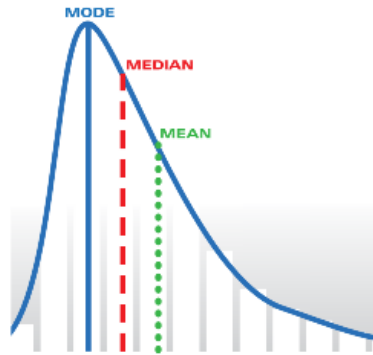




# Introduction to Particle Size Analysis



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[www.horiba.com/us/particle](http://www.horiba.com/us/particle)

# Why Particle Size?

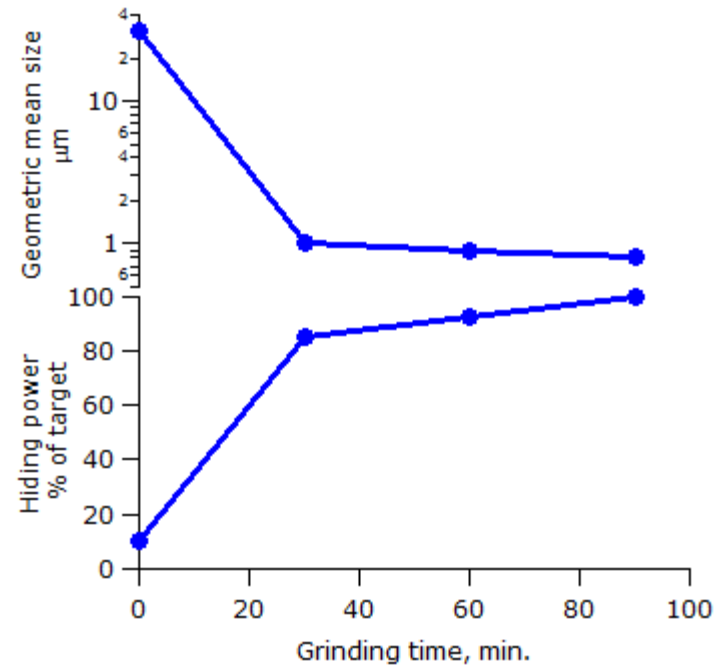
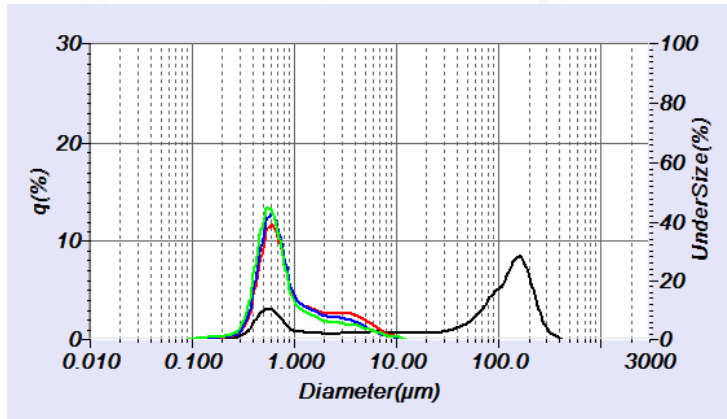
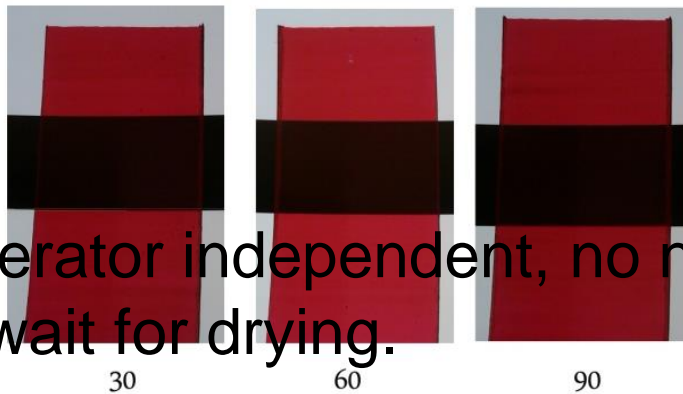
Size affects material behavior and processing across a number of industries.

Industry		Industry	
<b>Ceramic</b>		<b>Construction</b>	
<b>Oil/rubber</b>		<b>Chemical</b>	
<b>Battery</b>		<b>Pharmaceutical</b>	
<b>Electricity</b>		<b>Food/Drink</b>	
<b>Automobile</b>		<b>Paper/Pulp</b>	
<b>Mining</b>		<b>Ink/Toner</b>	

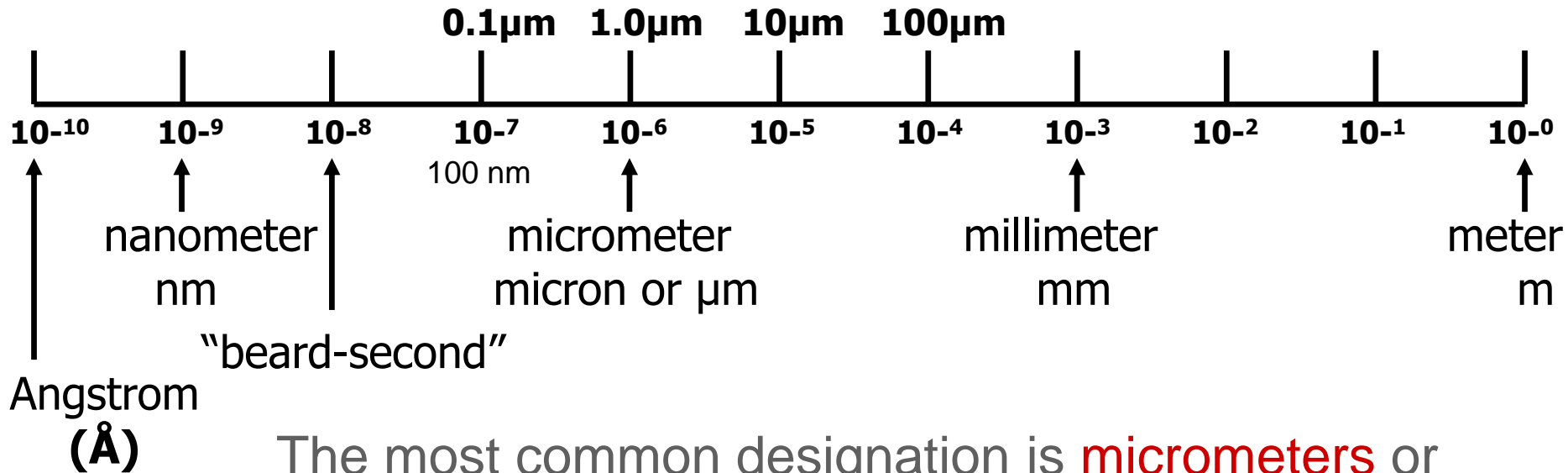
# Application: Pigment Hiding Power

Operator dependent, need to wait for drying.

Operator independent, no need to wait for drying.



# Size Terminology



C-H bond length

The most common designation is **micrometers** or **microns**. When very small, in colloid region, measured in **nanometers**, with electron microscopes or by dynamic light scattering.

Fun tip: Describing your work in terms of beard-seconds make it much more interesting at parties.



**Poll!**

**Which size ranges do you measure?**



# Size: Particle Diameter ( $\mu\text{m}$ )

0.001      0.01      0.1      1      10      100      1000

Sizes

Nano-Metric

Colloidal

Fine

Coarse

Apps

Macromolecules

Suspensions and Slurries

Powders

Methods

Electron Microscope

Acoustic Spectroscopy

Sieves

Light Obscuration

Laser Diffraction – LA-960

Electrozone Sensing

DLS – SZ-100

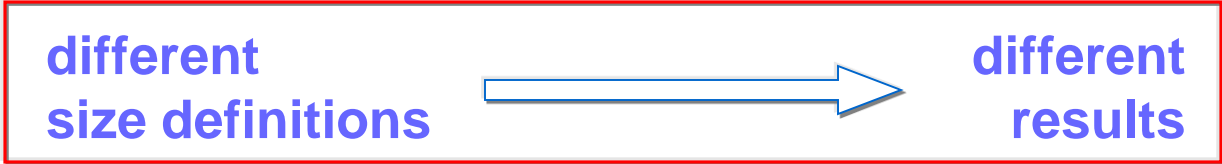
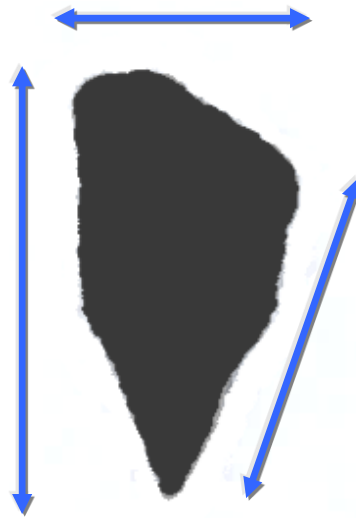
Sedimentation

Disc-Centrifuge

Optical Microscopy PSA300, Camsizer

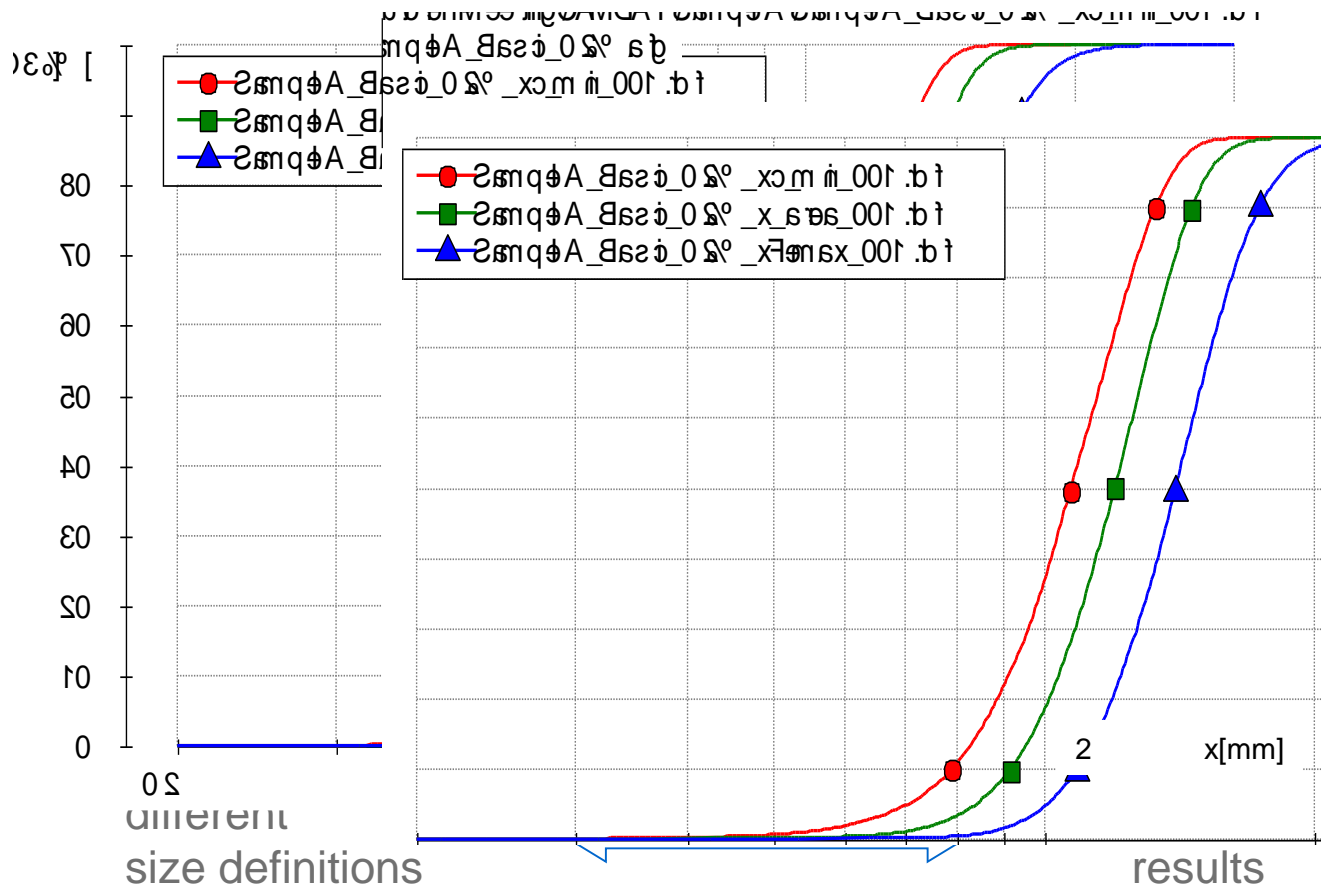
# The Basics

## Which is the most meaningful size?



# Same data, different size definitions give different results!

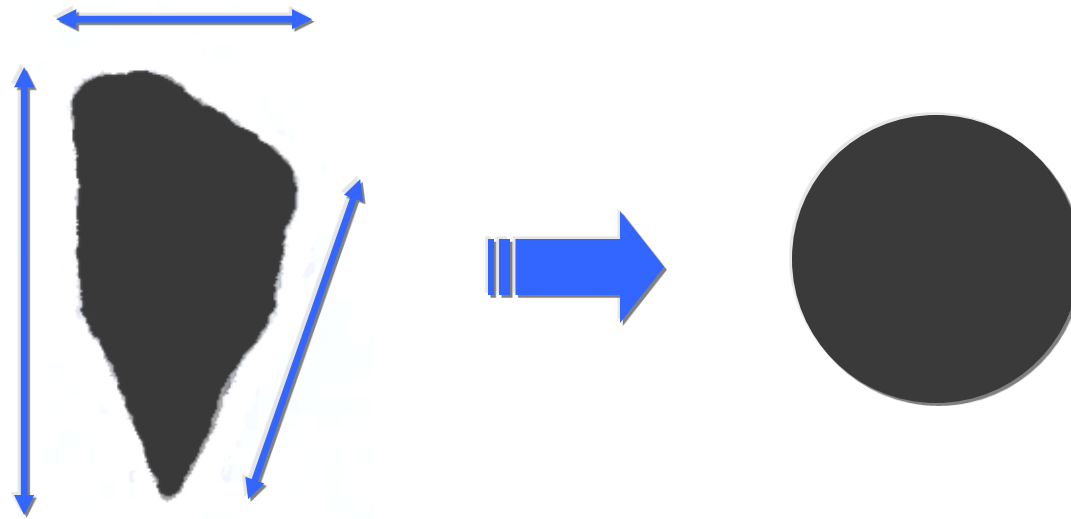
$X_{cmin}$  ↔  $X_{Area}$  ↔  $X_{Femax}$





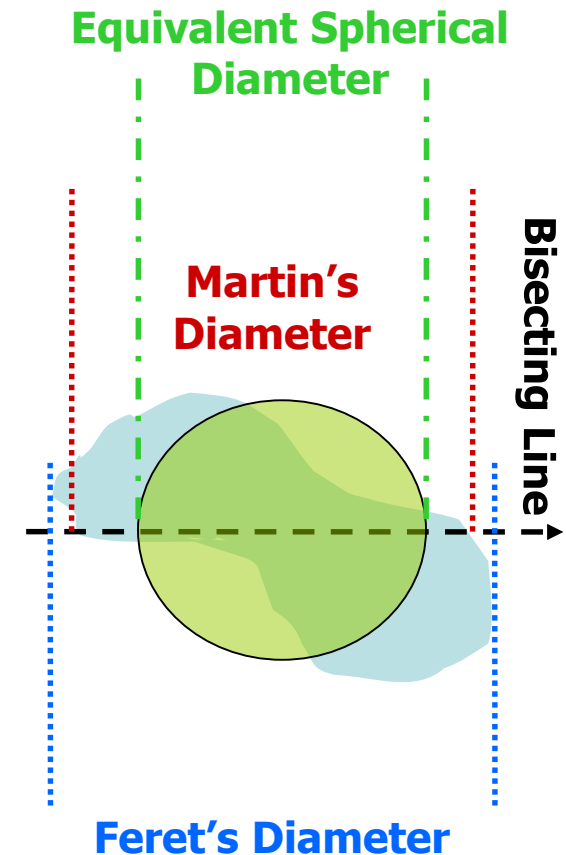
# The Basics

## What sizes can be measured?



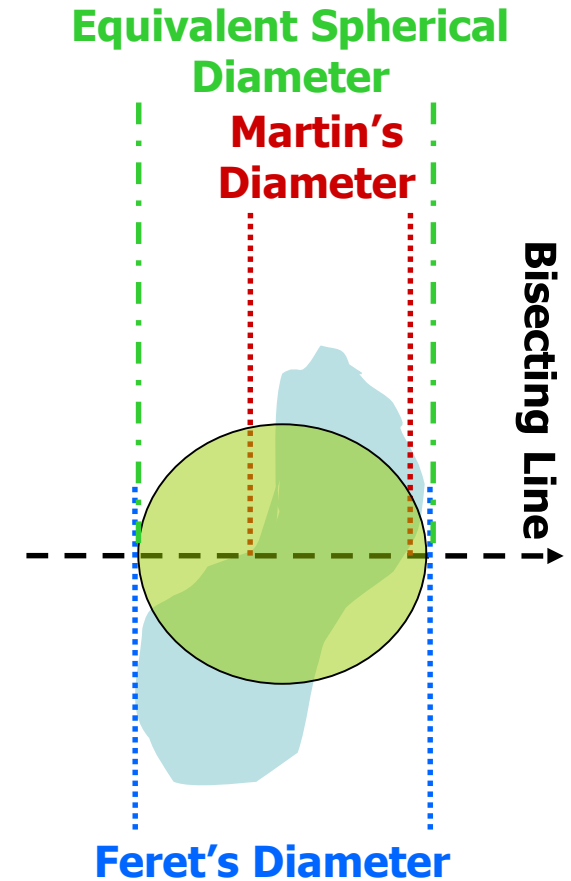
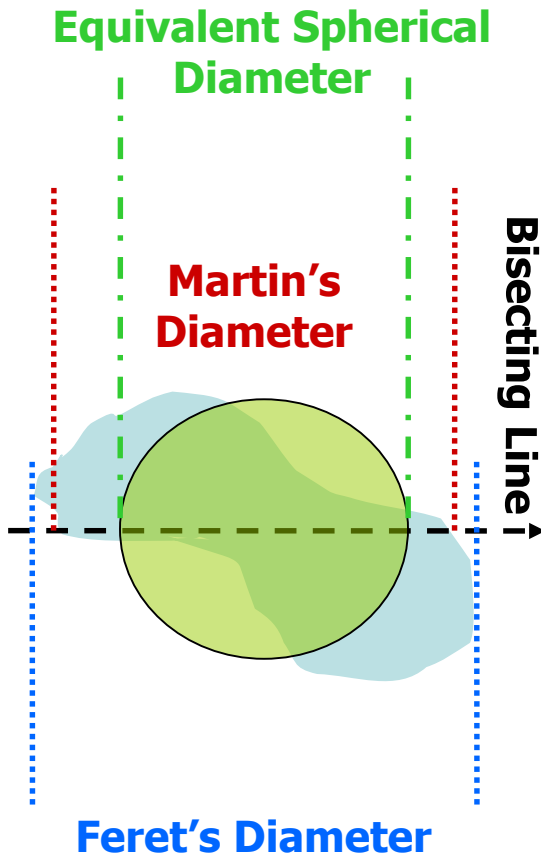
# Size Definitions

- **Martins' Diameter:** The distance between opposite sides of a particle measured on a line bisecting the projected area. To ensure statistical significance all measurements are made in the same direction regardless of particle orientation.
- **Feret's Diameter:** The distance between parallel tangents on opposite sides of the particle profile. Again to insure statistical significance, all measurements are made in the same direction regardless of particle orientation.
- **Note:** *Both Martin's and Feret's diameters are generally used for particle size analysis by optical and electron microscopy.*
- **Equivalent Circle Diameter:** The diameter of a circle having an area equal to the projected area of the particle in random orientation. This diameter is usually determined subjectively and measured by oracular micrometers called graticules.
- **Equivalent Spherical Diameter:** The diameter of a sphere that has the same volume as the irregular particle being examined.



# Particle Orientation

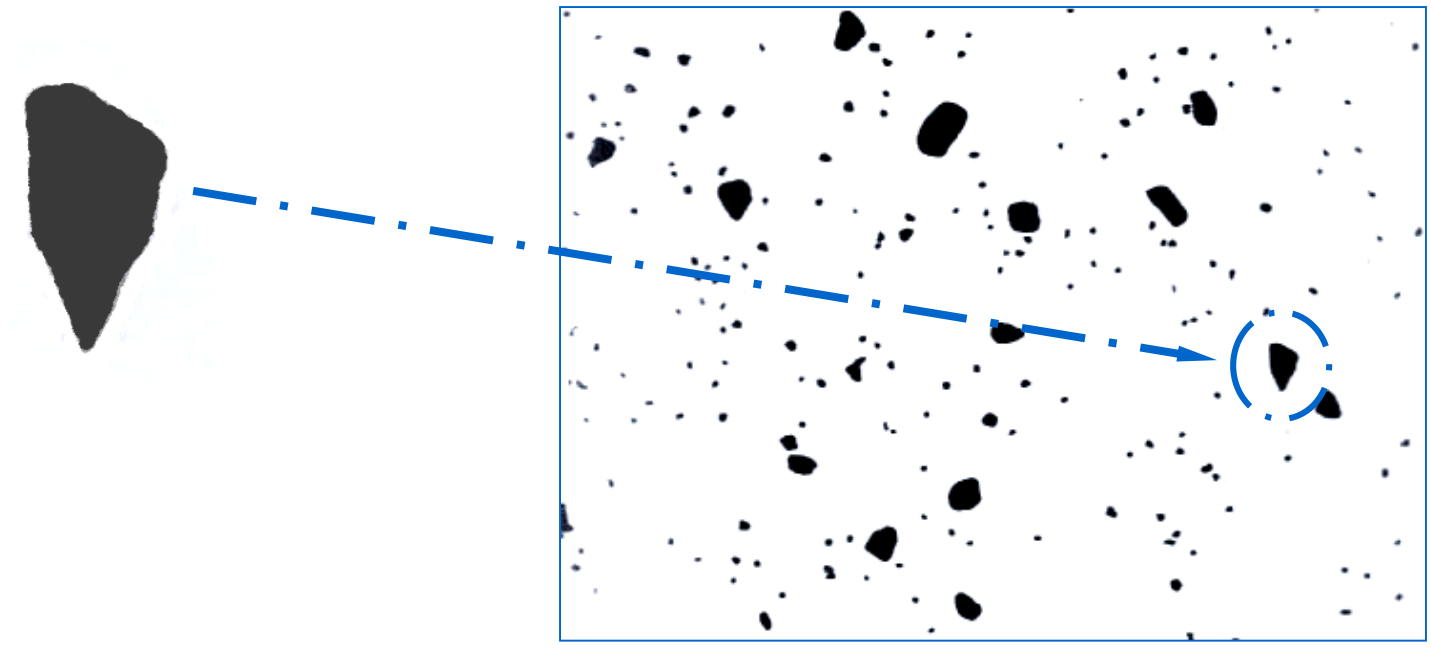
- Martin's and Feret's Diameter's will vary as particles are viewed in different orientations. The result will be a **DISTRIBUTION** from smallest to largest.



# The Basics

## Particle

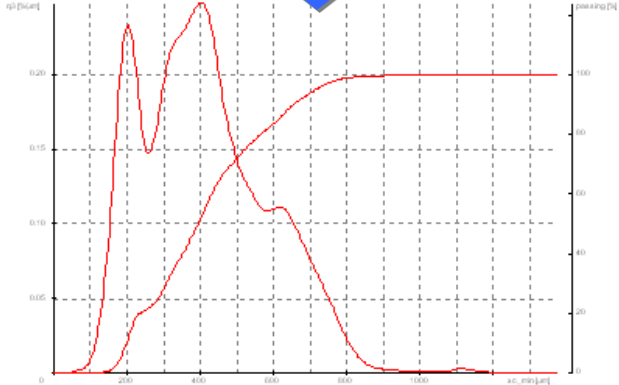
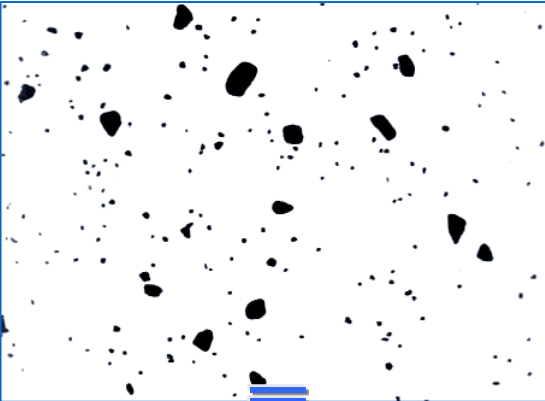
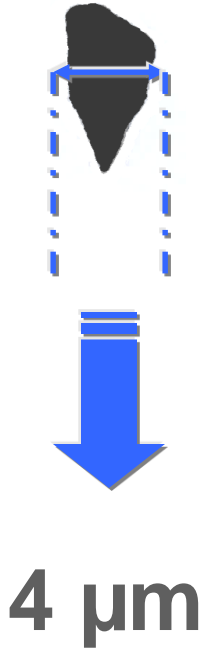
## Particle Distribution



# The Basics

## Particle Size

## Particle Size Distribution





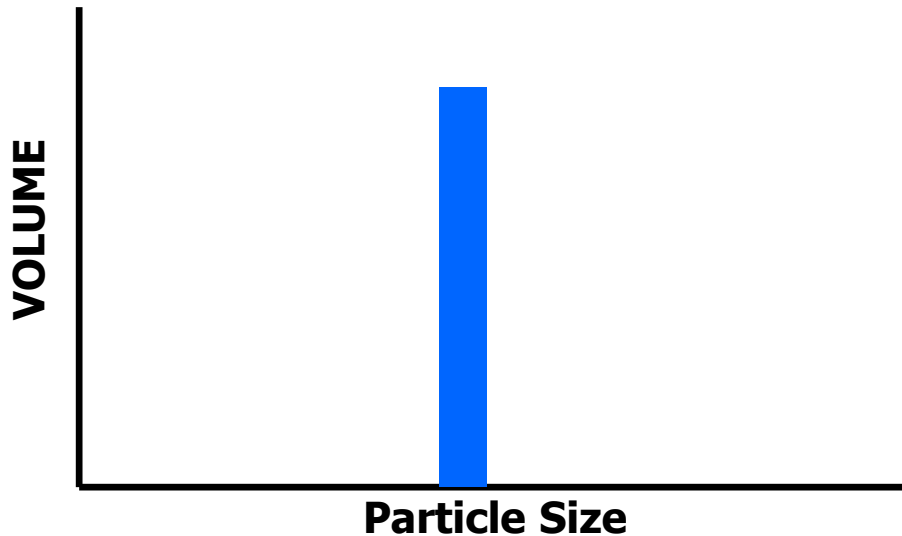
**Poll!**

**What size(s) are reported by your PSA?**



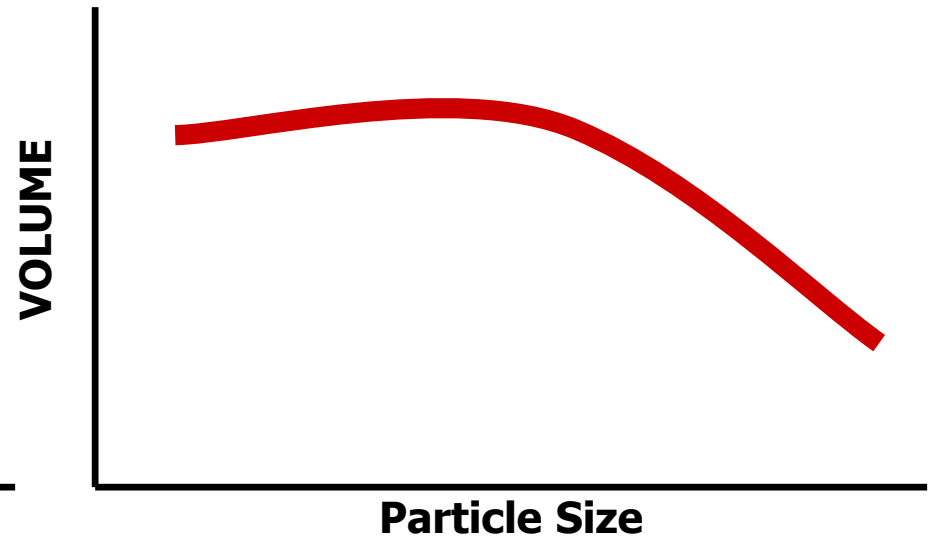
# Monodisperse vs. Polydisperse

## Monodisperse



- **Monodisperse Distribution:**
  - All particles are the same size
  - Latex standards

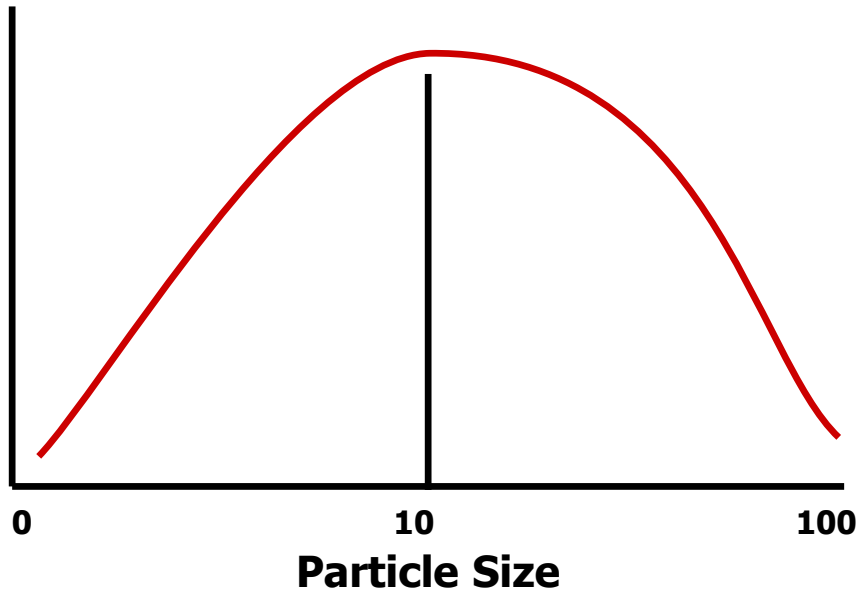
## Polydisperse



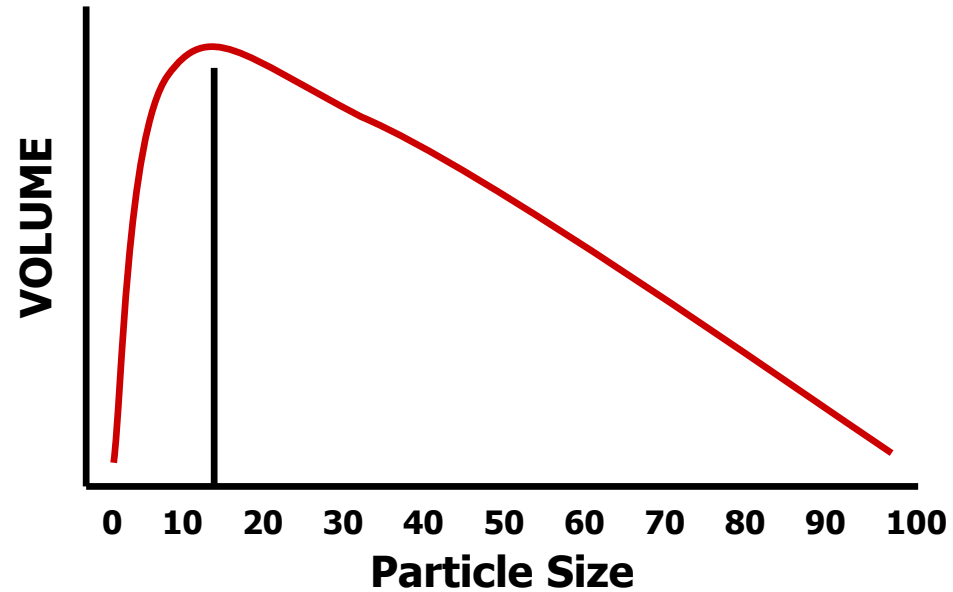
- **Wide Distribution:**
  - Particles of Many Sizes
  - Everything else

# Logarithmic vs. Linear Scale

- Logarithmic X-Axis Distribution

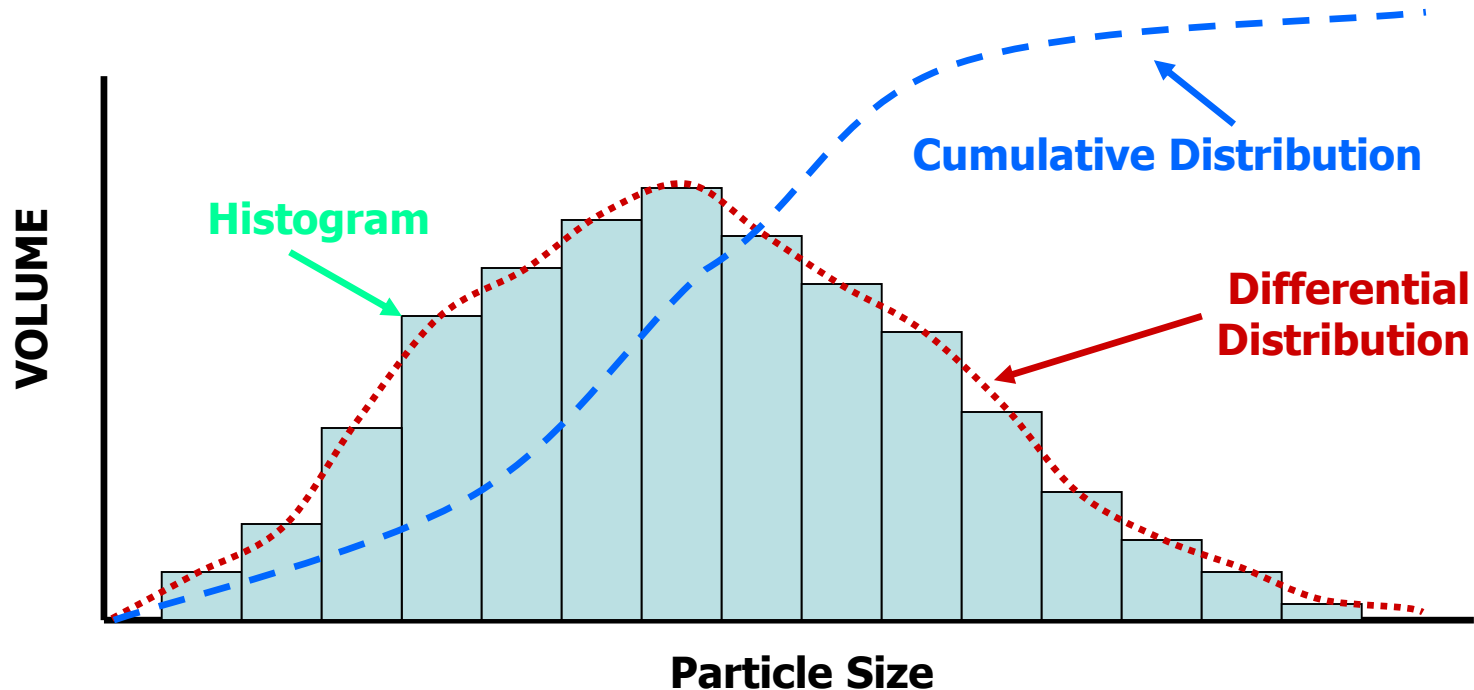


- Linear X-Axis Distribution



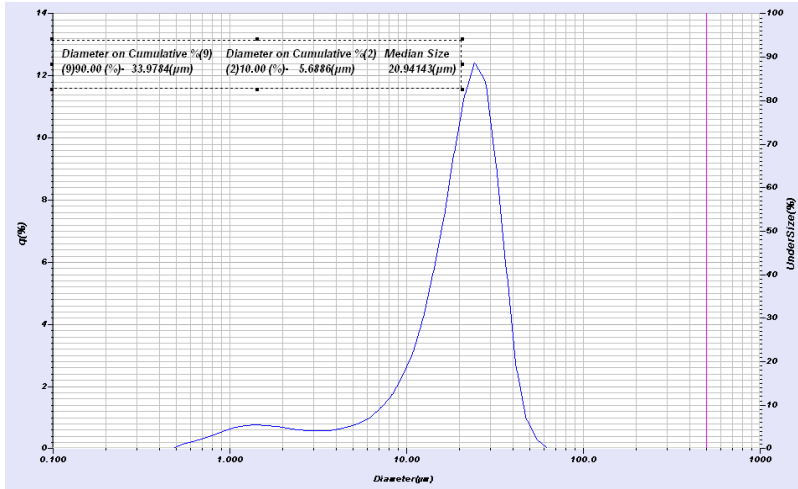


# Distribution Display

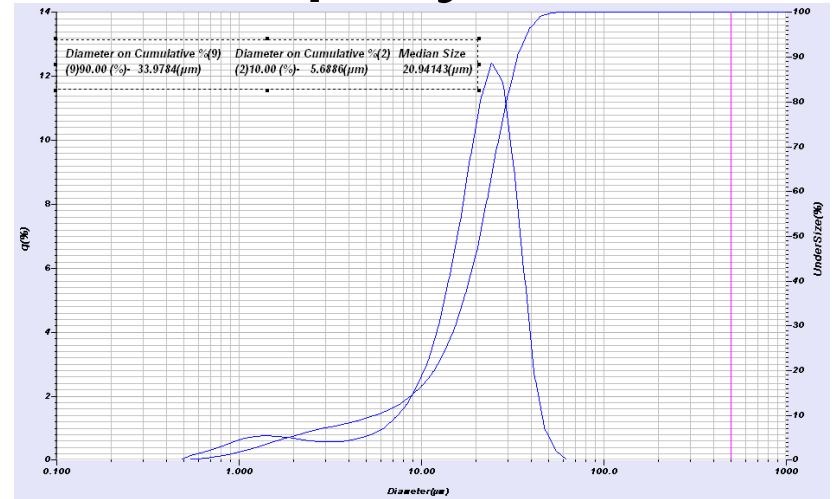


- Represented by series of segments or channels known as histogram.
- Number of channels based on design, practicality and aesthetics

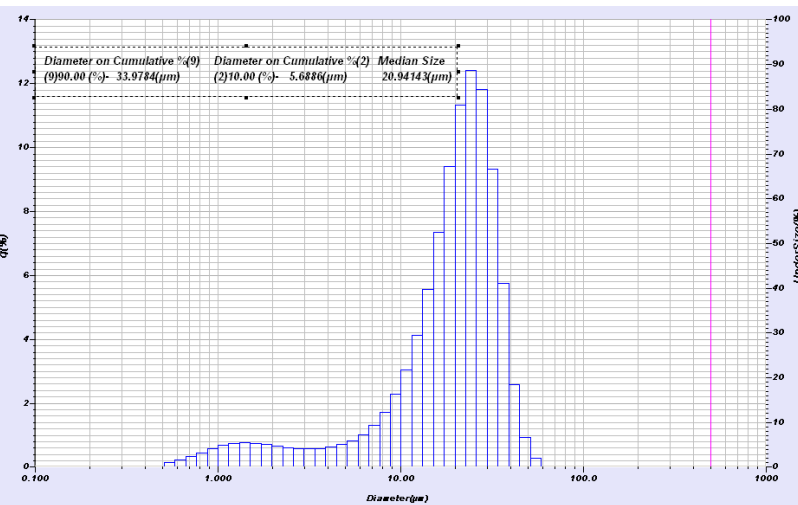
# Your Analyzer's Displays



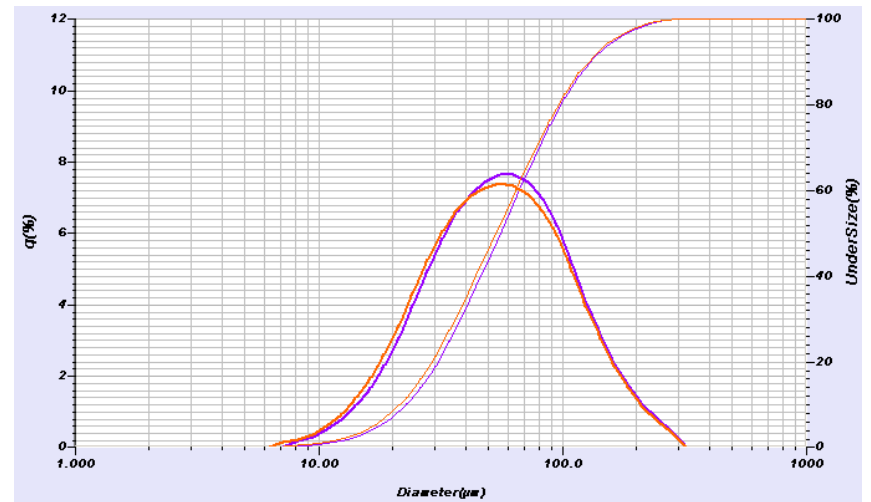
Frequency



Frequency + cumulative (undersize)



Histogram



Multiple frequency + cumulative (undersize)

# Central Values

## Mean

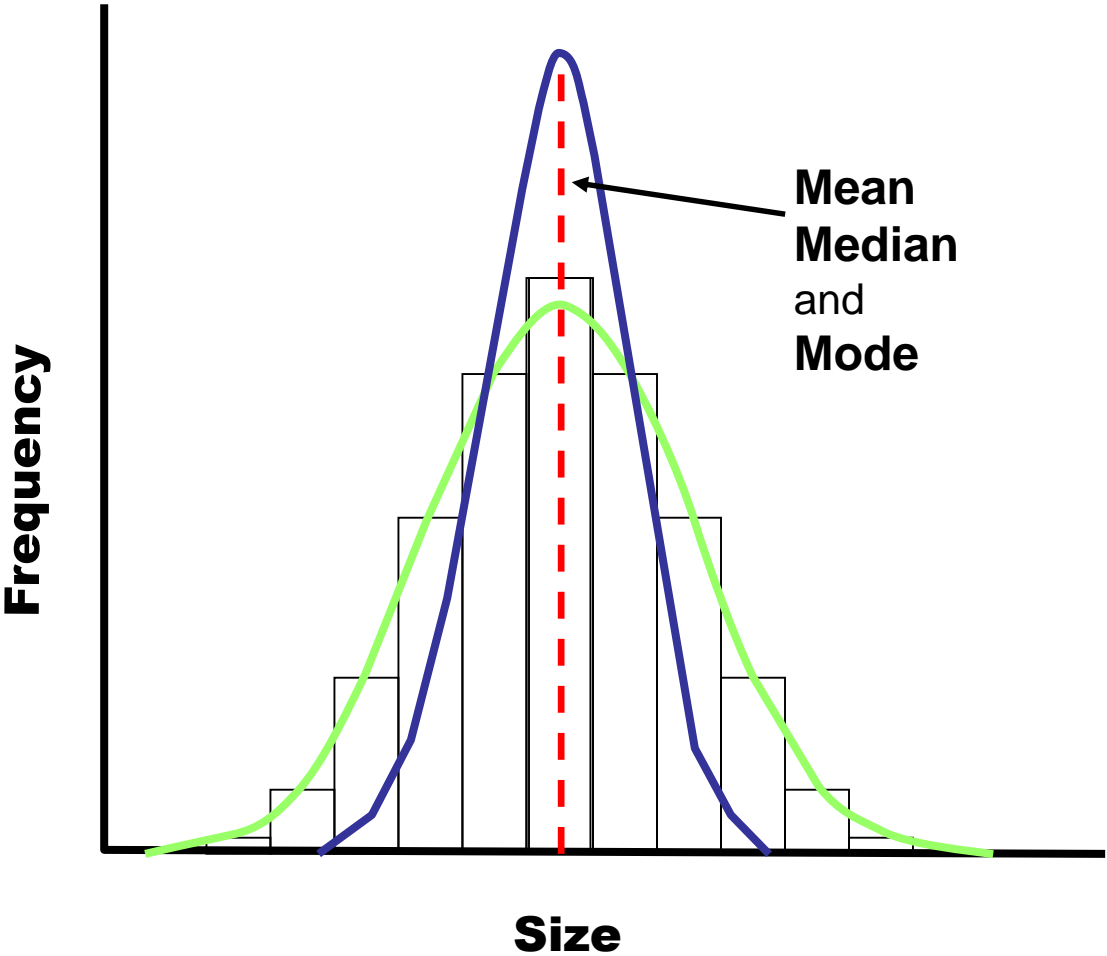
Weighted Average  
Center of Gravity

## Median

50% Point

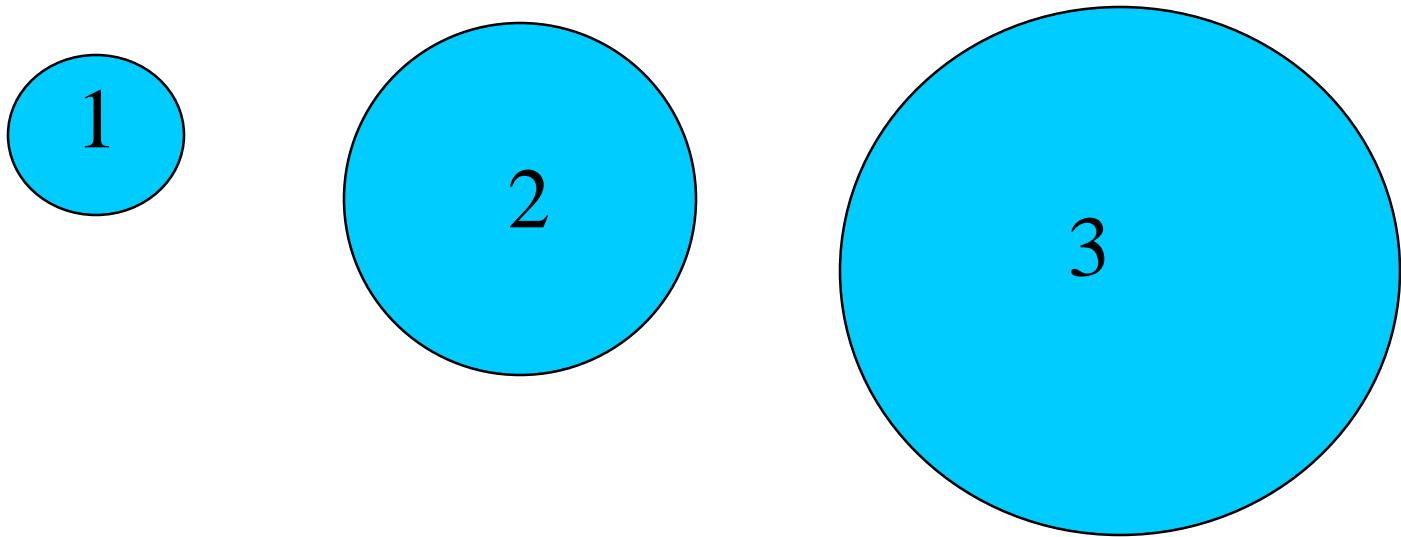
## Mode

Peak of the distribution  
Most common value



# What does “Mean” mean?

Three spheres of diameters 1,2,3 units



What is the average size of these spheres?

$$\text{Average size} = (1+2+3) \div 3 = 2.00$$

This is called the  $D[1,0]$  - the number mean

# Many possible Mean values

$$X_{nl} = D[1,0] = \frac{1+2+3}{3} = 2.00 \quad \text{Number weighted mean Diameter (length)}$$

$$X_{ns} = D[2,0] = \sqrt{\frac{1+4+9}{3}} = 2.16 \quad \text{Mean surface diameter}$$

$$X_{nv} = D[3,0] = \sqrt[3]{\frac{1+8+27}{3}} = 2.29 \quad \text{Mean volume diameter}$$

$$X_{sv} = D[3,2] = \frac{1+8+27}{1+2+3} = 2.57 \quad \text{Volume/surface mean,}$$

$$X_{vm} = D[4,3] = \frac{1+16+81}{1+8+27} = 2.72 \quad \text{Volume weighted mean diameter}$$

None of the answers are wrong they have just been calculated using different techniques

# Moment Ratios: ISO 9276-2

For your reference

$$D[p, q] = \left[ \frac{\sum n_i D_i^p}{\sum n_i D_i^q} \right]^{1/(p-q)} \quad p \neq q$$

$$D[p, q] = \exp \left[ \frac{\sum n_i D_i^p \ln D_i}{\sum n_i D_i^q} \right] \quad p = q$$

# Volume-based Mean diameter

D[4,3] which is often referred to as the Volume Mean Diameter [ VMD ]

$$D [4,3] = \frac{\sum D_i^4 n_i}{\sum D_i^3 n_i}$$

Monitoring the D[4,3] value in your specification will emphasize the detection of large particles

## Mean Size

The frequency distribution is found using the arithmetical mean diameter, as shown in the formula below.

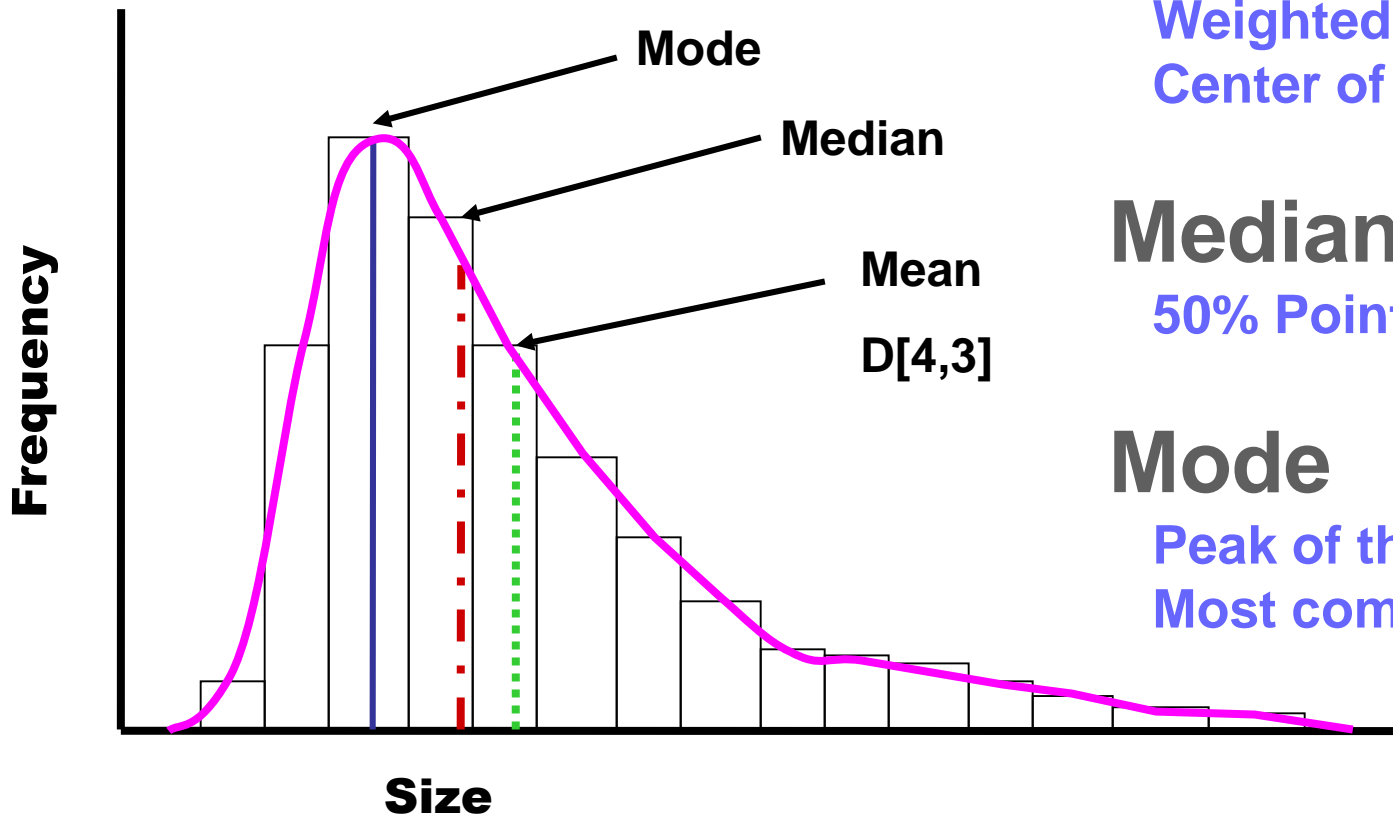
$$\text{Mean Diameter} = \frac{\sum \{q(J) \times X(J)\}}{\sum \{q(J)\}}$$

J : Particle Diameter Division Number

q(J) : Frequency Distribution Value (%)

X(J) : Jth Particle Diameter Range's Representative Diameter (μm).

# Central Values revisited



## Mean

Weighted Average  
Center of Gravity

## Median

50% Point

## Mode

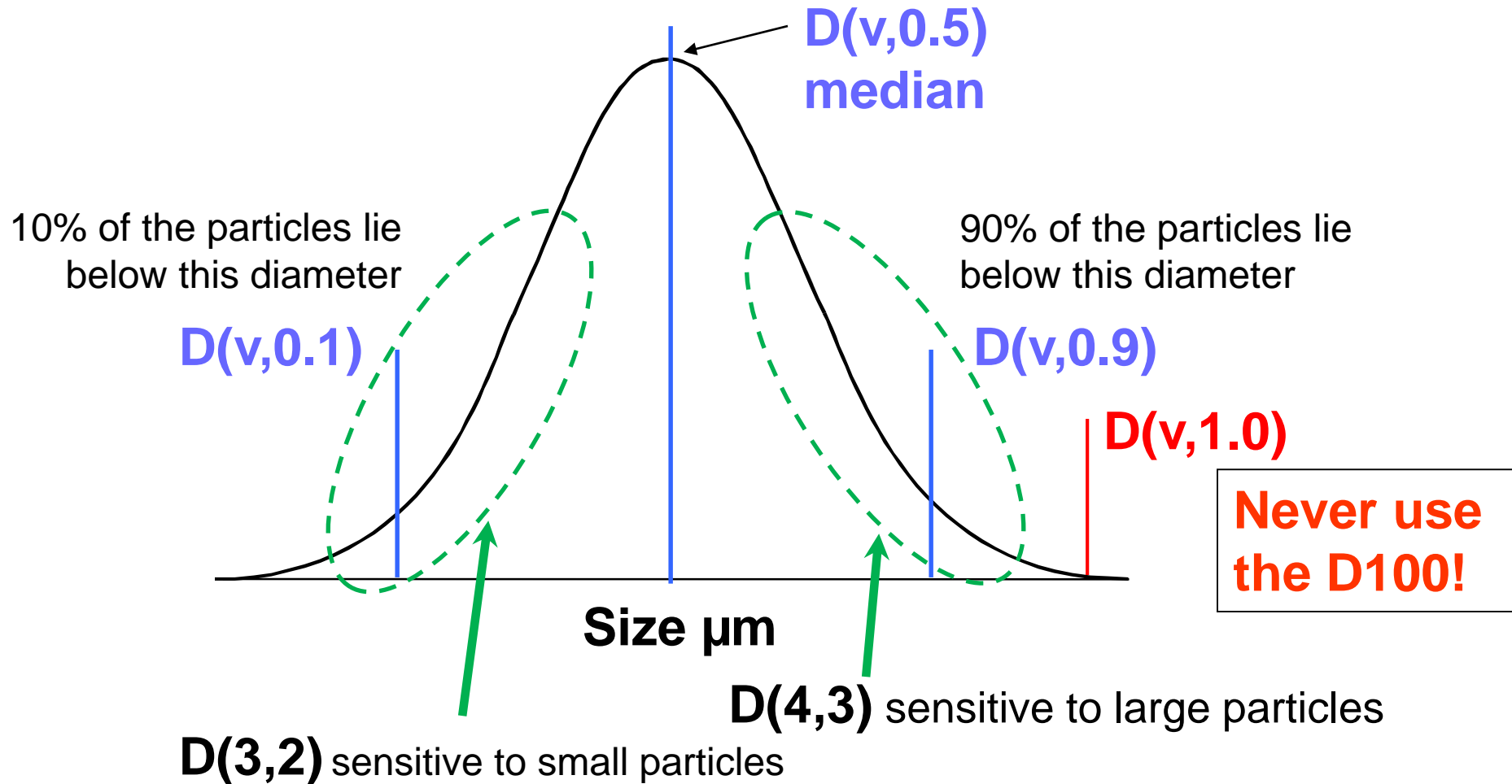
Peak of the distribution  
Most common value

Remember:  $D[4,3]$  is sensitive to large particles

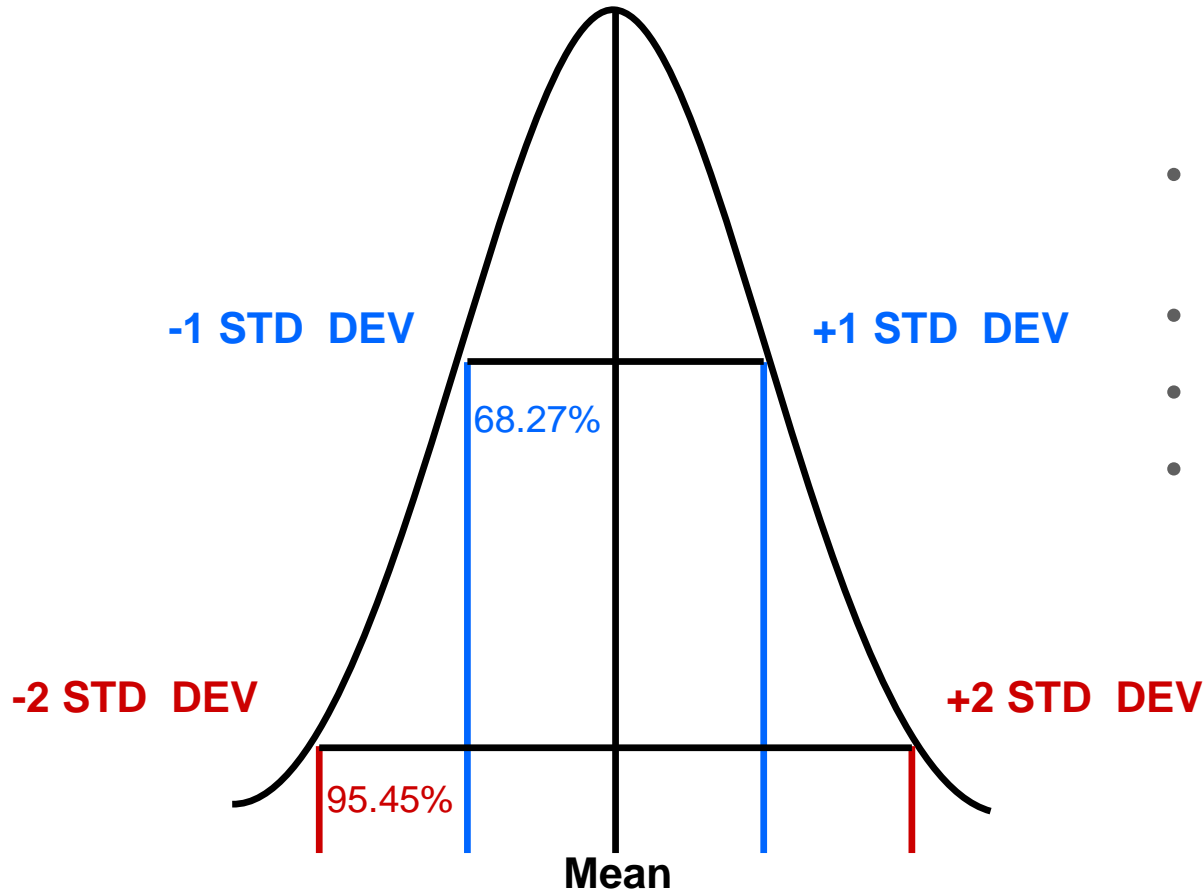


# Most Common Statistics

half are smaller than this diameter    half are larger than this diameter



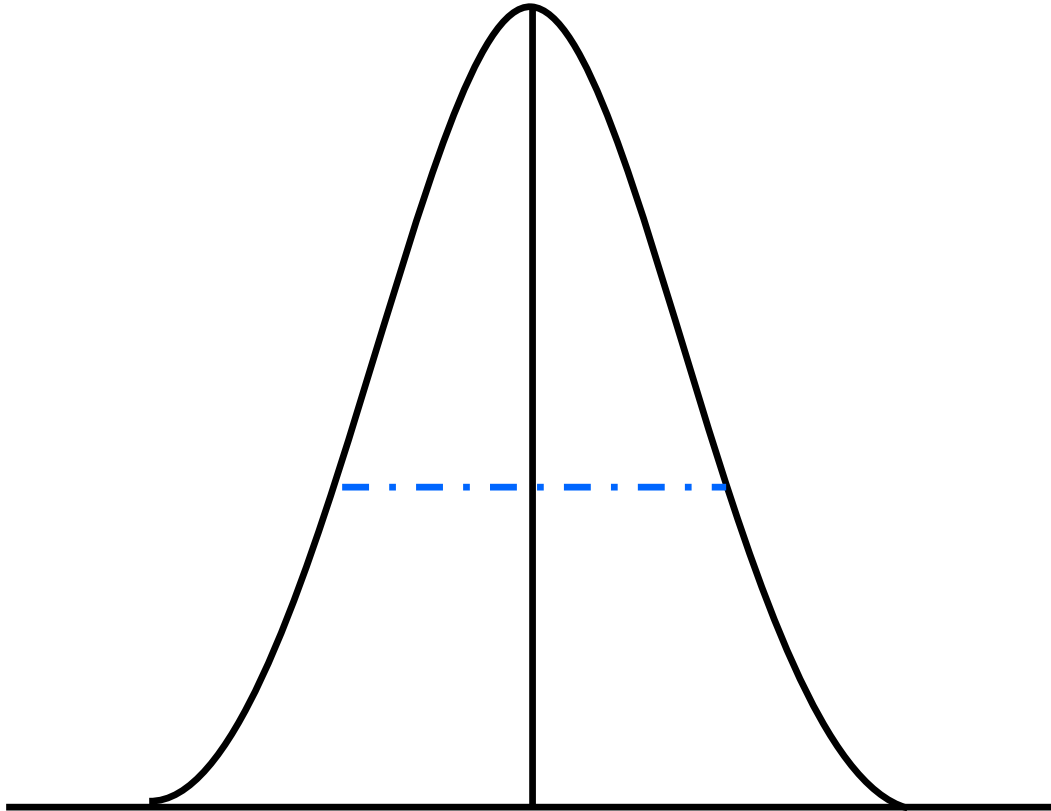
# Standard Deviation



- Normal (Gaussian) Distribution Curve
- $\mu$  = distribution mean
- $\sigma$  = standard deviation
- Exp = base of natural logarithms

$$Y = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[\frac{-(x-\mu)^2}{2\sigma^2}\right]$$

# Distribution Width



- **Polydispersity Index (PI, PDI)**
- **Span**
- **Geometric Std. Dev.**
- **Variance**
- **Etc...**

# For Your Reference

## Variance

The value for the expanded distribution condition is found using the formula below.

$$\text{Variance} = \sum \left[ (X(J) - \text{Mean})^2 \frac{q(J)}{100} \right]$$

J : Particle Diameter Division Number

q(J) : Distribution Graph Value(%)

X(J): Jth Particle Diameter Range's Representative Diameter (μm)

Mean: Arithmetic Mean Diameter (μm)

## Std. Dev.

Value taken from variance value's square root.

## Coefficient of Variation (CV)

This result of dividing the arithmetic standard deviation (Std. Dev.) by the mean diameter.

## Mode Size

Frequency distribution value's largest values that become particle diameters of the frequency distribution graph's peak.

## Span

Value that becomes the criteria for widening the distribution, as shown below.

Not displayed if both of the diameter on cumulative % are not set.

$$\text{Span Value} = \frac{(\text{Diameter on cumulative \% A} - \text{Diameter on cumulative \% B})}{\text{Median diameter}}$$

Diameter on cumulative % A: the first value set in the display conditions.

Diameter on cumulative % B: the second value set in the display conditions.

Note: Span typically =  $(d_{90} - d_{10}) / d_{50}$

# For Your Reference

## Geometric Mean Size

The frequency distribution is found using the geometric mean value, as shown in the formula below.

$$\text{Geometric Mean Diameter} = 10^{\frac{\sum (\log X(J) \times q(J))}{\sum q(J)}}$$

J : Particle Diameter Division Number

q(J) : Frequency Distribution Value (%)

X(J) : Jth Particle Diameter Range's Representative Diameter (μm)

## Geometric Variance

The value for the expanded distribution condition is found using the formula below.

$$\text{Geometric Variance} = 10^{\sum (\log X(J) - \log(\text{Mean}))^2 \cdot \frac{q(J)}{100}}$$

J : Particle Diameter Division Number

q(J) : Frequency Distribution Value (%)

X(J) : Jth Particle Diameter Range's Representative Diameter (μm)

Mean : Geometric Mean Diameter (μm)

## Geometric Standard Deviation

$$\text{Geometric Distribution Deviation} = 10^{\sqrt{\sum (\log X(J) - \log(\text{Mean}))^2 \cdot \frac{q(J)}{100}}}$$

J : Particle Diameter Division Number

q(J) : Frequency Distribution Value (%)

X(J) : Jth Particle Diameter Range's Representative Diameter (μm)

Mean : Geometric Mean Diameter (μm)

# For Your Reference

## Error Calculations in LA-960 only

### Chi Square

Indicates the degree of similarity between the refractive index used to produce the particle size distribution calculation result and the actual scattering data. The closer to "0", the greater the similarity. Becomes the selection's criterion when the refractive index is not known for the sample being measured. Chi Square ( $\chi^2$ ) is found using the following formula.

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

$y_i$  : Actual scattering measurement data

$y(x_i)$ : Scattering data found using refractive index file data and displayed particle size distributions

$\sigma_i$  : Scattering data standard deviation

### R Parameter

Indicates the degree of similarity between the refractive index used to produce the particle size distribution calculation result and the actual scattering data. The closer to "0", the greater the similarity.

Becomes the selection's criterion when the refractive index is not known for the sample being measured.

The Residual R Parameter is found using the following formula.

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

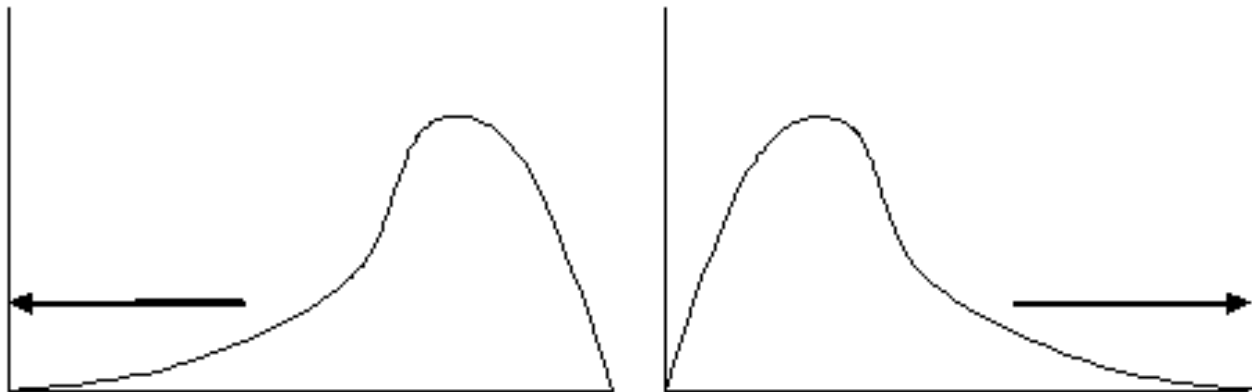
$y_i$  : i-th detector channel's actual scattering measurement data

$y(x_i)$ : Scattering data calculated by calculating backwards from the refractive index data and the displayed particle size distribution.

$N$  : Number of light detector channels

# Skewness

1. **positive skew:** The right tail is longer; the *mass* of the distribution is concentrated on the left of the figure. The distribution is said to be *right-skewed*.
2. **negative skew:** The left tail is longer; the mass of the distribution is concentrated on the right of the figure. The distribution is said to be *left-skewed*.



Negative Skew

Elongated tail at the **left**

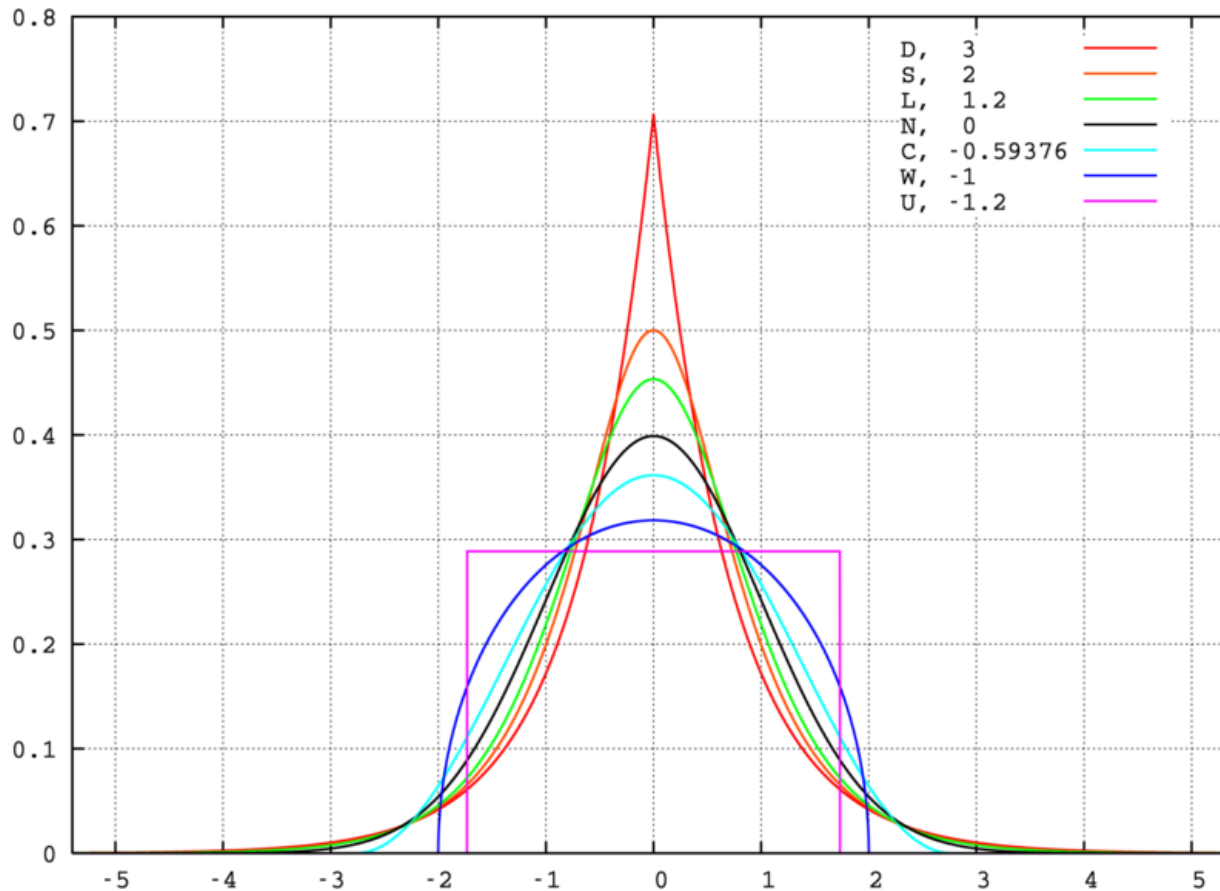
More data in the left tail than would be expected in a normal distribution

Positive Skew

Elongated tail at the **right**

More data in the right tail than would be expected in a normal distribution

# Kurtosis (Peakedness)



From highest to lowest peak:  
red, kurtosis 3  
orange, kurtosis 2  
green, kurtosis 1.2  
black, kurtosis 0,  
cyan, kurtosis -0.59376...  
blue, kurtosis -1  
magenta, kurtosis -1.2



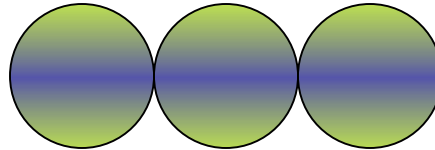
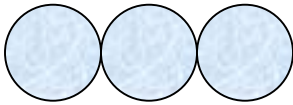
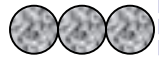
# Number vs. Volume Distributions

$r = 1 \mu\text{m}$   
 $v = 4$

$r = 2 \mu\text{m}$   
 $= 32$

$r = 3 \mu\text{m}$   
 $= 108$

$$V = \frac{4}{3} \pi r^3$$



$V \cdot 3 = 12$   
 $12/432 = 2.8\%$

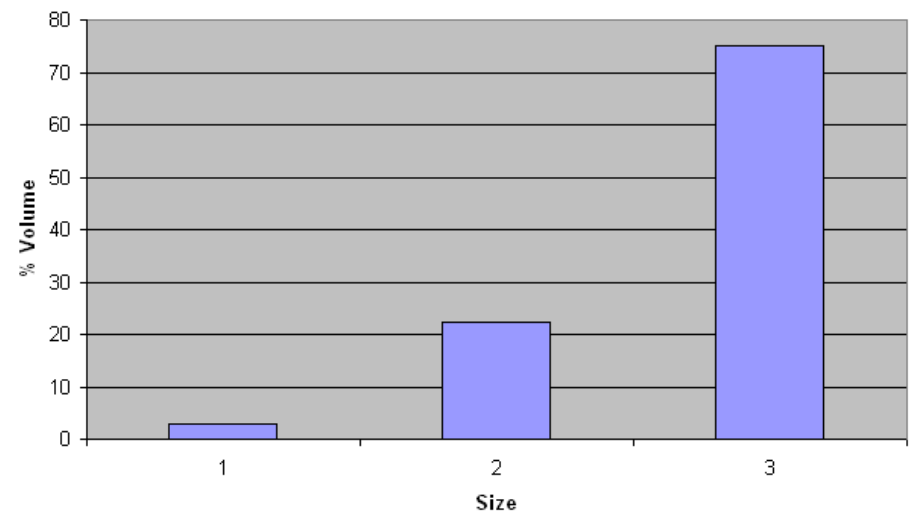
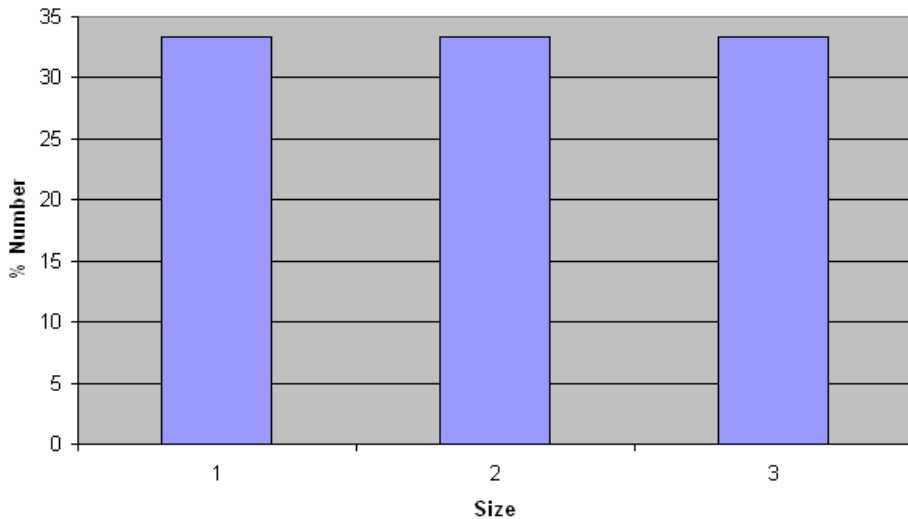
96  
 $96/432 = 22.2\%$

324  
 $324/432 = 75\%$

Total =  $12 + 96 + 324 = 432$

Number

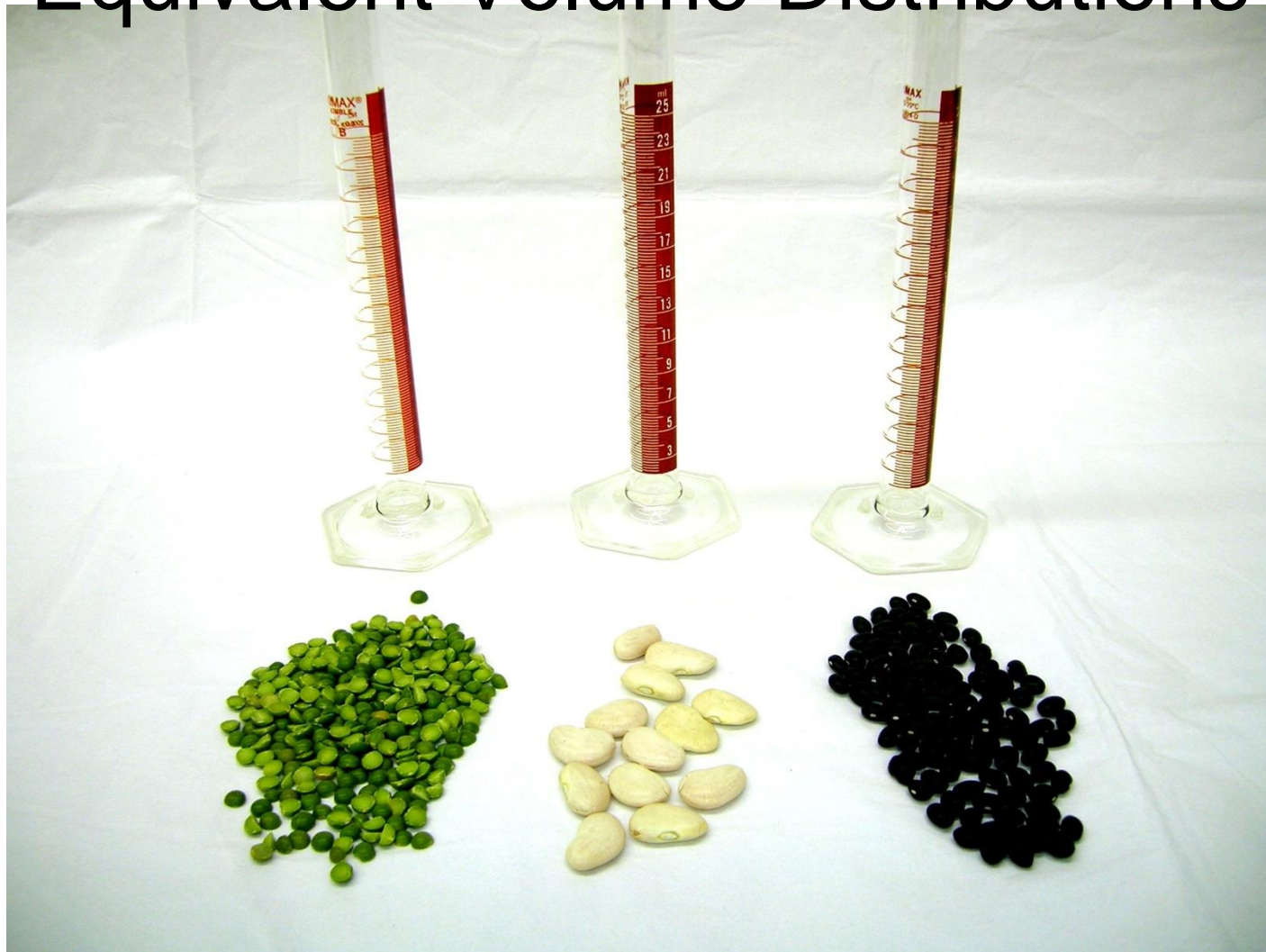
Volume



# Beans!



# Equivalent Volume Distributions



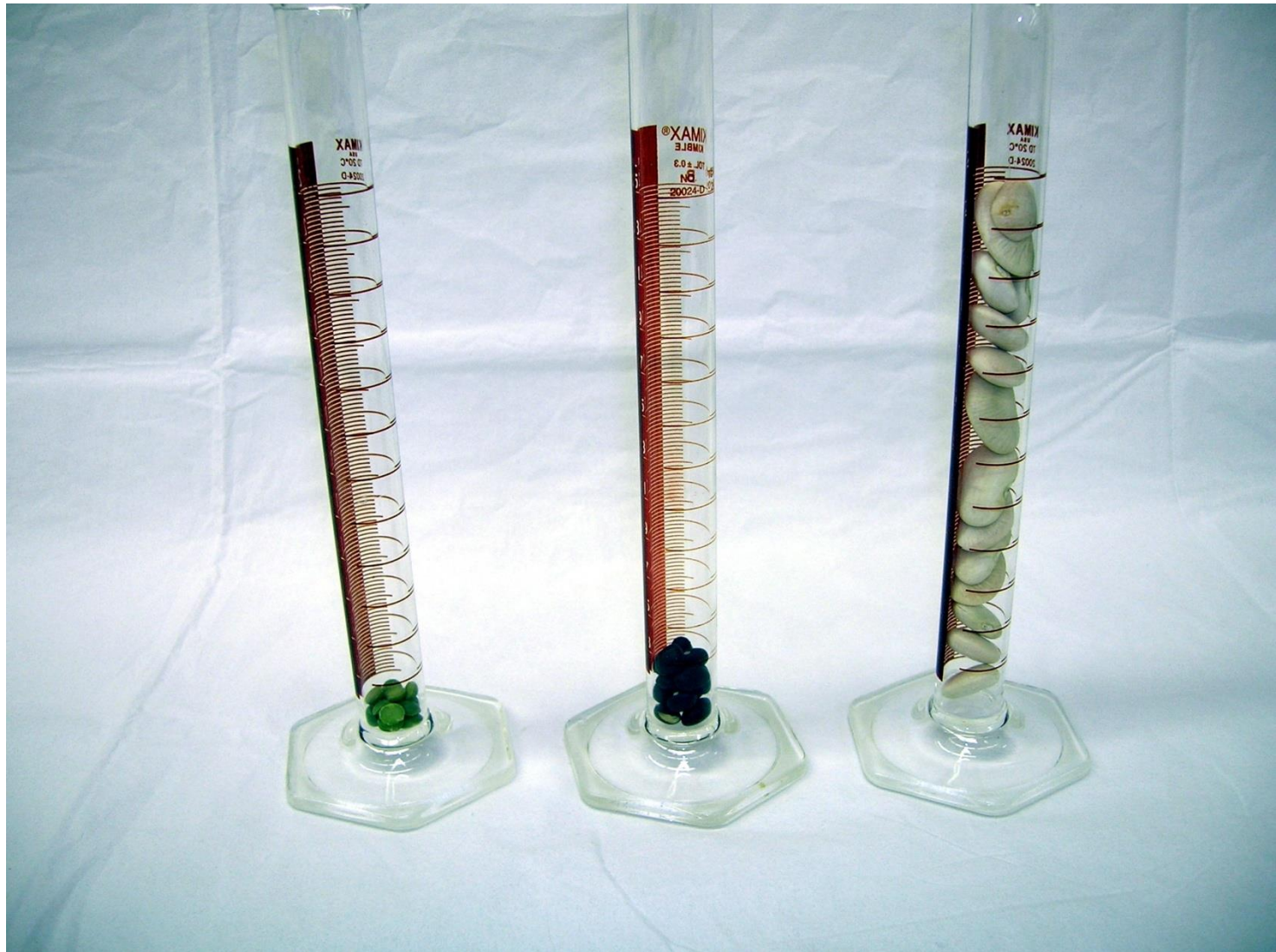
# Equivalent Volume Distributions



# Equivalent Number Distributions

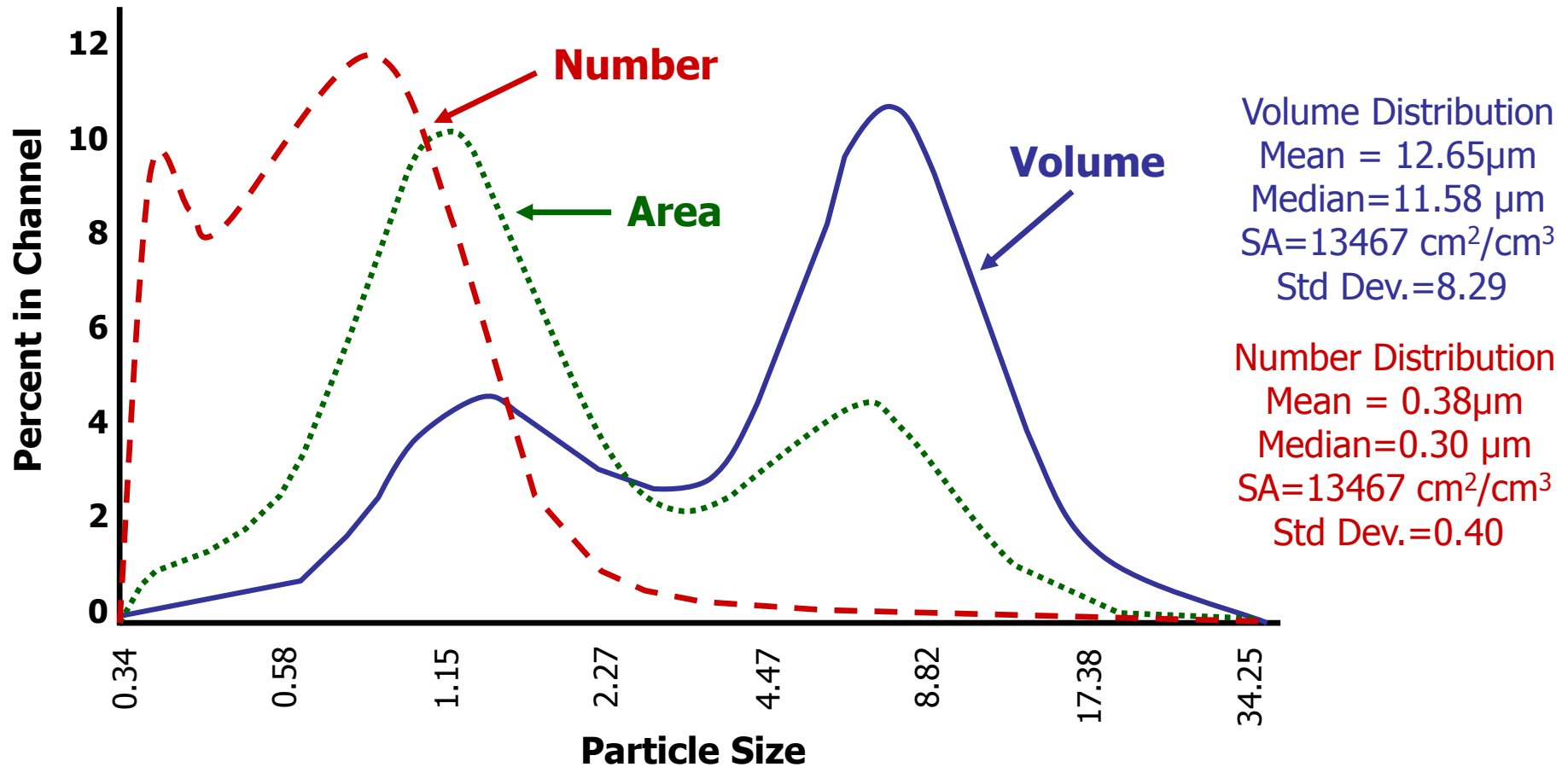


# Equivalent Number Distributions



# Comparing Distribution Bases

- Same material shown as volume, number and area distribution



# Statistical Issues with Distributions

- L Neumann, E T White, T Howes (Univ. Queensland) “What does a mean size mean?” 2003 AIChE presentation at Session 39 Characterization of Engineered particles November 16 - 21 San Francisco

## Other references:

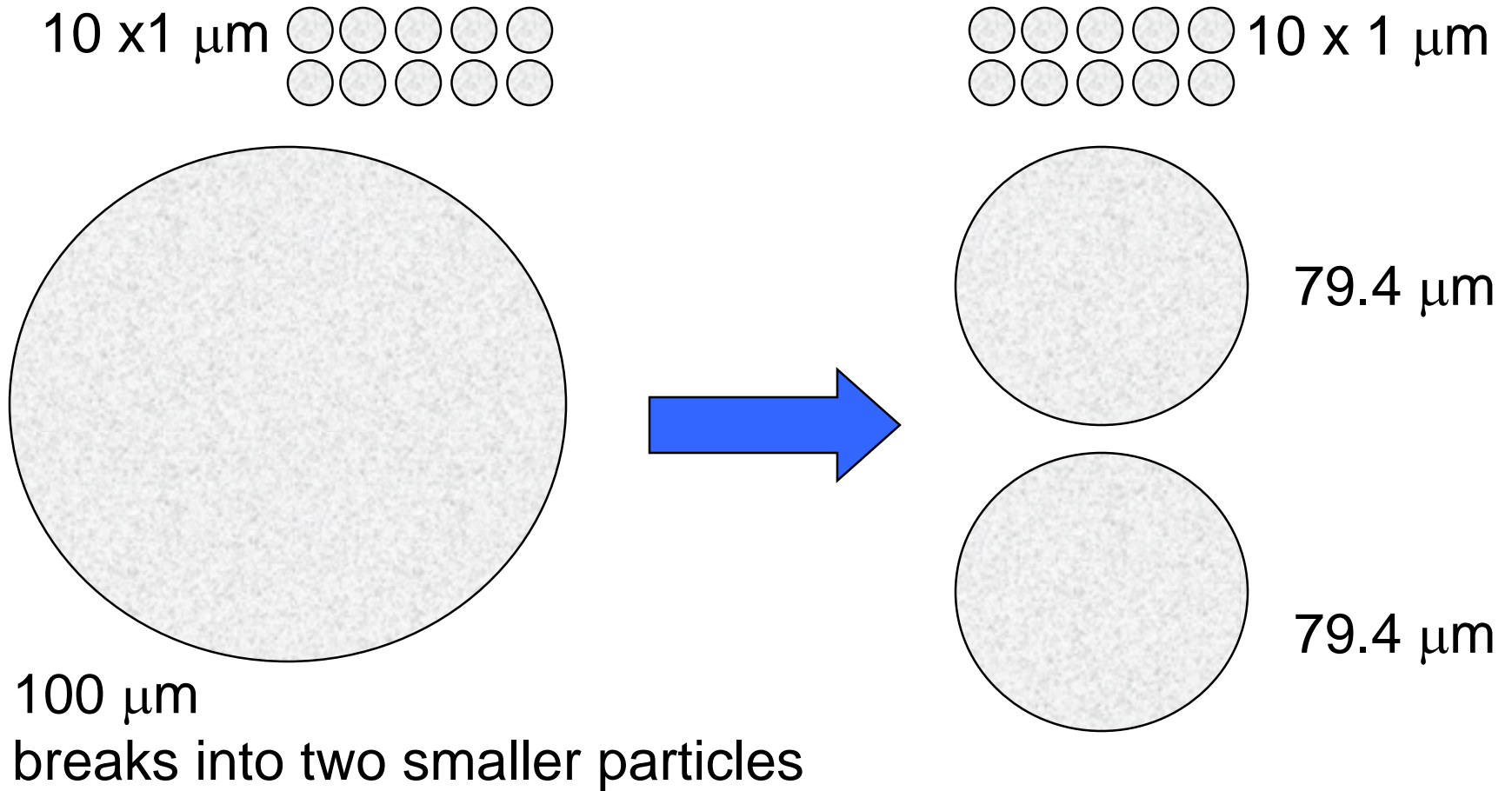
- L Neumann, T Howes, E T White (2003) Breakage can cause mean size to increase Dev. Chem. Eng. Mineral Proc. J.
- White E T, Lawrence J. (1970), Variation of volume surface mean for growing particles, Powder Technology,4, 104 - 107



# Does the Mean Match the Process?

- Particle size measurements often made to monitor a process
  - Size reduction (milling)
  - Size growth (agglomeration)
- Does the measured/calculated mean diameter describe the change due to the process?
- It depends on which mean used...

# Size Reduction Scenario



# Size Reduction: Number Mean

Ten particles of size 1; one of size 100 units

Number mean =  $D[1, 0] = (10*1 + 1*100)/11 = \underline{10}$  units

..

Largest particle (100) breaks into two of 79.37

(conserves volume/mass:  $2 @ 79.37^3 = 1 @ 100^3$ )

Have broken one

What happens to the number mean?

Mean =  $(10*1+2*79.37)/12 = \underline{14.06}$  units

Surprise, surprise a 40.6% increase!

# Size Reduction: Volume Mean

Ten particles of size 1; one of size 100 units

Volume Moment Mean

$$D[4, 3] = (10 \cdot 1^4 + 1 \cdot 100^4) / (10 \cdot 1^3 + 1 \cdot 100^3) \sim \underline{100} \text{ units}$$

..

Largest particle (100) breaks into two of 79.37  
(conserves volume/mass:  $2 @ 79.37^3 = 1 @ 100^3$ )

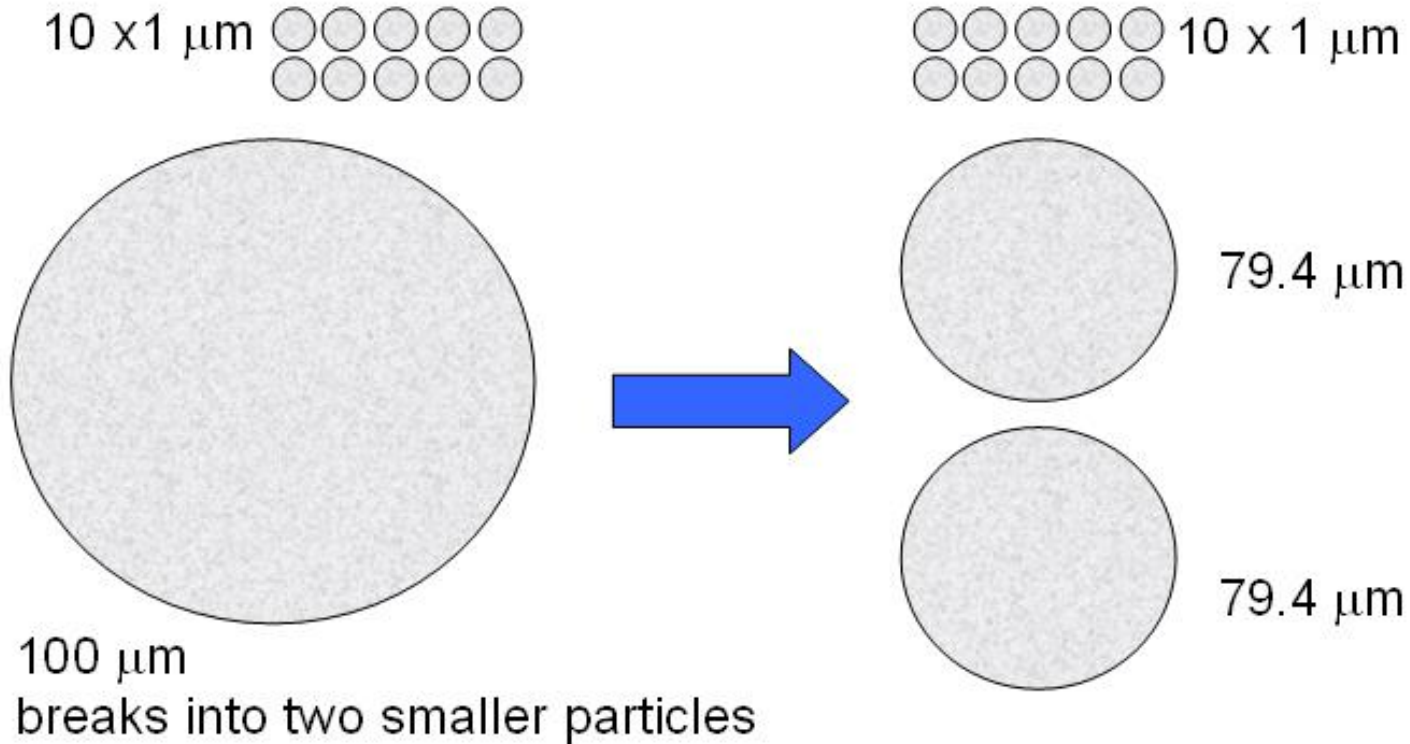
Have broken one

What happens to the  $D[4, 3]$ ?

$$\text{New } D[4, 3] = (10 \cdot 1^4 + 2 \cdot 79.37^4) / (10 \cdot 1^3 + 2 \cdot 79.37^3) \sim \underline{79.37} \text{ units}$$

This shows the expected behavior

# Can You See the Problem?



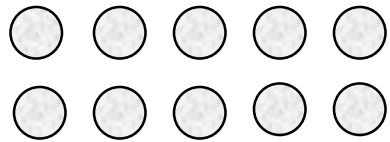
Number mean = 10

Number mean = 14  $\uparrow$

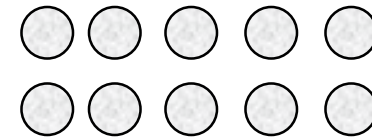
Volume mean = 100

Volume mean = 79  $\downarrow$

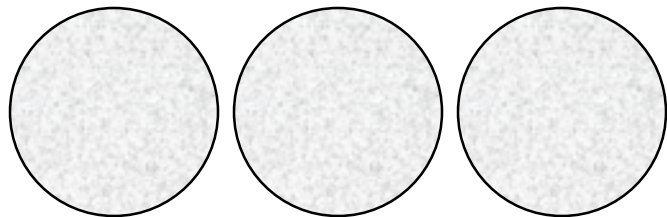
# Size Growth Scenario



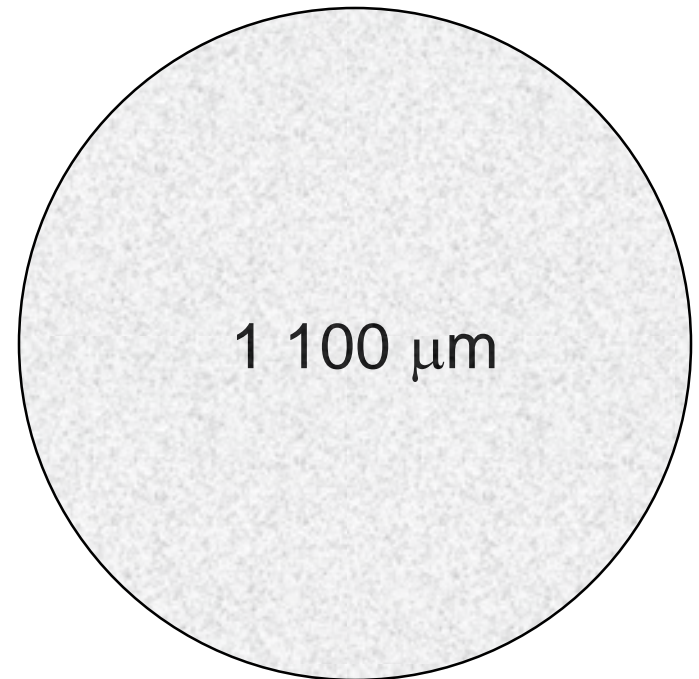
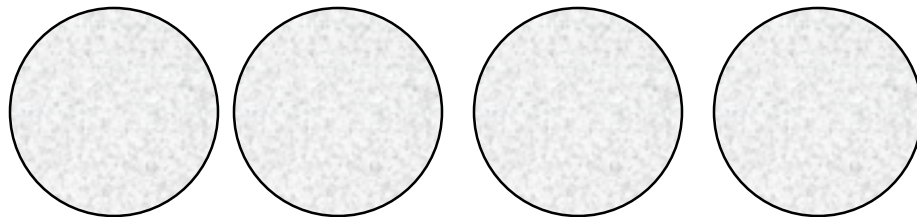
10 1  $\mu\text{m}$



10 1  $\mu\text{m}$



10 46.4  $\mu\text{m}$



1 100  $\mu\text{m}$

Ten 46.4  $\mu\text{m}$  particles agglomerate into one 100  $\mu\text{m}$  particle

# Growth: Number Mean

Ten particles of size 1; ten of size 46.42

$$D[1, 0] = (10*1 + 10*46.42)/20 = \underline{23.71} \text{ units}$$

Ten of 46.42 agglomerate into one of 100  
(conserves volume/mass:  $10 @ 46.42^3 = 1 @ 100^3$ )  
Have agglomerated half; does mean increase?

$$\text{Mean} = (10*1 + 1*100)/11 = \underline{10} \text{ units}$$

Over a 50% decrease!

# Growth: Volume Mean

Ten particles of size 1; ten of size 46.42

$$D[4, 3] = (10 \cdot 1^4 + 10 \cdot 46.42^4) / (10 \cdot 1^3 + 10 \cdot 46.42^3) \\ \sim \underline{46.4} \text{ units}$$

(Note again the volume moment mean is dominated by the large particles)

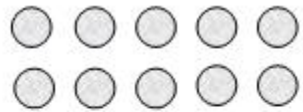
Ten of 46.42 agglomerate into one of 100  
(conserves volume/mass:  $10 @ 46.42^3 = 1 @ 100^3$ )  
Have agglomerated half; does mean increase?

$$D[4, 3] = (10 \cdot 1^4 + 1 \cdot 100^4) / (10 \cdot 1^3 + 1 \cdot 100^3) \sim \underline{100} \text{ units}$$

This shows the expected behavior



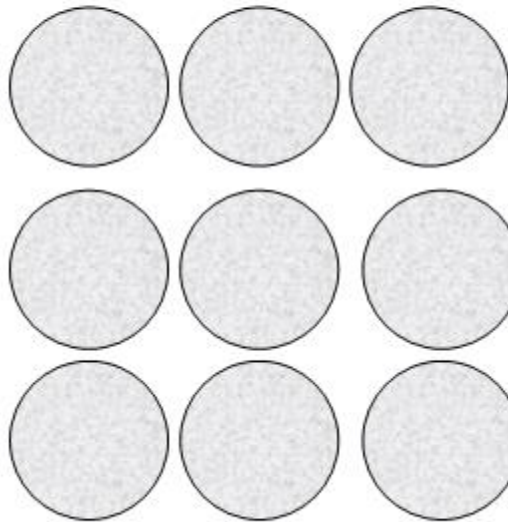
# Can You See the Problem?



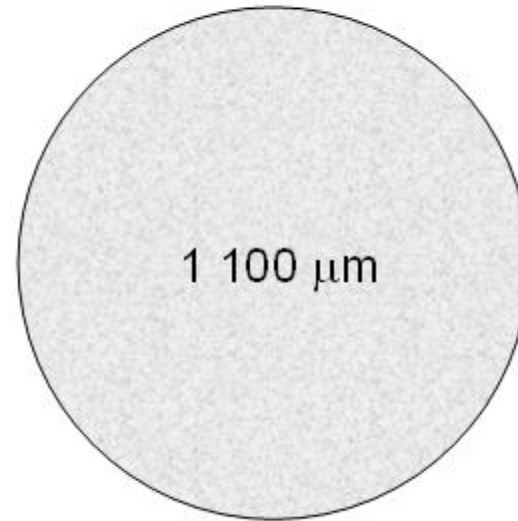
10 1  $\mu\text{m}$



10 1  $\mu\text{m}$



10 46.4  $\mu\text{m}$



1 100  $\mu\text{m}$

Ten 46.4  $\mu\text{m}$  particles agglomerate into one 100  $\mu\text{m}$  particle

Number mean = 24

Number mean = 10 ↓

Volume mean = 46

Volume mean = 100 ↑

# Practical Implications

- Not just a “party trick” topic!  
“Do you know you can break particles and the mean will increase?”
- Serious. “Did an experiment. I thought I broke particles but the mean has increased”  
(REAL experience)
- Should be aware it can happen!
- Analyse whole size distribution, not mean alone.



# METHODS OF ANALYSIS

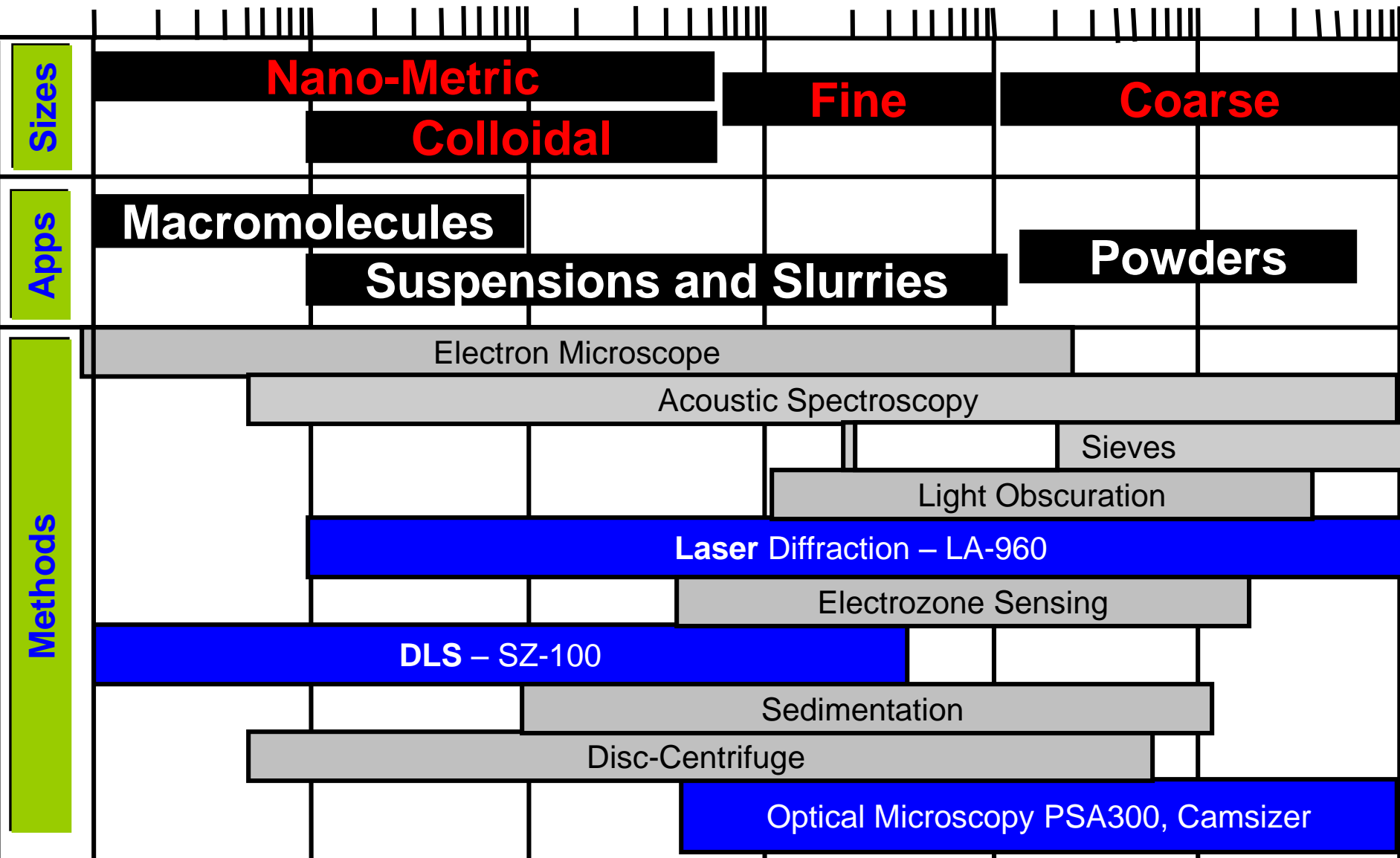
## PARTICLE MEASUREMENT METHODS

# PSA Method is Important

- Why should one consider various methods of particle size analysis?
  - Material suppliers and users employ many different types of instruments
  - Use a different technique = get a different answer
  - It is important to understand how analysis methods differ in order to know how to compare data

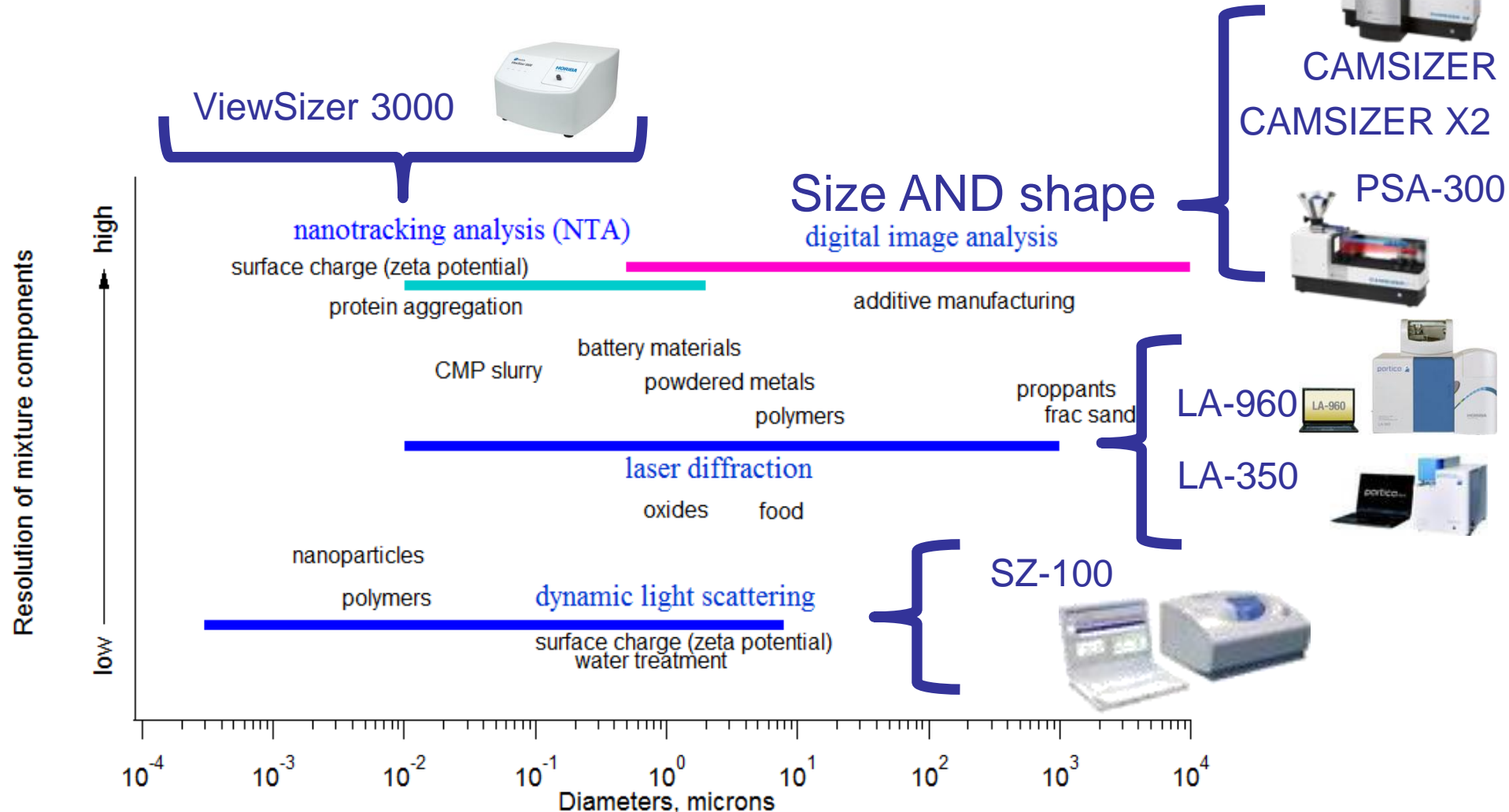
# Size Range by Technique (μm)

0.001      0.01      0.1      1      10      100      1000



# Which Analyzer?

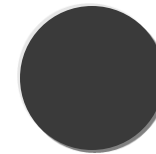
Size, desired resolution, and budget determine technology and product. For a given problem the choice is often clear.



# What Size is Measured?

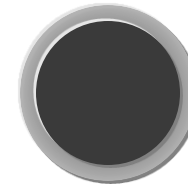
## Laser Diffraction

Equivalent Spherical Diameter



## Dynamic Light Scattering

Hydrodynamic Radius



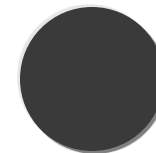
## Image Analysis

Lengths, Widths, Equivalent Spherical



## Acoustic Spectroscopy

Equivalent Spherical Diameter



# Particle Shape Definitions

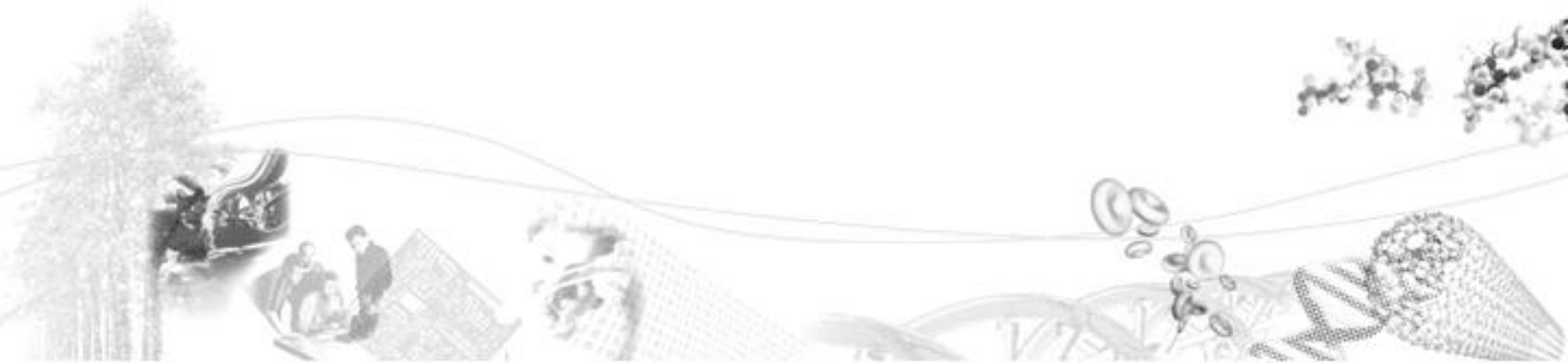
<b>Acicular:</b>	<b>Needle-shaped, rigid</b>
<b>Angular:</b>	<b>Edgy, hard angles</b>
<b>Fibrous:</b>	<b>Thread-like, non-rigid</b>
<b>Granular/Blocky:</b>	<b>Irregular-shaped, low aspect-ratio</b>
<b>Spherical:</b>	<b>Regular-shaped, unity aspect ratio</b>
<b>Aspect ratio:</b>	<b>Breadth / length OR Length / breadth</b>
<b>Sphericity:</b>	<b>How spherical is the particle?</b>
<b>Roundness:</b>	<b>How round is the particle?</b>





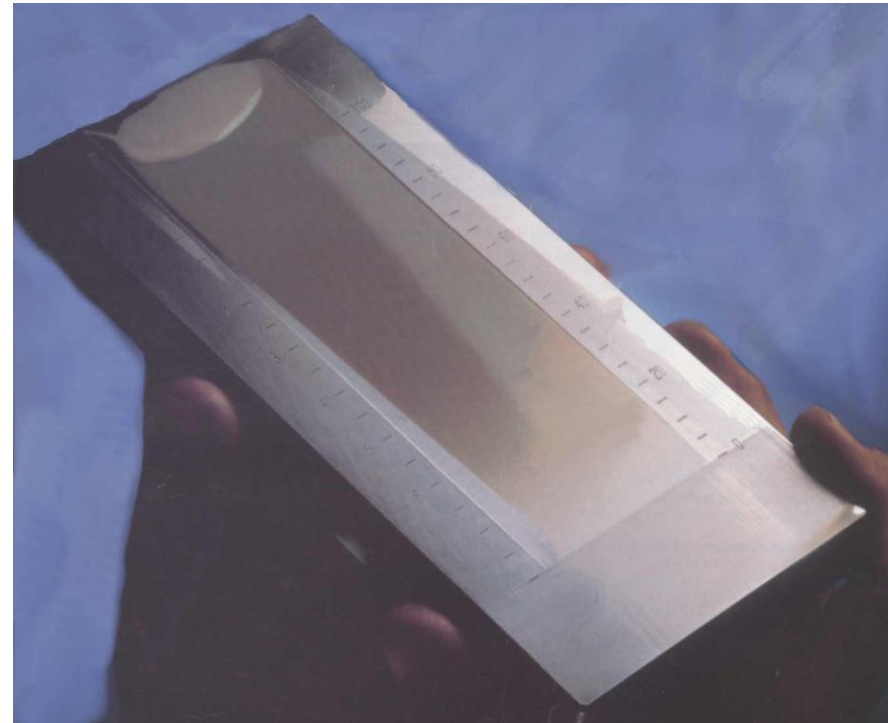
**Poll!**

**What are the shapes of your particles?**



# Hegman Gauge

- Used in paint and coatings industry
  - Device has tapered center channel
  - Slurry is placed in channel, then straight edge is drawn across it
  - “Hegman Number” is where particles disturb smooth surface of slurry
  - Information from largest particles only – no distribution



# Sieves

- Weigh % sample caught on known screen sizes
- Solid particles 30  $\mu\text{m}$  – 30 mm (and larger)

## Advantages:

- Low equipment cost
- Direct measurement method
- No practical upper limit

## Disadvantages:

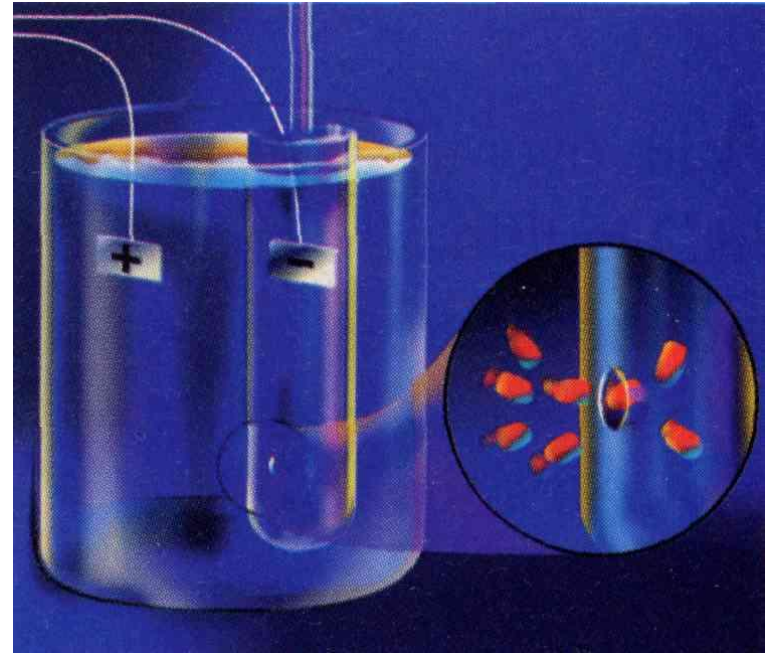
- Limited lower range
- Time Consuming
- High Labor Cost
- Need Large Sample

Available through [www.retsch.com](http://www.retsch.com)



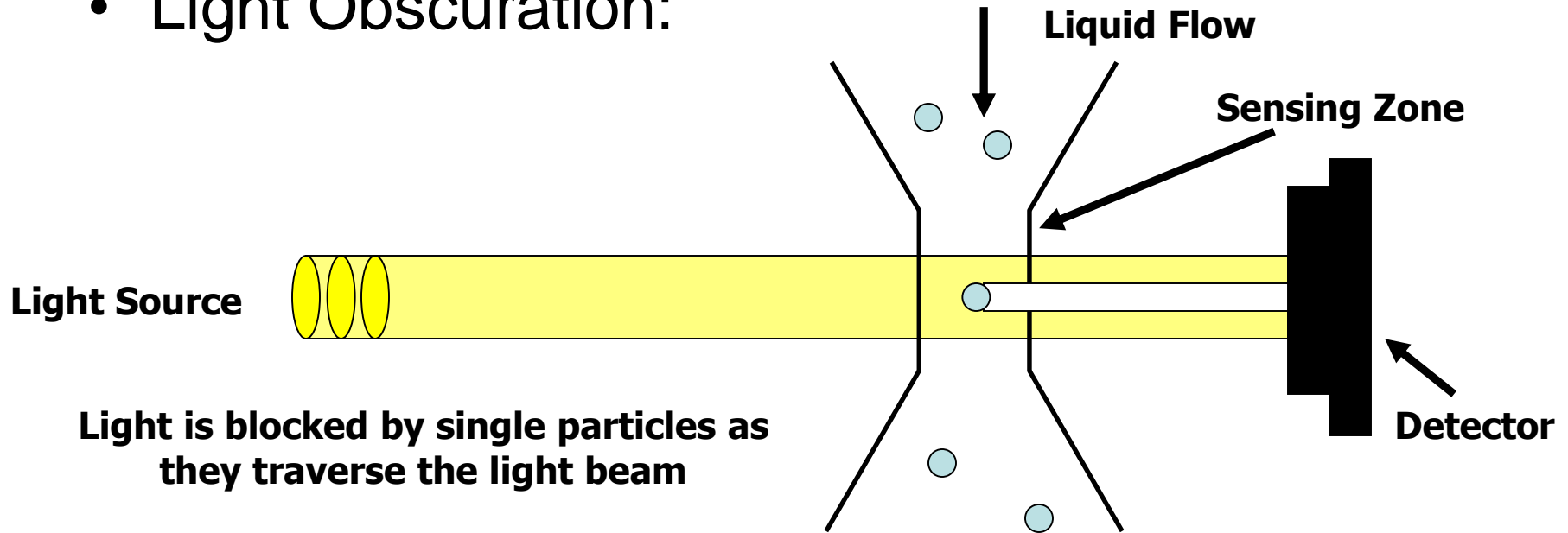
# Electrical Sensing Zone

- Coulter Principle
  - Based on change in conductivity of aperture as particle traverses.
  - Requires conducting liquid.
  - Directly measures particle volume and counts.
  - High resolution
  - Used for blood cell counting more than industrial applications



# Light Obscuration

- Light Obscuration:



## Advantages:

- Particle count available
- USP<788> testing
- High resolution histogram

## Disadvantages:

- Dilution required for particle size analysis
- Prone to cell clogging

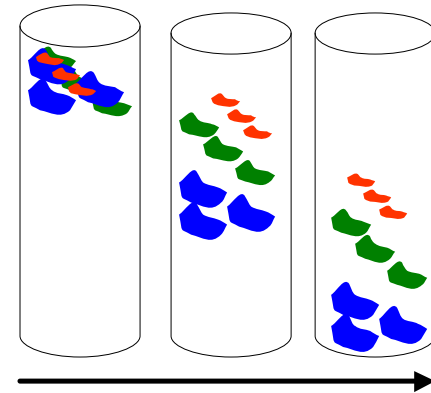
# Sedimentation

- Stokes Law

$$D = \sqrt{\frac{18\mu V_p}{(\rho_p - \rho_l)g}}$$

- $V_p$  = Settling velocity of discrete particle
- $g$  = Gravity constant
- $\rho_p$  = Density of Particle
- $\rho_l$  = Density of Carrier Fluid
- $\mu$  = Viscosity of Carrier Fluid

Sedimentation of same density material in a viscous medium



**Time**



Note: assumes settling of spherical particle  
Under-sizes compared to other techniques if non-spherical

# Sedimentation Issues

- **Comparison of Brownian Motion and Gravitational Settling** (Movement in 1 second; Particle density of 2.0 grams/cc)

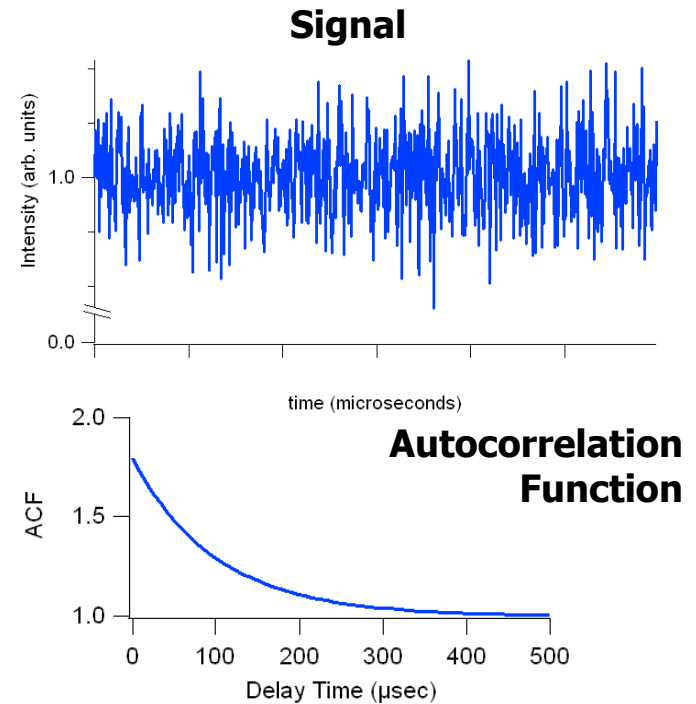
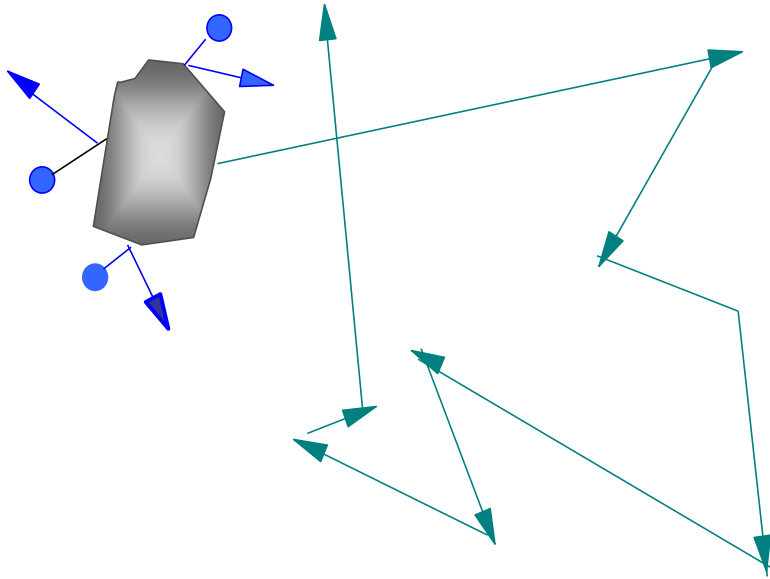
Particle Diameter (In micrometers)	Movement due to Brownian Motion		Movement due to Gravitational Settling
0.01	2.36	>>	0.005
0.25	1.49	>	0.0346
0.50	1.052	>	0.1384
1.0	0.745	~	0.554
2.5	0.334	<	13.84
10.0	0.236	<<	55.4

- Below 1 micrometer, Brownian motion becomes an appreciable factor in particle dynamics. Gravity sedimentation may not be an appropriate measurement technique for very small particles.

# Dynamic Light Scattering

Most common technique for sub-micron sizing

Range: 1 nm – 1  $\mu\text{m}^*$



Particles in suspension undergo Brownian motion due to bombardment by solvent molecules in random thermal motion.

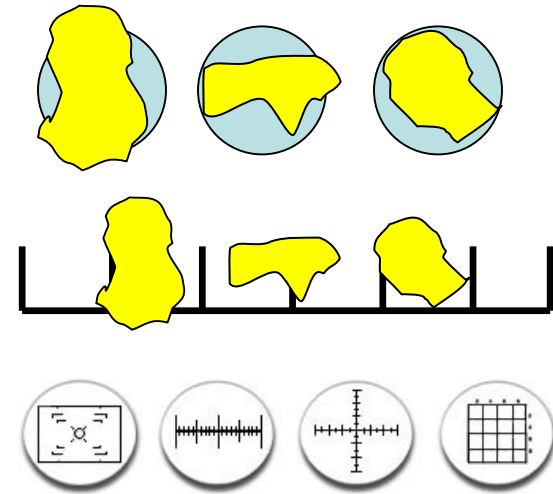
$$\textit{Stokes-Einstein} \quad R_H = \frac{kT}{6\pi\eta D}$$

\* Density dependent, when does settling become prominent motion?



# Manual Microscopy

- Count particles in a given field of view
- Use graticule to obtain size
- Repeat this process for a number of fields
- At least hundreds of particles must be sized



## Advantages:

- Simple
- Inexpensive
- Can see shape

## Disadvantages:

- Slow
- Measures very few particles
- Very tedious

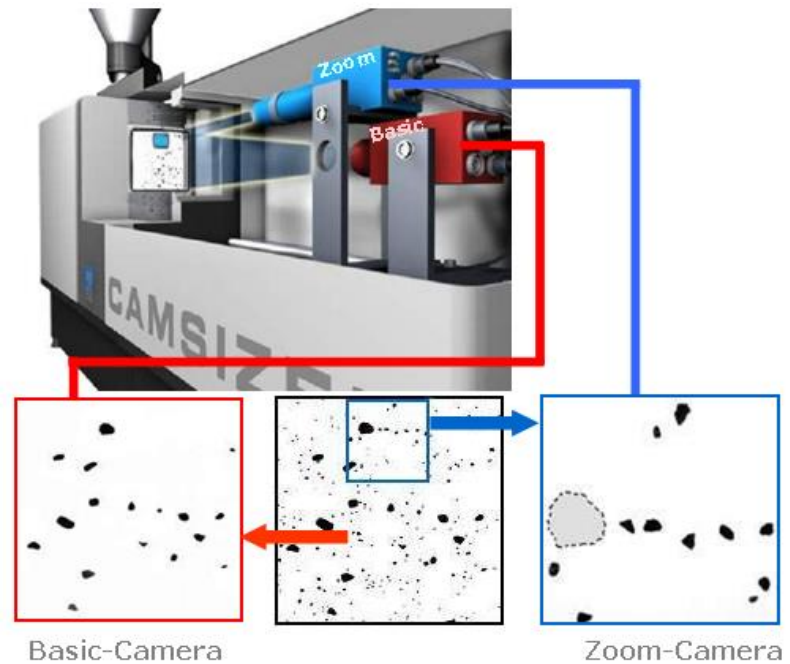
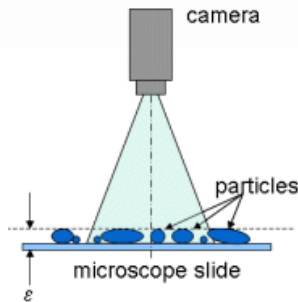
# Automated Microscopy

Static:

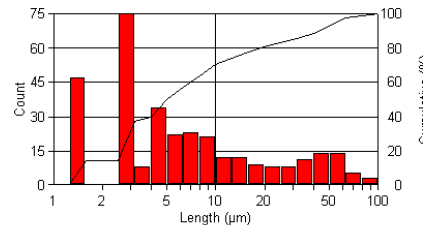
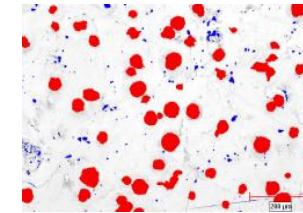
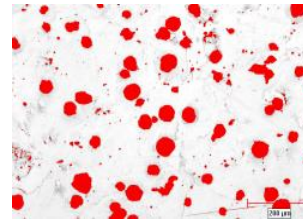
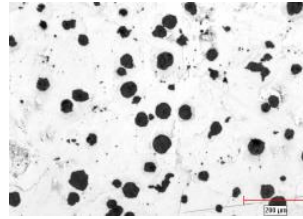
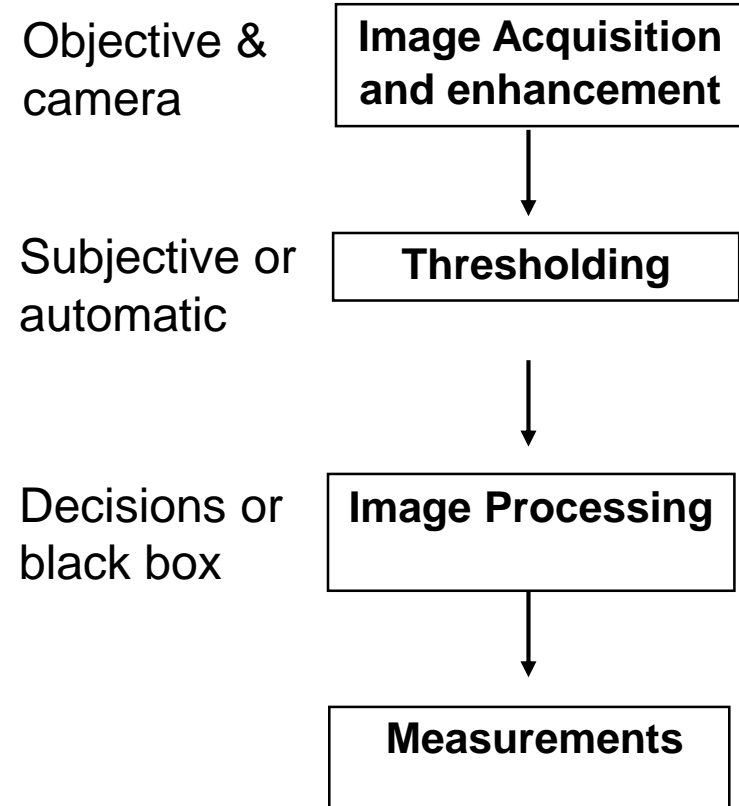
Particles fixed on slide,  
stage moves slide

Dynamic:

Particles flow past camera(s)



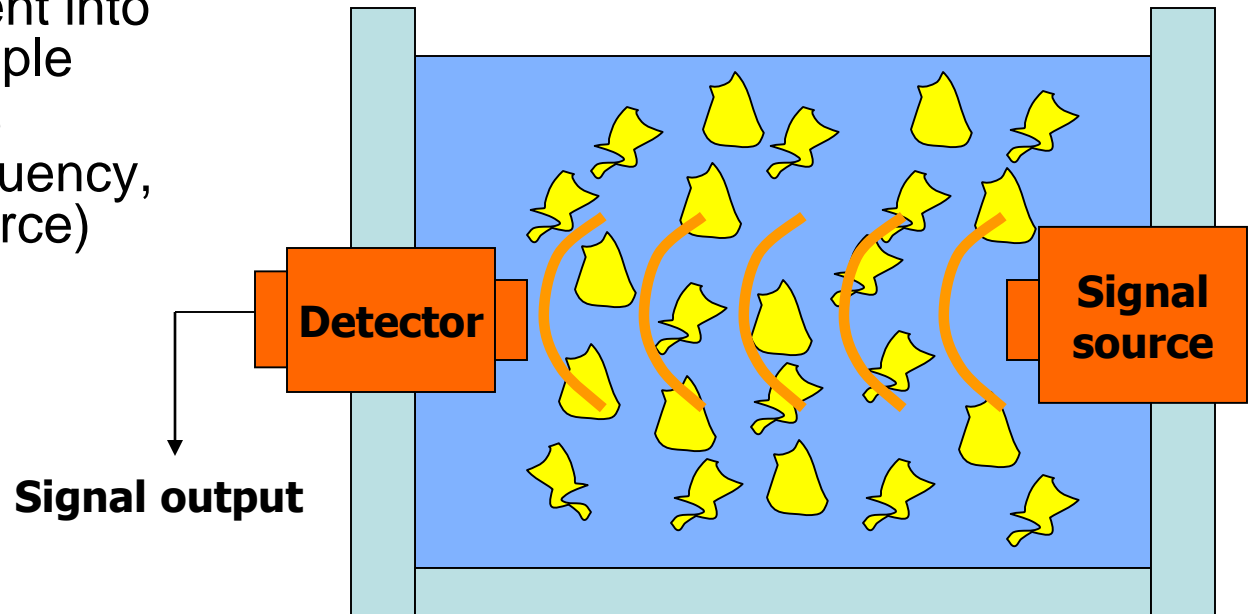
# Automated Microscopy



- Advantages:
  - Quick size + shape info
  - Statistically valid
  - High resolution
  - Particle images
- Disadvantages:
  - Expense
  - Knowing which numbers are important

# Acoustic Spectroscopy

- Acoustic signal sent into concentrated sample
- Detector measure attenuation  $f$  (frequency, distance from source)



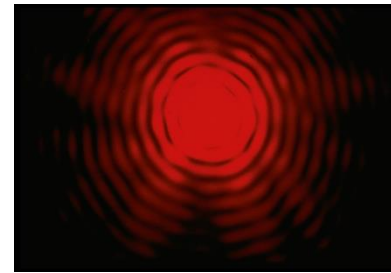
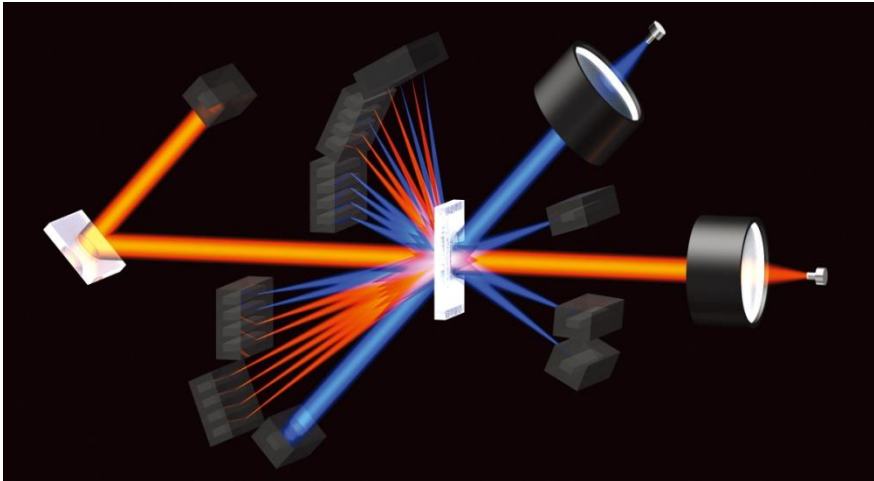
## Advantages:

- Can accommodate high sample concentrations (no dilution)
- Rheological properties
- Also measure zeta potential

## Disadvantages:

- Need at least 1 wt% particles
- Need to know wt%
- Minimum sample = 15 ml

# Laser Diffraction



- Converts scattered light to particle size distribution
- Quick, repeatable
- Powders, suspensions
- Most common technique

# Key Points

- Particle Analysis is about distributions
- Define terms (results) exactly
  - Volume vs. Number
- Different techniques give different answers since they measure different things
  - All are correct...
- Discuss results in terms of technique.

Thank you

# Thank you

Omoshiro-okashiku  
Joy and Fun

おもしろおかしく  
ありがとう



감사합니다

Cảm ơn

ありがとうございました

Dziękuję

धन्यवाद

Grazie

Merci

谢谢

நன்ற

ขอบคุณครับ

Obrigado

Σας ευχαριστούμε

Tack ska ni ha

شكرا

Большое спасибо

Danke

Gracias