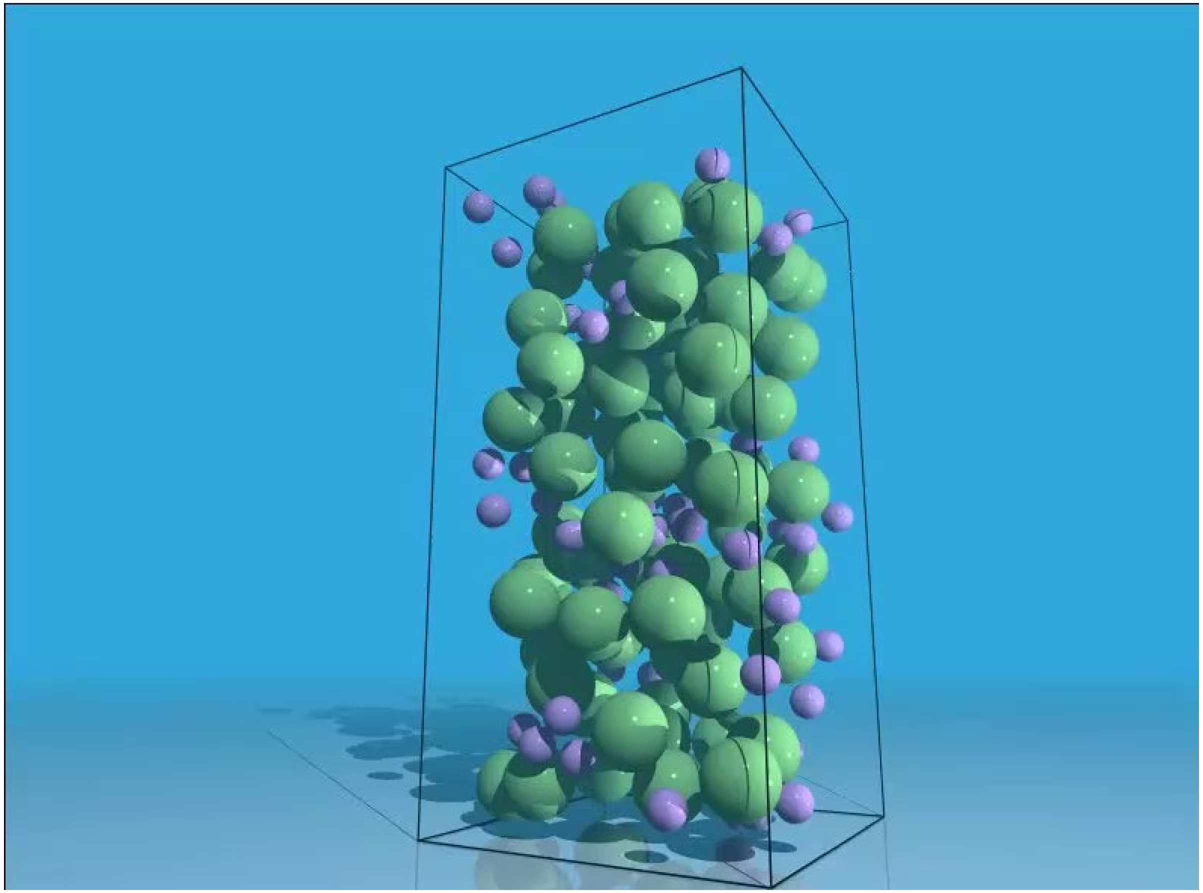
"Novices in the size measurement field must understand that most errors in size measurement arise through poor **sampling** and **dispersion** and not through instrument inadequacies."

T. Allen, Advances in Ceramics, Vol 21: Ceramic Powder Science, page 721, The American Ceramic Society Inc. (1987)

How much sample do I need to measure?

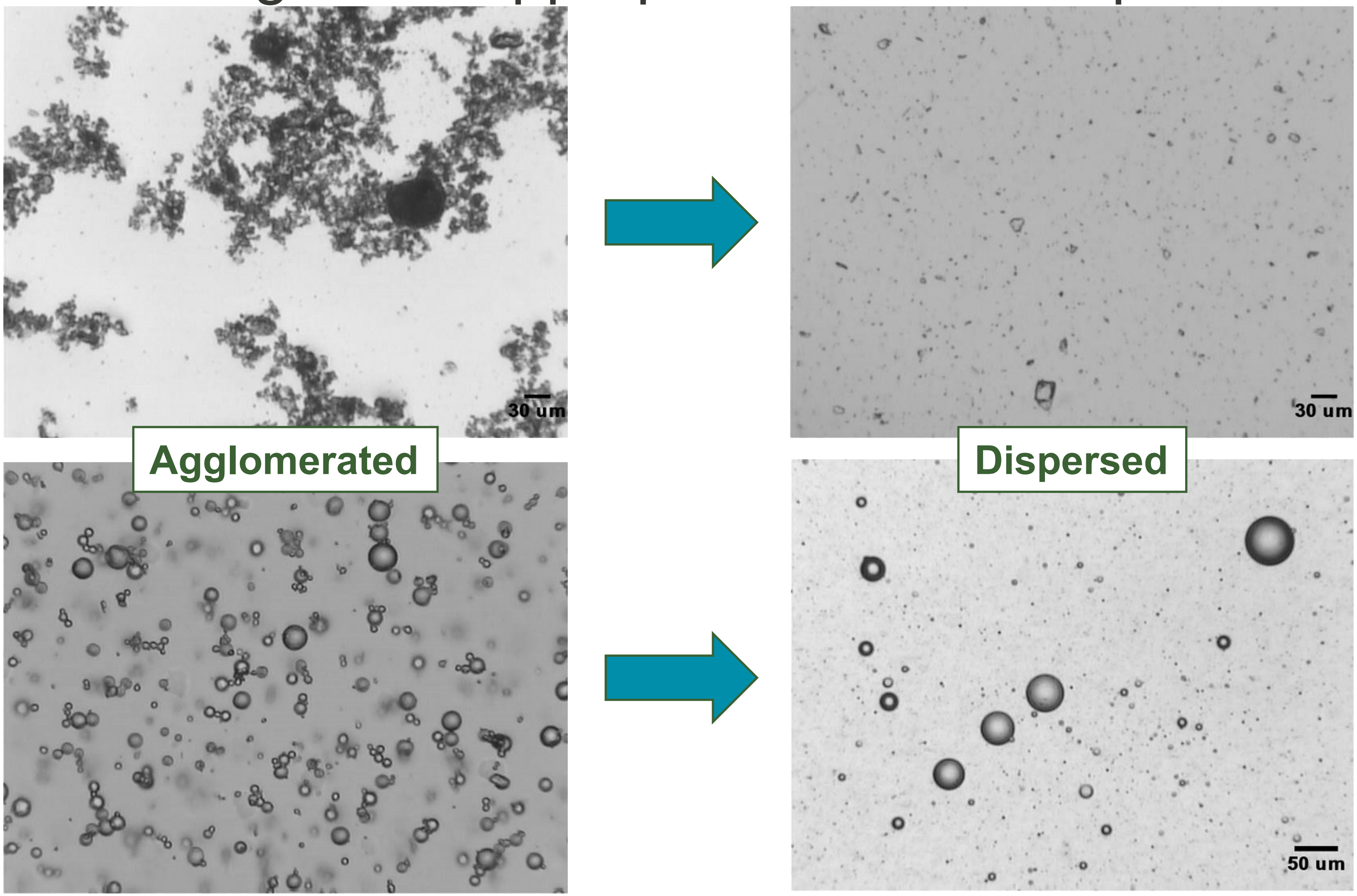


What happens to particles in transit?



Courtesy of A.J. Morris, M. Glover and M. Probert

Measuring in the appropriate state of dispersion



The wet dispersion process

Malvern Panalytical

Wetting the sample

Choose an appropriate dispersant

Carry out a beaker test

Use surfactant to improve the dispersion

Adding energy to improve dispersion

Stirring/pumping by the dispersion unit

Ultrasonics

Stabilising the dispersion

Check repeatability after ultrasound

Additives can be used to prevent re-agglomeration

Wetting the sample

Choose an appropriate dispersant

Carry out a beaker test

Use surfactants to improve wetting

Dispersant
Water/DI water
Organic acids
Alcohols (methanol / ethanol / isopropyl alcohol)
Simple alkanes (hexane / heptane/ iso-octane / cyclohexane)
Long-chain alkanes and alkenes (dodecane / mineral oils / sunflower oils / palm oil)

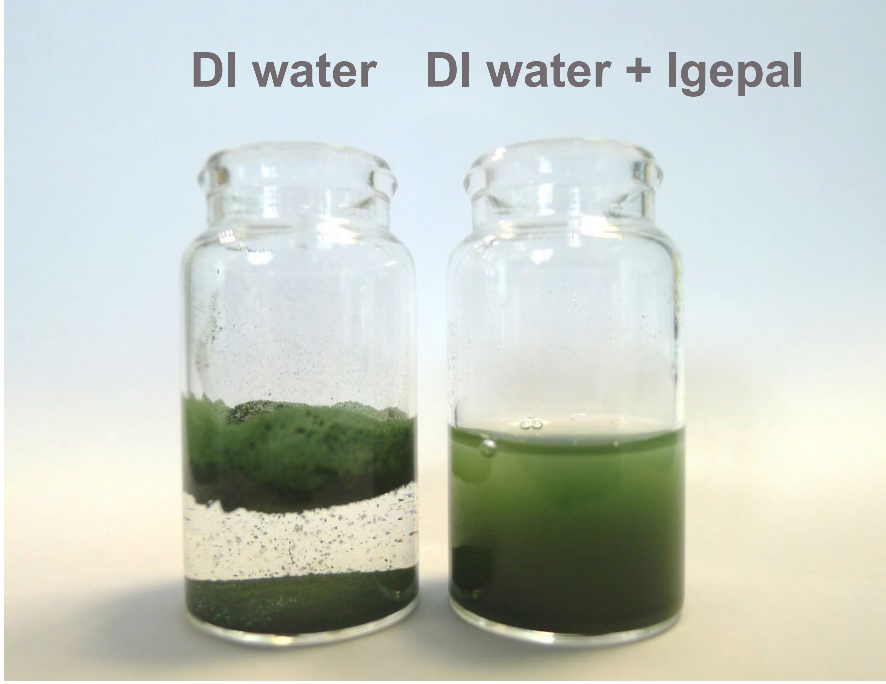
Polarity

Wetting the sample

Choose an appropriate dispersant

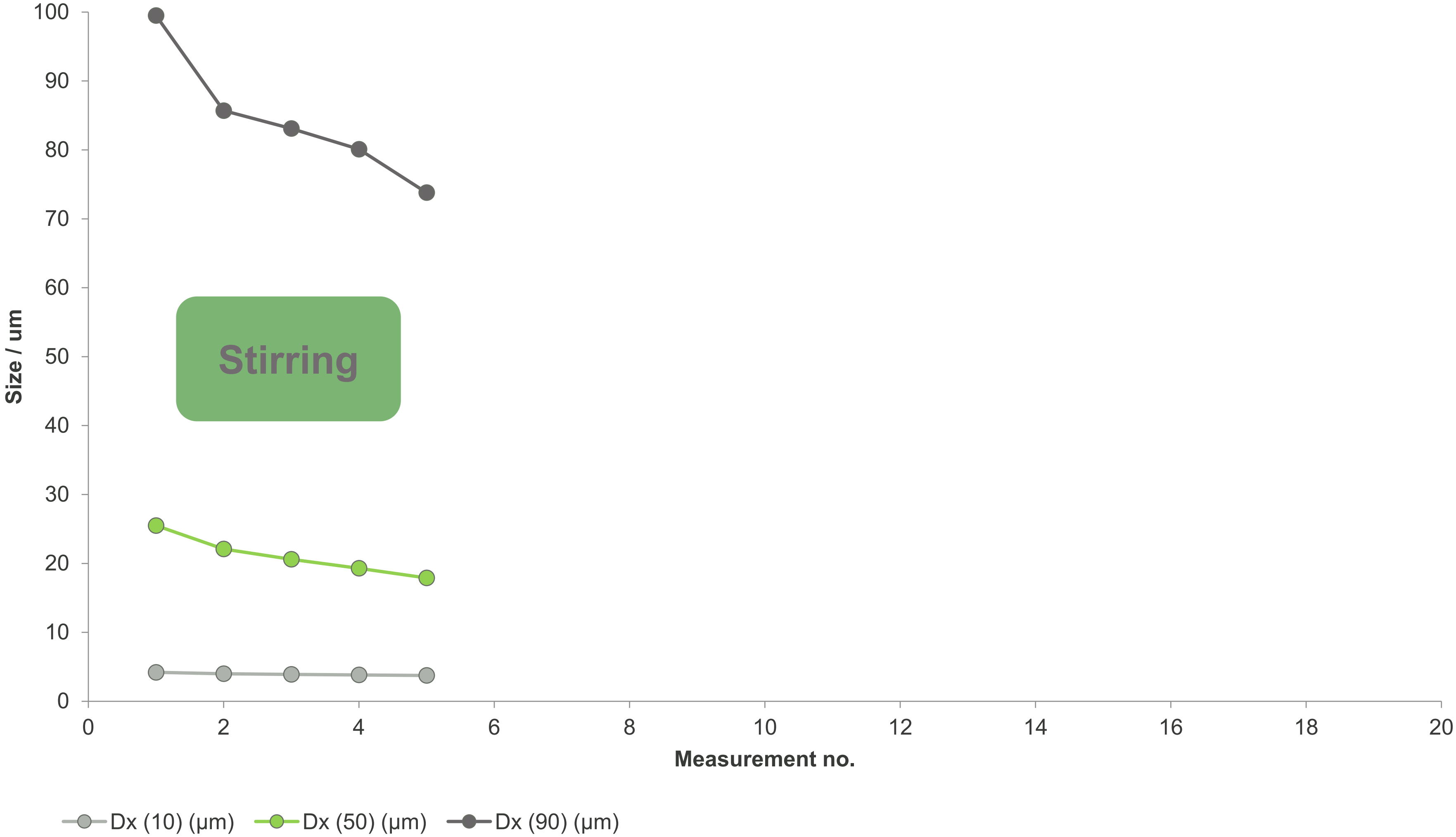
Carry out a beaker test

Use surfactants to improve wetting

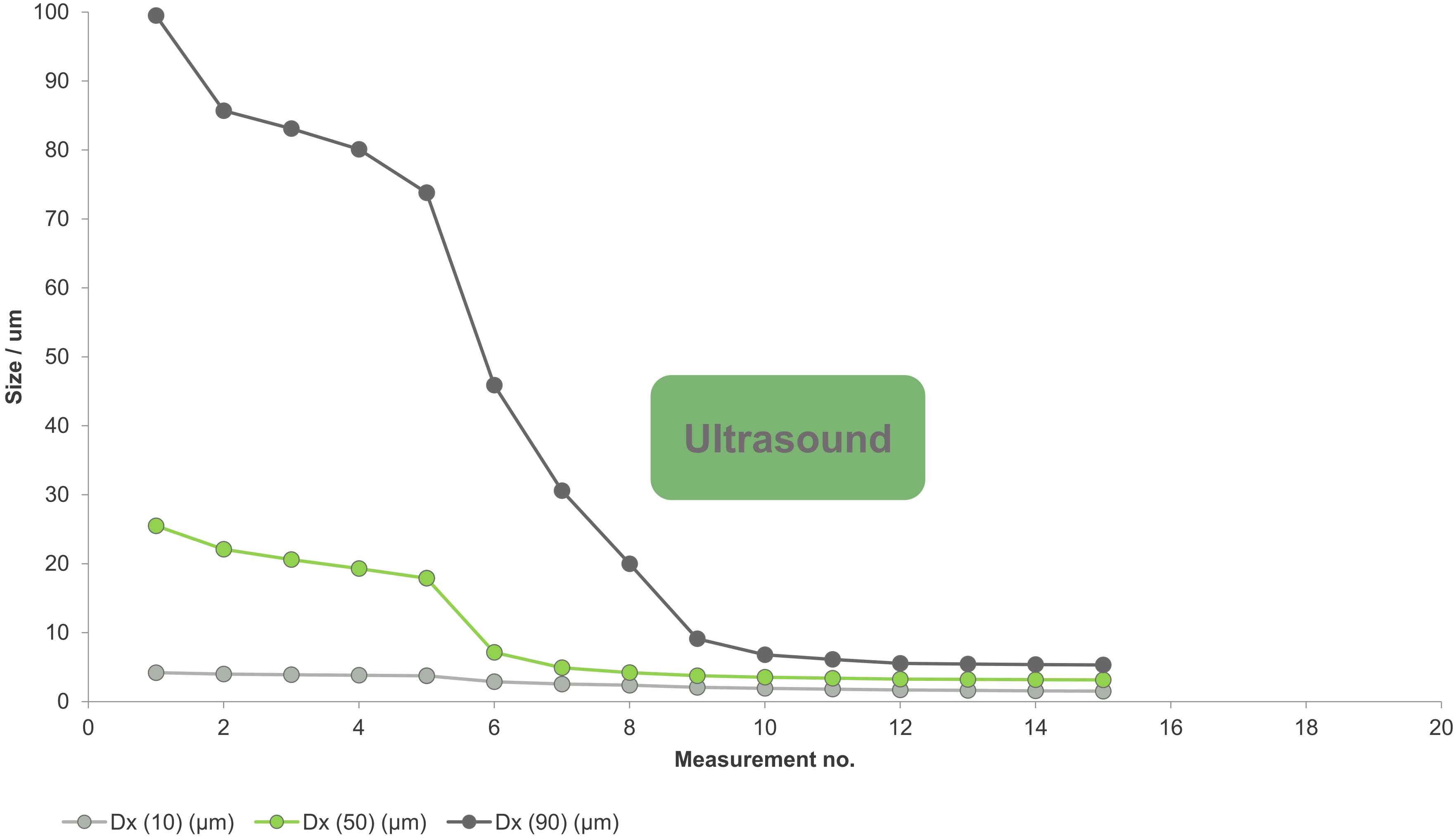


Stabilization	Examples
Steric	Igepal CA-360, Tween 20/80, Span 20/80
Electrosteric	Anionic: SDS (sodium dodecylfulfate), AOT (sodium-bis-2-etheylhexylsulfosuccinate)
	Cationic: CTAB (cetyltimethlammonium bromide)

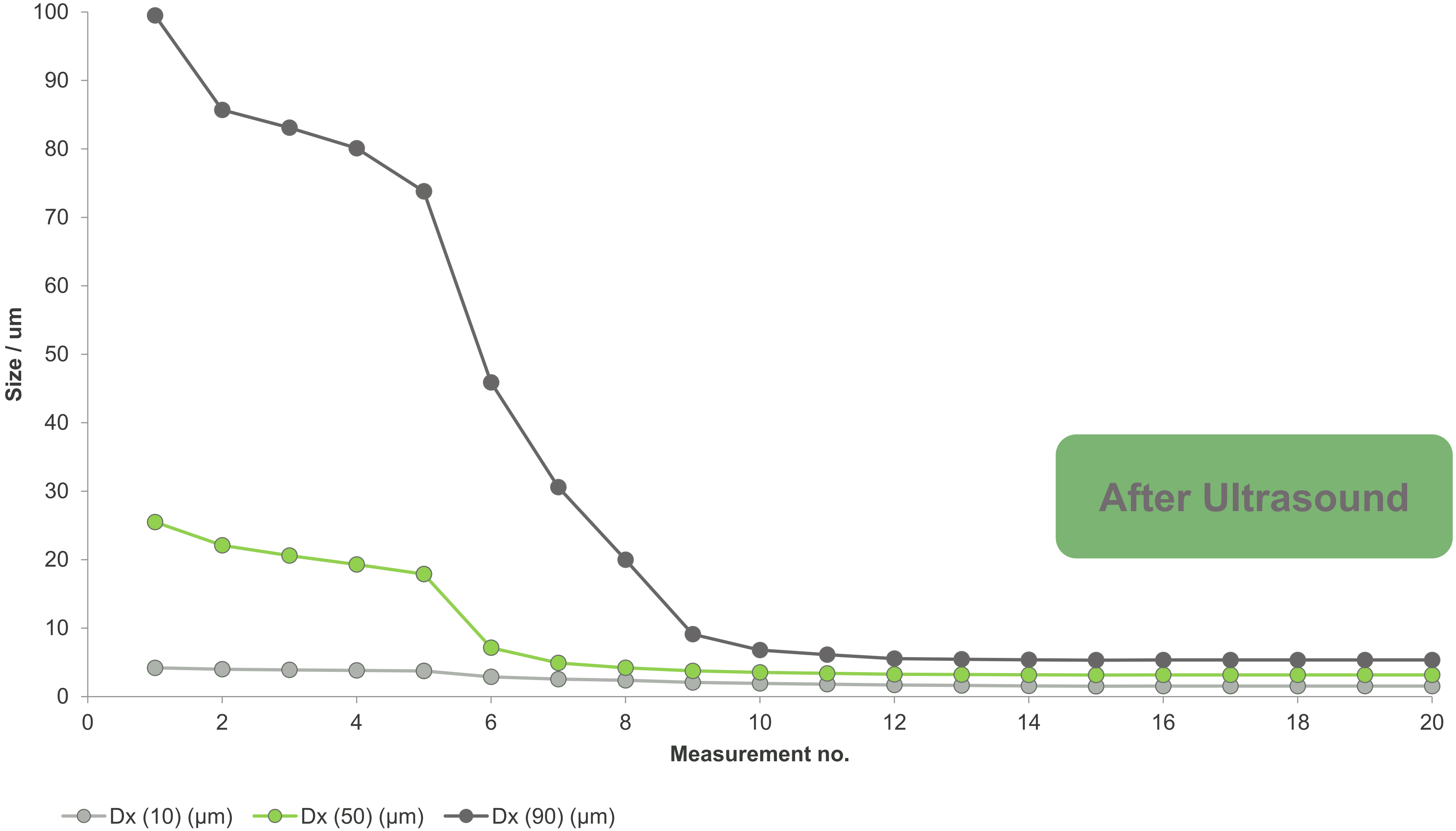
Adding energy to improve dispersion



Adding energy to improve dispersion

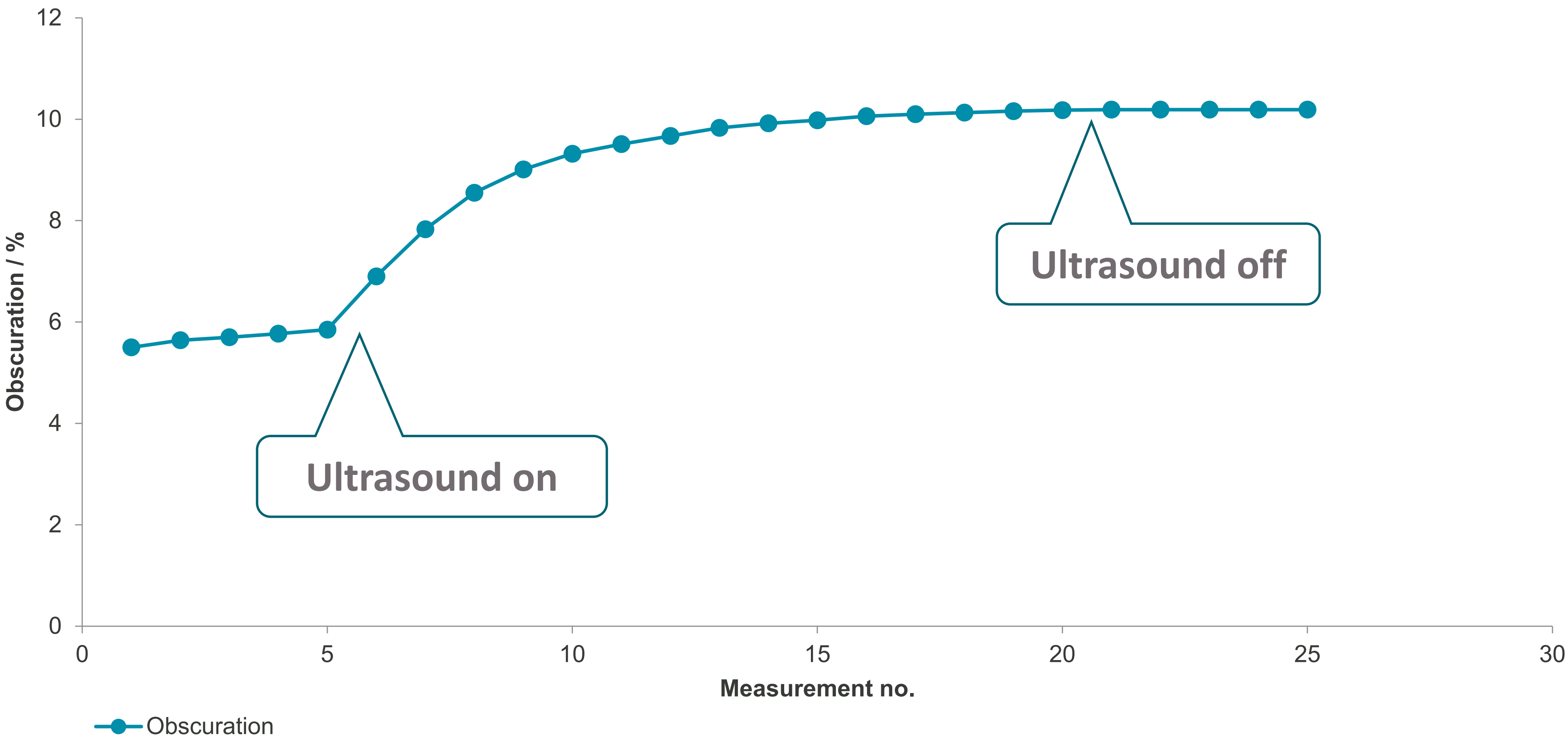


Adding energy to improve dispersion



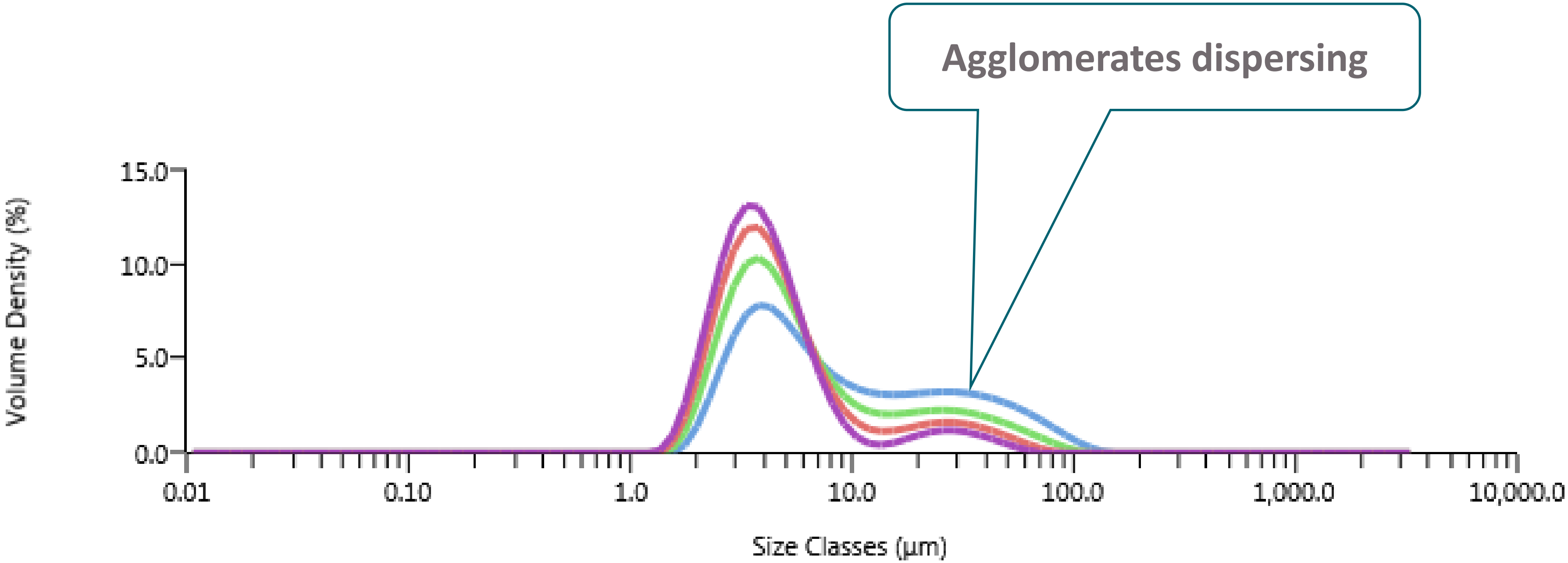
Identifying dispersion: obscuration

- Obscuration increases as agglomerates disperse



Dispersion trend: Particle size distribution

- Overlay the results of an ultrasound titration
  - Should show gradual dispersion



Following trends on the records view: dispersion

Record View

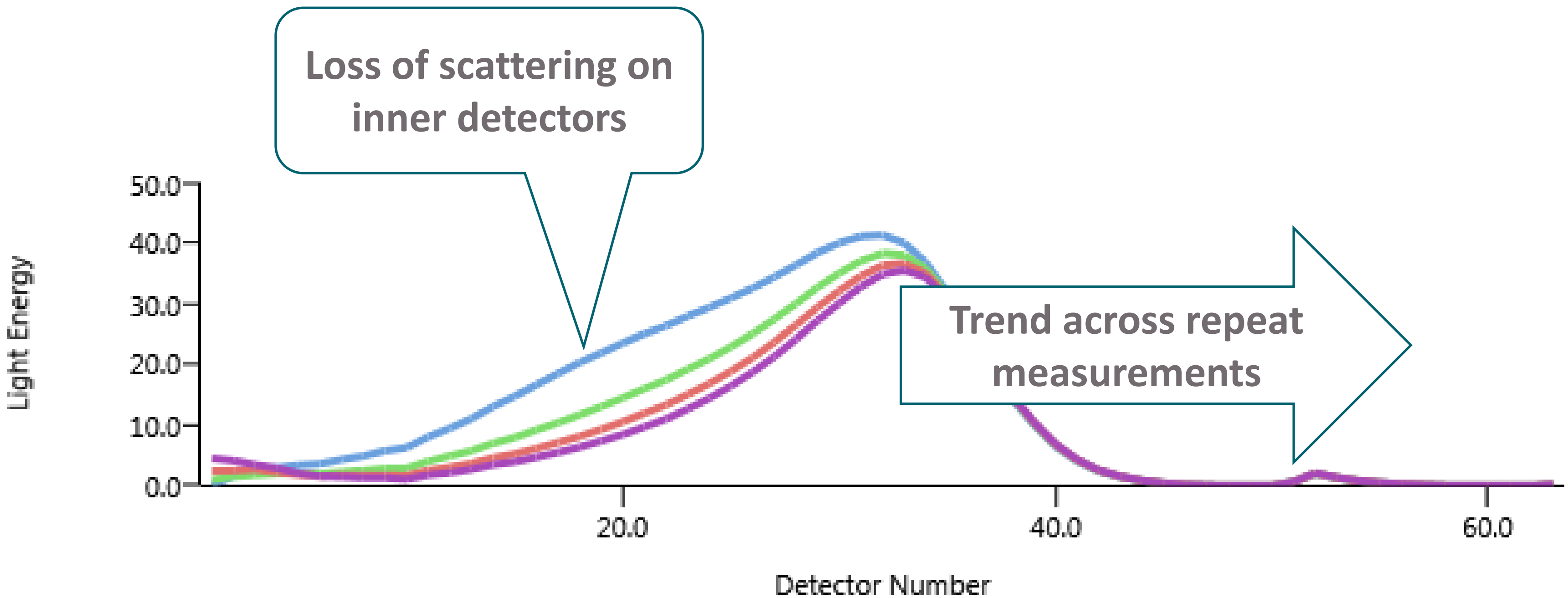
* Measurement file 40

Drag column header here to group by that column

Record Number	Sample Name	Laser Obscuration (%)	Dx (10) (µm)	Dx (50) (µm)	Dx (90) (µm)
1	Toner	5.50	4.84	20.2	325
2	Toner	5.64	4.86	21.2	341
3	Toner	5.70	4.83	19.6	329
4	Toner	5.77	4.81	18.7	337
5	Toner	5.85	4.86	21.7	349
6	Toner with ultrasound	6.90	4.60	11.2	295
7	Toner with ultrasound	7.83	4.32	8.35	211
8	Toner with ultrasound	8.55	4.18	7.44	65.3
9	Toner with ultrasound	9.01	4.09	6.95	29.6
10	Toner with ultrasound	9.32	4.02	6.60	12.4
11	Toner with ultrasound	9.51	4.17	6.48	10.9
12	Toner with ultrasound	9.67	4.21	6.38	10.2
13	Toner with ultrasound	9.83	4.22	6.30	9.68
14	Toner with ultrasound	9.92	4.20	6.24	9.49
15	Toner with ultrasound	9.98	4.15	6.16	9.19
16	Toner with ultrasound	10.06	4.17	6.14	9.05
17	Toner with ultrasound	10.10	4.22	6.12	8.82
18	Toner with ultrasound	10.13	4.24	6.10	8.67
19	Toner with ultrasound	10.16	4.27	6.08	8.60
20	Toner with ultrasound	10.18	4.29	6.07	8.51

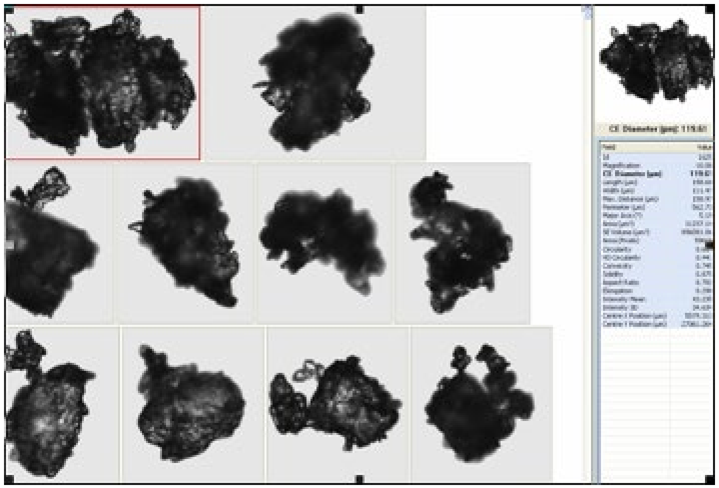
Dispersion trend: scattering data

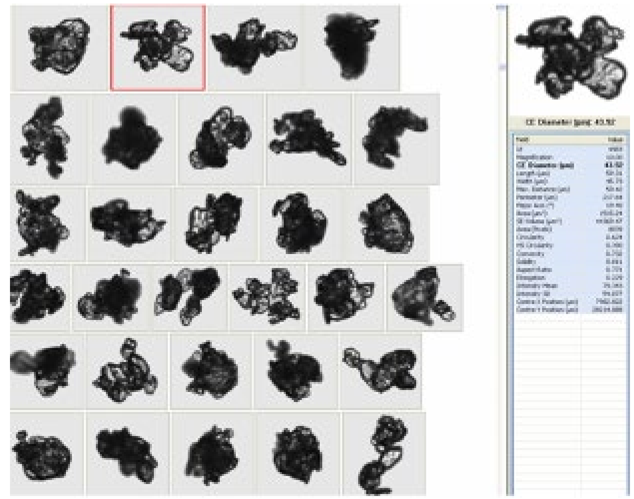
- During dispersion, as the particles get smaller
  - Scattering on inner detectors decreases
  - Peak shifts to higher angle detectors



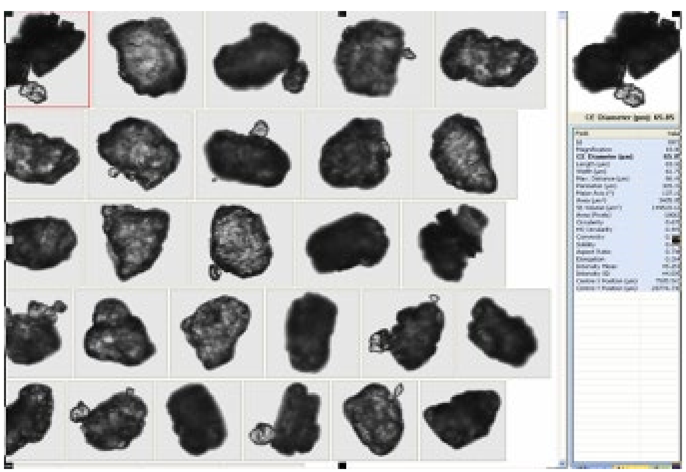
Reminder: detector number increases with angle
Scattering from larger particles falls on low angle detectors

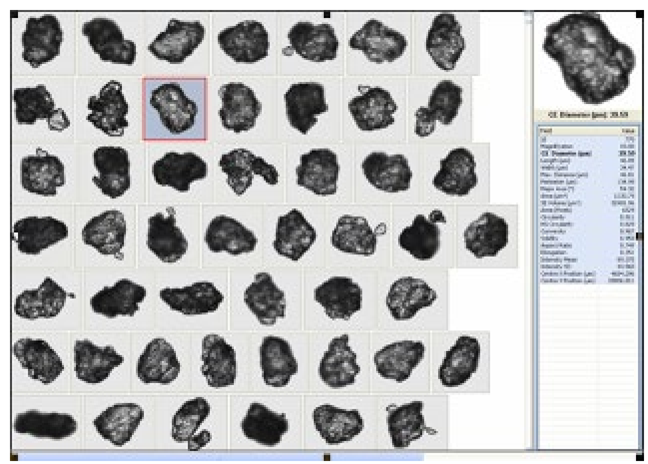
The dispersion process: Verification





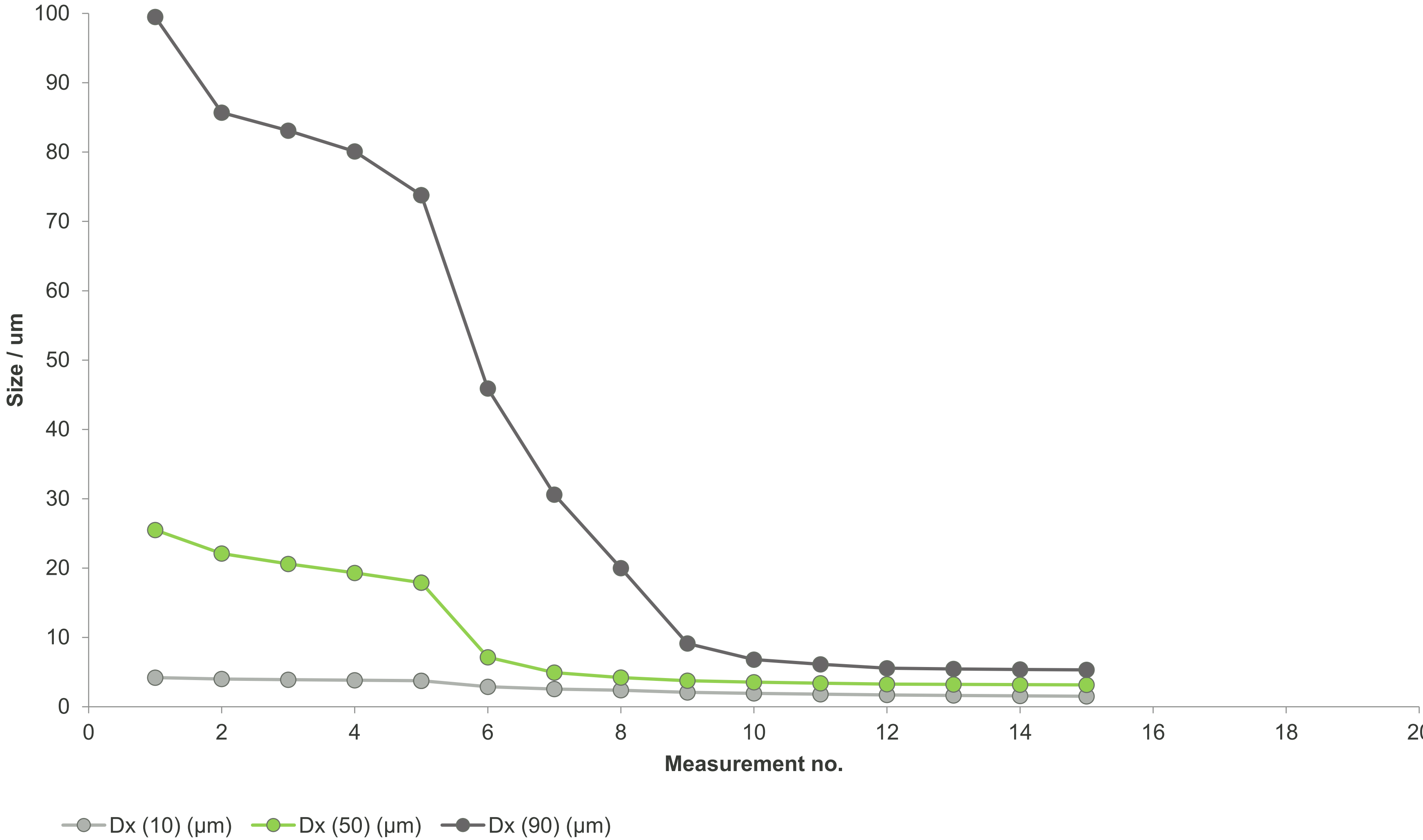
Without sonication



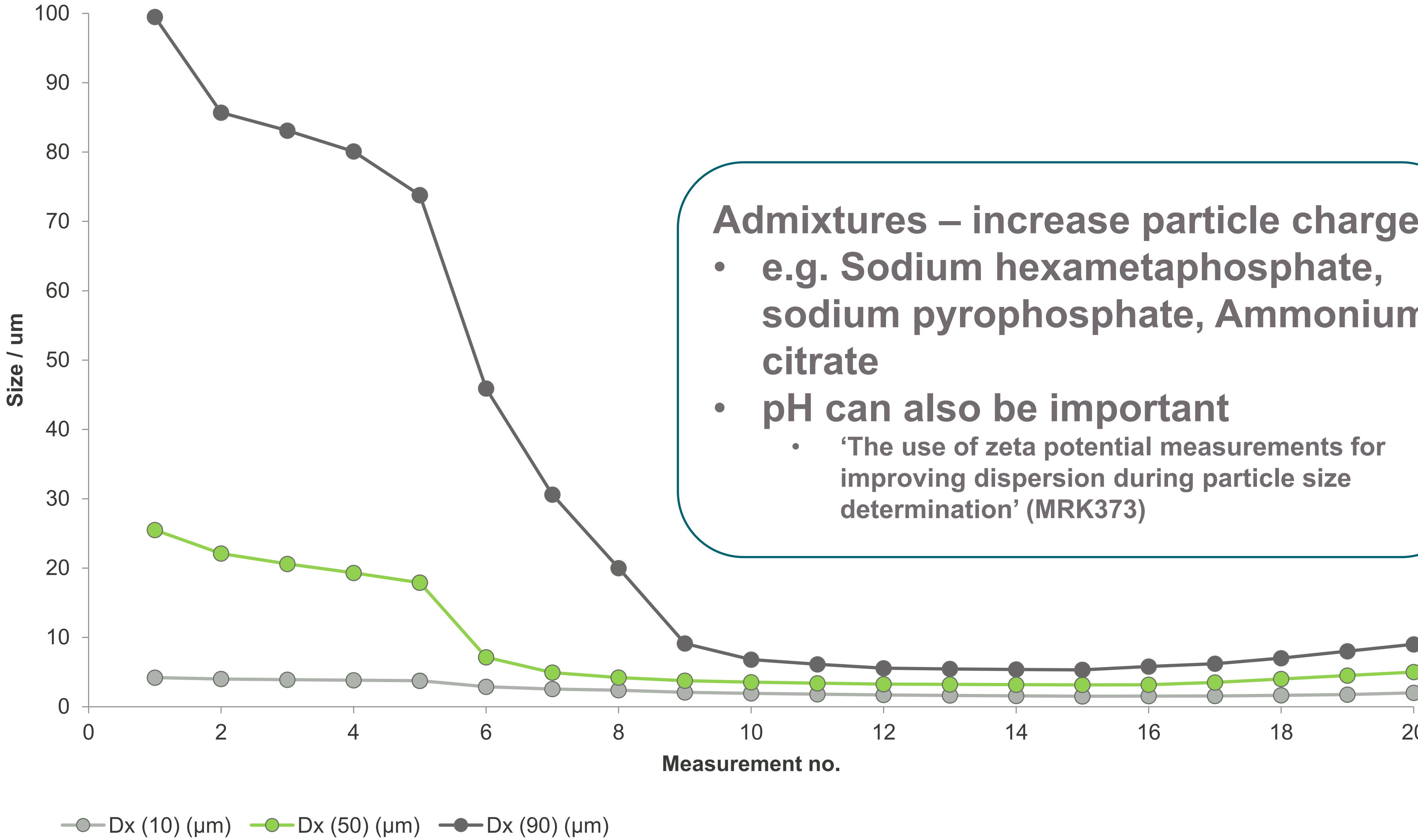


With sonication

Stabilising the dispersion



Stabilising the dispersion



Admixtures – increase particle charge

- **e.g. Sodium hexametaphosphate, sodium pyrophosphate, Ammonium citrate**
- **pH can also be important**
  - **'The use of zeta potential measurements for improving dispersion during particle size determination' (MRK373)**

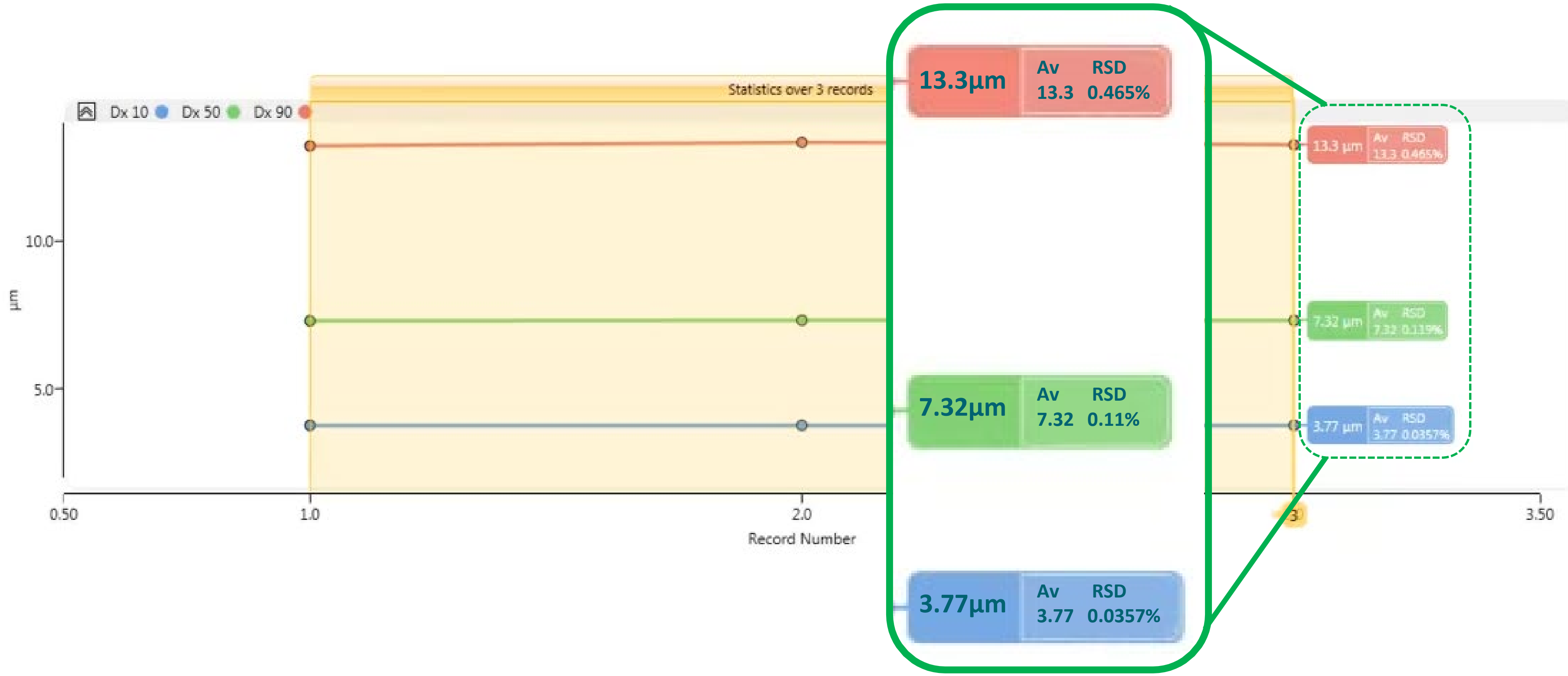
How stable should the results be?

- ISO13320-1: Section 6.4
  - Dv50 - 5 different readings: COV < 3%
  - Dv10 and Dv90: COV < 5%
  - “Below 10µm, these maximum values should be doubled.”
  - Coefficient of variance = relative standard deviation (RSD)
- In ideal conditions
  - 0.5% COV on parameters >1µm
  - 1% COV on parameters <1µm

$$\%COV = \frac{standard\ deviation}{average} \times 100$$

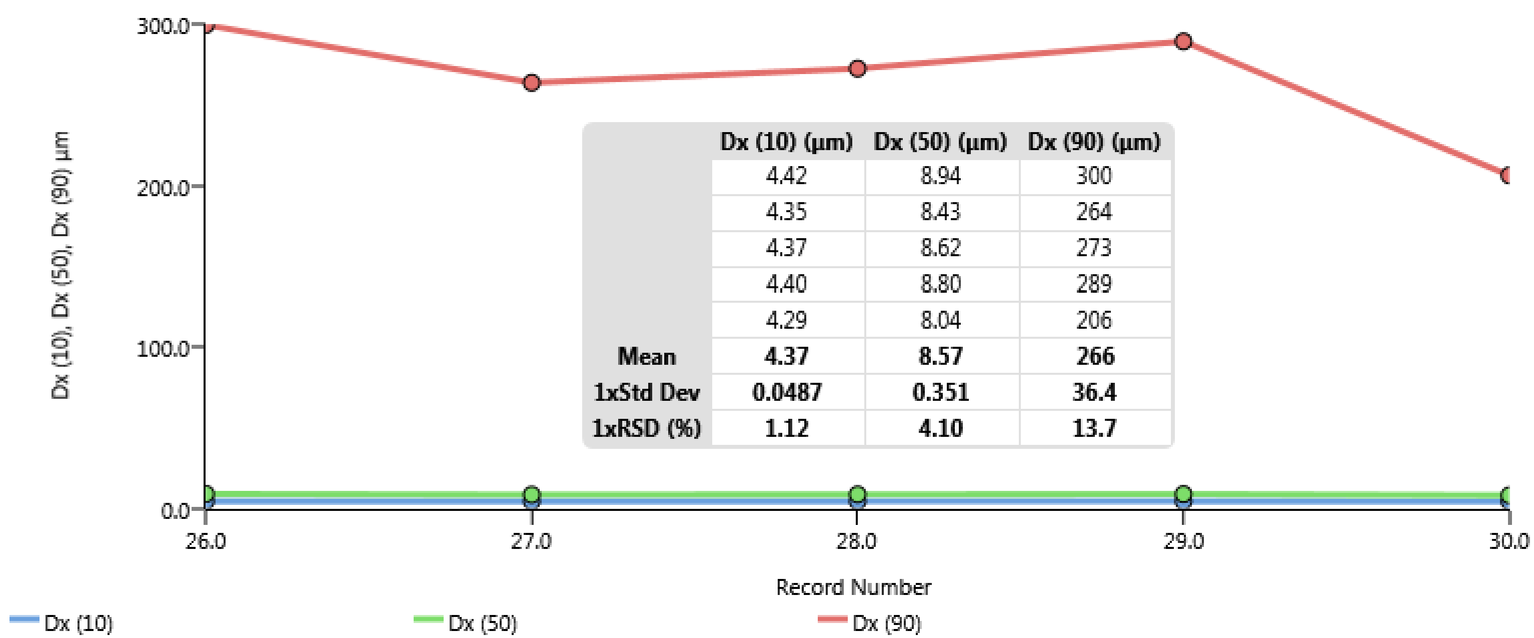
Checking the stability of the results

- The live trend shows the variability of the results
  - RSDs should be within ISO limits



What if the results are not stable?

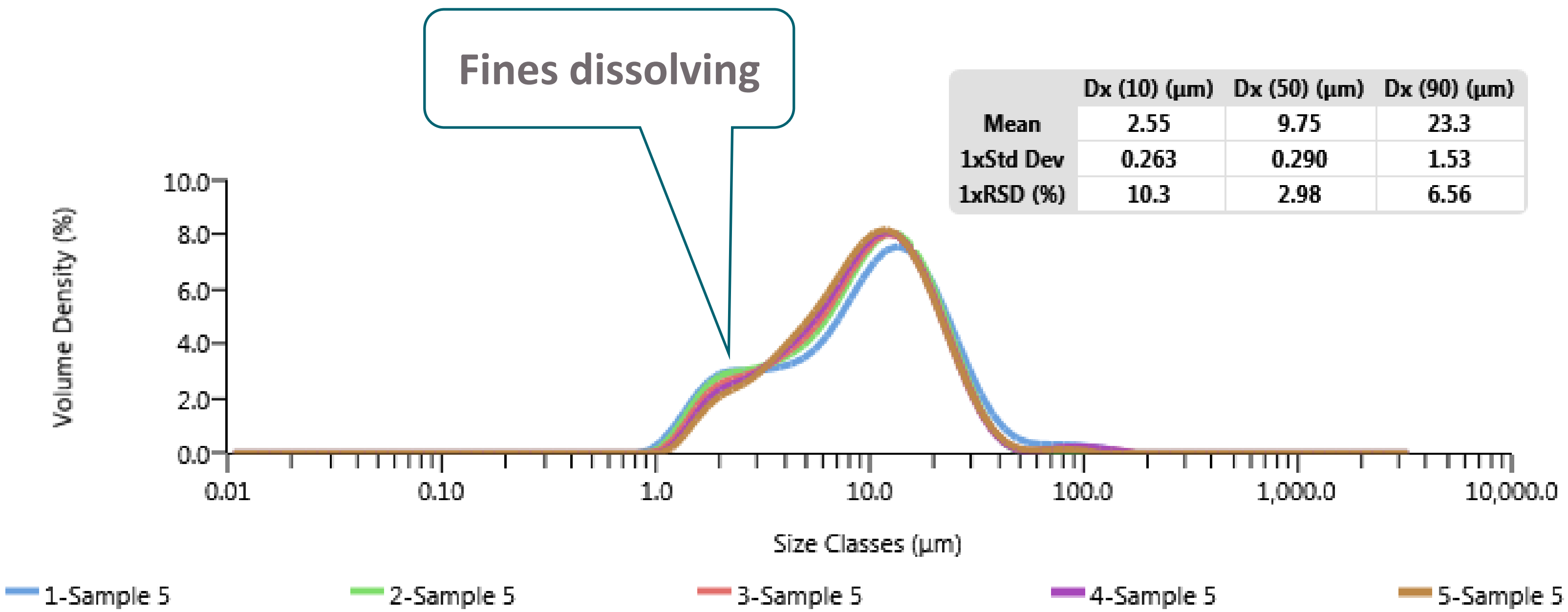
- If the results are not stable the sample could be:
  - Dissolving
  - Agglomerating
  - Breaking due to excessive ultrasound
  - Incomplete dispersion



	Dx (10) (µm)	Dx (50) (µm)	Dx (90) (µm)
	4.42	8.94	300
	4.35	8.43	264
	4.37	8.62	273
	4.40	8.80	289
	4.29	8.04	206
Mean	**4.37**	**8.57**	**266**
1xStd Dev	**0.0487**	**0.351**	**36.4**
1xRSD (%)	**1.12**	**4.10**	**13.7**

Identifying sample dissolution

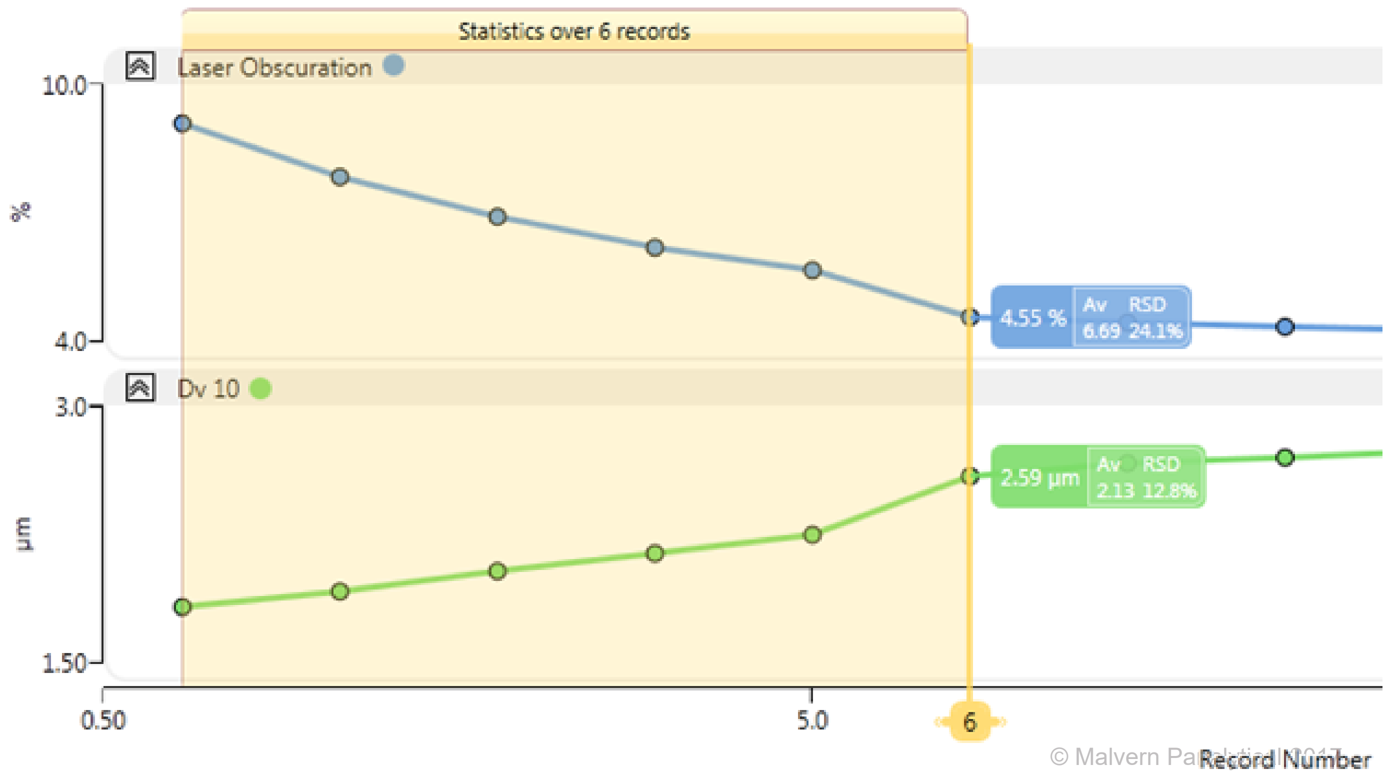
- If the particles are dissolving
  - The obscuration will decrease
  - The fine particles will get smaller and then disappear
    - The Dv10 will increase
  - The coarse fraction will become more dominant



	Dx (10) (μm)	Dx (50) (μm)	Dx (90) (μm)
Mean	2.55	9.75	23.3
1xStd Dev	0.263	0.290	1.53
1xRSD (%)	10.3	2.98	6.56

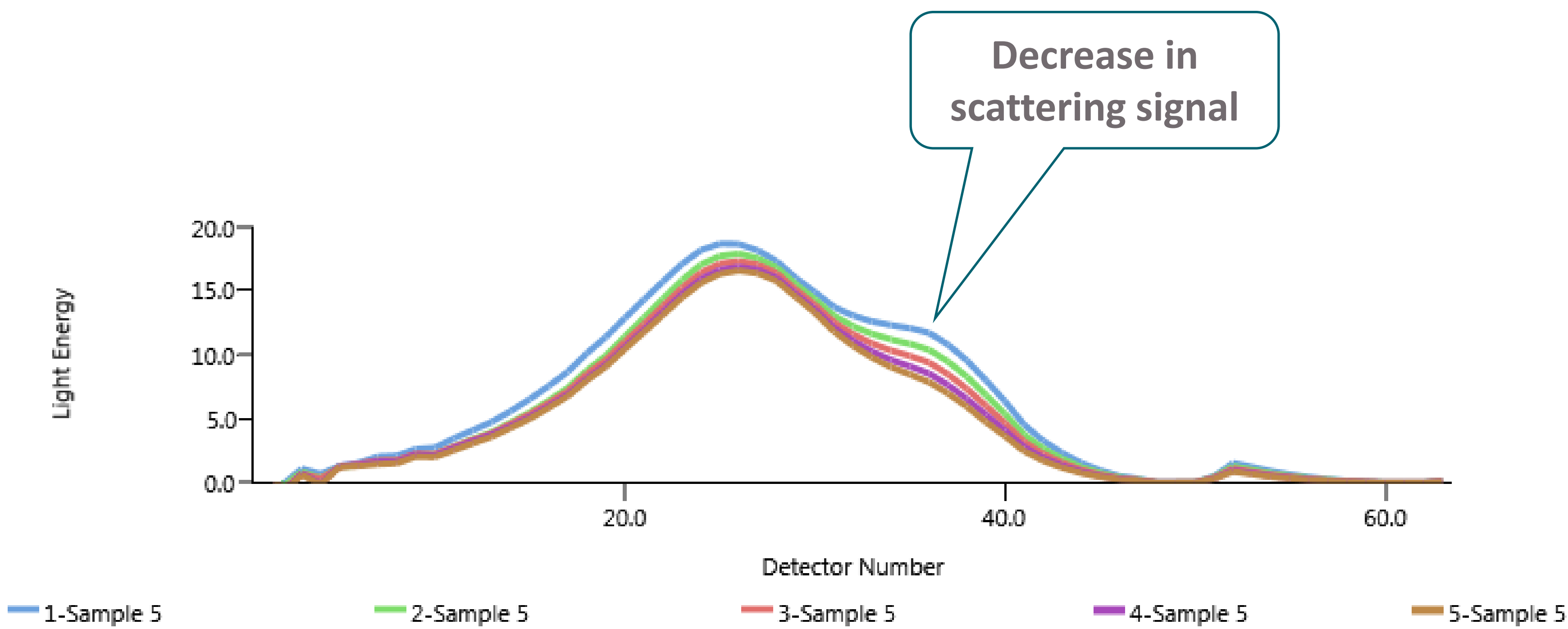
Identifying sample dissolution: Trend view

- Plotting the obscuration and Dv10 on the live trend can help to identify dissolution
  - Decreasing obscuration
  - Increasing Dv10



Identifying sample dissolution: Scattering data

- Scattering signal level decreases as sample dissolves
  - Fewer particles scatter less light



Remedies for sample dissolution

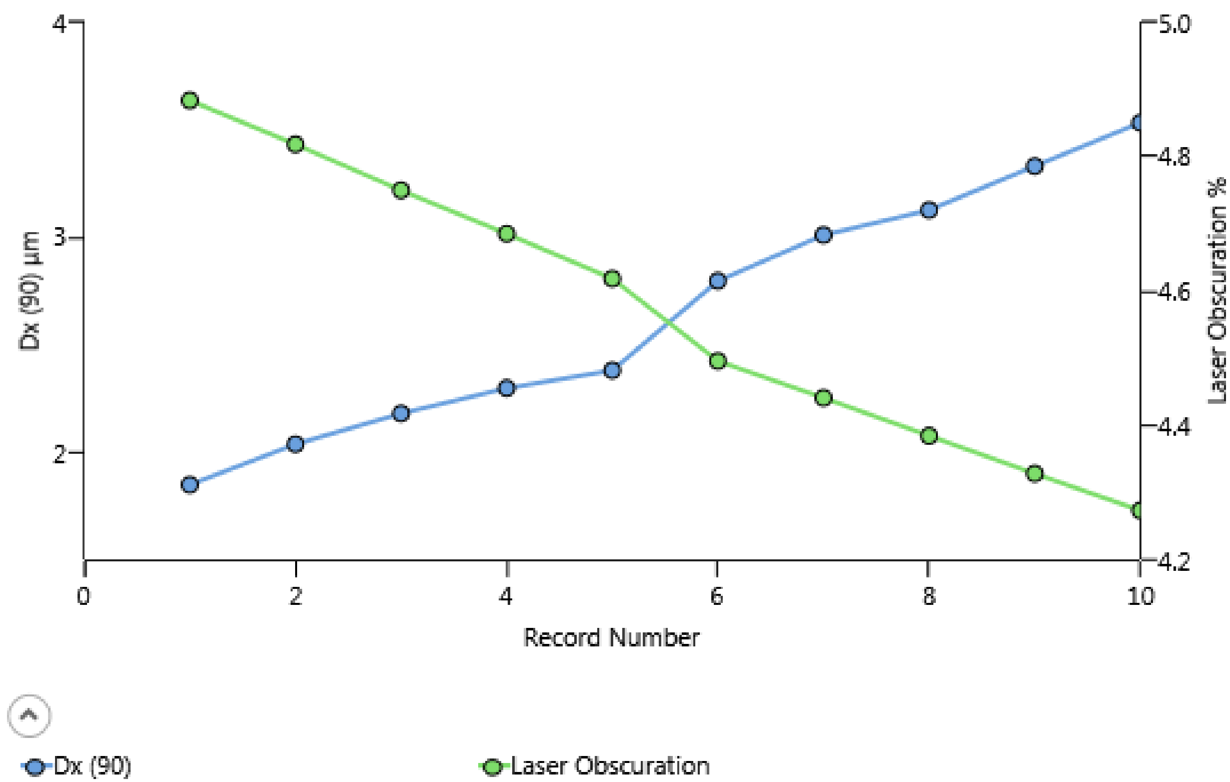
- Try other dispersants
  - As listed on slide 6
- Select the dispersant with the least dissolution
  - Determined from repeatability
- If unavoidable, measurements can be made with slight dissolution
  - Sample prep and measurement time must be controlled
- As a last resort, saturated solutions can be used
  - Must be used carefully
    - Temperature control etc.

Identifying sample agglomeration

- If the sample is agglomerating
  - A tail of large particles will appear in the distribution
  - The obscuration will decrease gradually
    - As individual particles become agglomerates
  - Using ultrasound may remove the agglomerates
    - If the sample is not chemically stable then ultrasound can cause agglomeration

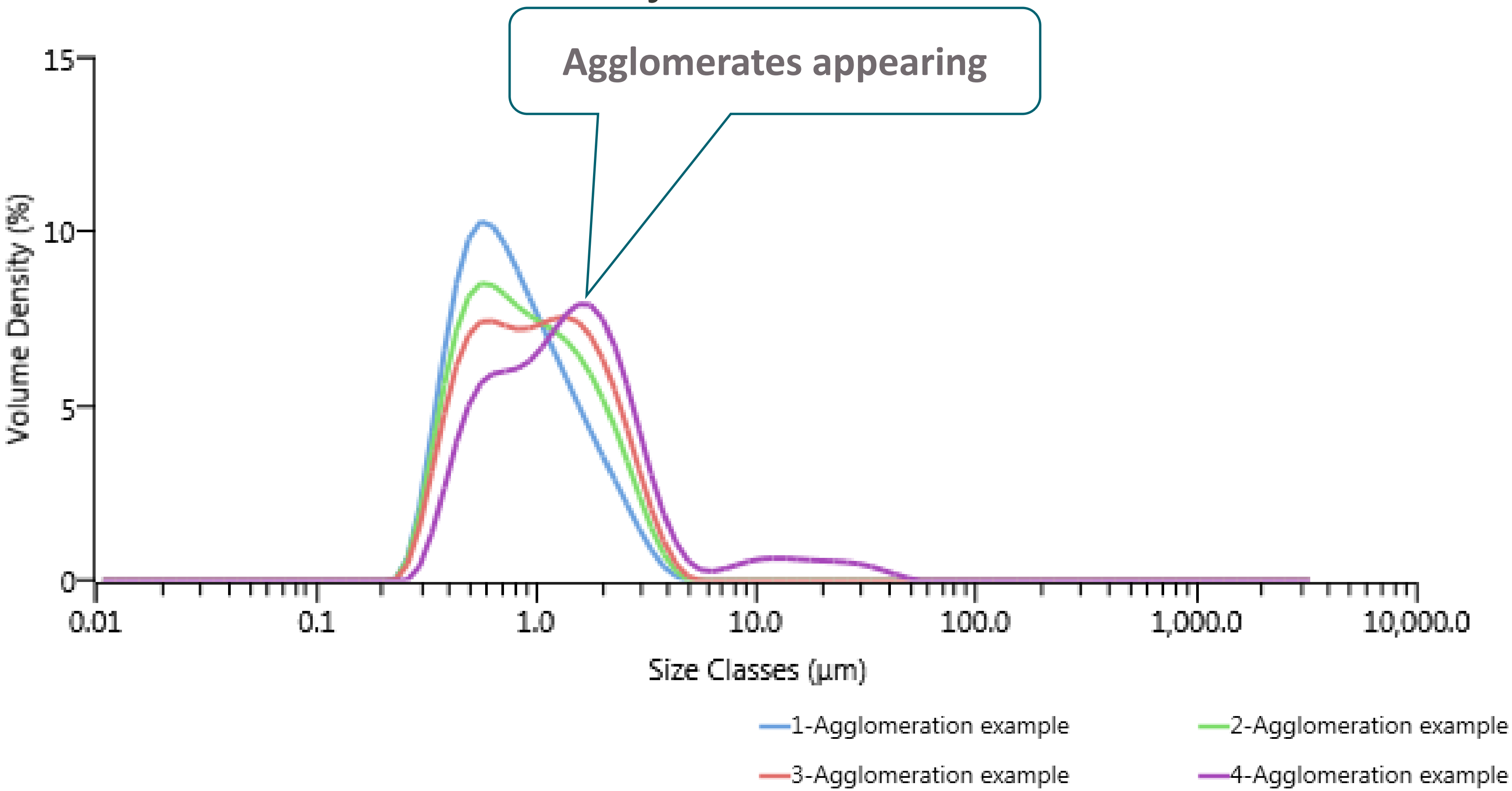
Identifying sample agglomeration: Trend view

- When the sample is agglomerating
  - The obscuration will decrease gradually
  - The Dv90 will increase



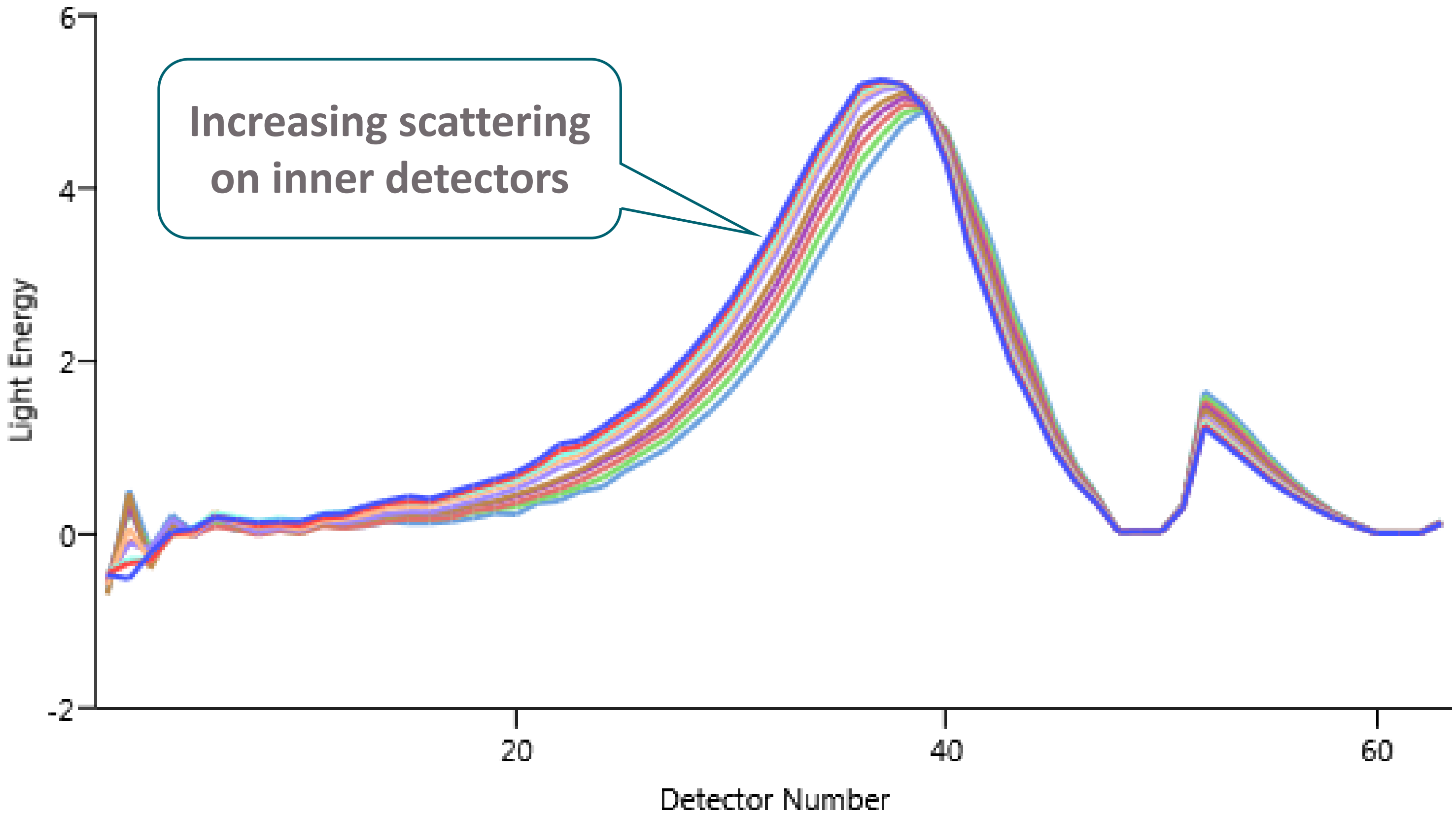
Identifying sample agglomeration: Size distribution

- The volume in the coarse fraction may increase
- Or the coarse fraction may increase in size



Identifying sample agglomeration: Scattering data

- Scattering data will increase and move towards inner detectors.



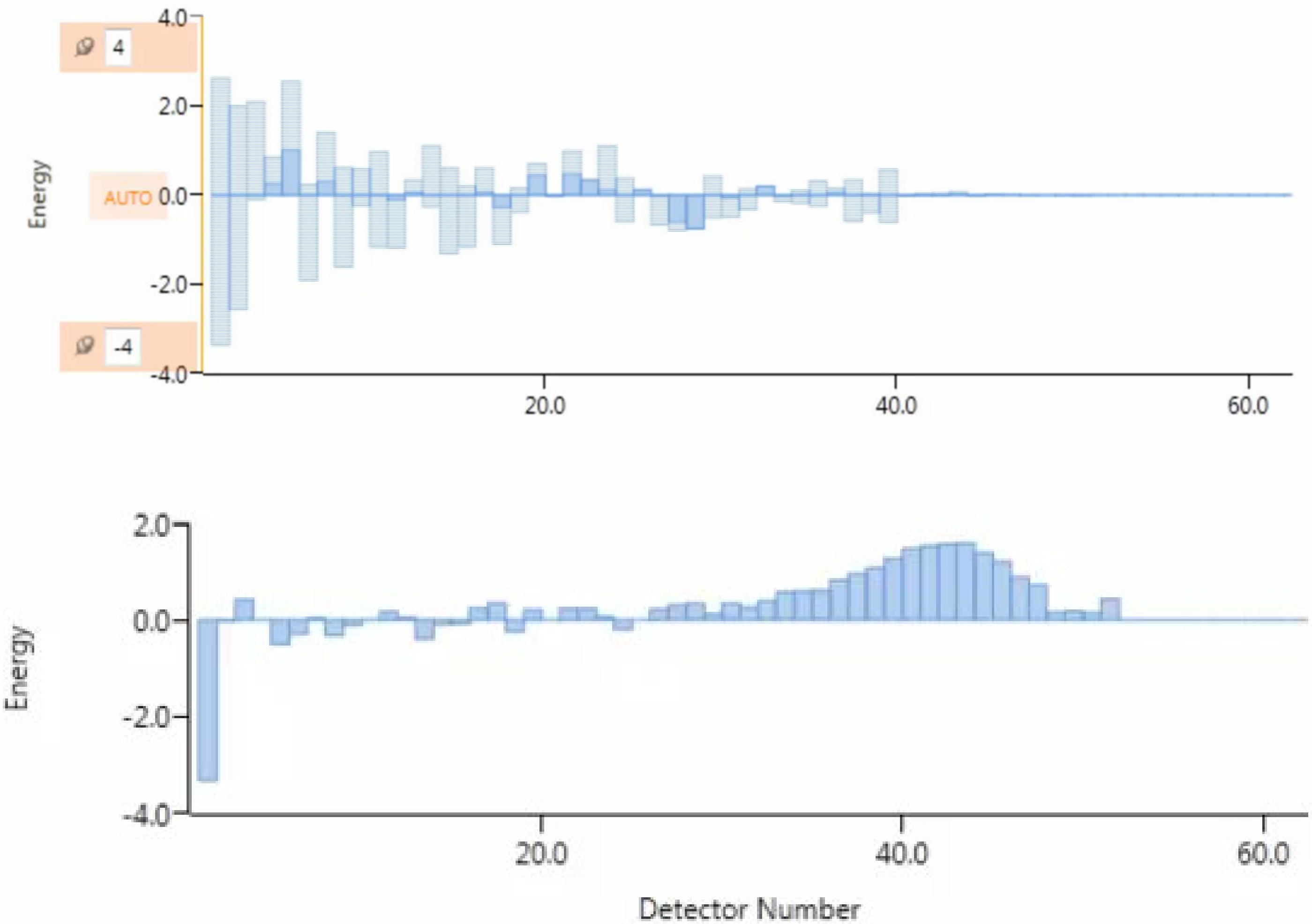
Remedies for sample agglomeration

- Surfactants or additives can be used to stabilise dispersions
  - Surfactants decrease interfacial tension
    - List on slide 7
  - Additives increase particle charge
    - Specific adsorption of ions to particle surface
    - E.g. Sodium Hexametaphosphate, Sodium Pyrophosphate, Ammonium Citrate
  - pH can also affect dispersion
- Use low concentrations, a few w/v%
  - as too much can cause agglomeration
  - too much surfactant can also cause foaming

How do measurement conditions affect results

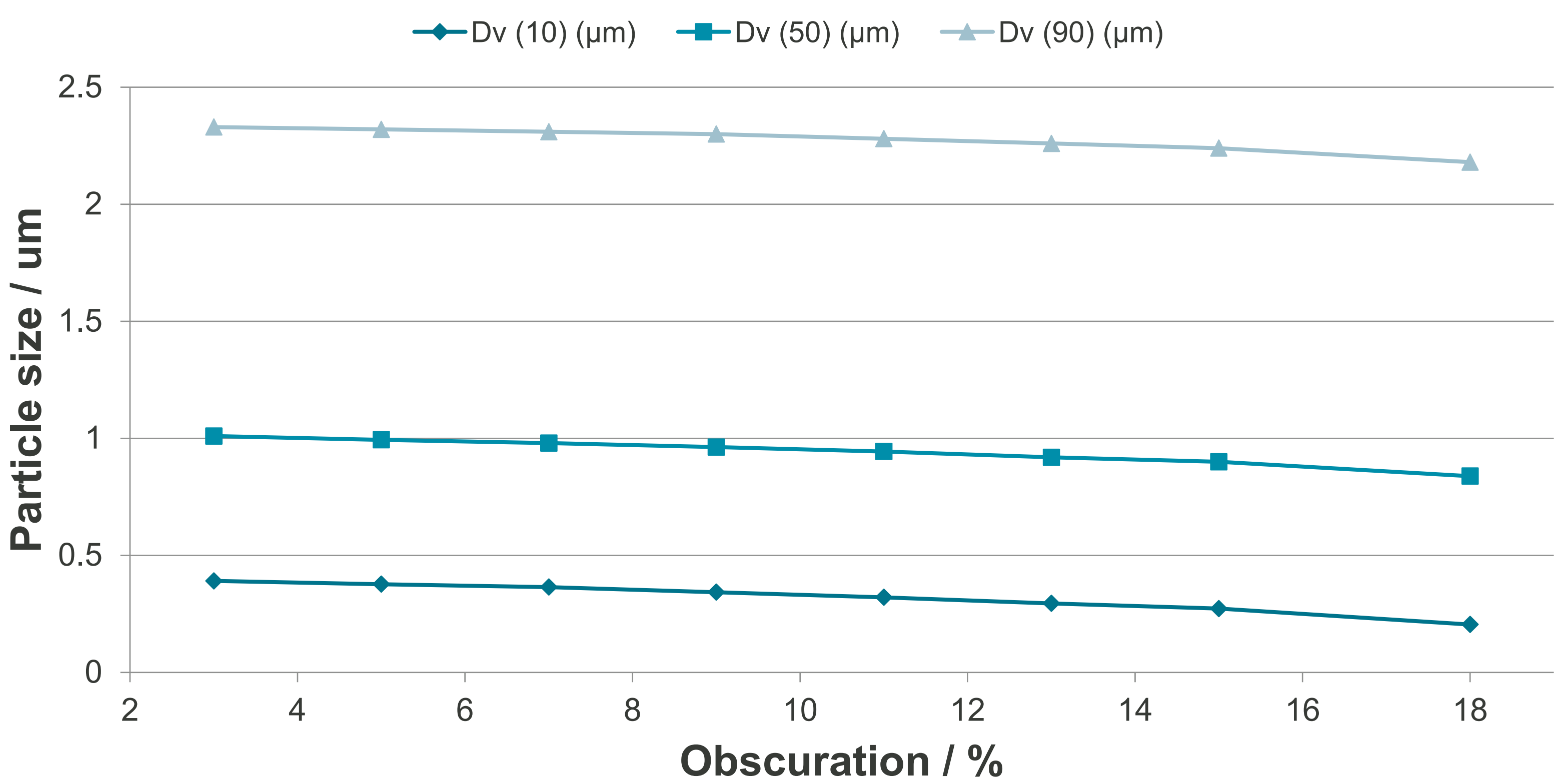
- Appropriate amount of sample
  - Good signal to noise ratio
  - Avoid multiple scattering
- Correct stir speed
  - Fast enough to prevent sedimentation for large/dense particles
  - Slow enough not to break emulsions
- Correct measurement duration
  - Long enough to sample all of the particles in the dispersion unit

Low obscuration limit: signal to noise ratio

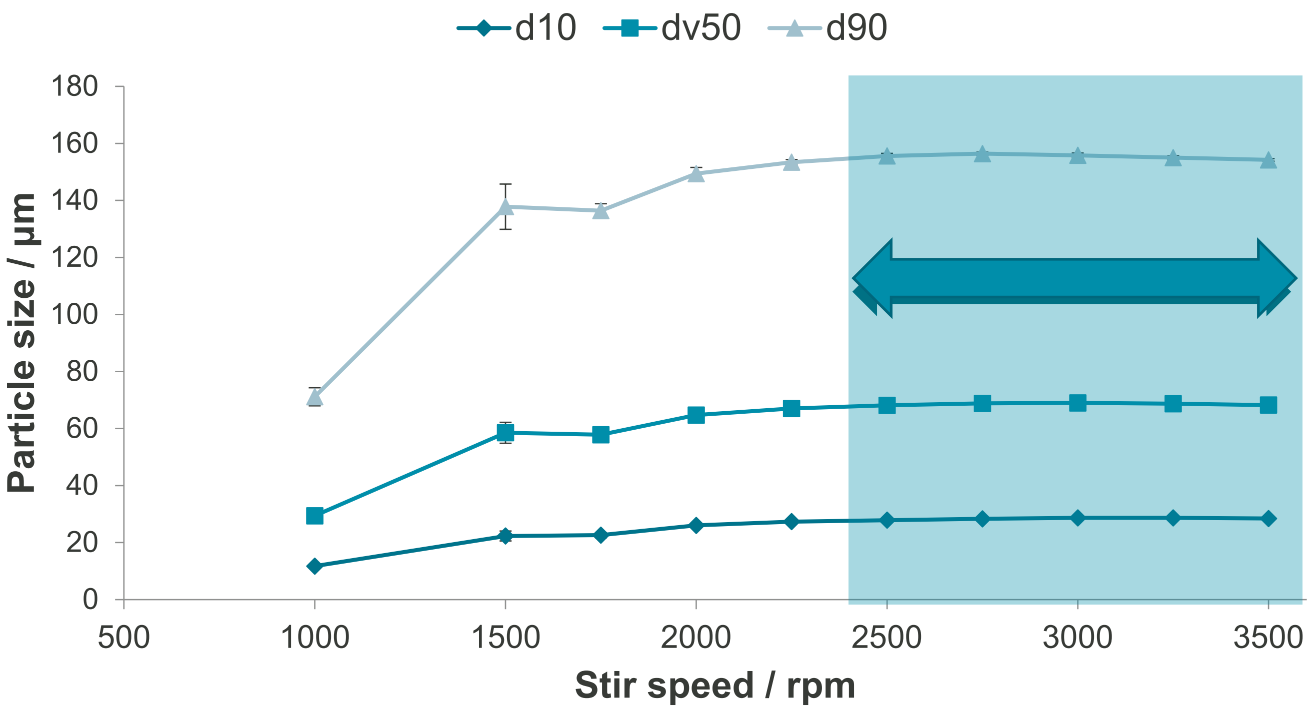


High obscuration limit: multiple scattering

- The upper limit of the obscuration range depends on multiple scattering:
  - Sample should be measured in the range where size is stable with obscuration.

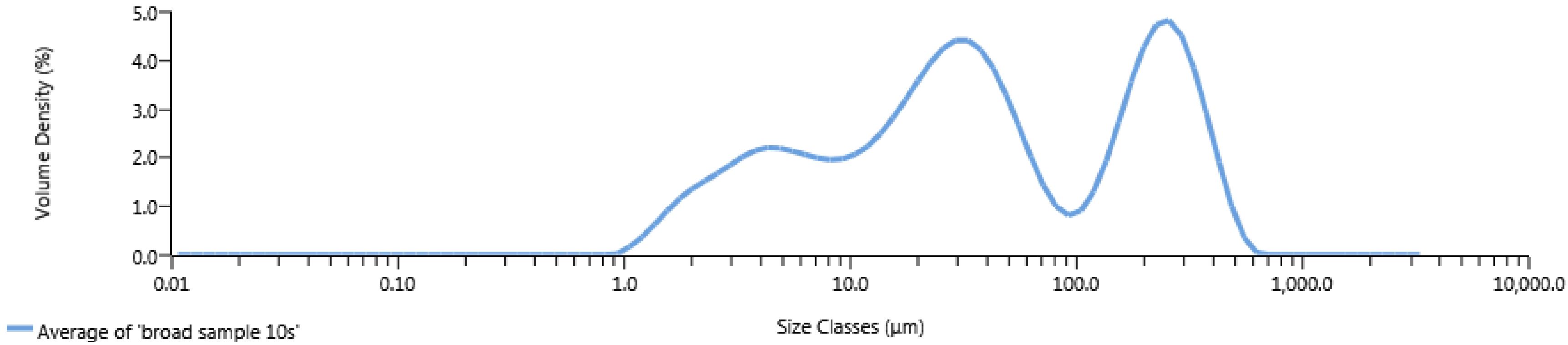


Determine the correct stir speed



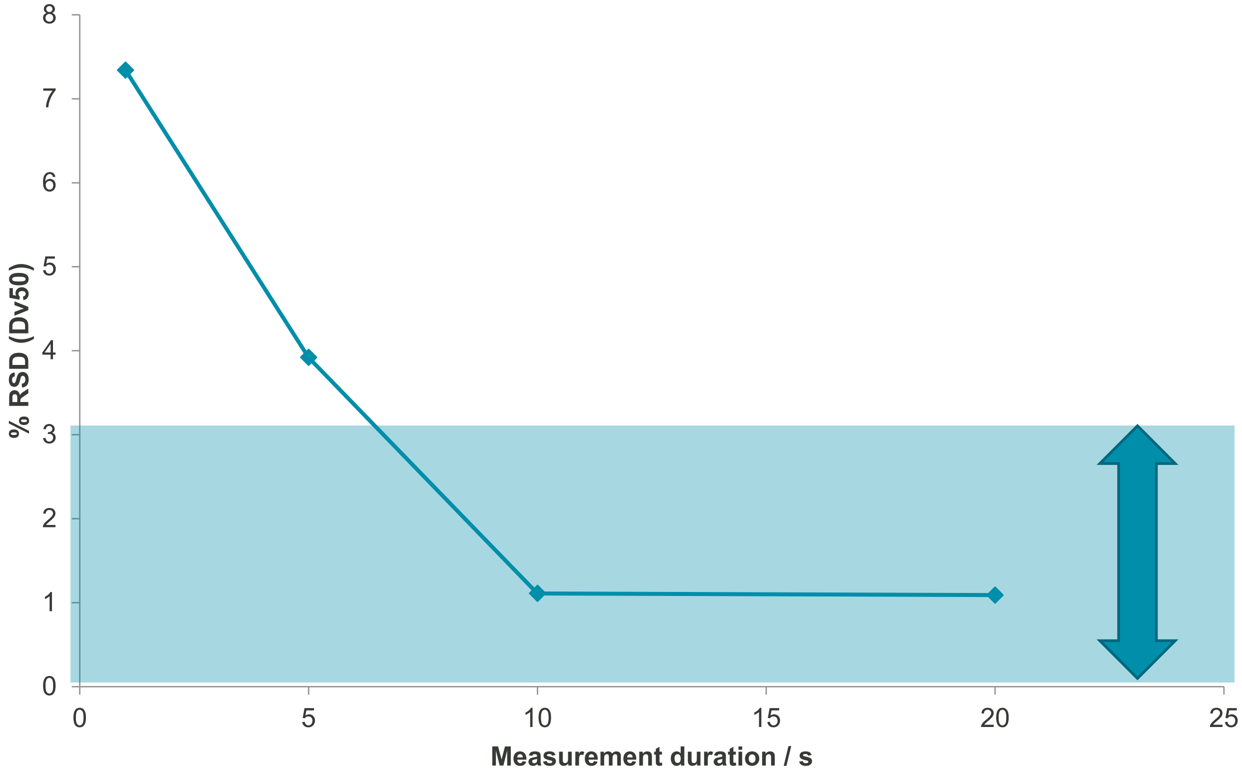
- For coarse or dense materials particle size will increase with stir speed until all particles are suspended
  - A stable particle size is obtained above 2500rpm

Determine the correct measurement duration



- For broad distributions measurement duration must be sufficient to sample all particles in the system.

Affect of measurement duration on variability



- Result variability is reduced as measurement duration is increased
  - Variability is within ISO limits when duration ≥10s

General rules for good measurements

- Measurement and background times
  - Background duration should be at least as long as the measurement duration
  - Make short repeat measurements before, during and after ultrasound to establish dispersion
  - For coarse or polydisperse materials the measurement duration may need to be increased to improve repeatability
- Ultrasound: generates heat in the dispersant
  - In organic solvents, allow a pre-measurement delay to let this heat dissipate

The purpose of method development

- A laser diffraction measurement requires

‘a representative sample, dispersed at an adequate concentration in a suitable liquid or gas’

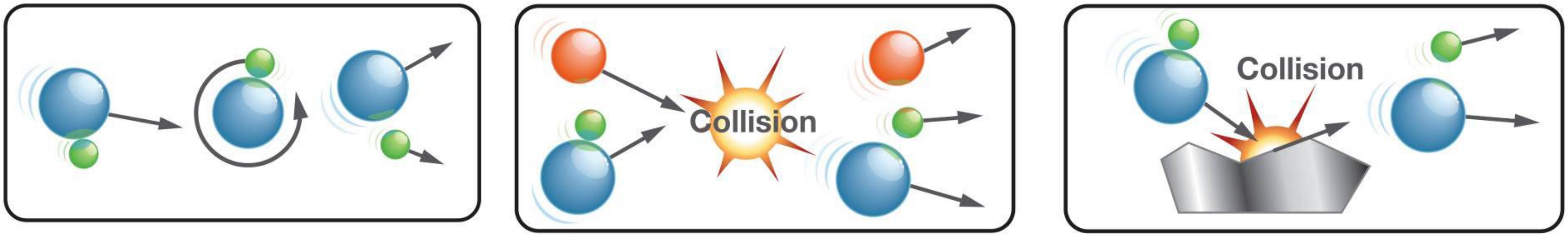
<USP429>

- Method development must define appropriate
  - Sampling
  - Dispersion
  - Measurement conditions

Mastersizer 3000 Part 4:

Method development for dry powder dispersion

Dry powder dispersion: Mechanisms



Velocity gradients caused by shear stress

Particle-to-particle collisions

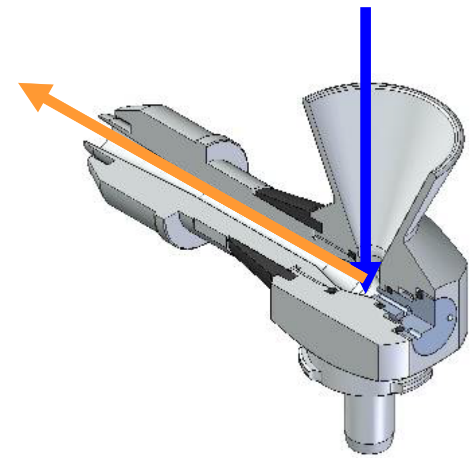
Particle-to-wall collisions

Energy/aggression

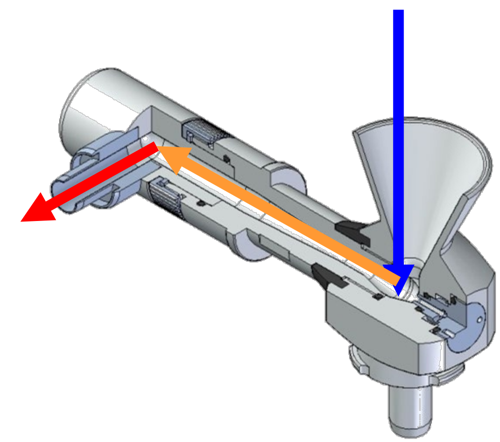
- Importance of each mechanism depends on:
  - Disperser geometry
  - Flow rate or pressure drop
  - Material type
- Higher impact energies may improve the dispersion effectiveness
  - Needs to be balanced against the risk of particle break-up

Dry powder dispersion: Disperser design

- Standard disperser
  - Straight through design
  - No direct wall impaction
  - Suitable for most types of sample



- High energy disperser
  - Elbow design
  - Direct impaction surface
  - Suitable for robust aggregated samples



Setting up the feed rate: sample tray

- General-purpose sample tray
  - Designed for bulk powders
  - Hopper – designed to regulate the flow flowing powders
  - Hopper height can be adjusted to control powder flow

Step 1: Setting up the feed rate

- Use a manual measurement to test the feed rate
  - Set up a long measurement
    - This gives you time to adjust the feed rate and see the response
  - Use high pressure, 4bar
    - High obscurations are likely to be observed at higher pressures
- Set up obscuration range
  - Coarse particles: ~0.5% to ~6%
  - Fine particles: ~0.5% to ~3%
- Turn on obscuration filtering
- Increase the feed rate until the obscuration is in range
  - And within range for the majority of the measurement

Unrestricted Document

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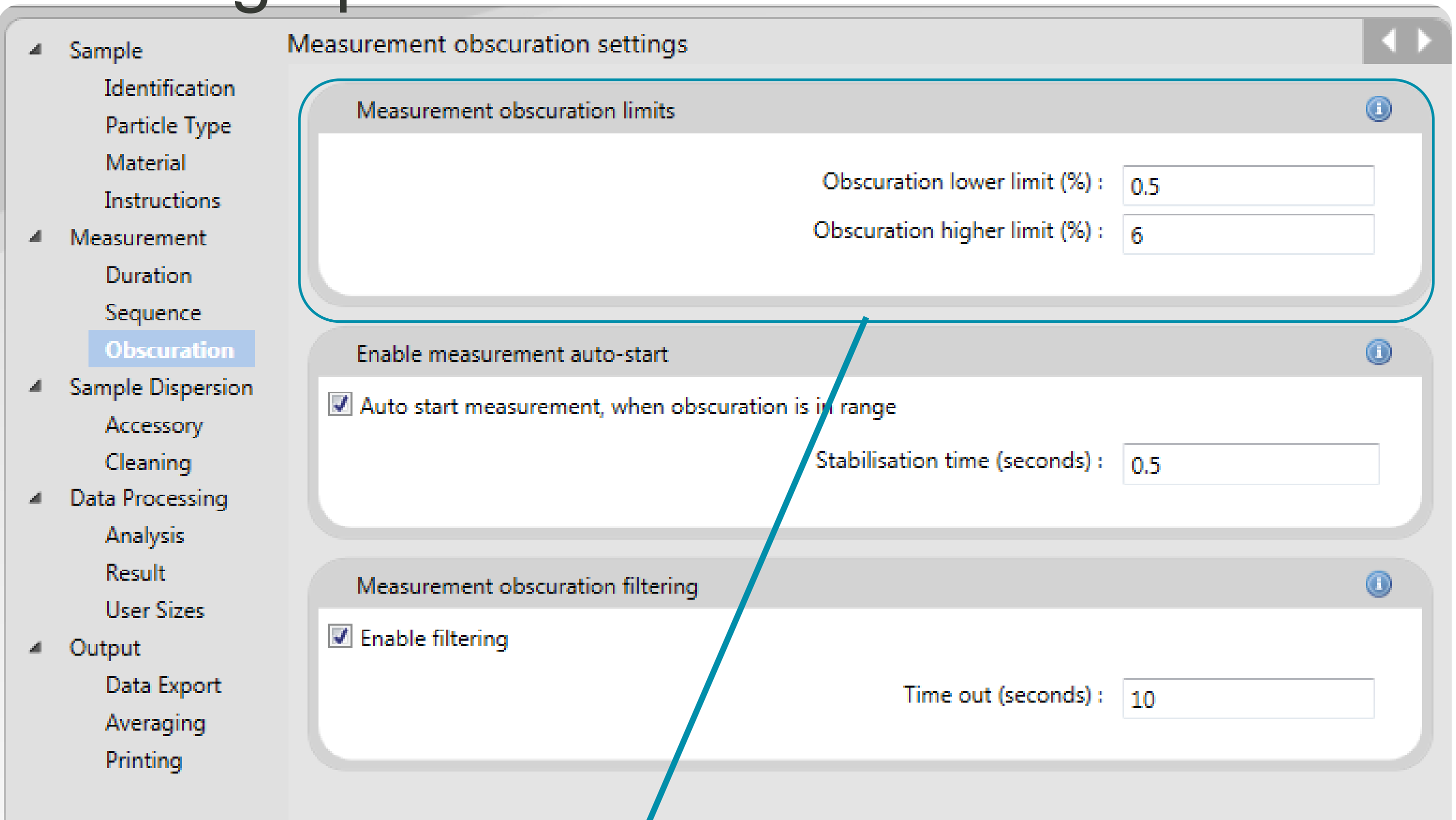
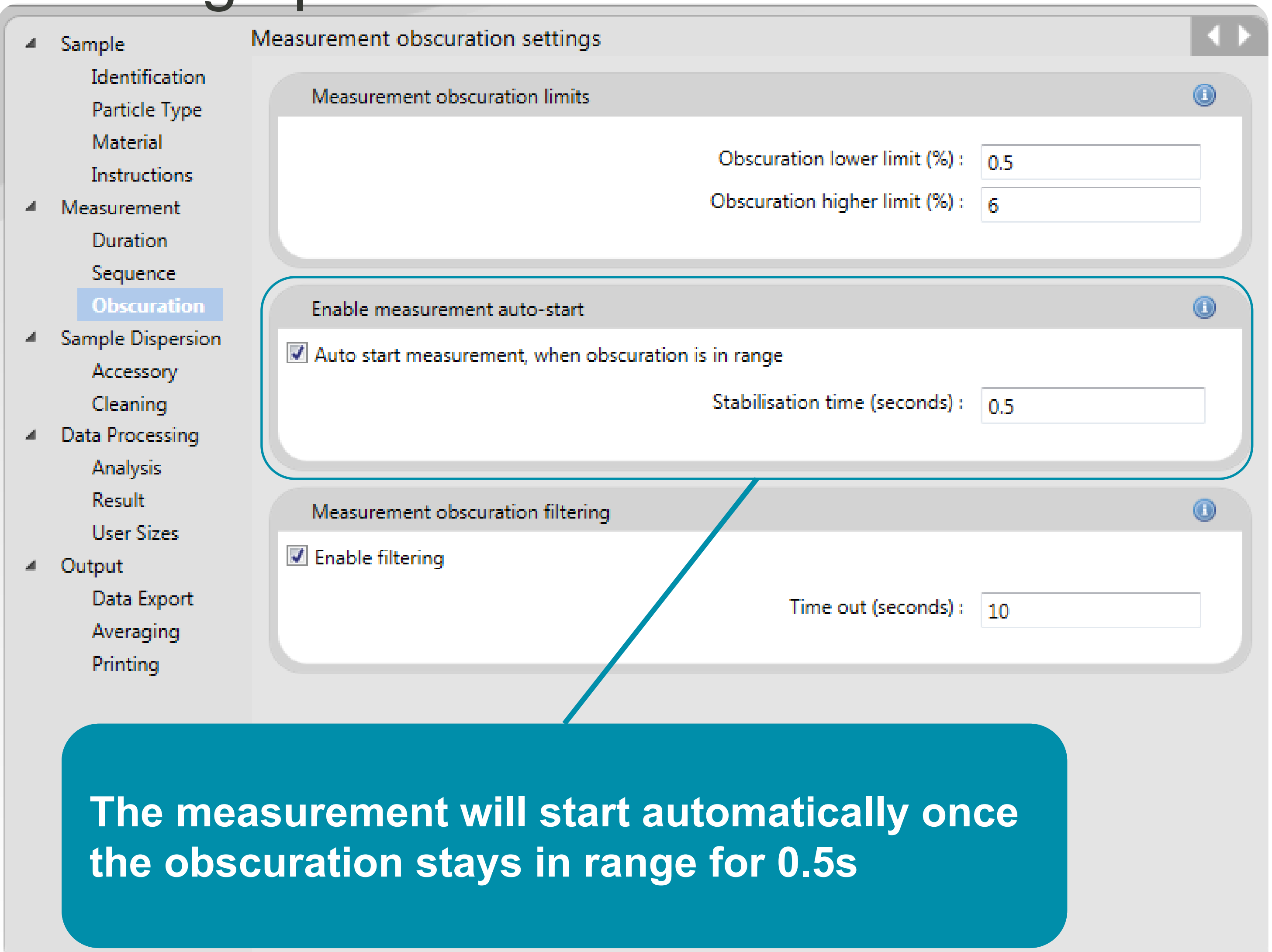
Step 1: Setting up the feed rate



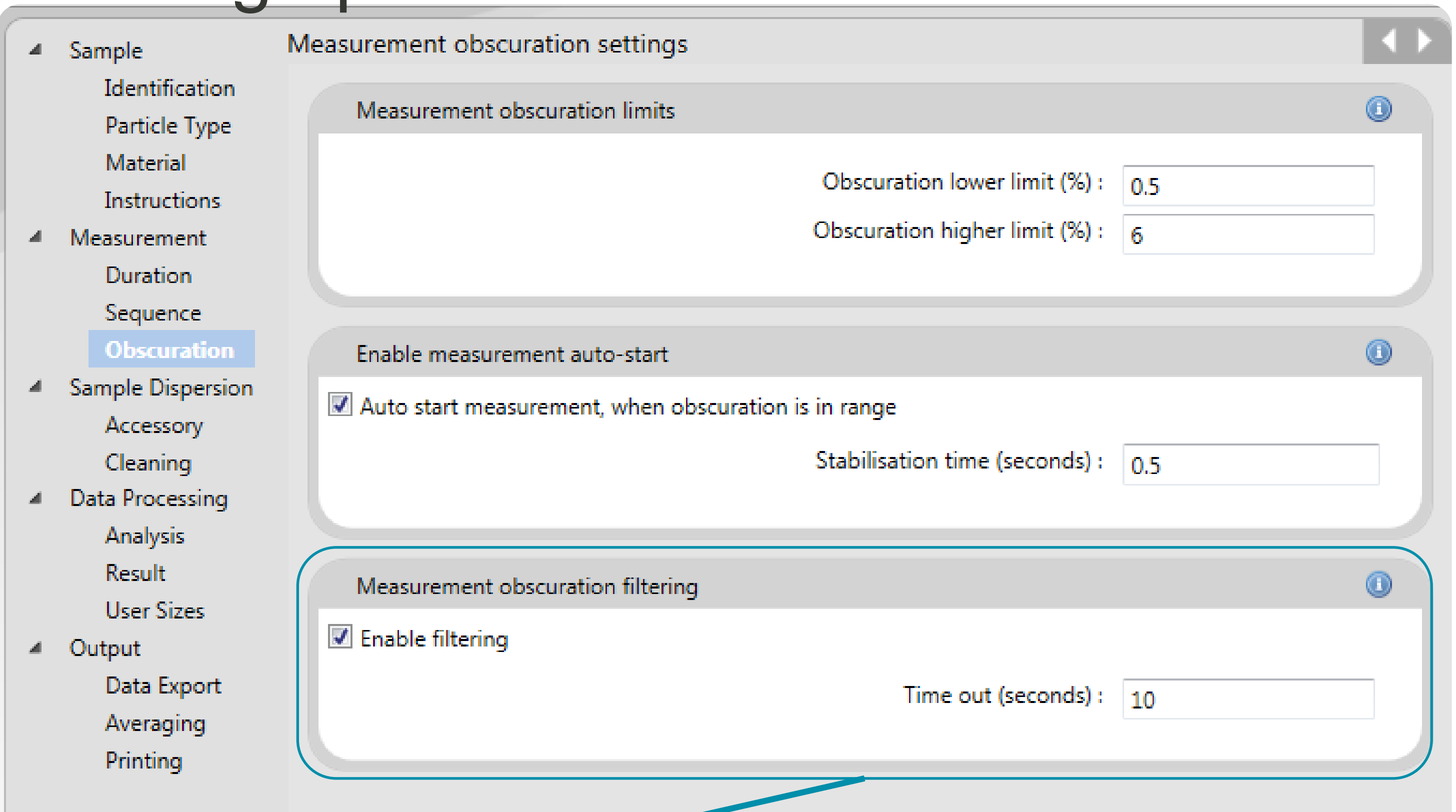
Set up the obscuration range

- **Coarse particles: ~0.5% to ~6%**
- **Fine particles: ~0.5% to ~3%**

Step 1: Setting up the feed rate



Step 1: Setting up the feed rate

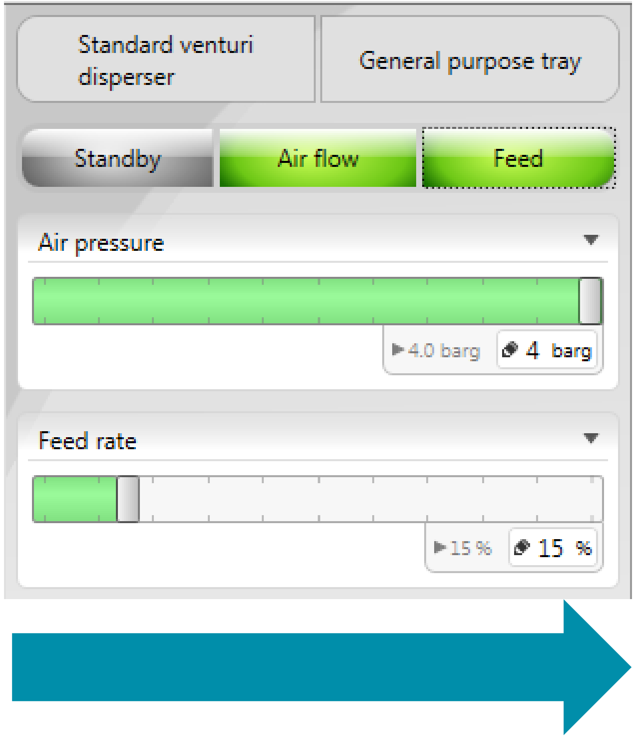


Only include measurements when the obscuration is in range

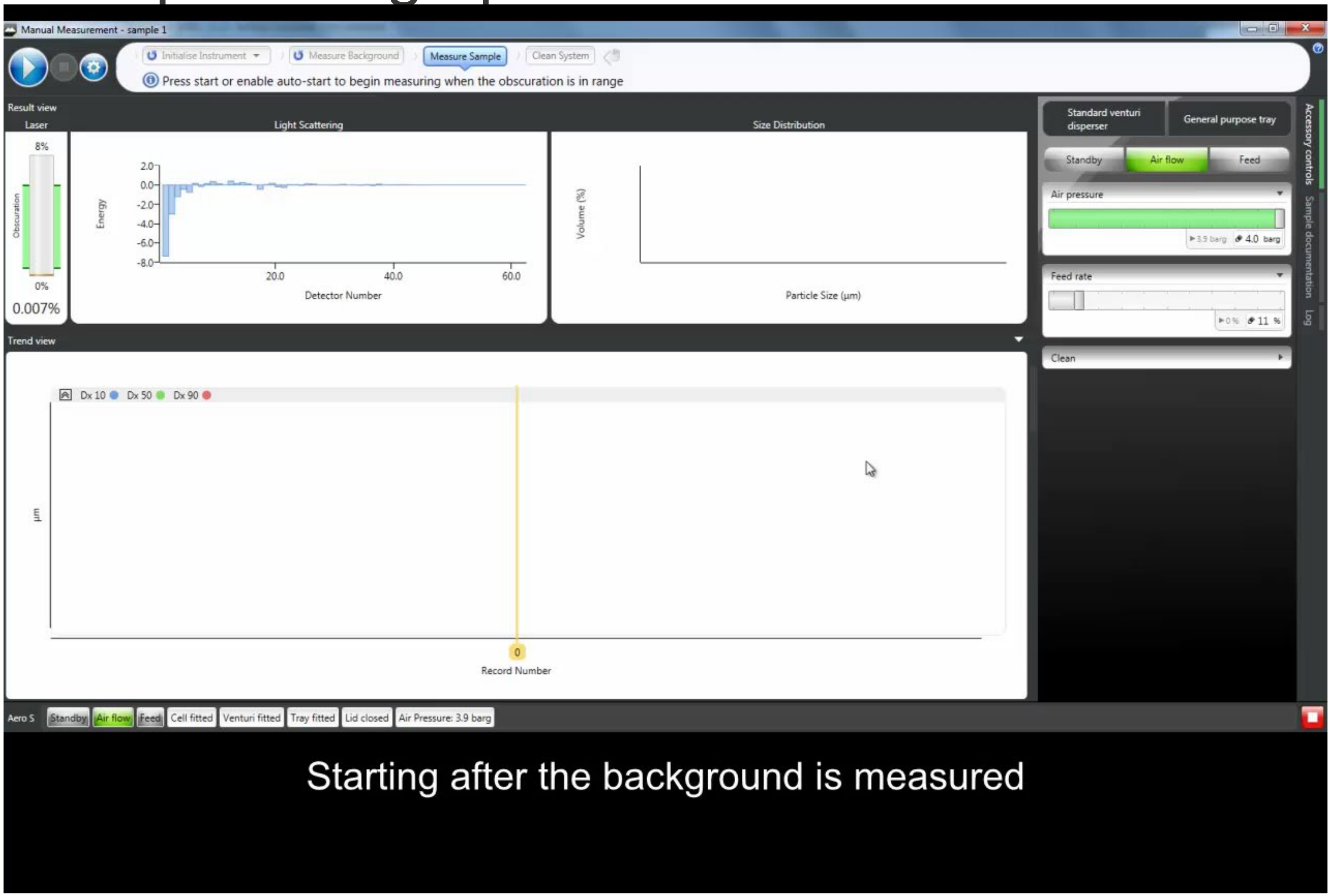
- **If the measurement is out of range for 10 seconds it will stop automatically**

Step 1: Setting up the feed rate

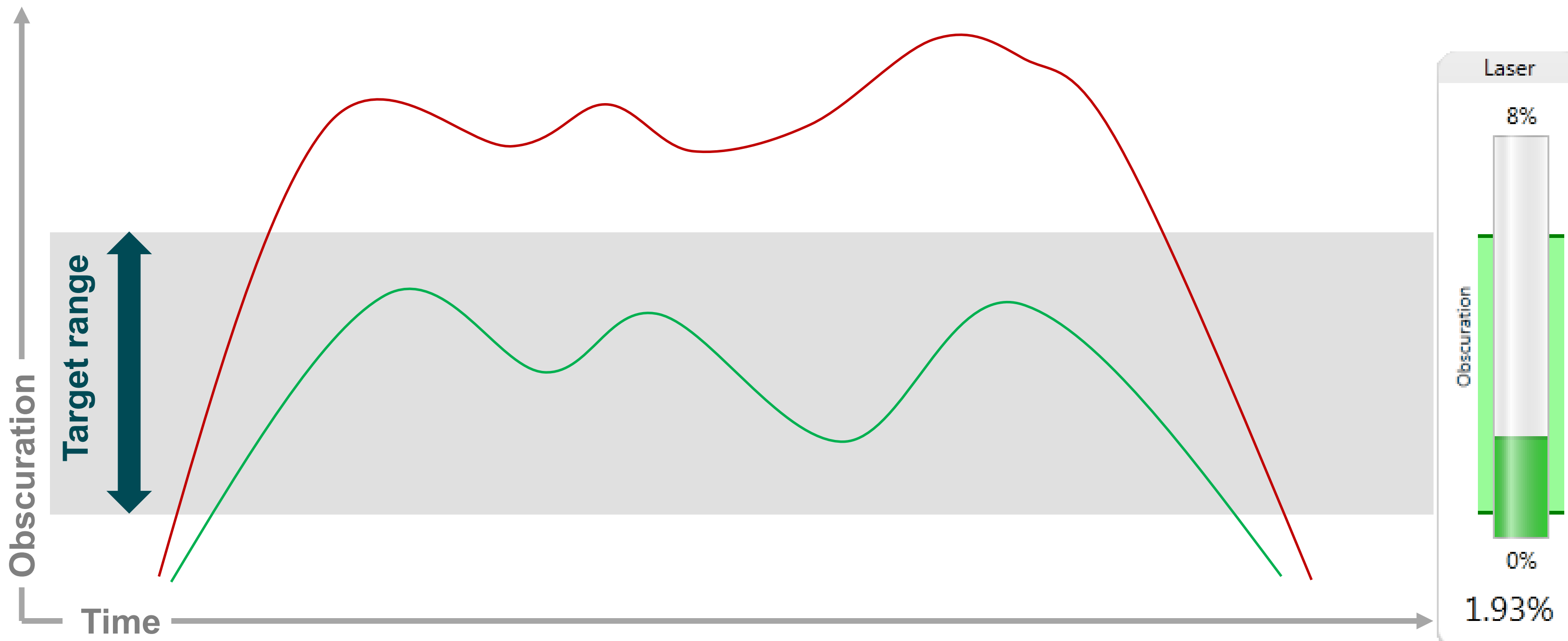
- Increase the feed rate until the obscuration is in range
  - And stays within range for the majority of the measurement

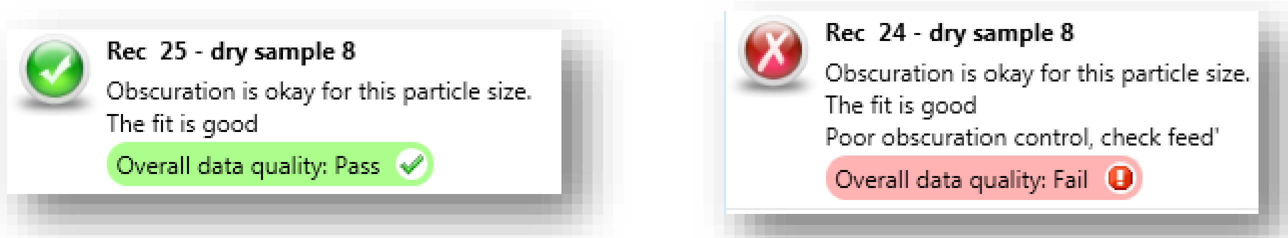


Video clip: setting up the feed rate



Feed rate is selected to keep obscuration in range





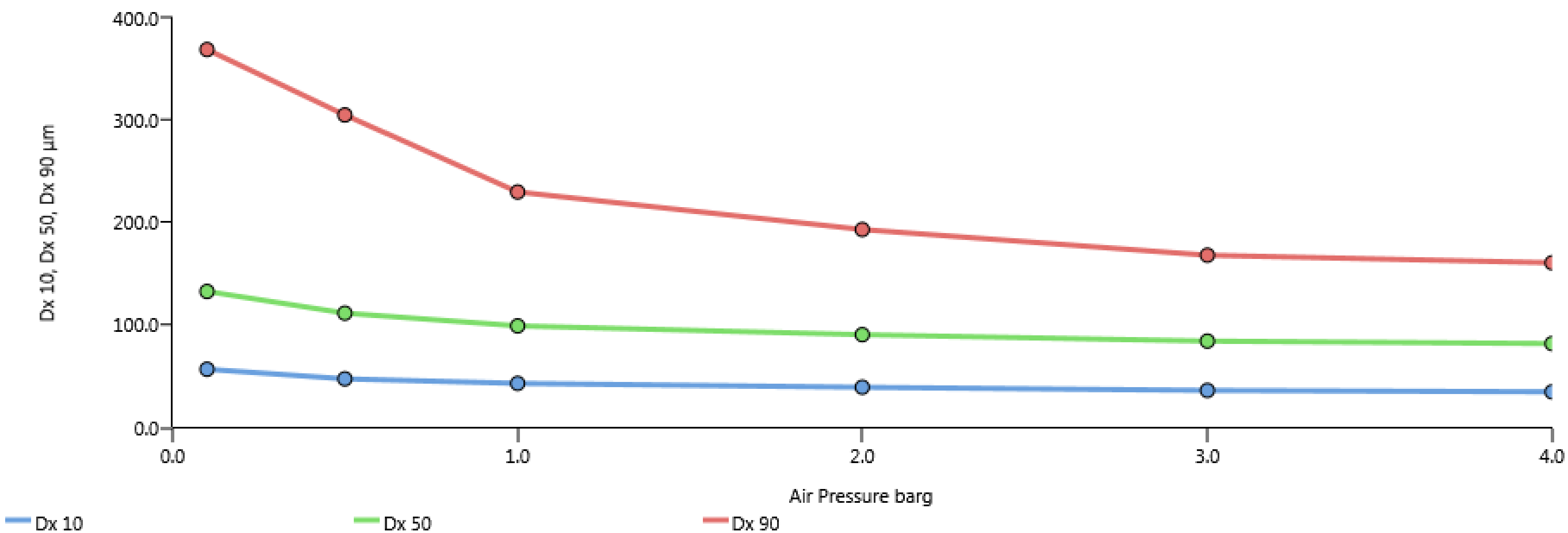
Dry powder dispersion: ISO guidance

- Degree of dispersion is controlled by primary air pressure
  - Monitor change in size distribution with pressure
    - Carry out pressure titration – **Step 2**

- Check that particle comminution (milling or particle break up) has not occurred
  - Compare dry results to a well dispersed wet measurement – Step 3
  - Choose the pressure which agrees with the wet results
    - Shows dispersion and not particle breakage

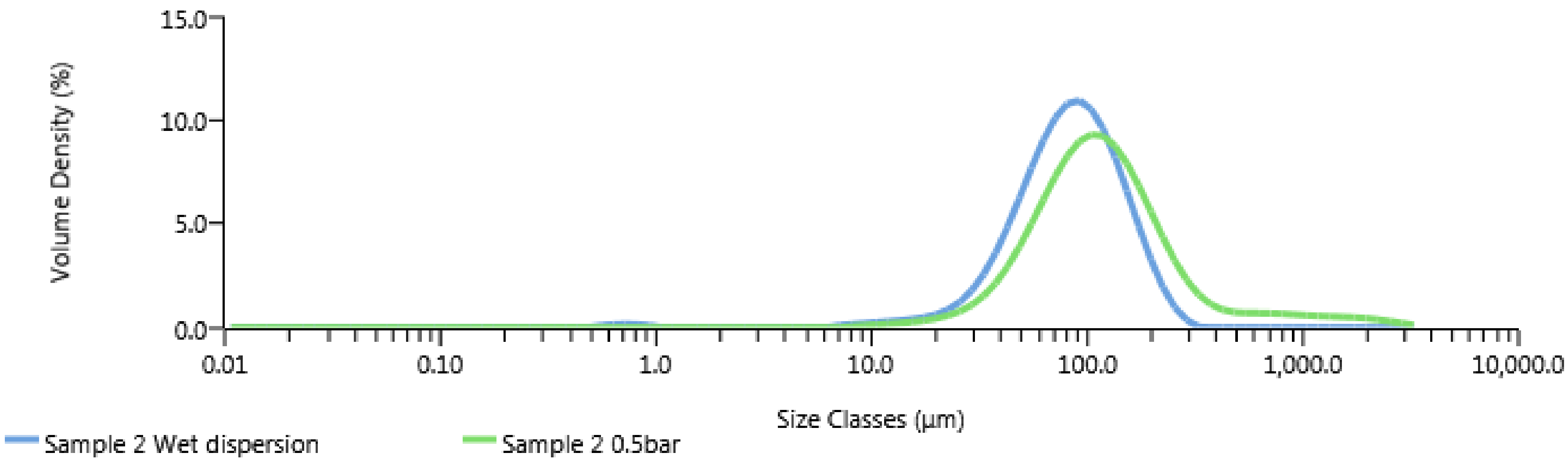
Step 2: Measure a pressure titration

- Make measurements at 4, 3, 2, 1, 0.5 and 0.1 bar.
- Make repeat measurements at each pressure to check for sample segregation



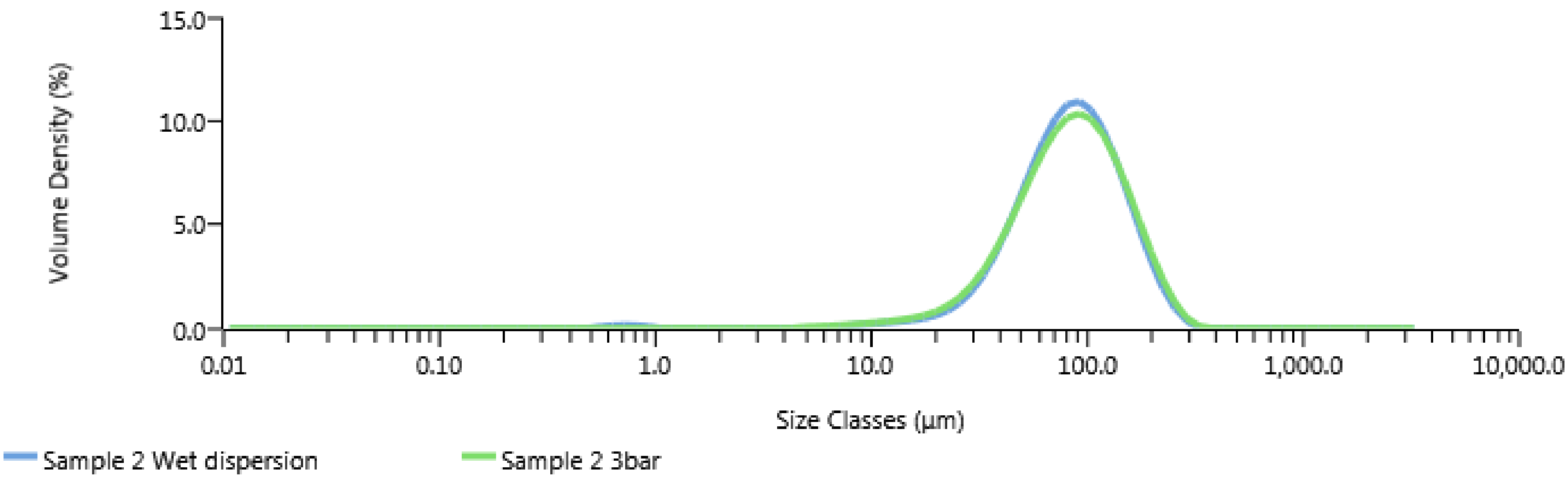
Step 3: Compare dry results to wet

- Low pressure dry result shows larger result
  - Indicates sample is not fully dispersed



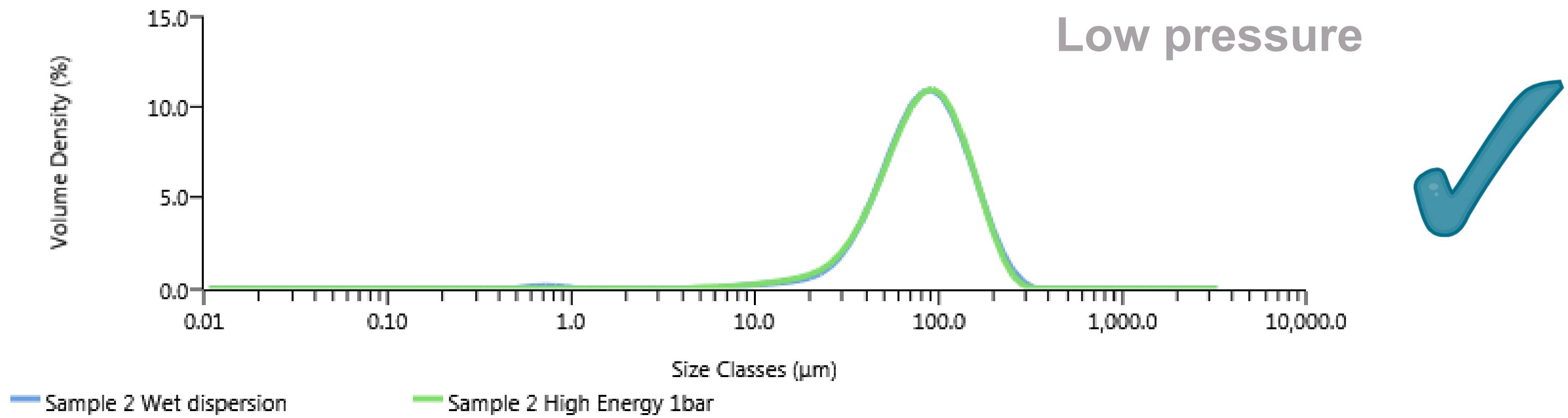
Step 3: Compare dry results to wet

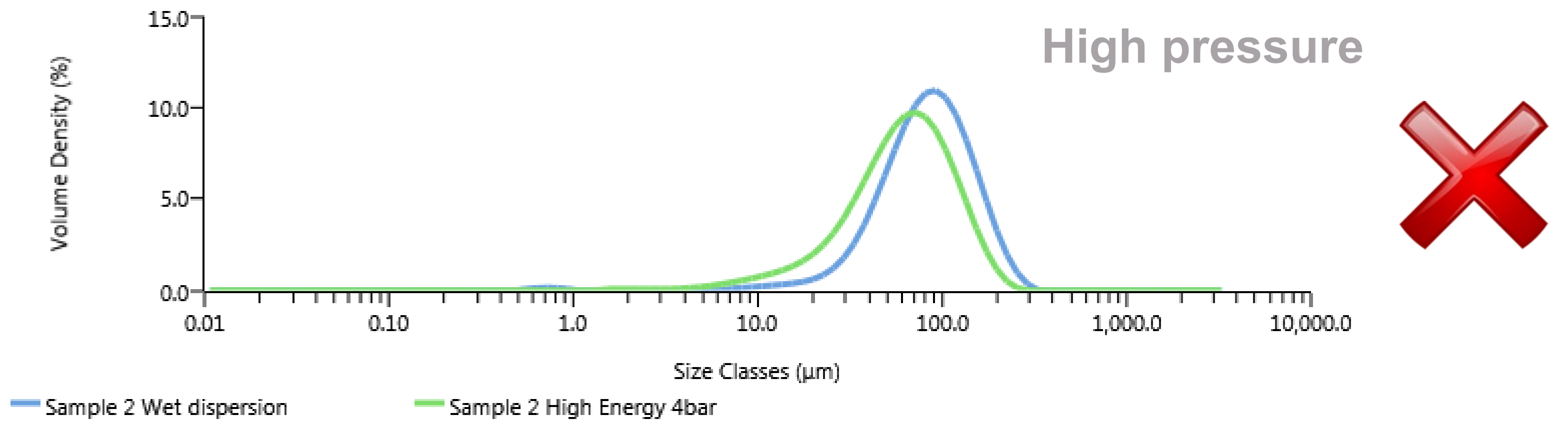
- High pressure shows good agreement
  - Suggests the material is dispersed



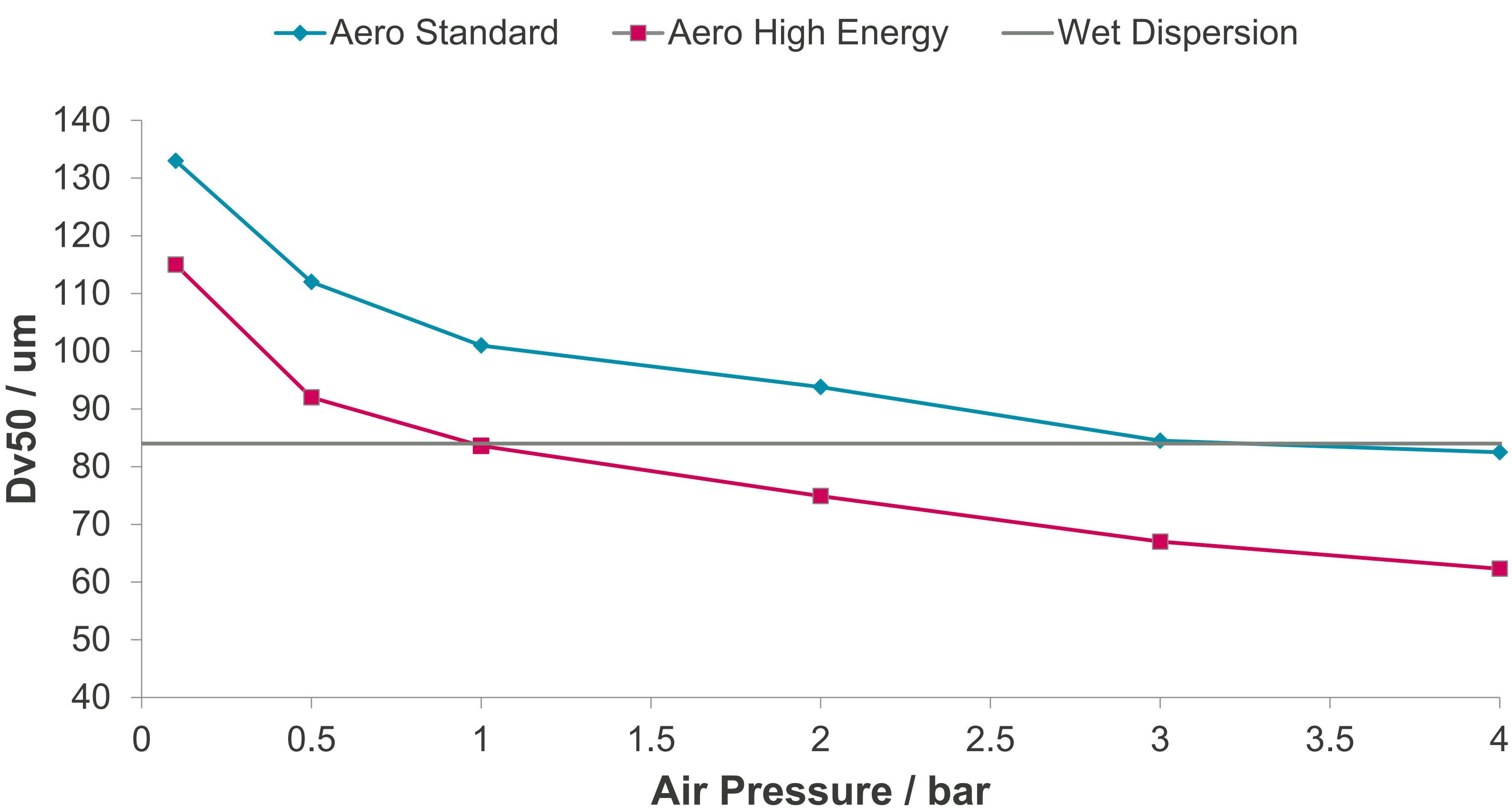
Step 4 : High energy venturi

- For robust, highly agglomerated materials the high energy venturi may be required.



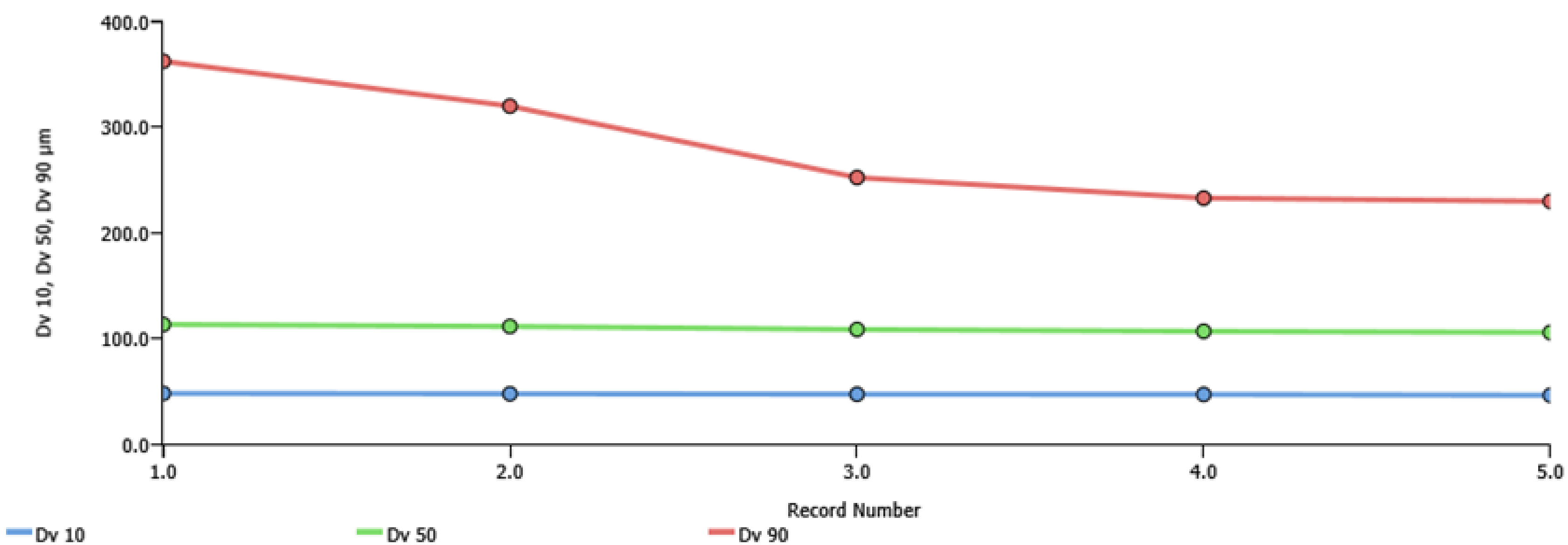


Comparing standard and high energy venturis



Segregation in dry measurements

- Segregation can occur with free-flowing powders with wide particle size distributions
  - Characterized by a decrease in size over repeat measurements
  - Make several quick repeat measurements at each pressure
  - This can be done as part of the pressure titration



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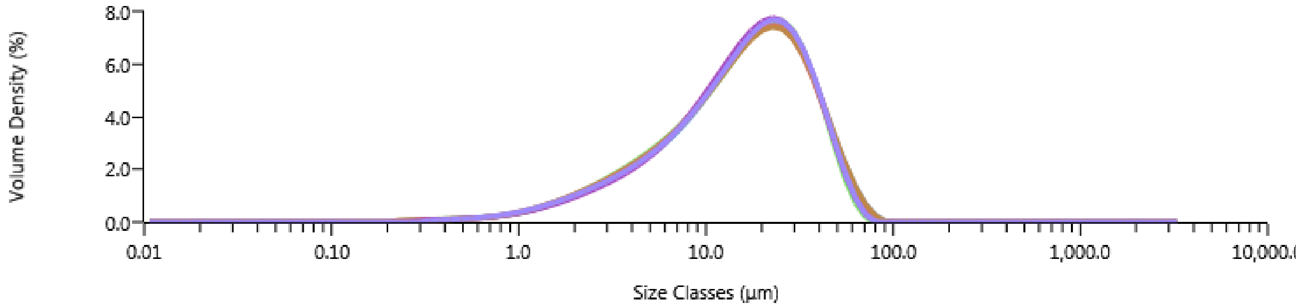
Segregation in dry measurements

- Segregation can occur with free-flowing powders with wide particle size distributions
  - Characterized by a decrease in size over repeat measurements
  - Make several quick repeat measurements at each pressure
  - This can be done as part of the pressure titration
- Always measure the whole sample, either by:
  - Making enough short measurements to use the whole sample and then create an average
  - Make one long measurement long enough to use up all of the sample.

Definitions of repeatability, reproducibility etc.

- Repeatability
  - Same sample run time and time again
  - Critical Factors:
    - Instrument
    - Dispersion i.e. any changes occurring during a measurement
- Reproducibility
  - Another sample, operator, instrument, technique, day, etc……..
  - Critical Factors:
    - Instrument
    - Dispersion
    - Sampling methodology
- Robustness
  - Capacity of method to remain unaffected by small, deliberate, variations in method parameters

Reproducibility: Sampling



	Record Number	Sample Name	Dx 10 (µm)	Dx 50 (µm)	Dx 90 (µm)
	1	Baby Powder 50mg	3.62	16.6	40.4
	2	Baby Powder 40mg	3.47	16.2	38.1
	3	Baby Powder 30mg	3.51	16.2	39.4
	4	Baby Powder 20mg	3.79	16.5	38.8
	5	Baby Powder 10mg	3.57	16.5	40.4
	6	Baby Powder 5mg	3.61	16.5	38.9
Mean			**3.59**	**16.4**	**39.3**
1xStd Dev			**0.112**	**0.180**	**0.917**
1xRSD (%)			**3.12**	**1.10**	**2.33**

- Reproducible results can be achieved for very small sample masses.

General rules for good dry measurements

- Ensure that the obscuration filtering is on
  - Eg 0.5 to 6%
  - Set the feed rate to keep the obscuration in range
- Always measure the whole sample
  - In several short measurements, which are averaged
  - Or one long measurement
- Measure several sub samples from the same batch to assess reproducibility

The purpose of method development

- A laser diffraction measurement requires

‘a representative sample, dispersed at an adequate concentration in a suitable liquid or gas’

<USP429>

- Method development must define appropriate
  - Sampling
  - Dispersion
  - Measurement conditions