Particle Size Data Interpretation and Communication

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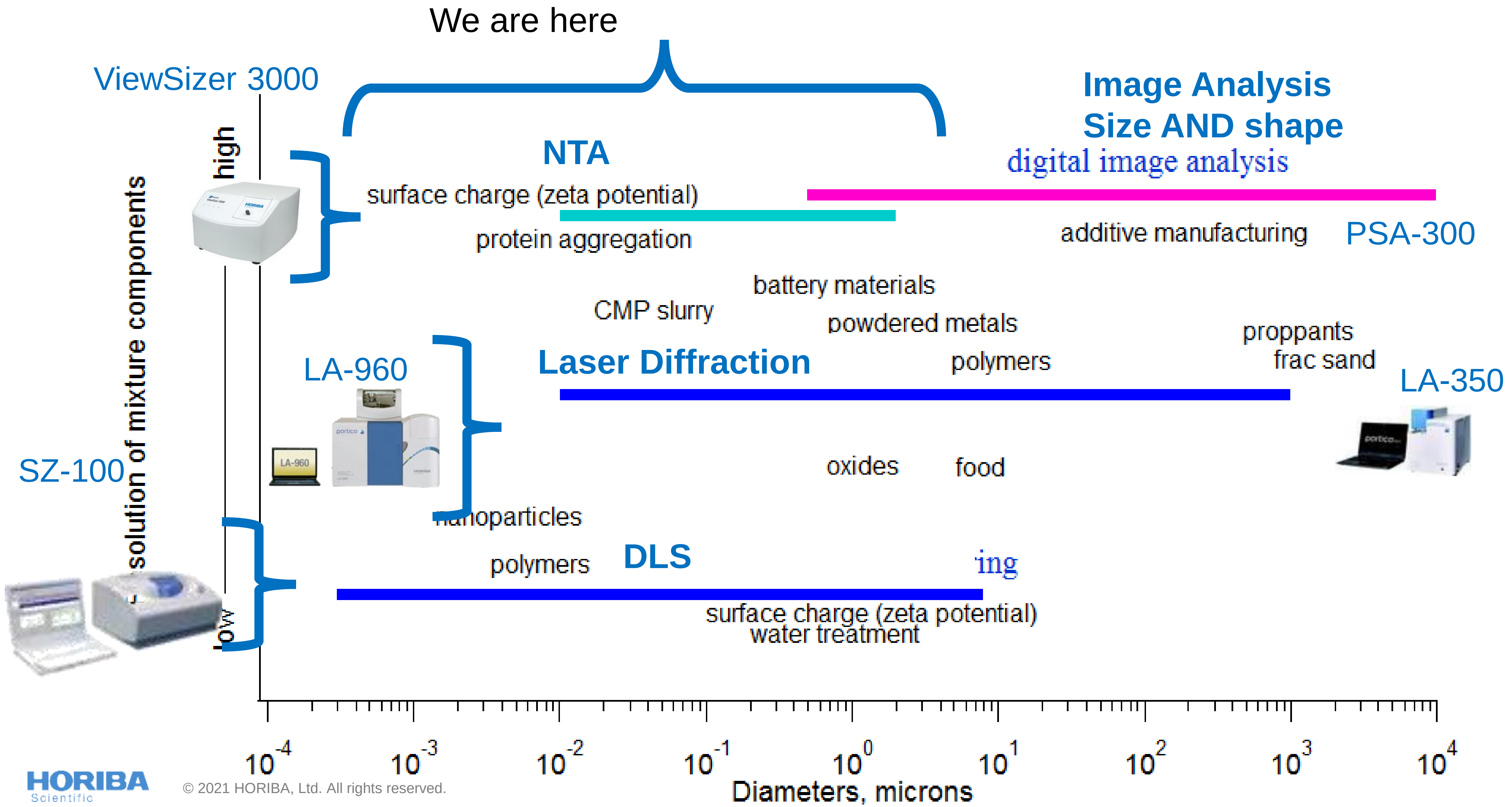
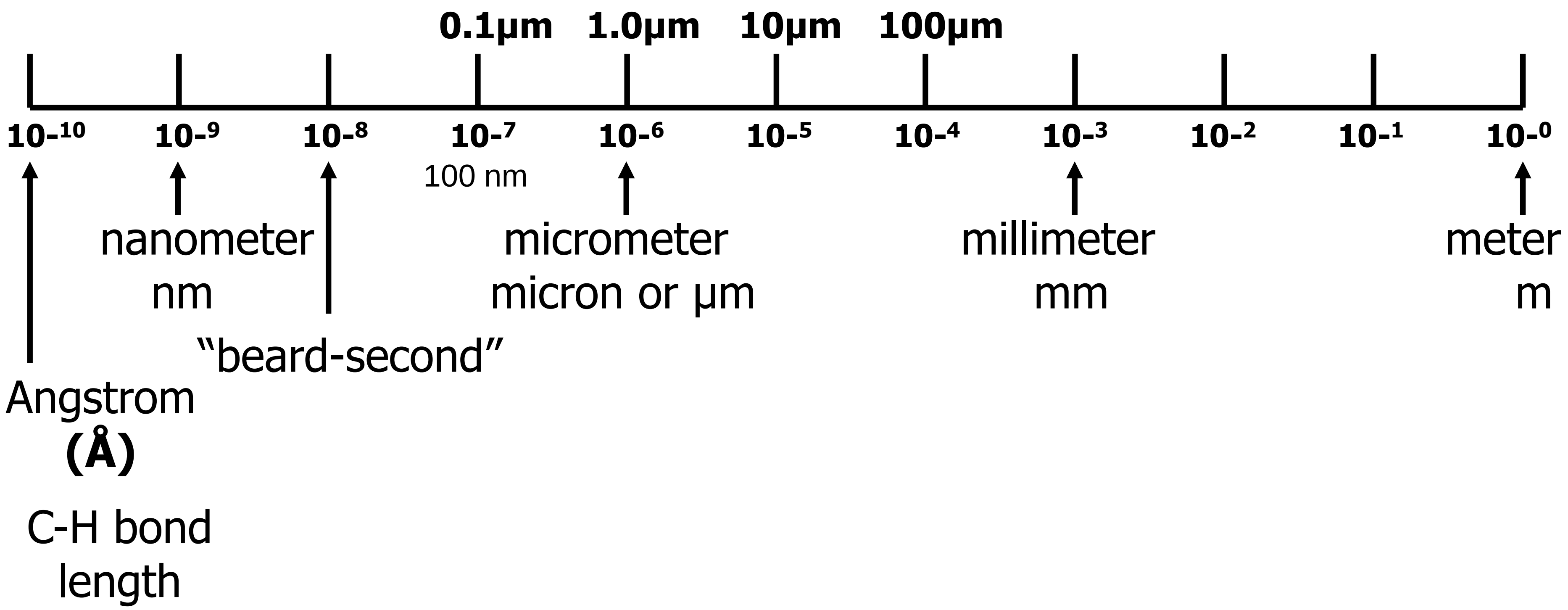
Analysis Techniques



Size Terminology

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.



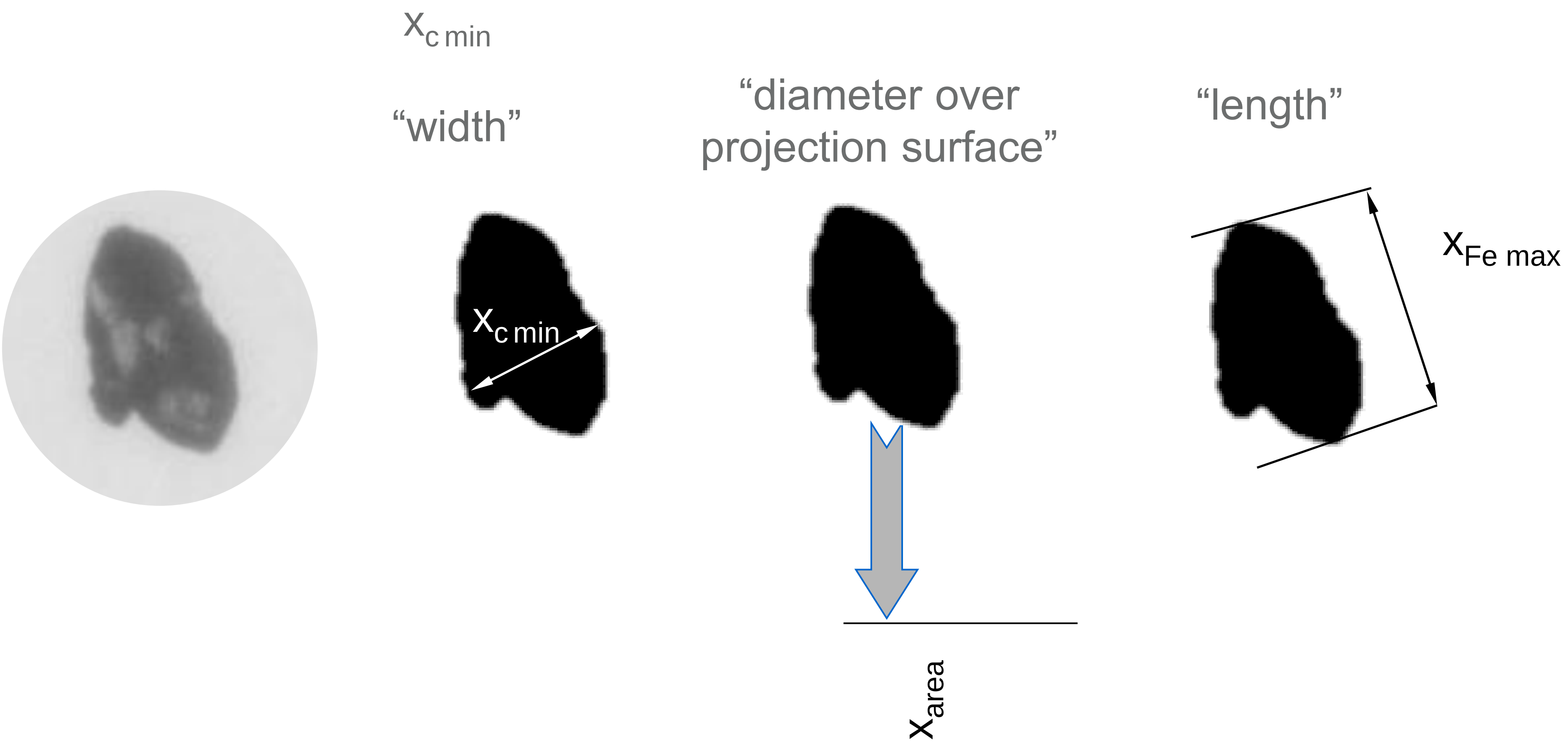
Fun tip: Describing your work in terms of beard-seconds make it much more interesting at parties.

Sieve Sizes

Microns	US Mesh	Tyler Mesh
4750	4	4
1180	16	14
250	60	60
63	230	250

As size goes down, mesh goes up.

What is the most meaningful size?

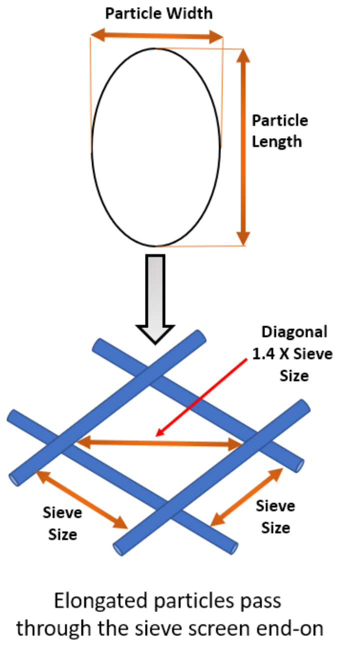


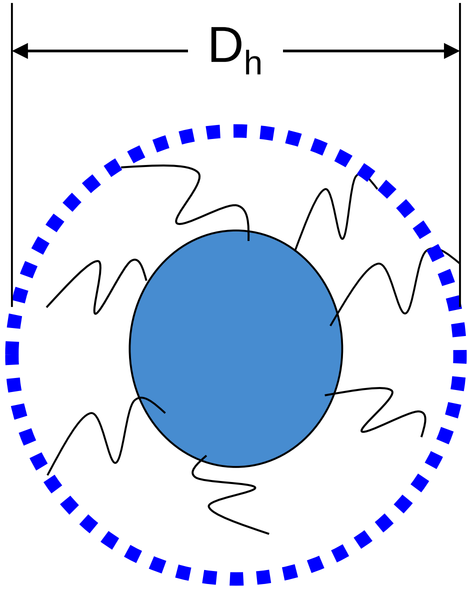
different size definitions → **different results**

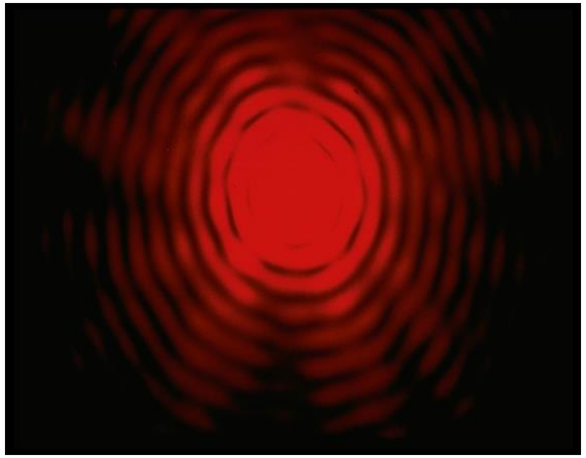
HORIBA Scientific

What size can you measure?

Economics means many size parameters are a little odd.







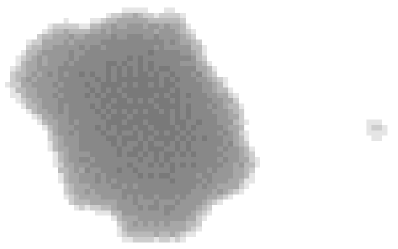
Fits through a grid
Sieve

Same viscous drag
Hydrodynamic Diameter
DLS, NTA, Centrifugation

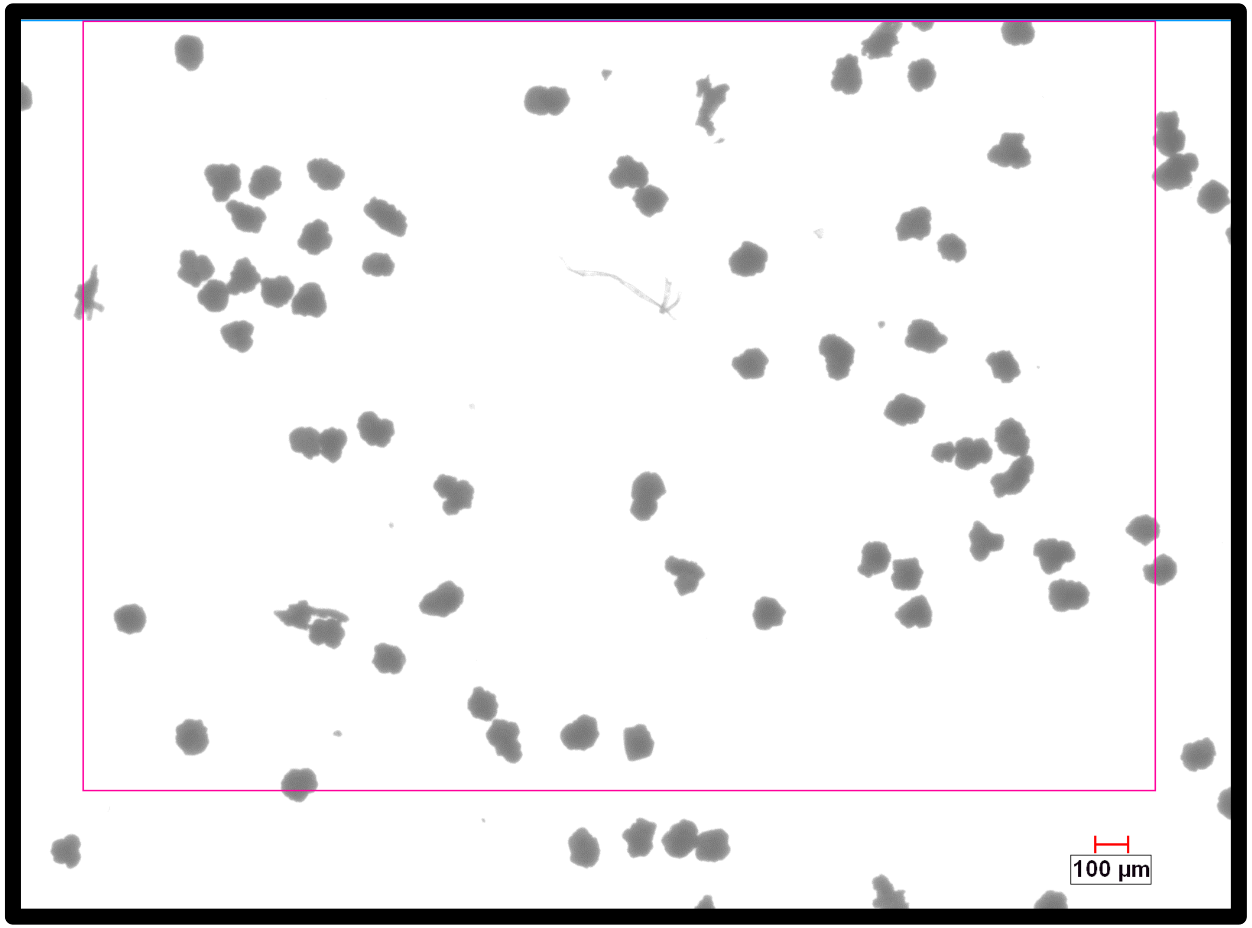
Same scattering pattern
Laser diffraction

Particle distribution

So far talked trying to get a size from one particle.

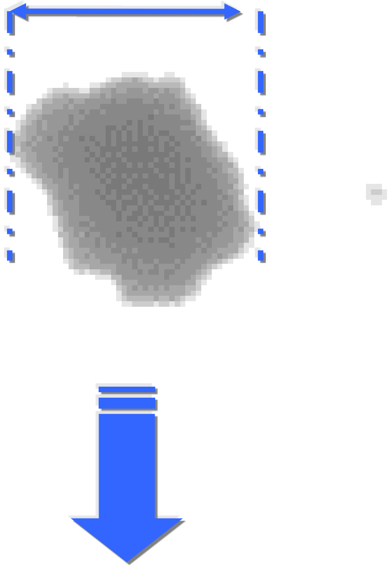


A real sample is a mixture of many sizes



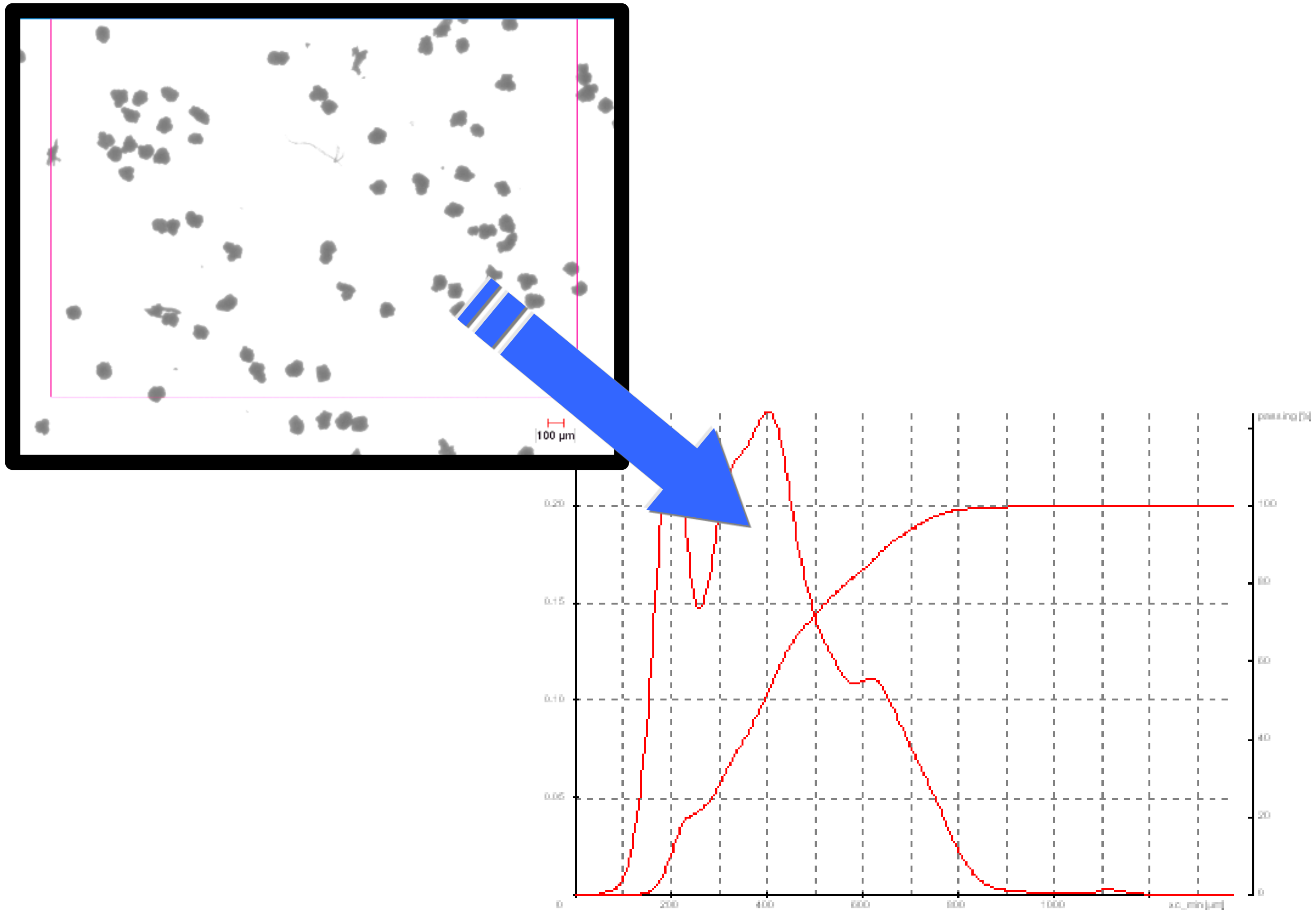
Things are more complicated

Particle Size



4 microns

Particle Size Distribution

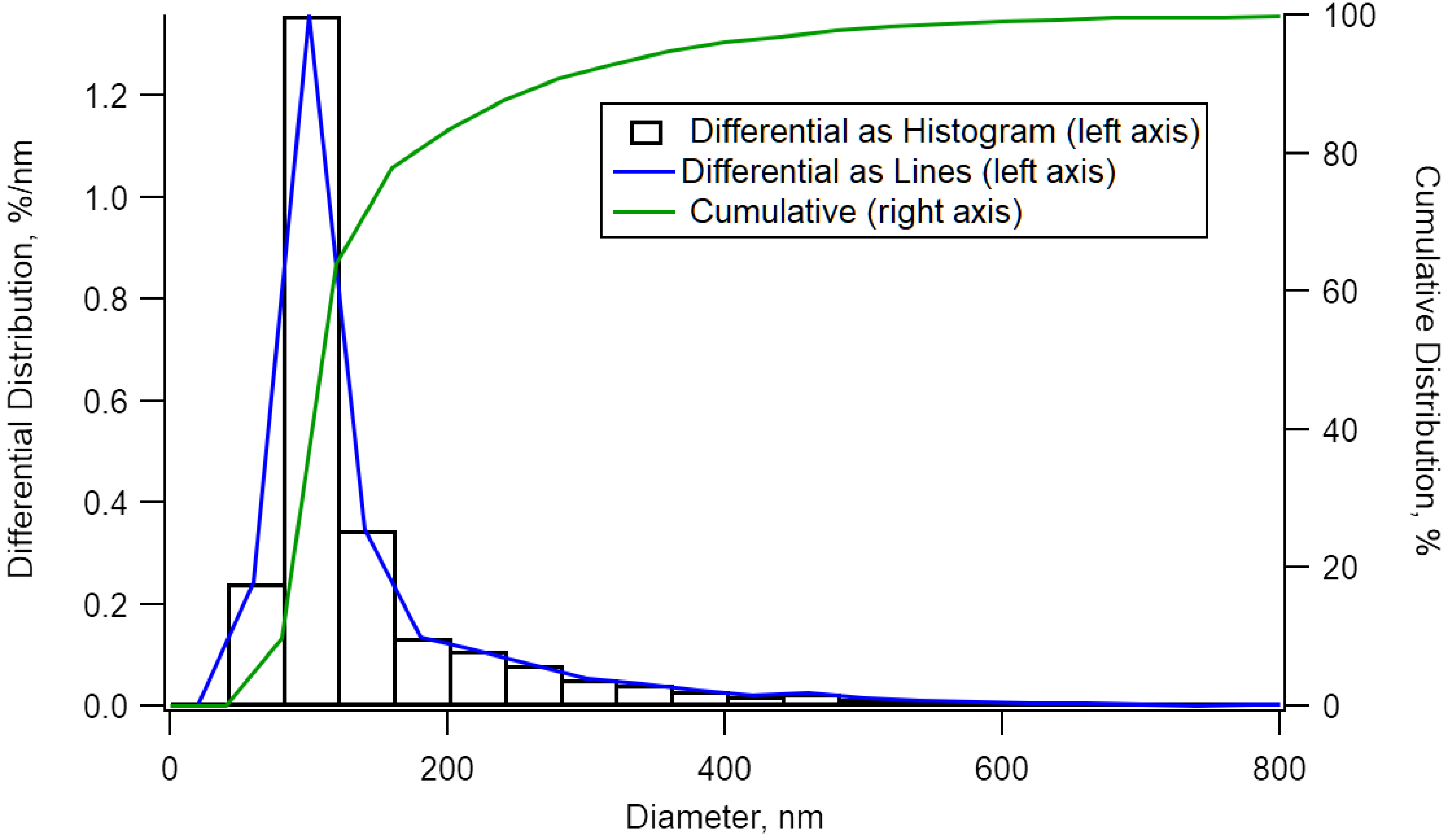


Showing a distribution

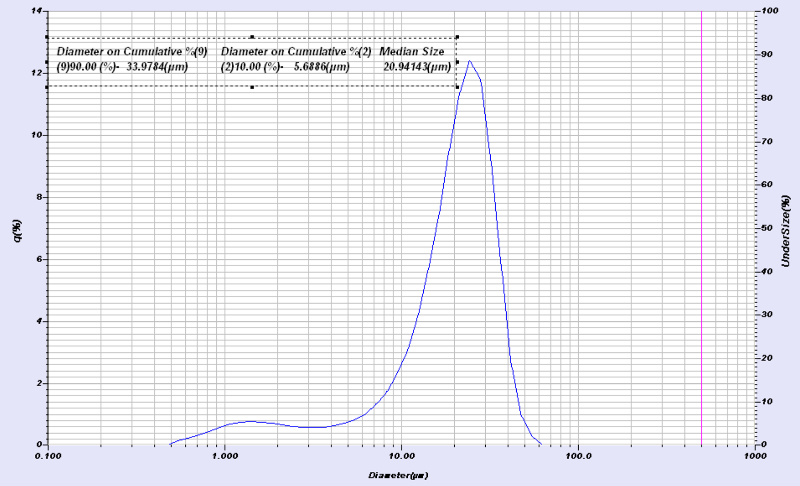
Displayed as a histogram, a line plot of the differential distribution, or as a cumulative plot.

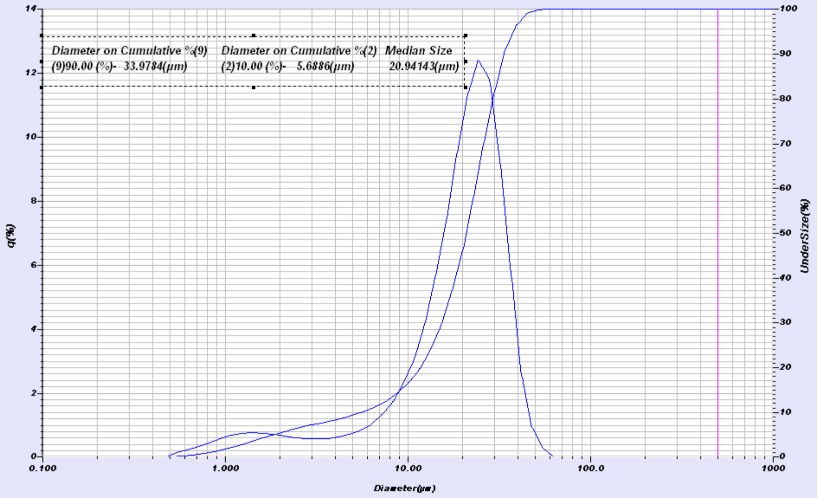
All represent the same data.

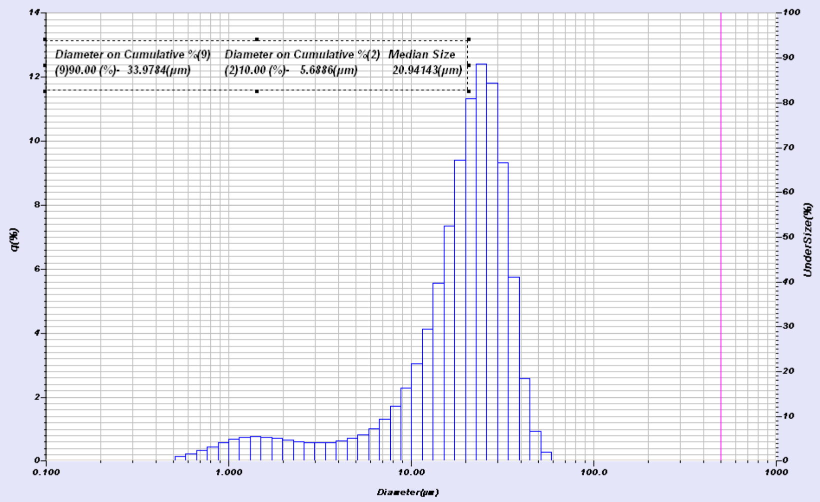
Histogram overlays do not look very good.

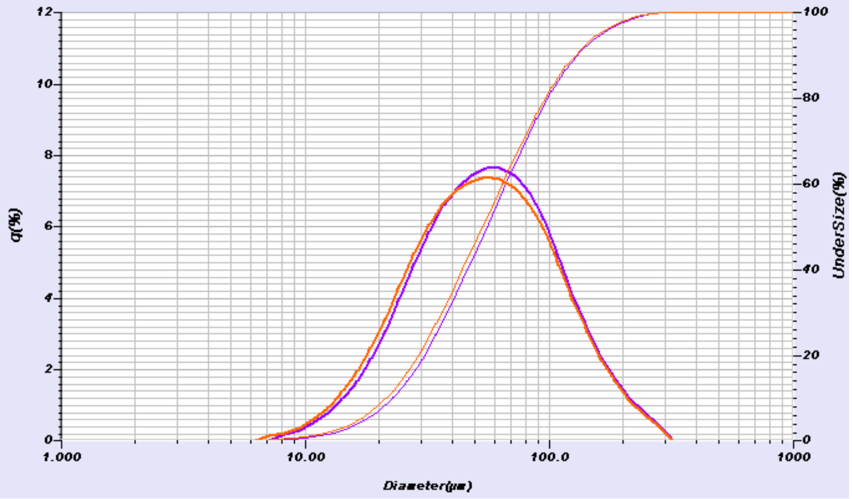


Your analyzer's displays





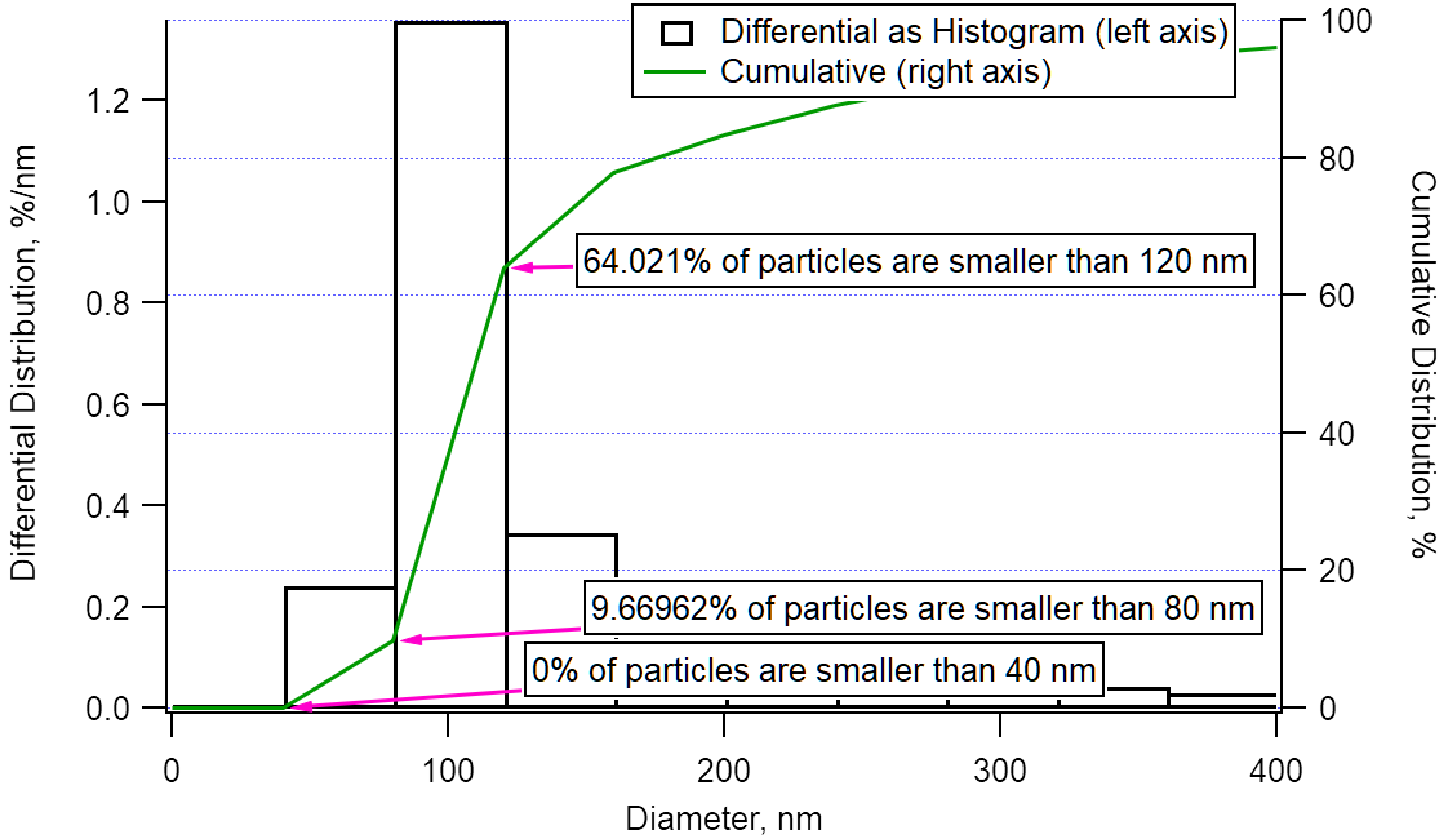




Interpreting a cumulative distribution

Cumulative distributions show the fraction of particles smaller than a particular size.

The plot on the right shows how to interpret the points of the cumulative distribution.



Summarize: Central values

Mean

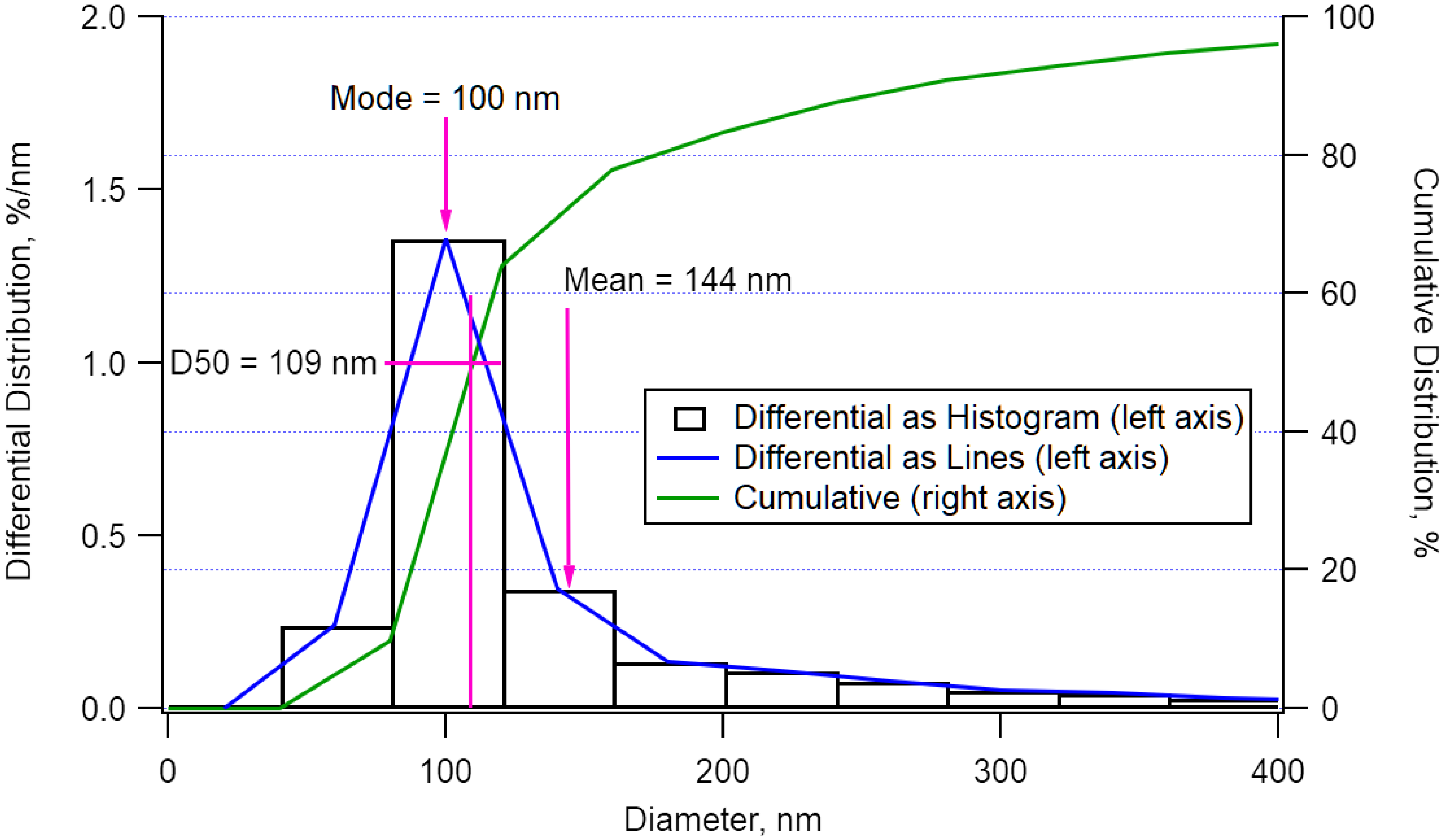
Weighted Average
Center of Gravity

Median

50% Point

Mode

Peak of the distribution
Most common value

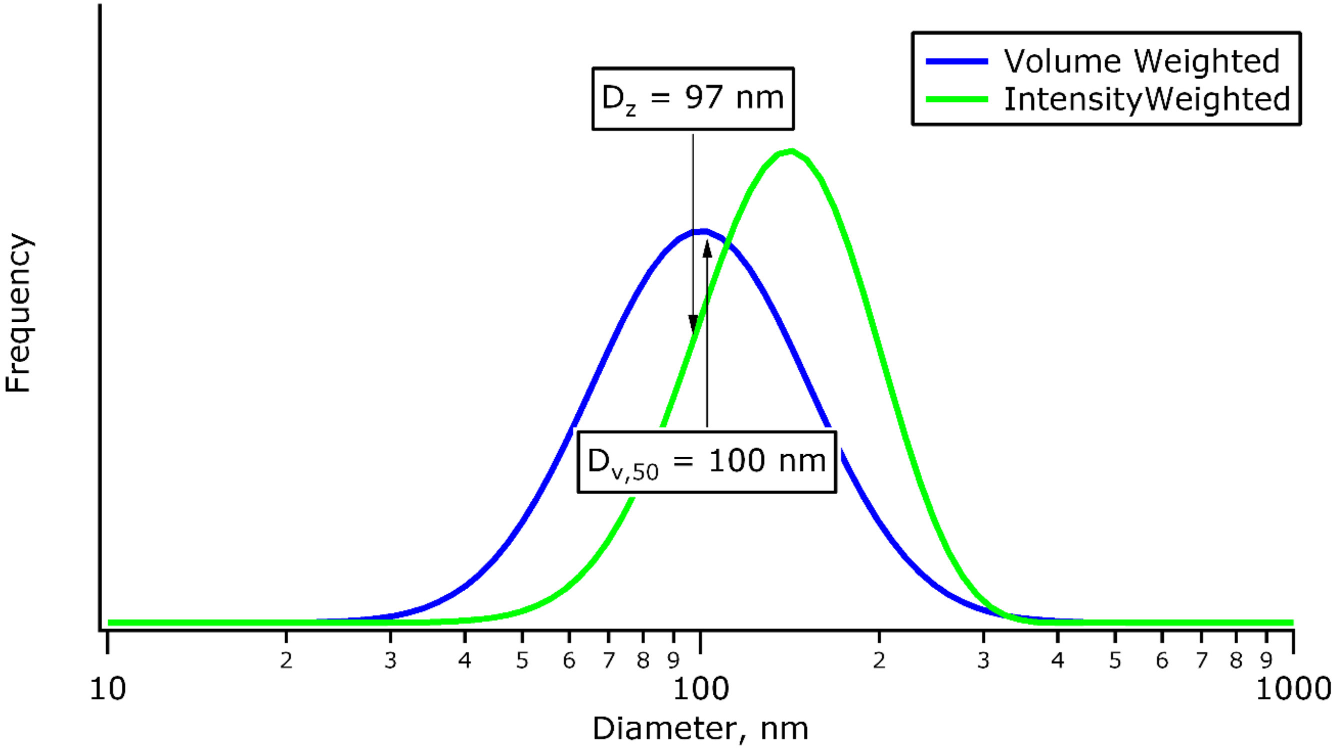


Z-average (DLS)

Size determined from intensity weight diffusion coefficient ~1/D

Intensity weighted harmonic mean size

$$1/D_z = \sum D_i S_i / \sum S_i$$



D_z = z-average
S_i = total scattering from all of species i
D_i = Diameter of species all

As size goes up, so does D_z.

What are D values?

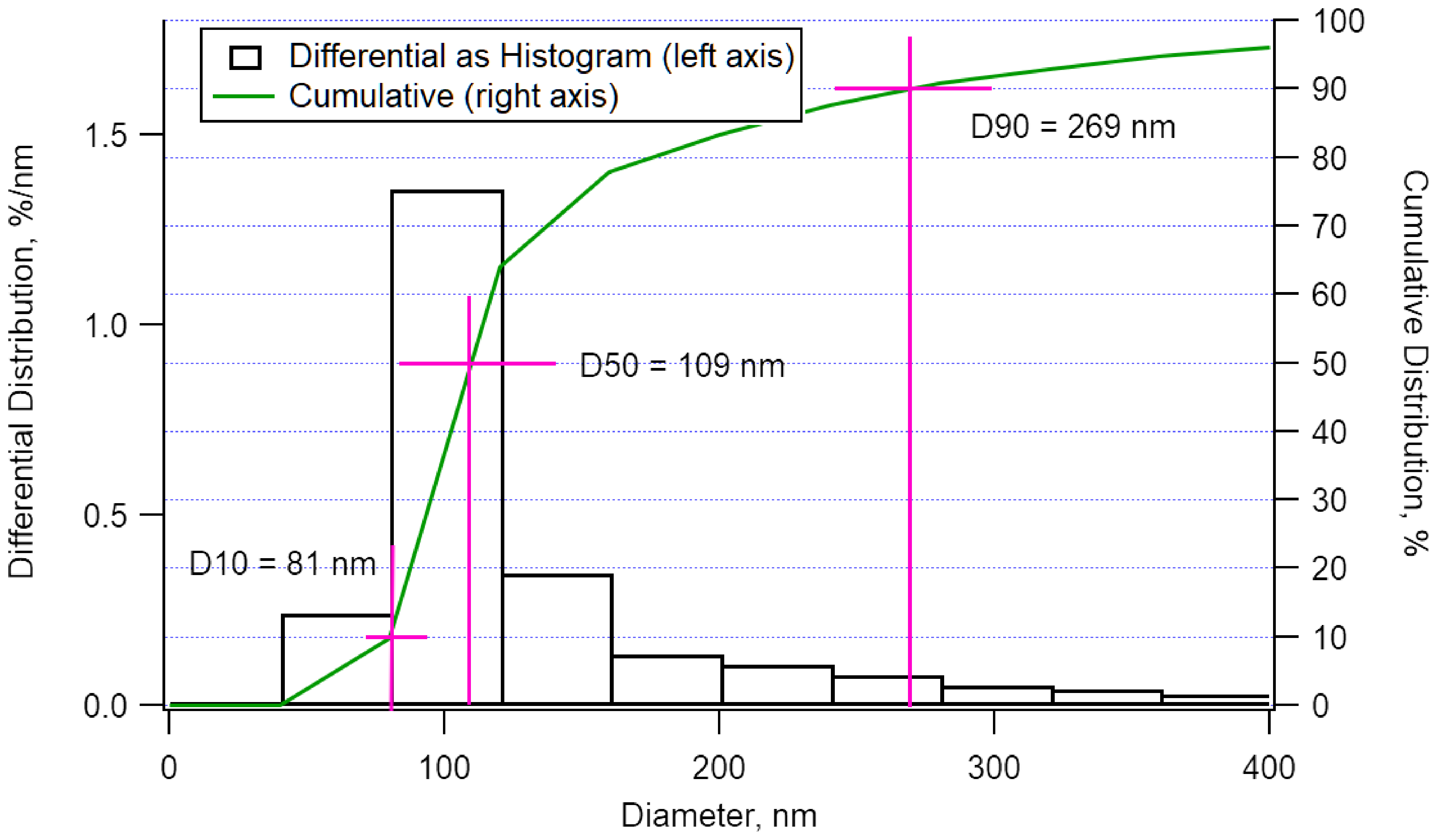
Here we show how to extract “D” values.

Use the cumulative distribution to find size corresponding to fraction.

For D10, 10% of particles are smaller than 81 nm.

D50 is the median of the size distribution (half of particle larger, half smaller).

Note D90 is further from D50 than D10.

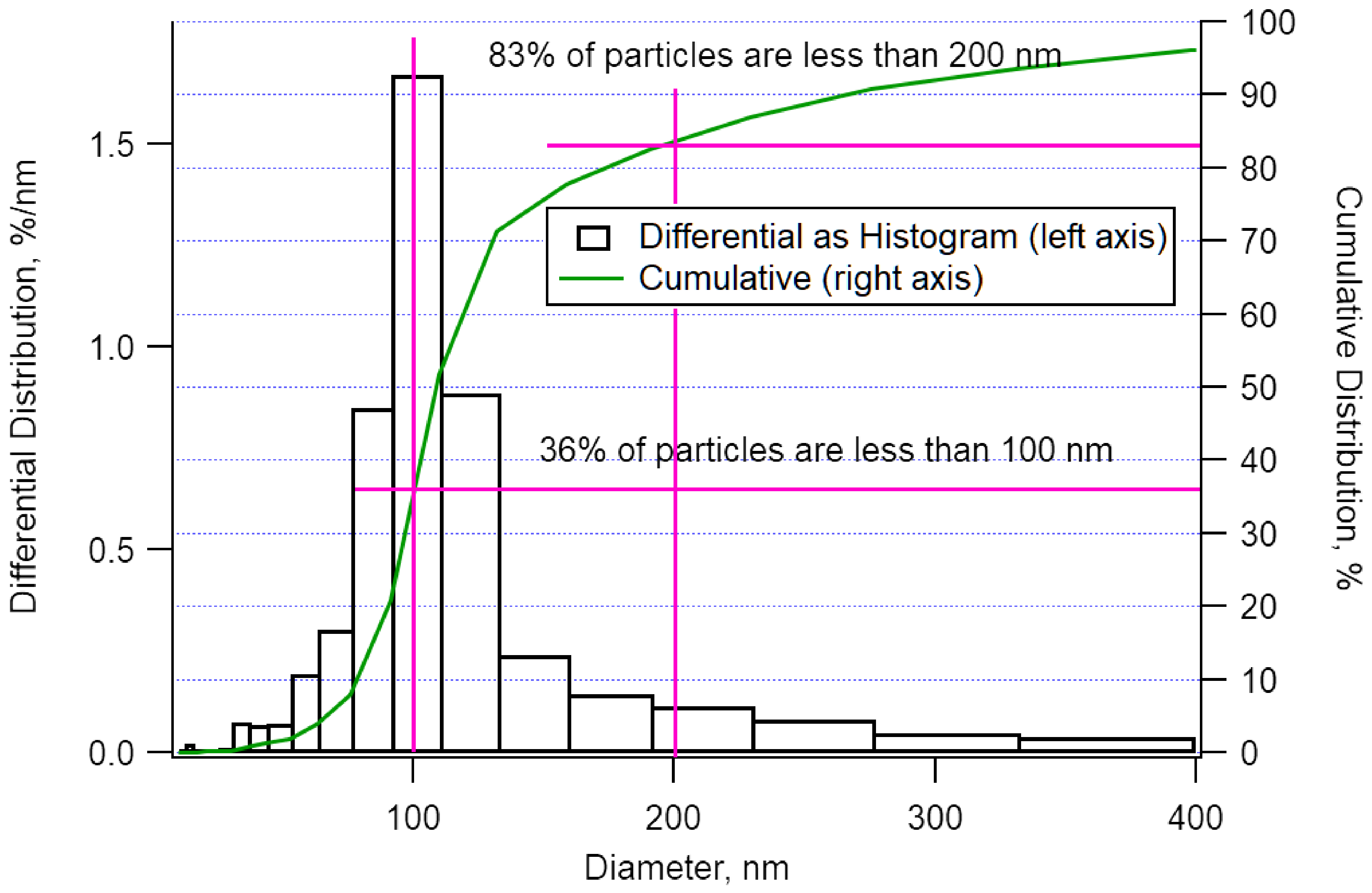


% less than

Another way of expressing the data is % less than.

For example, you may wan to find the fraction of particles that are smaller than a cutoff value (say a nominal filter size).

This is the D value interpretation reversed.

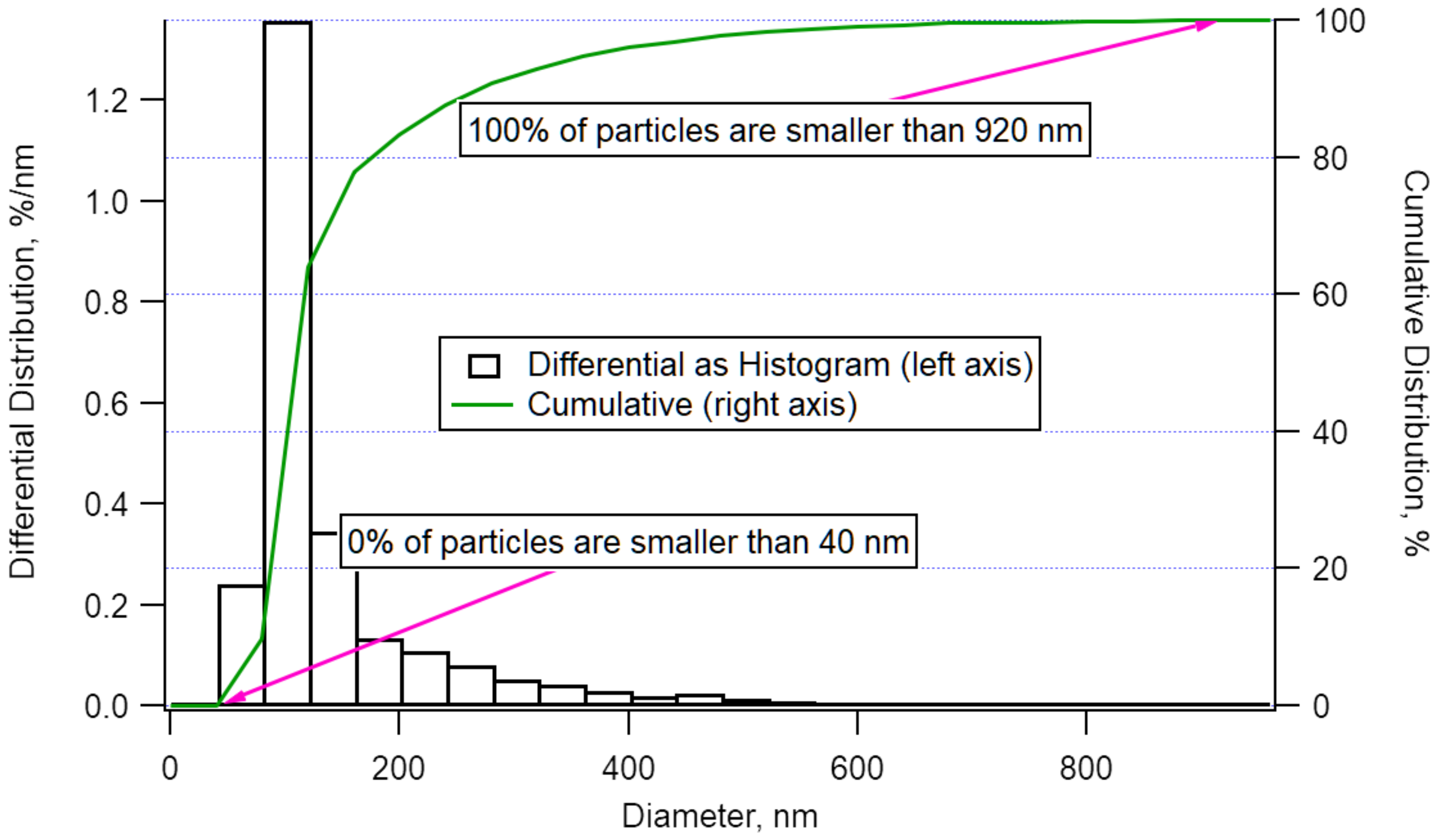


Why not use D100?, D0?

The graph shows there are no particles less than 40 nm. And there are no particles larger than 920 nm. That is,
D0= 40 nm and D100 = 920 nm.

BUT, this is data from your <u>sample</u>.

To really claim you have no particles of a size, you have to measure all of your particles. That is generally not reasonable.

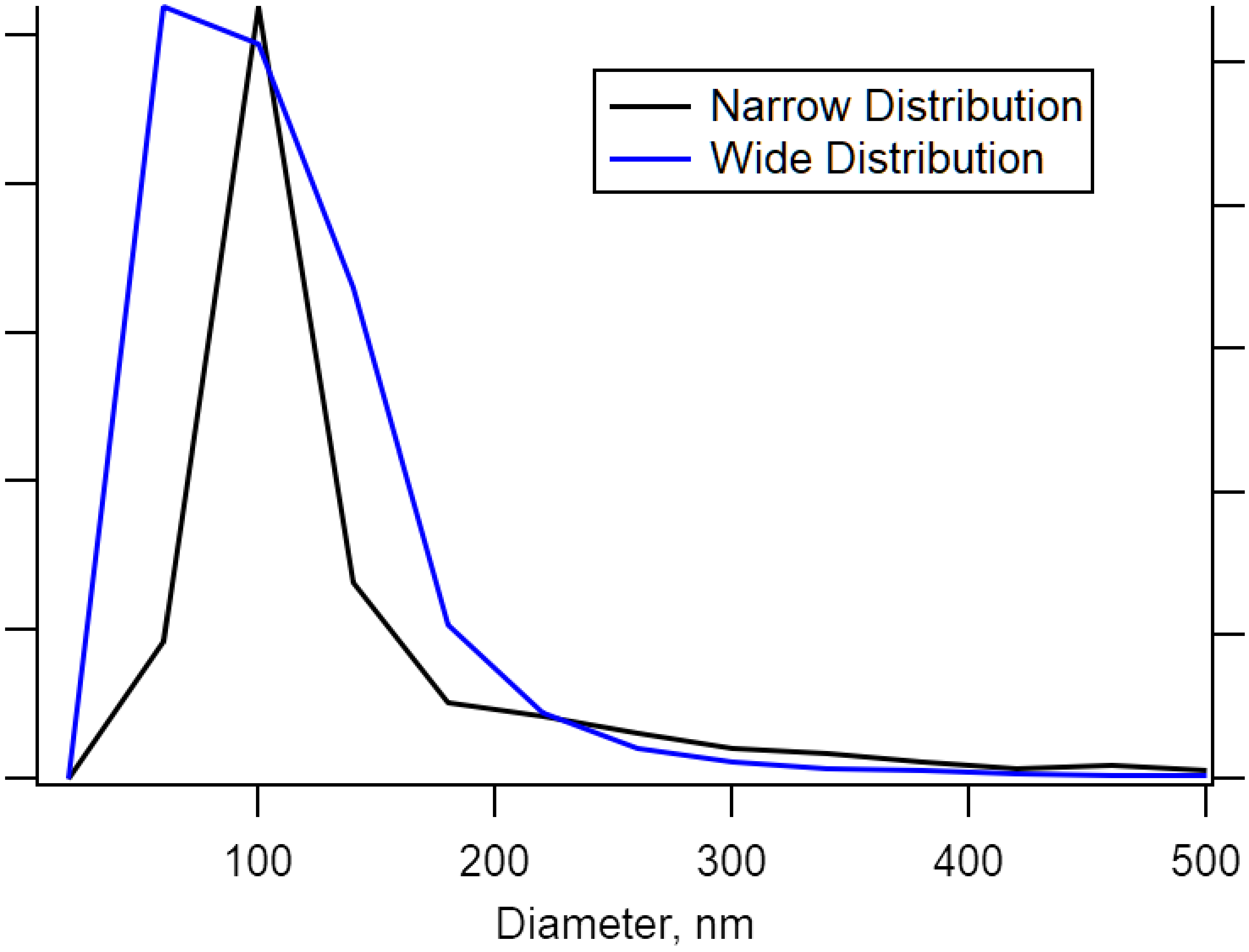


What about width?

Monodisperse: all particles the same size.

Narrow: Not a wide range of sizes

Wide: Broad (a decade?) range of sizes

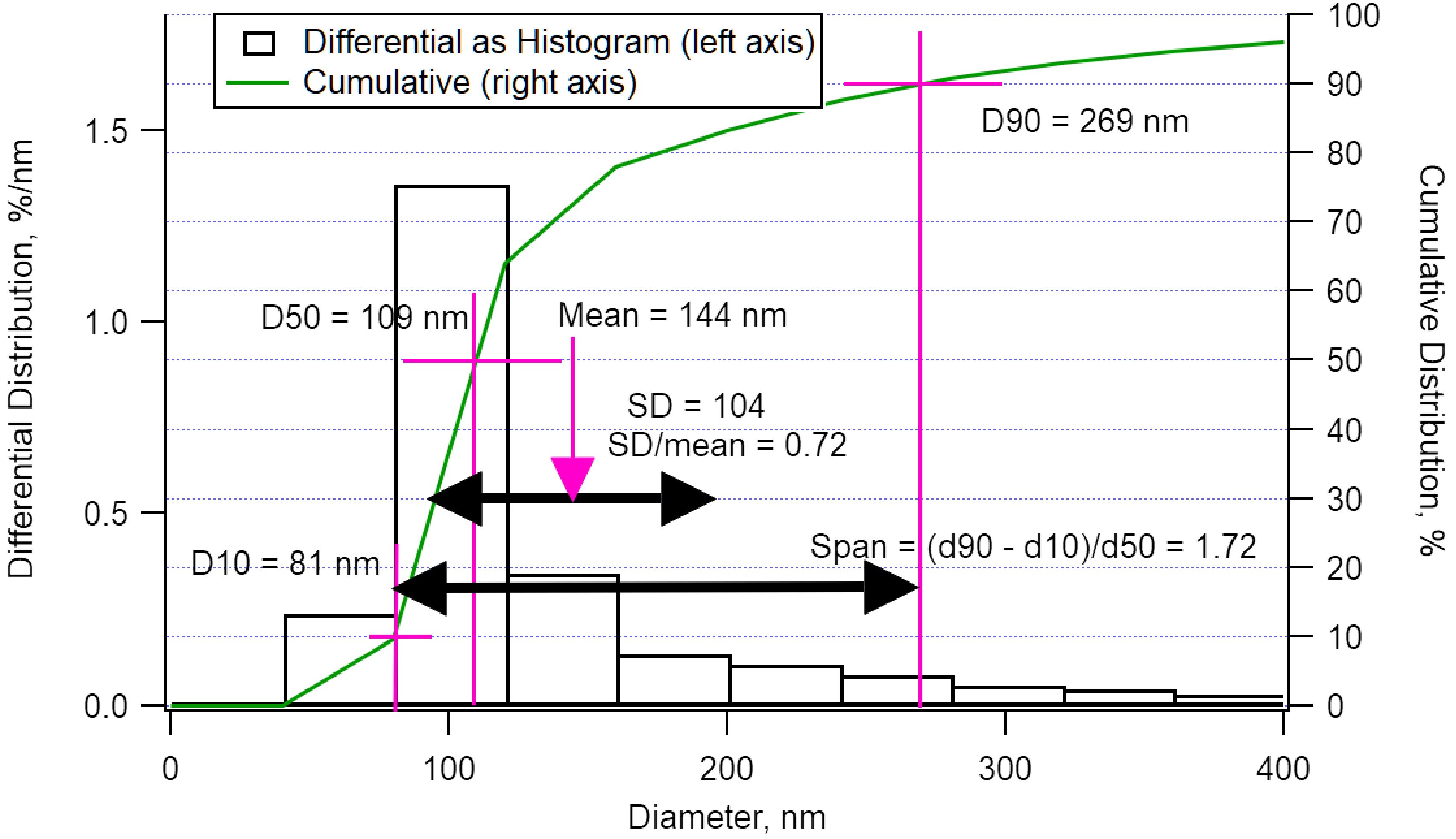


Distribution Width

Width is also be used to describe a distribution.

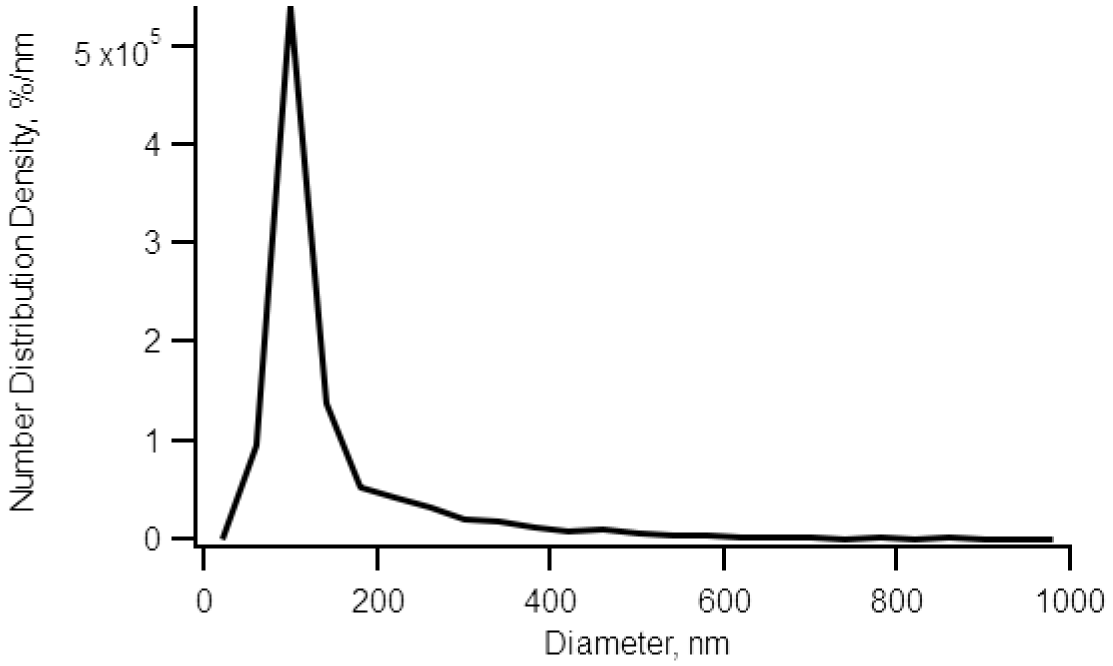
Values can include
-Standard Deviation
-Span (D90-D10)/D50
    or (D85-D15)/D50
-Geometric Standard Deviation

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

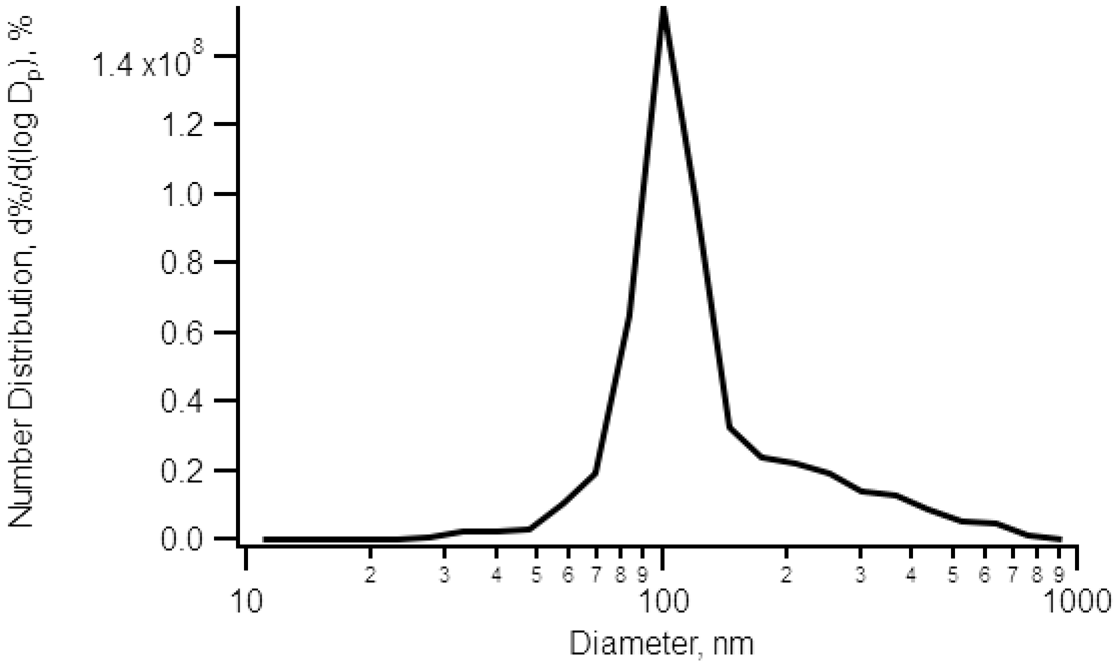


Linear vs logarithmic X axis

Linear X-Axis Distribution



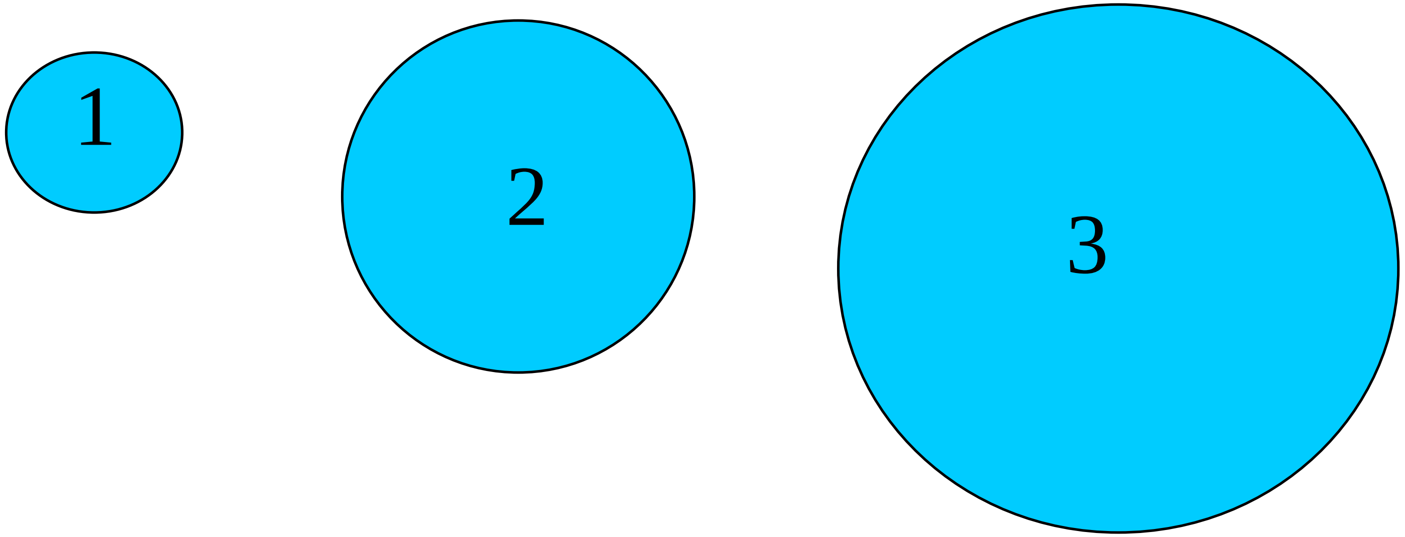
Logarithmic X-Axis Distribution



Same number of bins for both over same range.
Note that log data uses equal areas convention (ISO-9276-1).
That is, we plot dC/d(logX)

What does Mean mean?

Three spheres of diameters 1,2,3 units



What is the average size of these spheres?

Average size = (1+2+3) ÷ 3 =2.00

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

Many possible mean values

$$X_{nl} = D[1,0] = \frac{1+2+3}{3} = 2.00$$

Number weighted mean Diameter (length)

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

Mean surface diameter

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

Mean volume diameter

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

$$X_{sv} = D[3,2] = \frac{1+8+27}{1+2+3} = 2.57$$

Volume/surface mean,

$$X_{vm} = D[4,3] = \frac{1+16+81}{1+8+27} = 2.72$$

Volume weighted mean diameter

Moment Ratios: ISO 9276-2

For your reference

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

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

Common summations

$$D[1,0] = \frac{d_1\ (d_1^0) + d_2\ (d_2^0) + d_3\ (d_3^0) + \ ....}{(d_1^0) + (d_2^0) + (d_3^0) + \ ...} = \frac{d_1\ + d_2\ + d_3\ + \ ....}{1 + 1 + 1 + \ ...}$$

$$D[3,2] = \frac{d_1\ (d_1^2) + d_2\ (d_2^2) + d_3\ (d_3^2) + \ ....}{(d_1^2) + (d_2^2) + (d_3^2) + \ ...}$$

$$D[4,3] = \frac{d_1\ (d_1^3) + d_2\ (d_2^3) + d_3\ (d_3^3) + \ ....}{(d_1^3) + (d_2^3) + (d_3^3) + \ ...}$$

D[3,2] Sauter mean

D[3,2] is the volume/surface mean or Sauter mean.

Diameter of a particle having the same volume/surface area ratio as the population of particles.

This is useful where specific surface area is important, such as catalysis, dissolution, and bioavailability

Volume 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.

Mean Diameter = Σ{q(J) × X(J)} / Σ{q(J)}
J : Particle Diameter Division Number
q(J) : Frequency Distribution Value (%)
X(J) : Jth Particle Diameter Range's Representative Diameter (μm).

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)

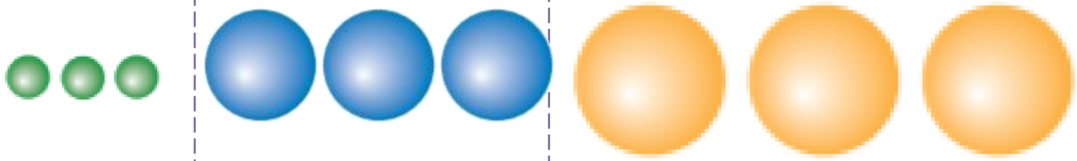
Number vs volume distributions

r = 1 µm
v = 4

r =2 µm
= 32

r = 3 µm
= 108

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

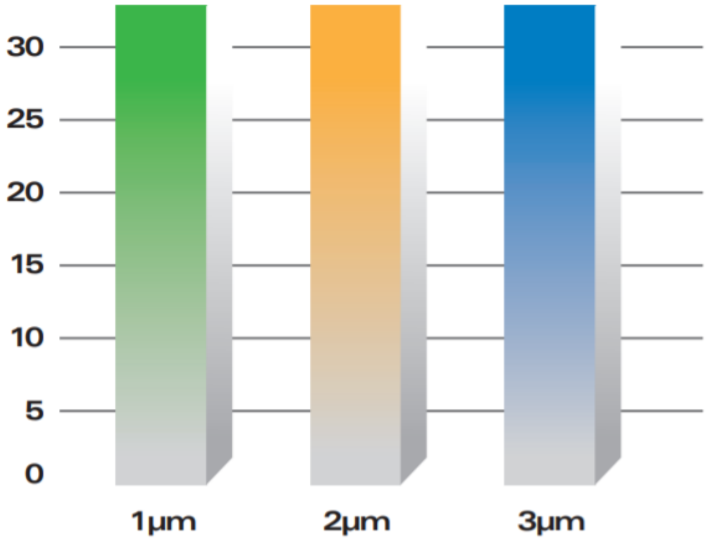


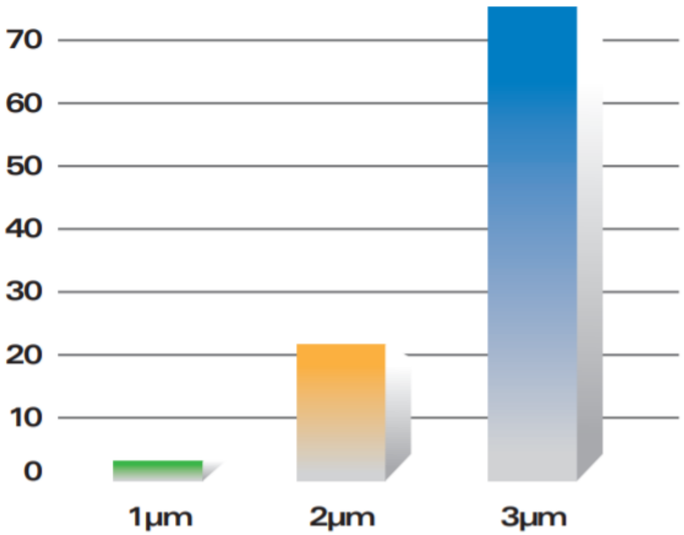
V*3 = 12
12/432=2.8%

96
96/432=22.2%

324
324/432=75%

Total = 12+96+324 = 432





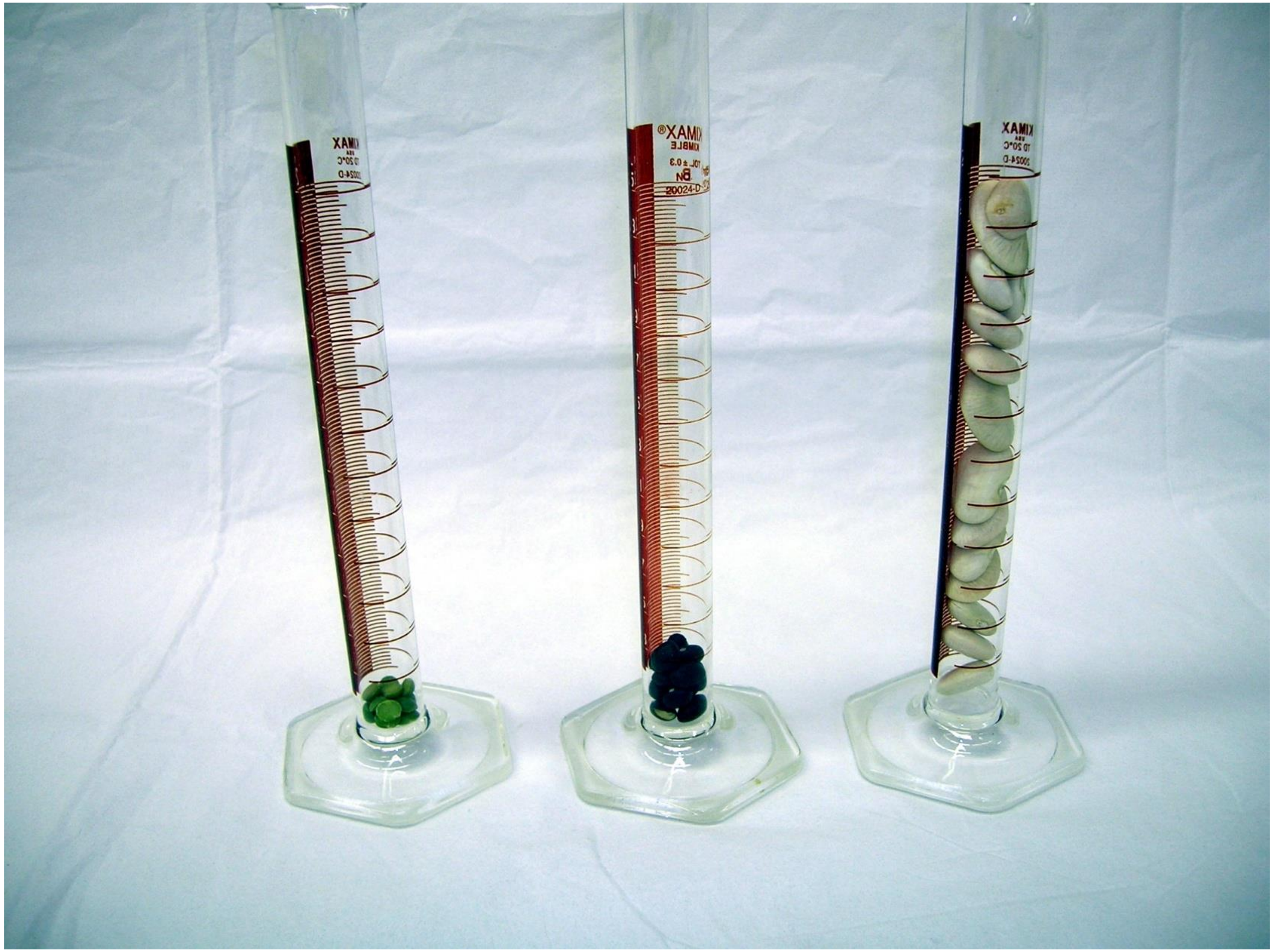
Beans (Lima, Black Bean, Mung Beans)

Equal volumes of beans

Different numbers of beans

Equal number of beans

Different volumes



Number vs volume distributions

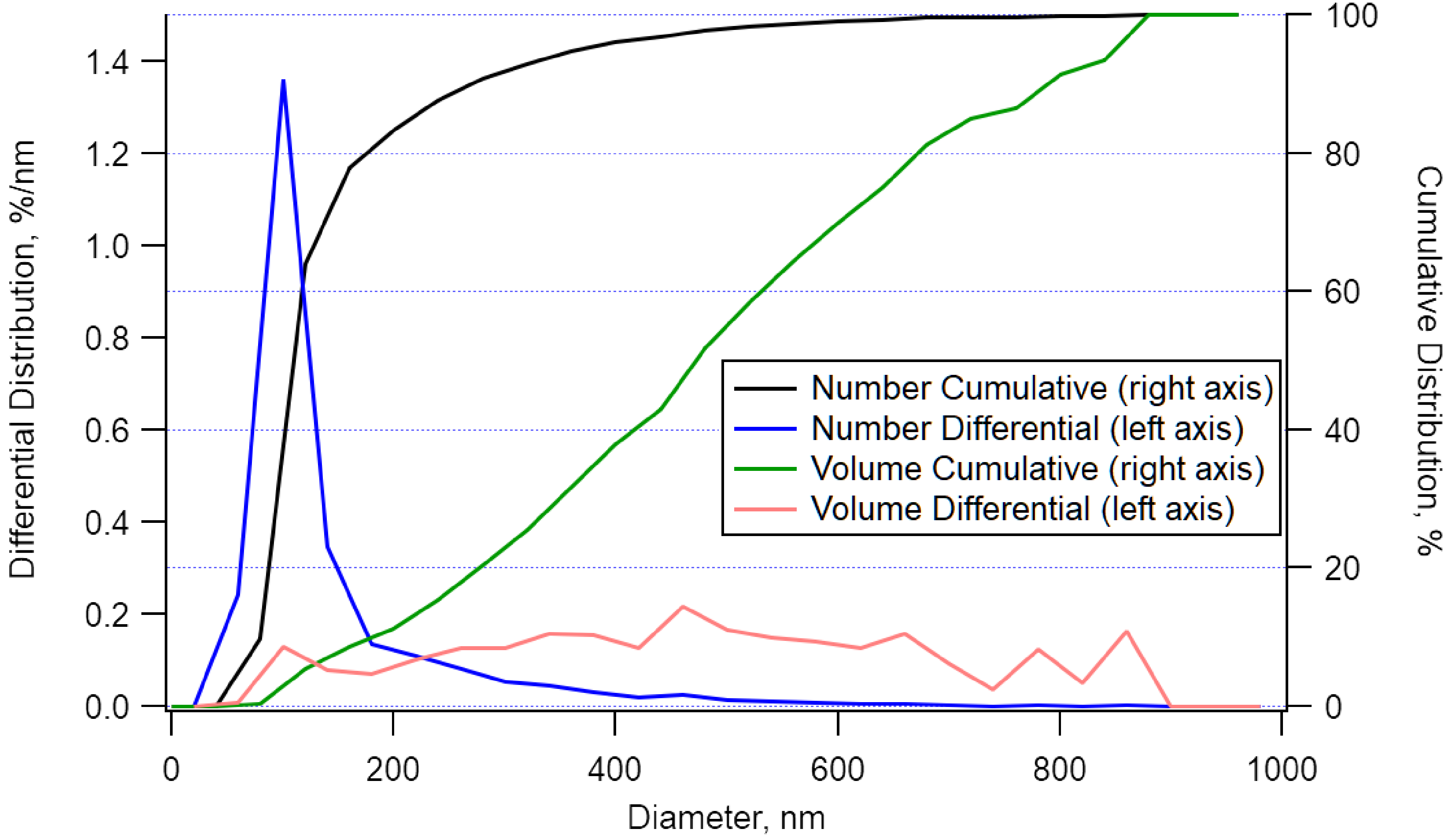
Number mean: 145 nm

Volume mean: 475 nm

Dn50: 109

Dv50: 468

Note you need to express the distribution base in your results!



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?

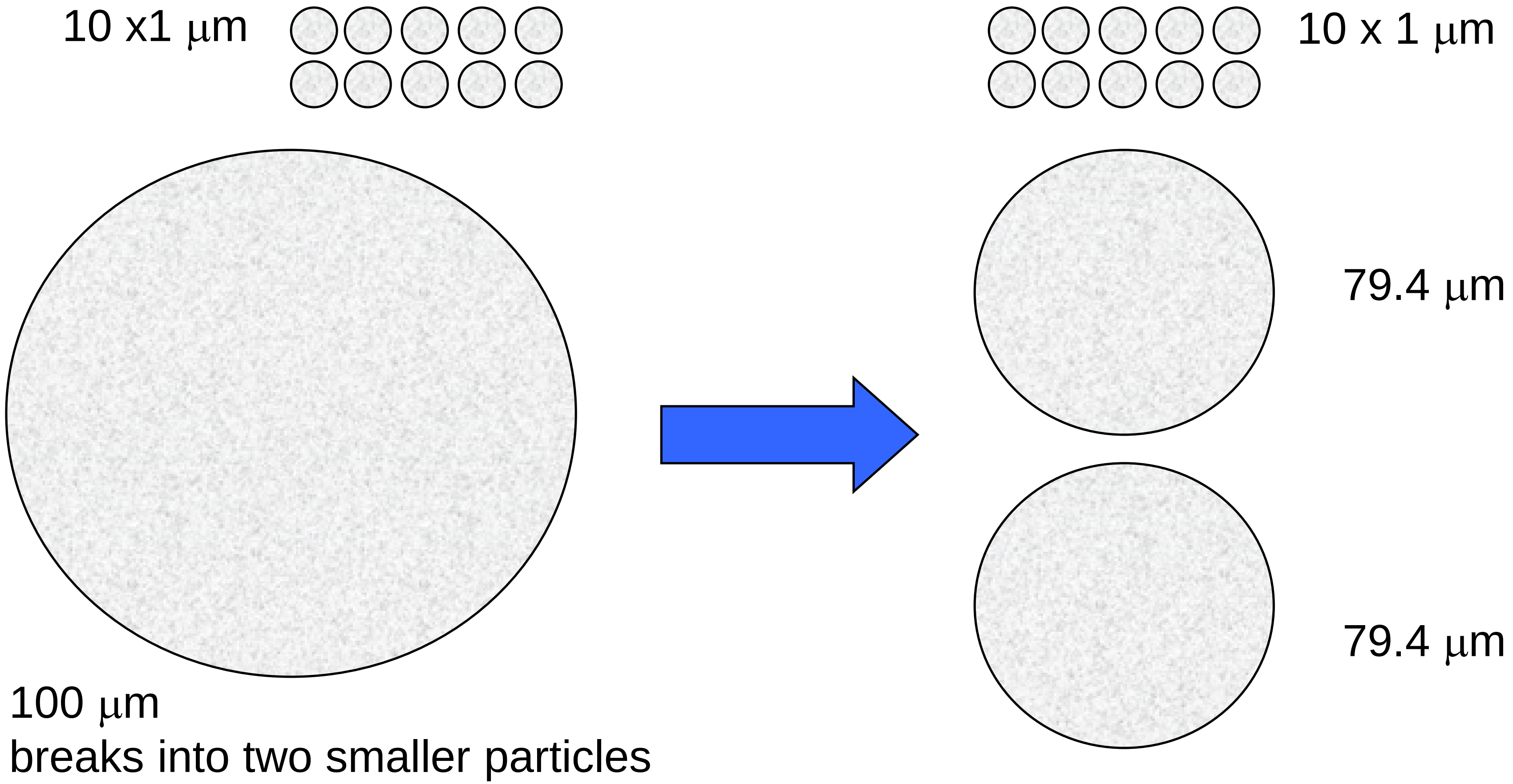
Particle size measurements often made to monitor a process

- 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



Size reduction: number mean

Ten particles of size 1; one of size 100 units

Number mean = D[1, 0] = (10*1 + 1*100)/11 = <u>10</u> 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?

Number Mean (broken = (10*1+2*79.37)/12 = <u>14.06</u> units

Surprise, surprise a 40.6% increase!

Size reduction: volume mean

Ten particles of size 1; one of size 100 units

Volume Moment Mean

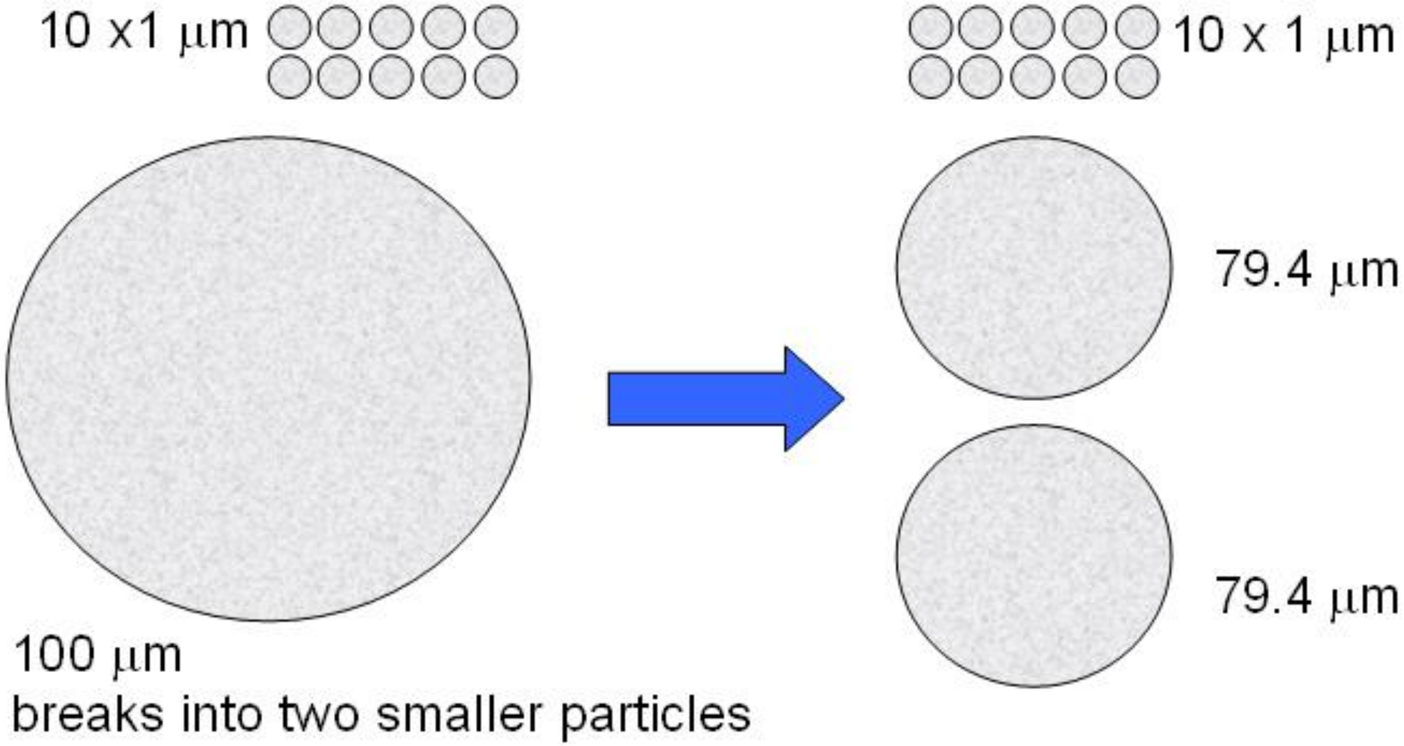
$D[4, 3] = (10*1^4 + 1*100^4)/(10*1^3 + 1*100^3) \sim \underline{100}$ units

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]?

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

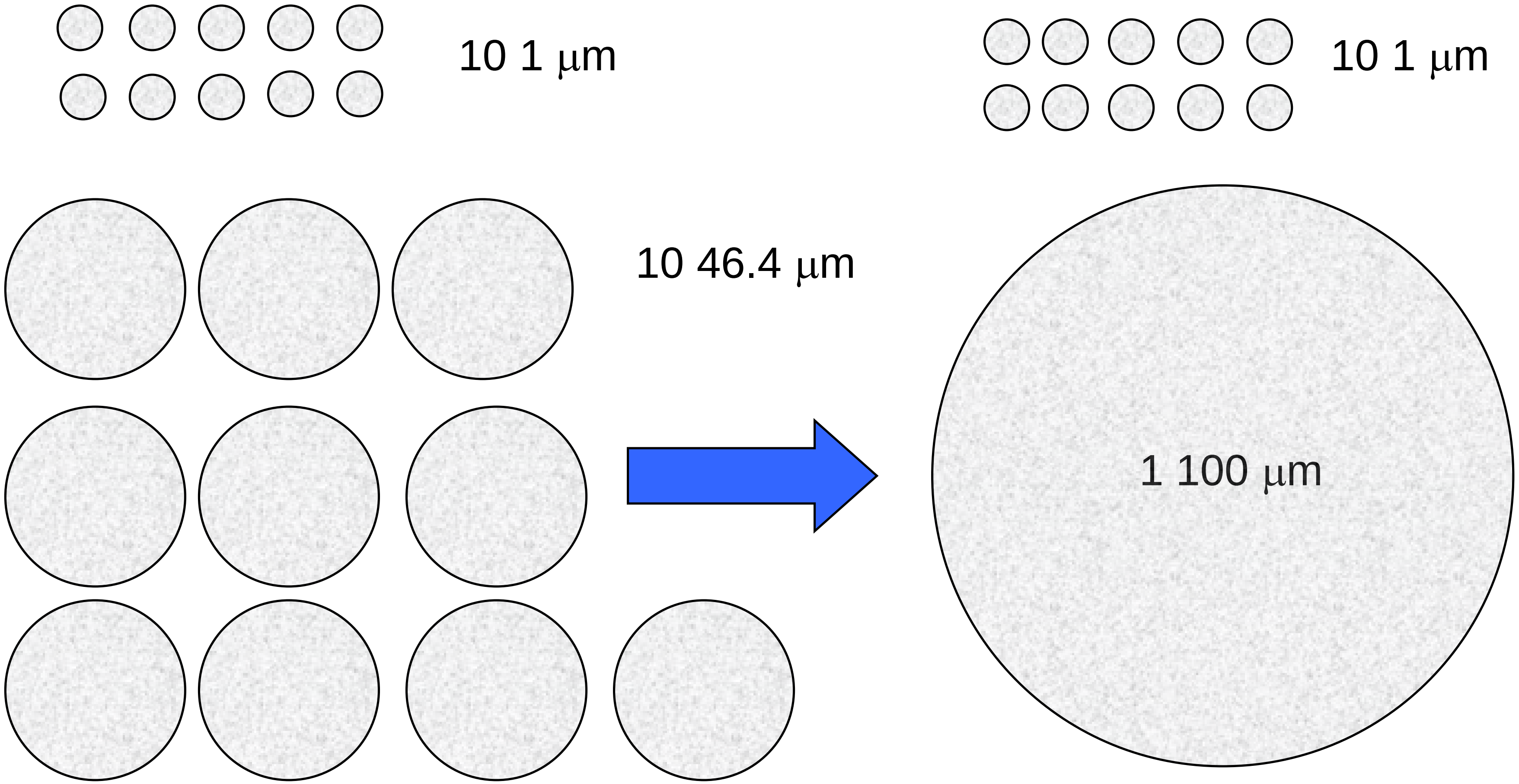
This shows the expected behavior

The problem



Number mean = 10	Number mean = 14 ↑
Volume mean = 100	Volume mean = 79 ↓

Size growth



Ten 46.4 mm particles agglomerate into one 100 mm particle

Growth: number mean

Ten particles of size 1; ten of size 46.42

D[1, 0] = (10*1 + 10*46.42)/20 = <u>23.71</u> 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?

Mean = (10*1+1*100)/11 = <u>10</u> units

Over a 50% decrease!

Growth: volume mean

Ten particles of size 1; ten of size 46.42

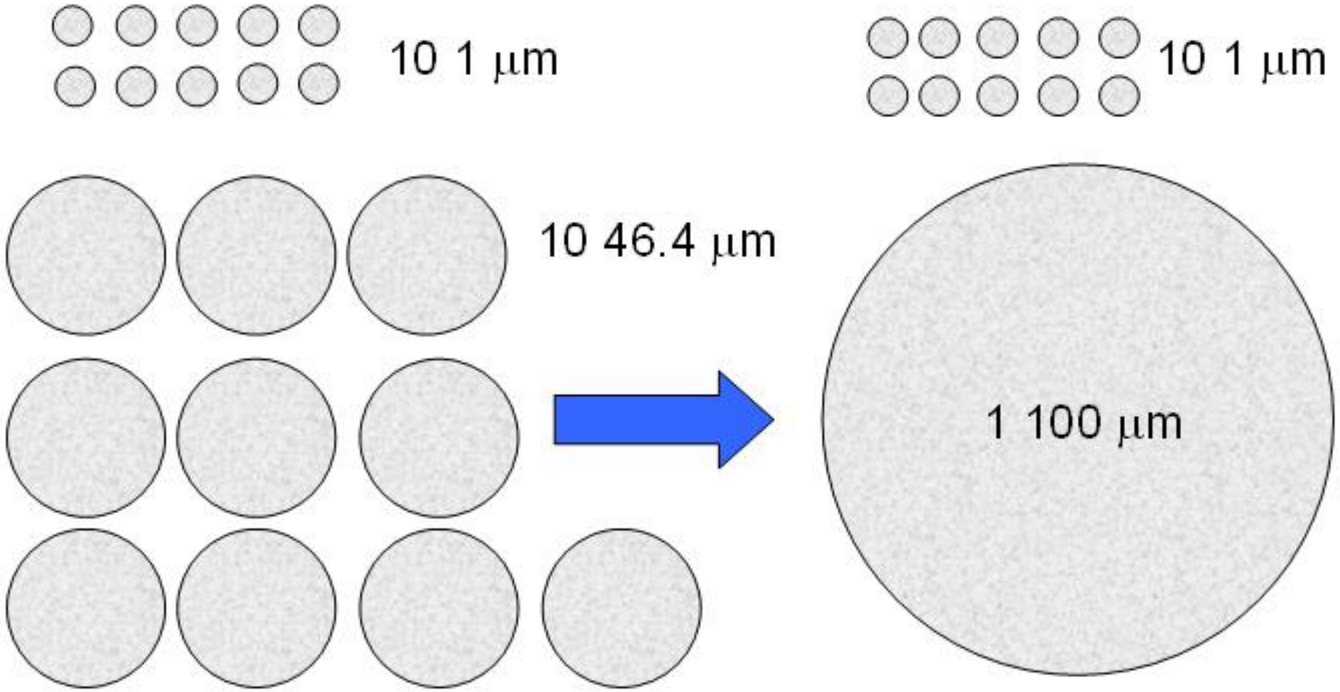
$D[4, 3] = (10*1^4 + 10*46.42^4)/(10*1^3 + 10*46.42^3) \sim \underline{46.4}$ units

(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?

$D[4, 3] = (10*1^4+1*100^4)/10*1^3 + 1*100^3 \sim \underline{100}$ units
This shows the expected behavior

The problem



Ten 46.4 µm particles agglomerate into one 100 µm 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.**

Only use volume??

Volume is good for many processes as illustrated

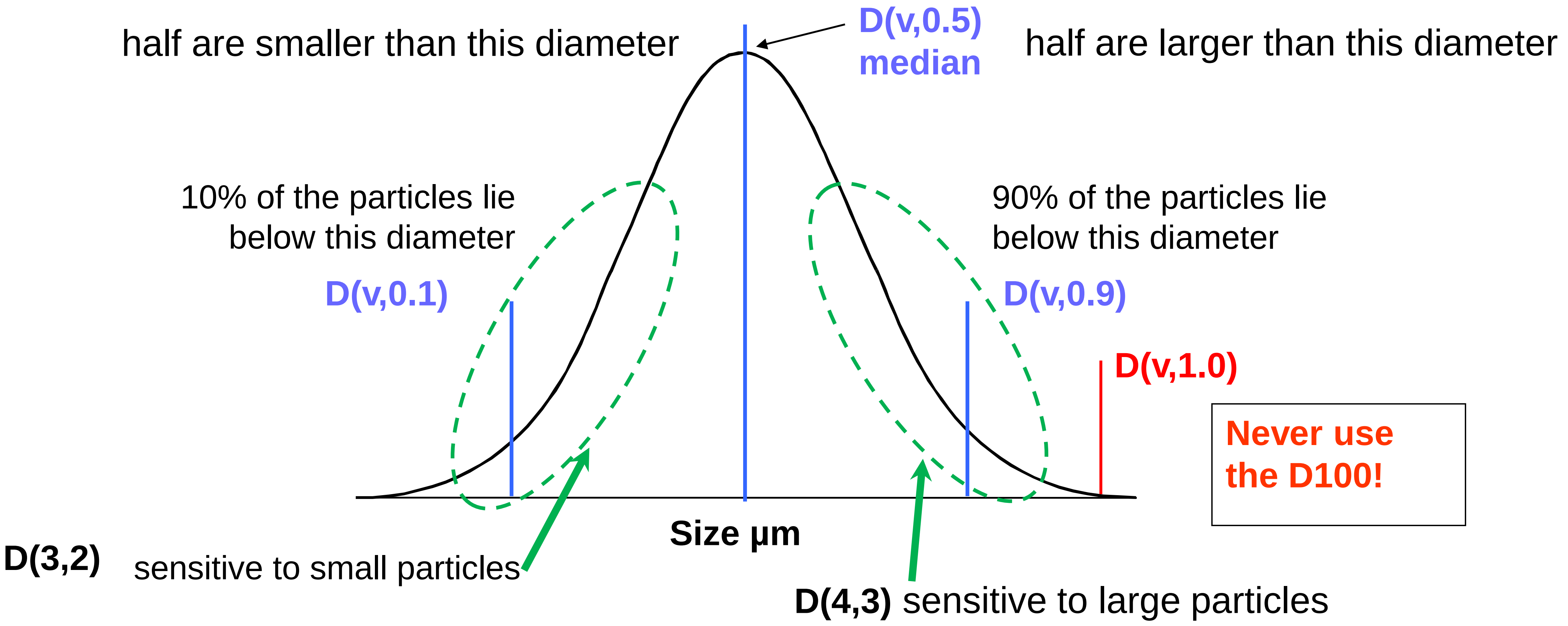
Some processes depend on small particles, so number is more valuable.

- dust
- suspension viscosity

It is generally easier to convert from number to volume than volume to number.

Concluding comments: common measures

How was it measured? What technique/analyzer?
What parameter (median, mean, mode)?
What basis (volume, number, surface area)?



Never use the D100!

Omoshiro-okashiku

Joy and Fun

Terima kasih

நன்றி

Gracias

谢谢

Tack ska du ha

Danke

Σας ευχαριστώ πάρα πολύ

Grazie

THANK YOU

धन्यवाद

شكرًا

ขอบคุณครับ

Obrigado

Большое спасибо

ありがとうございました

Cảm ơn

Merci

감사합니다

Dziękuję