



Solving Powder Challenges Using Particle Size and Shape Analysis



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www.horiba.com/us/particle



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Liam approaches light speed



What we'll talk about

- **Importance of size and shape**
- **State of the art technologies for size and shape measurement**
- **Tips and best practices**

Additional resources

- Data interpretation (larger topic, TR008)
- Laser diffraction theory (TE017, TR002)
- Image analysis theory (TR009)
- Dynamic light scattering (TE012, TR012, TR014)
- Shape data from light scattering



Influence of size and shape

- Particle size and size distribution directly affect compaction, flow, dissolution, texture, and much more
- Particle shape less so with some exceptions
- Together they influence
 - Particle processes, making products
 - Product performance
 - Making measurements
- So in other words, almost everything

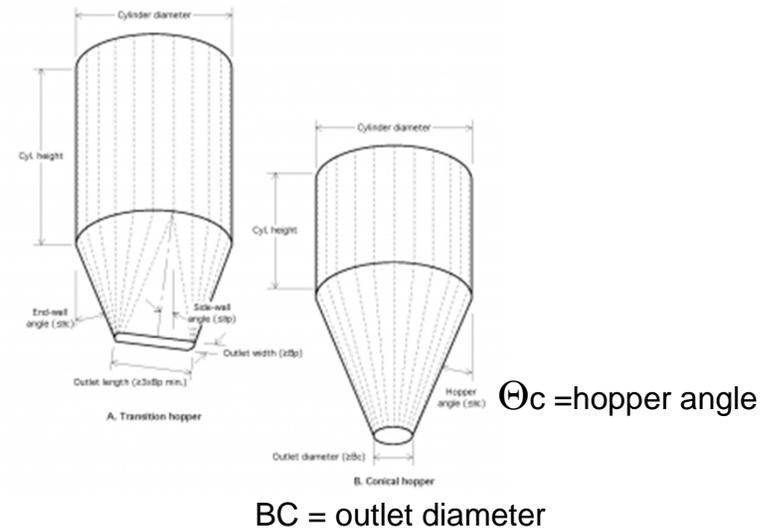
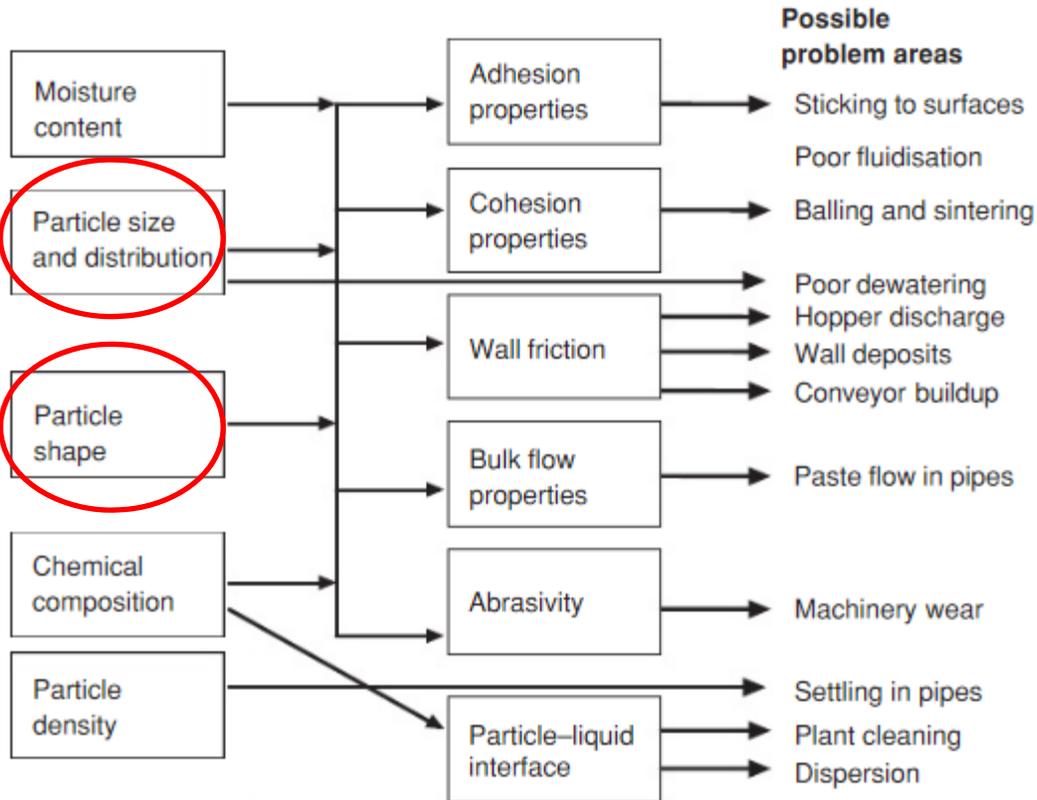
Particle processes affected by shape

- Powder flow; spheres flow easily, needles do not
- Powder mixing; blend time may change with shape
- Also VERY associated with size, hard sometimes to separate size and shape

Powder flow

- Understand that spheres flow more easily than needles
- How to quantify? Need to first know something about powder flow testing
- Won't go into great detail in today's talk
- Just show results including particle shape

Powder flow*



* **Bulk Solids Handling**
Equipment Selection and Operation

Edited by

Don McGlinchey

Reader

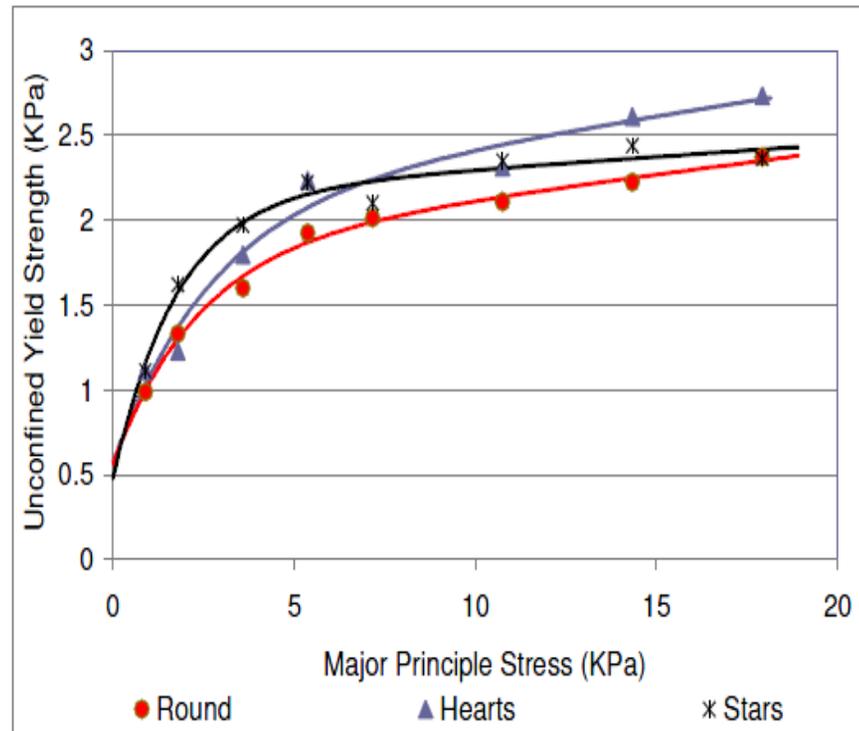
Centre for Industrial Bulk Solids Handling

Glasgow Caledonian University

UK

Powder flow

- Unconfined Yield Strength
- Major principle stress that causes an unconfined bulk material to fail in shear
- Directly proportional to arching & formation of rat holes
- Influences by # contact points



Round



Heart

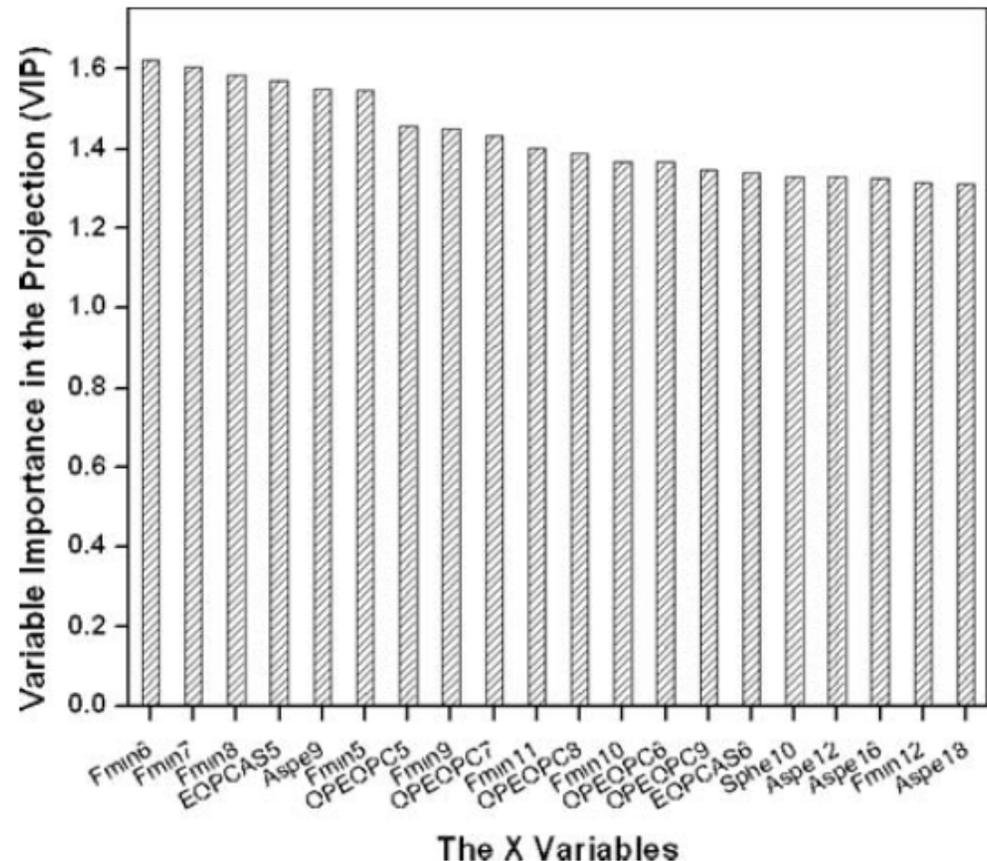


Star

From: Johansen, Effect of Particle Shape on Unconfined Yield Strength, Material Flow Solutions, Inc.

Influence of size and shape

- Study of pharma powders using DIA to determine which size and shape descriptors best predict FFC
- Minimum Feret, equivalent circle, aspect ratio shown to be most predictive

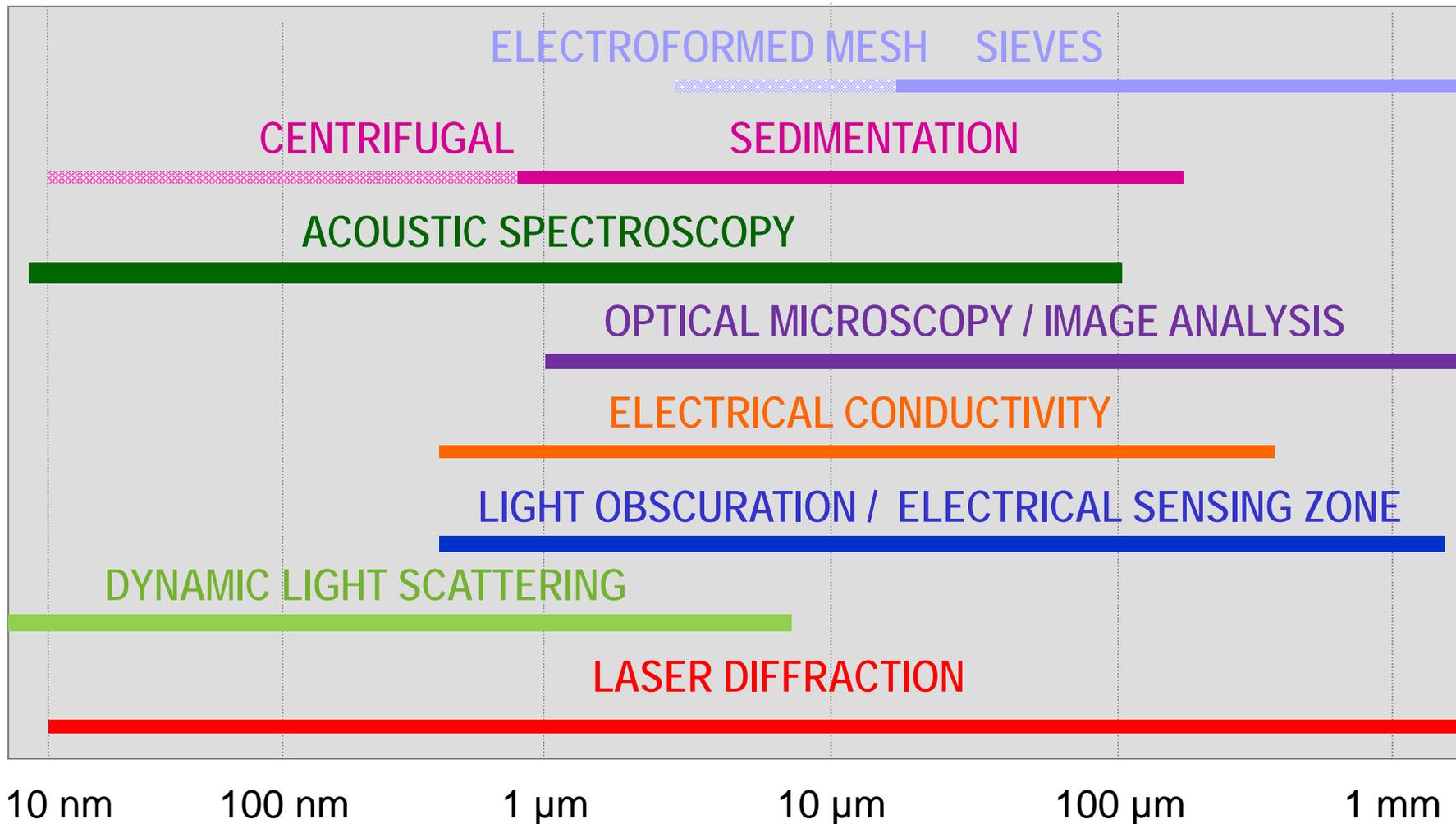


Weili, Yu, et al. 2011. Prediction of Bulk Powder Flow Performance Using Comprehensive Particle Size and Particle Shape Distributions. Journal of Pharmaceutical Sciences, 100(1) <http://onlinelibrary.wiley.com/doi/10.1002/jps.22254/abstract>

What we'll talk about

- Importance of size and shape
- **State of the art technologies for size and shape measurement**
- Tips and best practices

Size range by technique



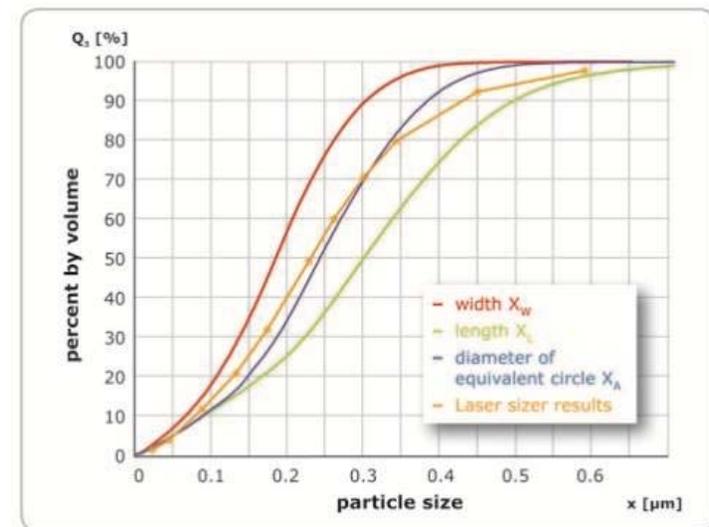
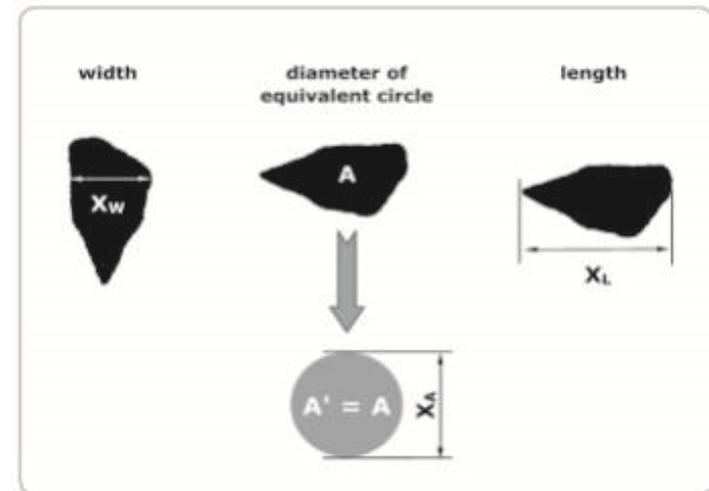
Size descriptors

■ Laser diffraction

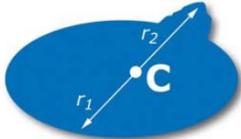
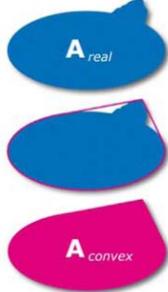
- Equivalent spherical diameter

■ Image analysis

- Equivalent circular diameter
- Minimum chord length (width)
- Maximum feret (length-ish)
- Minimum Martin's diameter (width)
- Many more for special cases (curved particles, true length)



Shape descriptors (IA only)

- Sphericity  $\frac{4\pi A}{P^2}$
- Symmetry  $\frac{1}{2} \left(1 + \min \left(\frac{r_1}{r_2} \right) \right)$
- Aspect ratio  $\frac{X_{c \ min}}{X_{Fe \ max}}$
- Convexity  $\sqrt{\frac{A_{real}}{A_{konvex}}}$

Featured technologies

- **LA-960**

Laser Diffraction

- **SZ-100**

Dynamic Light Scattering & Zeta Potential

- **CAMSIZER & CAMSIZER XT**

Dynamic Image Analysis

- **PSA300**

Static Image Analysis

- **SA-9600**

Flowing Gas BET Surface Area

LA-960: Laser Diffraction

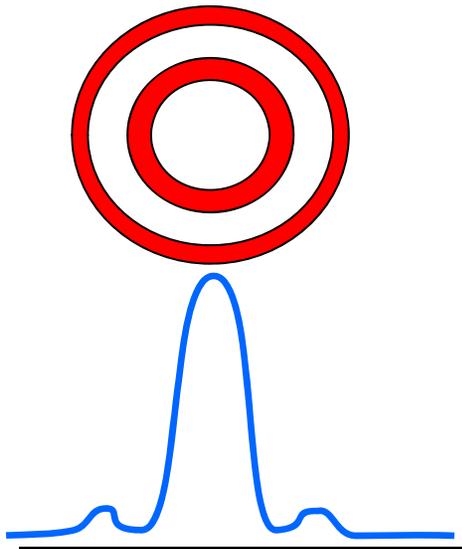
- Particle size performance leader
- Tenth generation
- Ultra durable
- Lowest total cost of ownership
- Suspension, emulsion, powder, paste, gel
- 10 nanometer – 5 mm



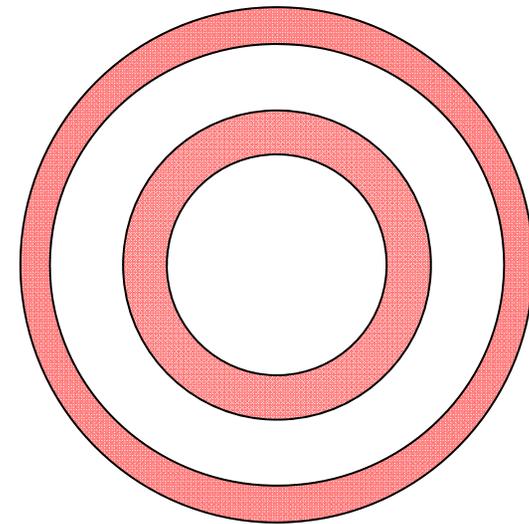
Diffraction measurement principle

■ LARGE PARTICLE:

- Peaks at low angles
- Strong signal



Narrow Pattern - High intensity

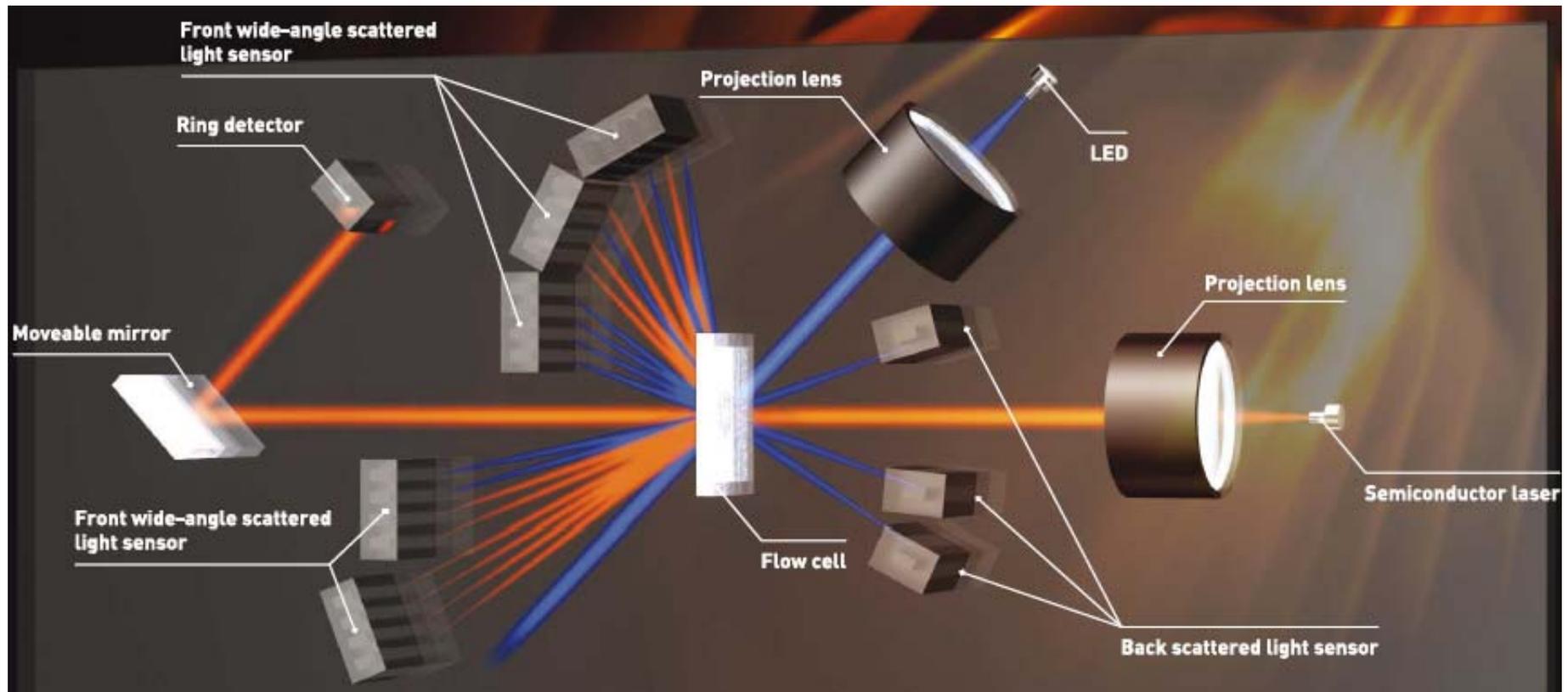


Wide Pattern - Low intensity

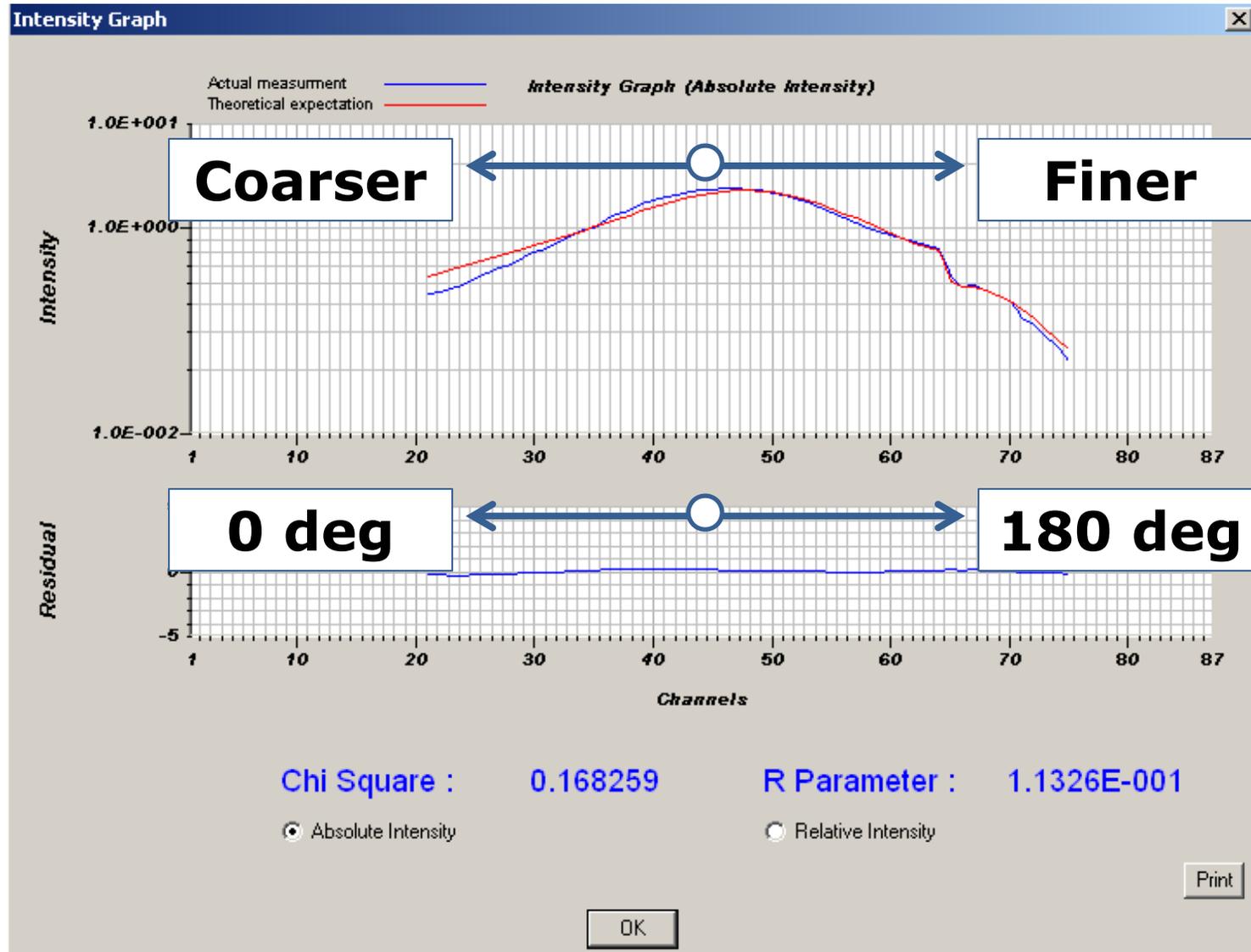
■ SMALL PARTICLE:

- Peaks at larger angles
- Weak Signal

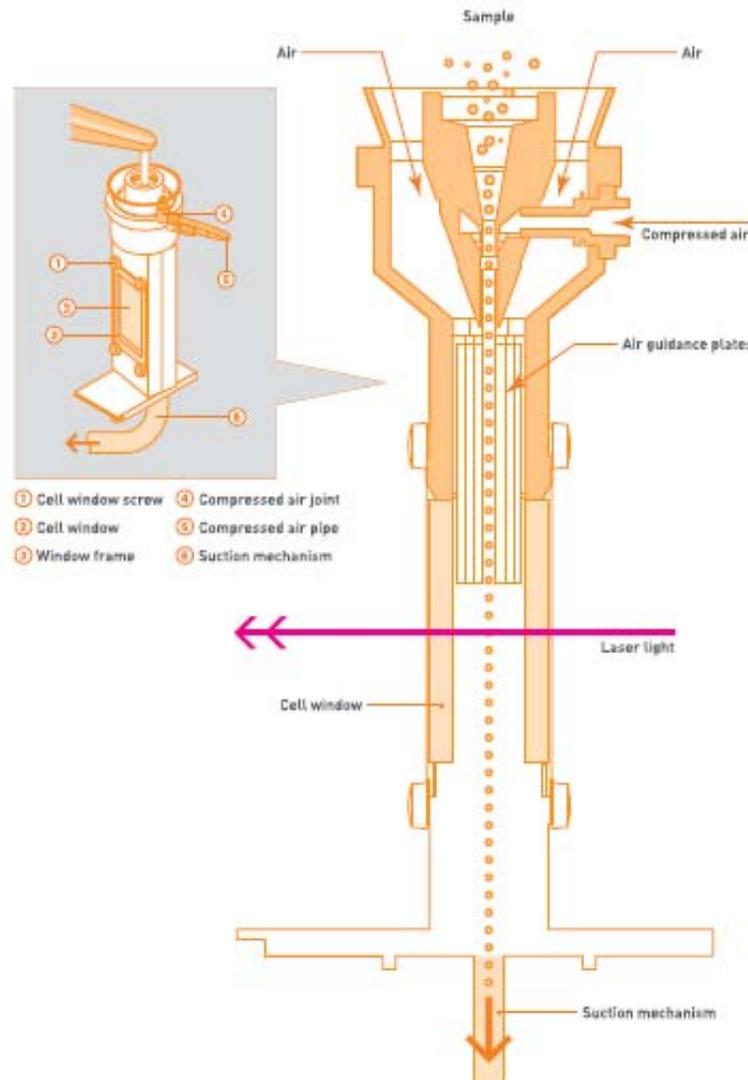
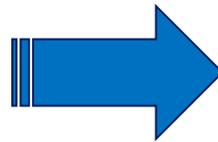
Example optical design



Diffraction measurement principle



LA-960 PowderJet



- Sits on top of LA-960
- No impaction surfaces prevents breakage
- Feedback control for maximum precision
- Fully automated
- Wet to dry switch in 30 seconds

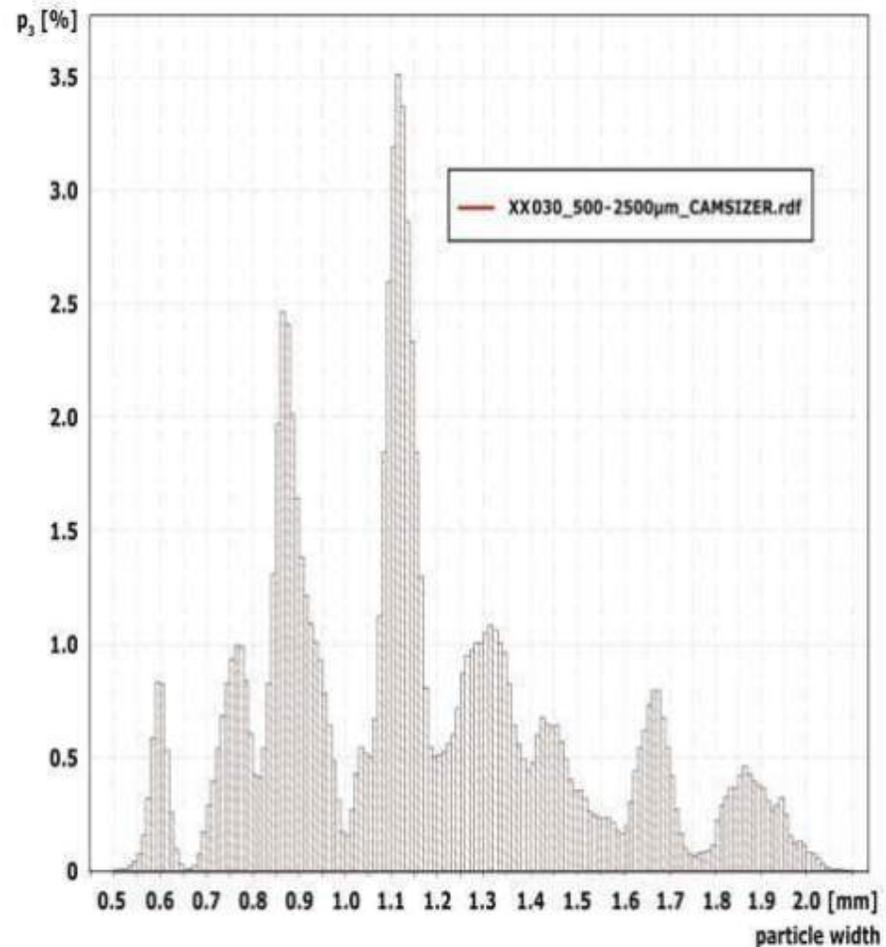
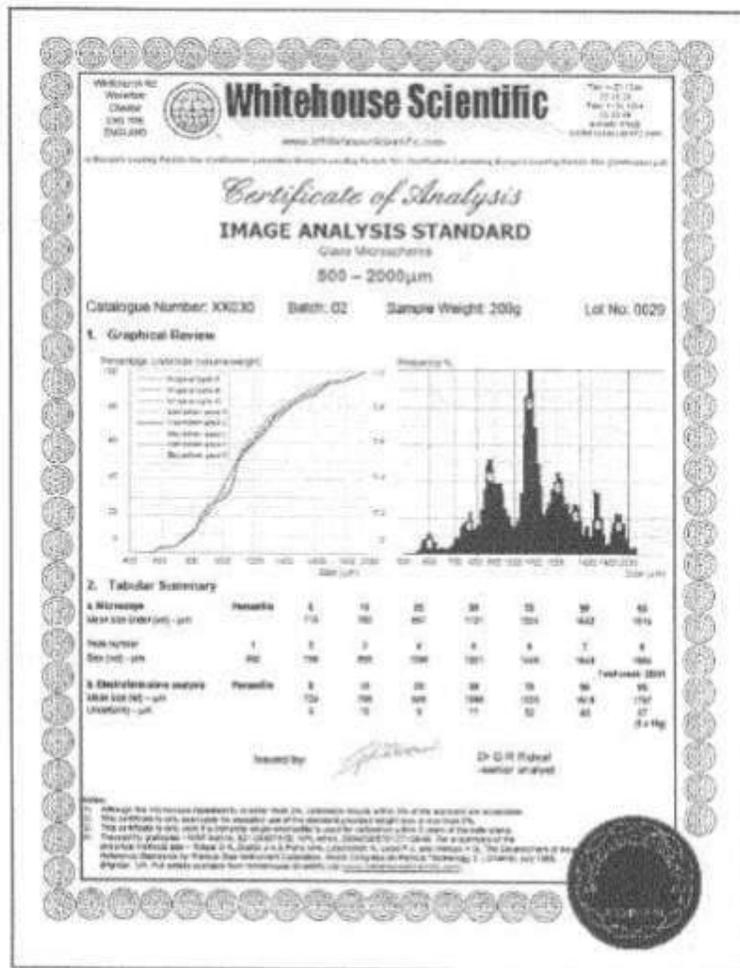
CAMSIZER XT: Dynamic Image Analysis

- High resolution size & shape
- Intelligent sieve correlation
- Patented dual capture
- CAMSIZER XT
 - 1 μm – 8 mm
 - Cohesive or free flowing powders
 - Suspensions with accessory



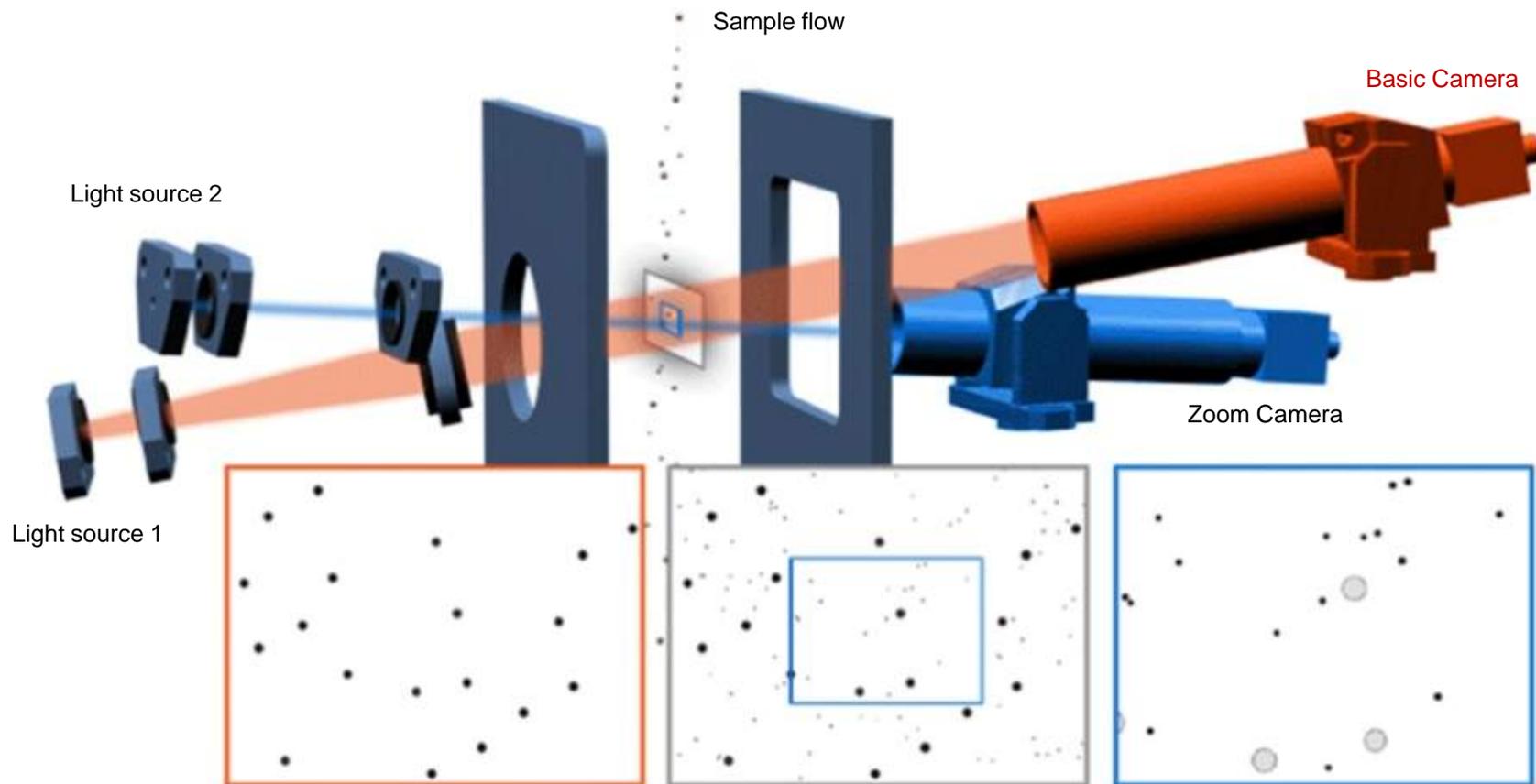
High resolution measurement

Whitehouse Glass Bead Standard XX030

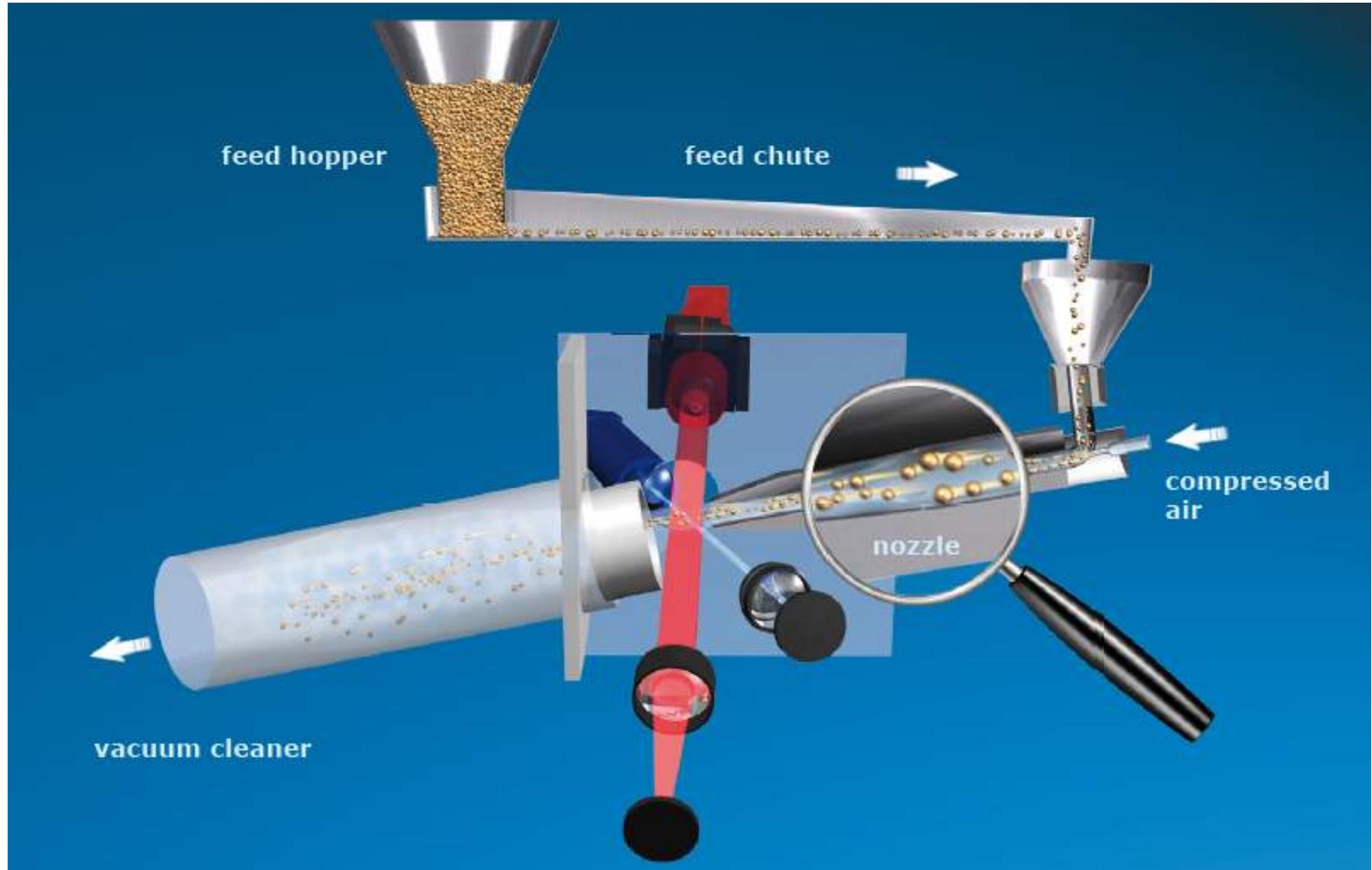


CAMSIZER XT measurement

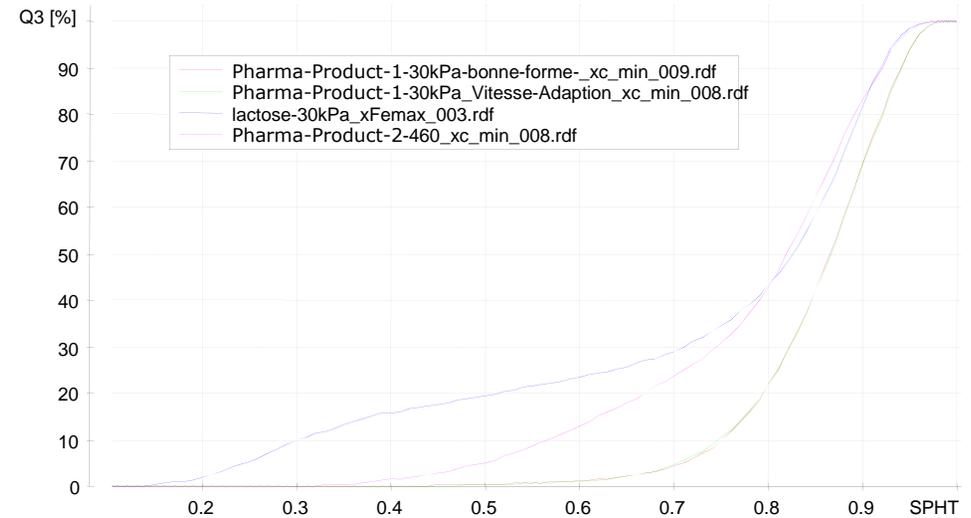
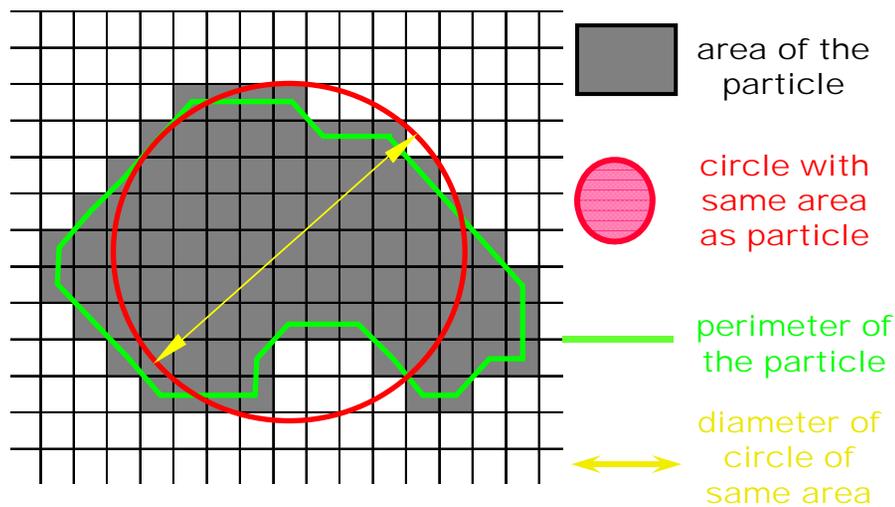
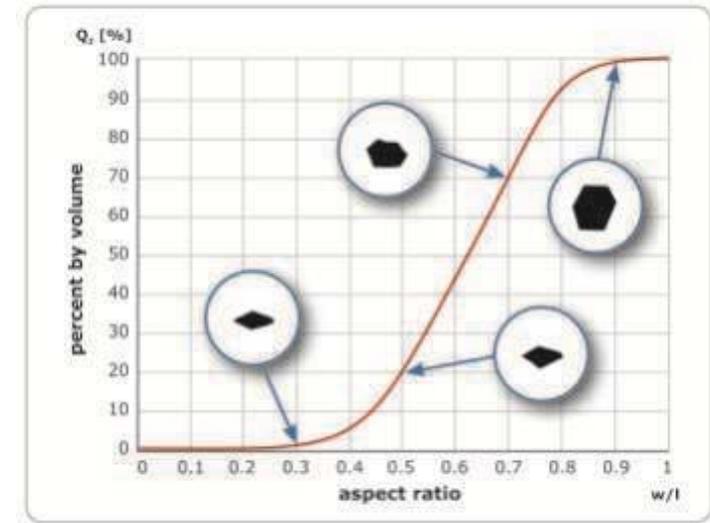
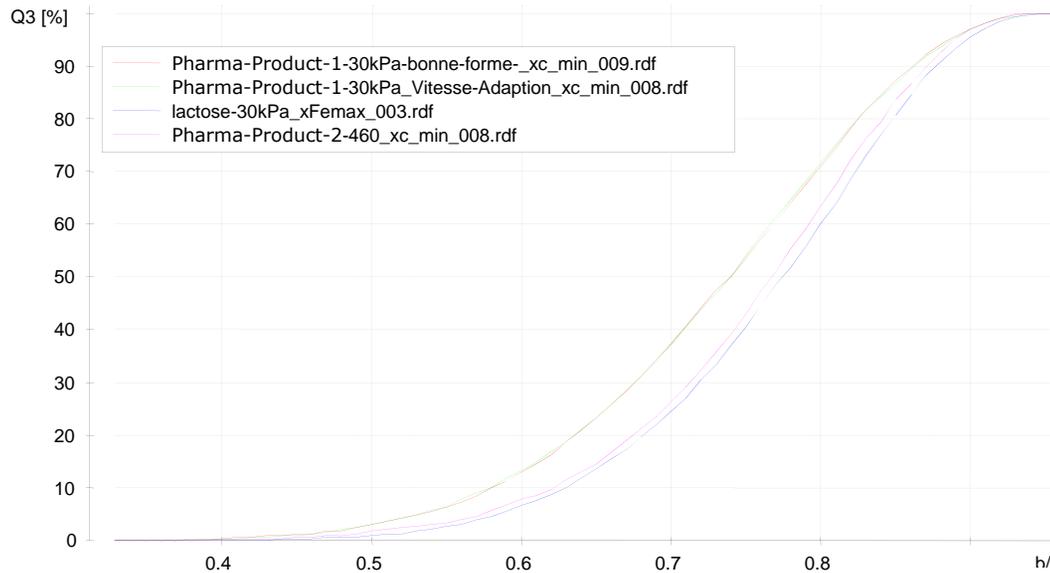
Advanced, patented optics design



CAMSIZER XT measurement

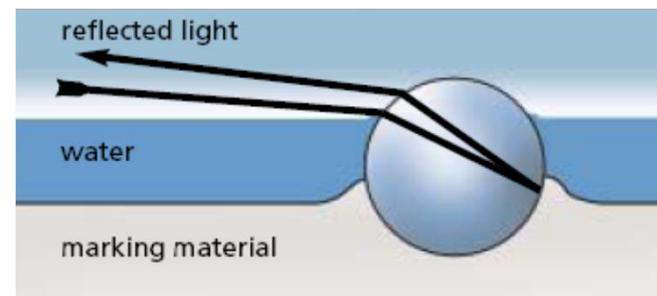
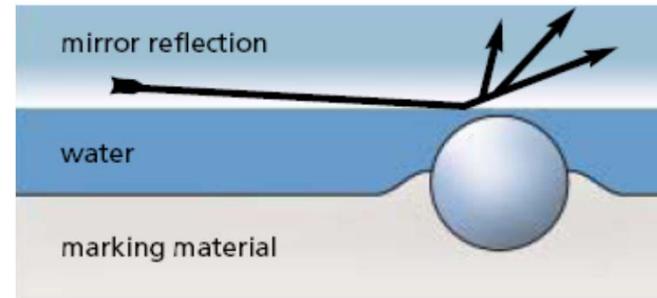


Shape analysis with the XT



Glass beads for road markings

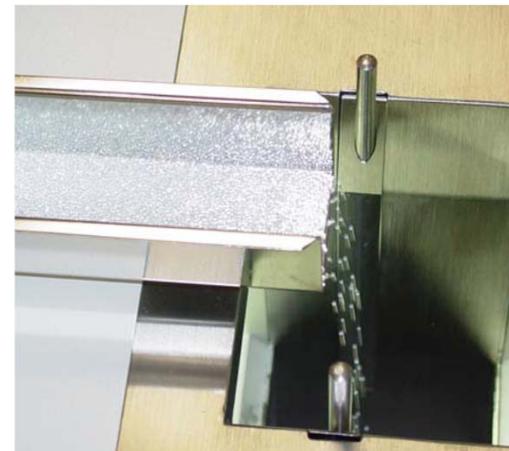
- Size and shape critical to reflective properties
- More round = more reflectivity back to source
- CAMSIZER uses b/l ratio to quantify roundness
- Traditional techniques: sieves and “round-o-meter”



Dry



In paint



Proppants



Sand proppant



Resin coated sand

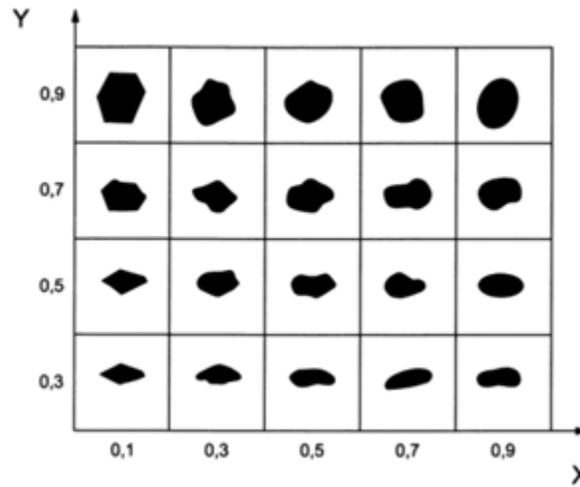


Ceramic proppant

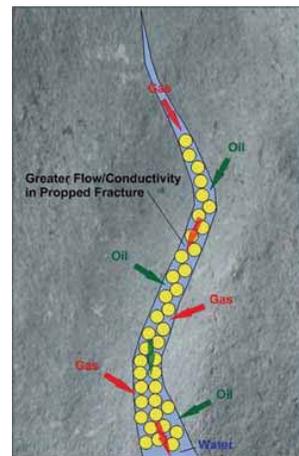
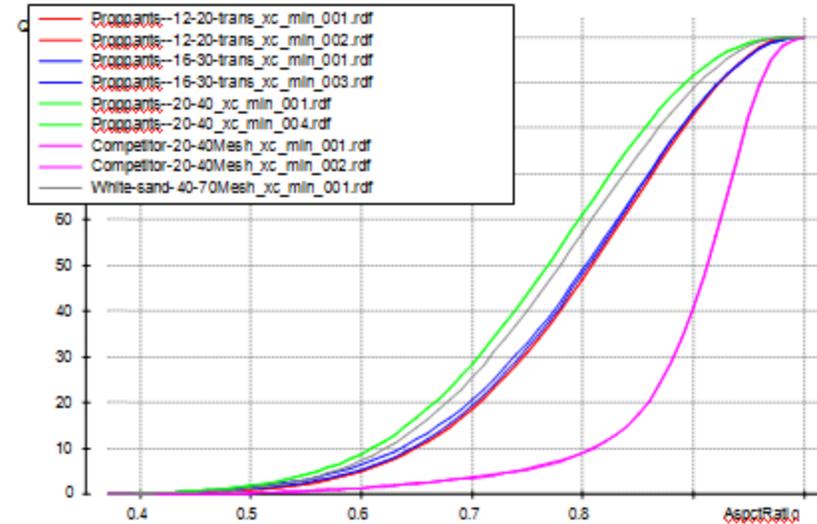


Resin coated ceramic proppant

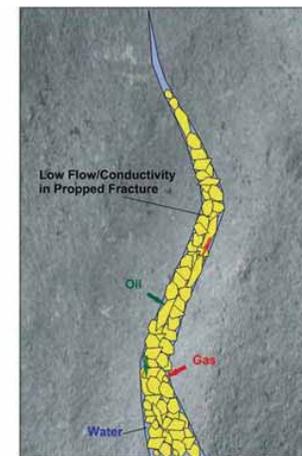
Traditional method



CAMSIZER Technology



a. Well Rounded Ceramic Proppant



b. Poorly Sorted Angular Proppant Sand

Laser diffraction advantages

- Fastest measurement: less than 1 min.
- Excellent intermediate precision
- Most common modern sizing technique
- Flexible design also supports measurement of suspensions, emulsions, gels, pastes, creams



Image analysis advantages

- Faster measurement: less than 5 mins.
- Superior resolution
- Improved intermediate precision
- Quantify clusters, satellites, broken particles, mixtures
- Capture images for backup



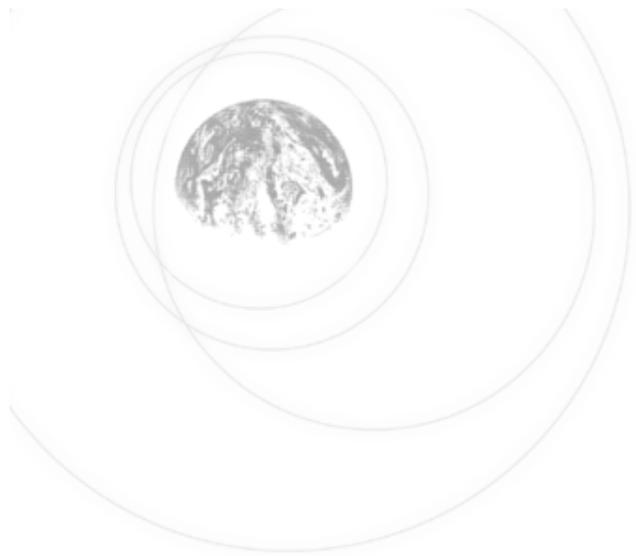
Must-have features for dry analysis

- Feedback control of powder flow to maximize precision
- Wide dynamic range
- Easy operation via method files
- Maintenance-free operation



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- **Tips and best practices**



Sampling

Webinar TR011
White Paper WP004



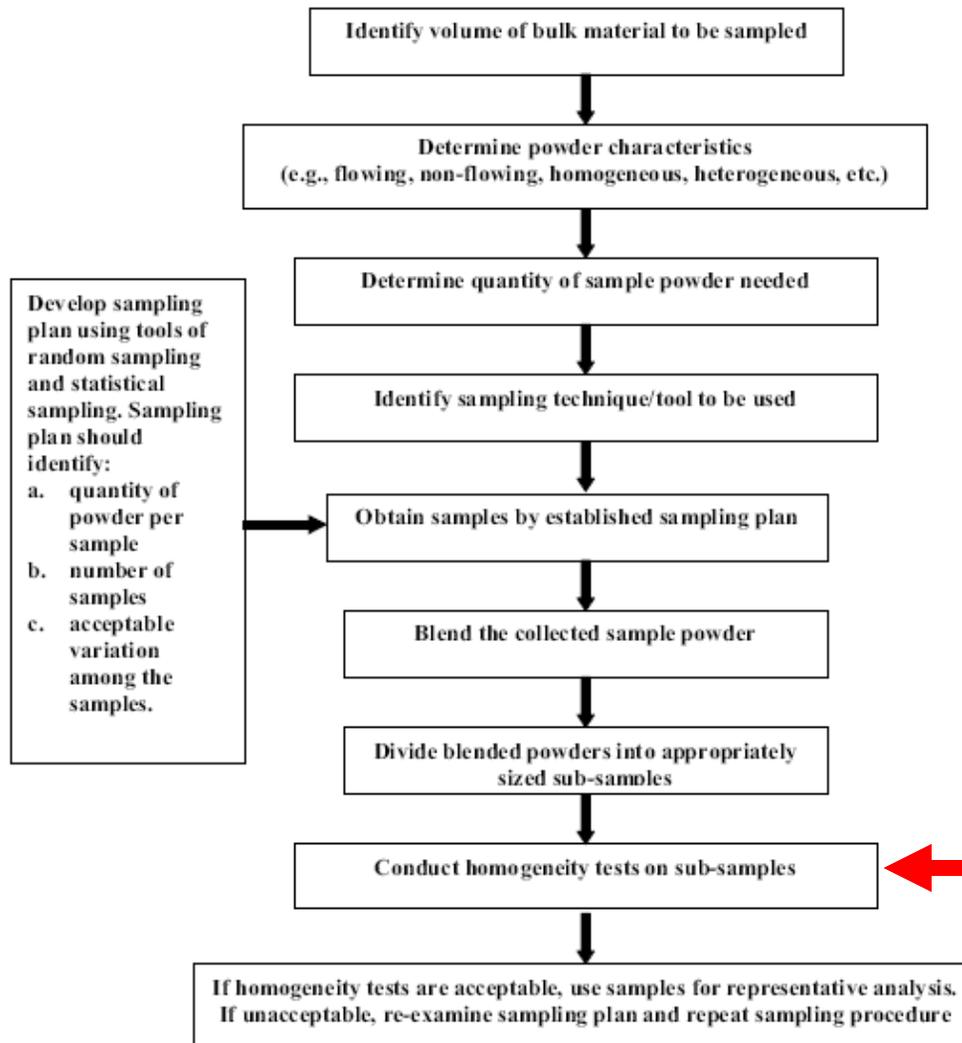
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Sampling workflow



Excellent strategy
not sure how often followed

From: NIST Recommended Practice Guide
Special Publication 960-1
Particle Size Characterization
Ajit Jillavenkatesa, Stanley J. Dapkunas, Lin-Sien H. Lum
Materials Science and Engineering Laboratory
January 2001

Must do this

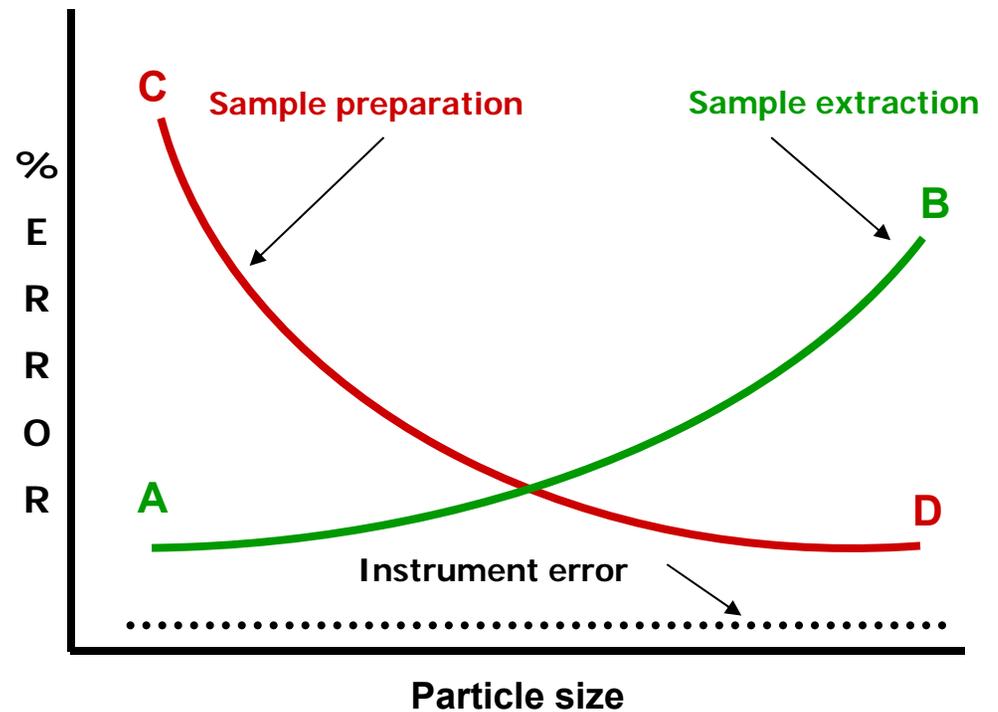
Measurement error sources

Small particles

- Smaller extraction errors (A)
- Larger sample prep errors (C)

Large particles

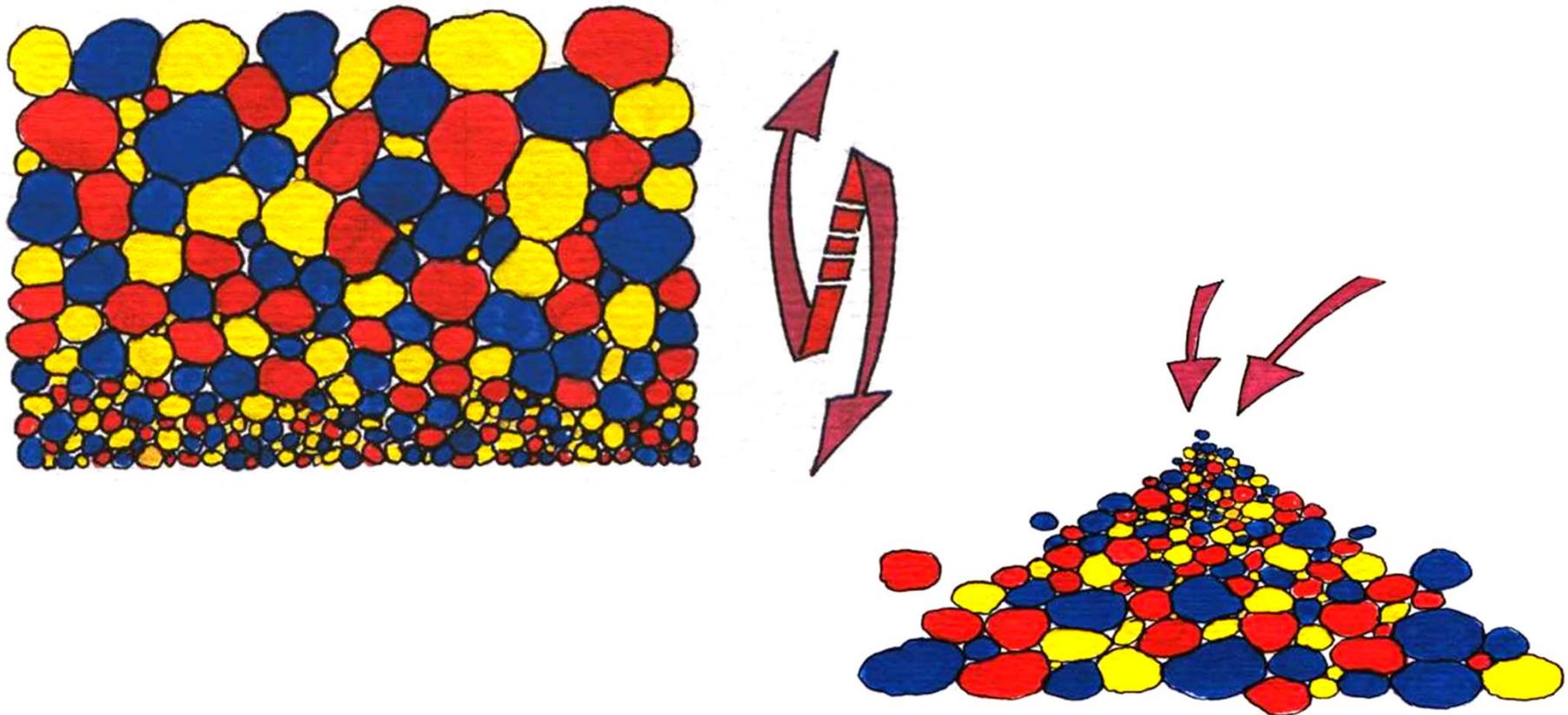
- Larger extraction errors (B)
- Smaller sample prep errors (D)



Instrument error relatively small

May increase w/decreasing particle size (less so w/LA-960)

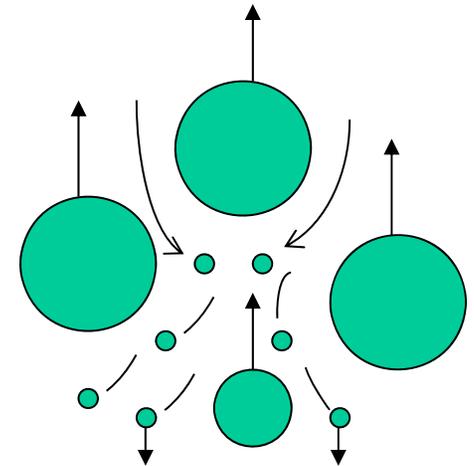
Why sampling matters



Separation happens with any materials having a polydisperse particle size distribution

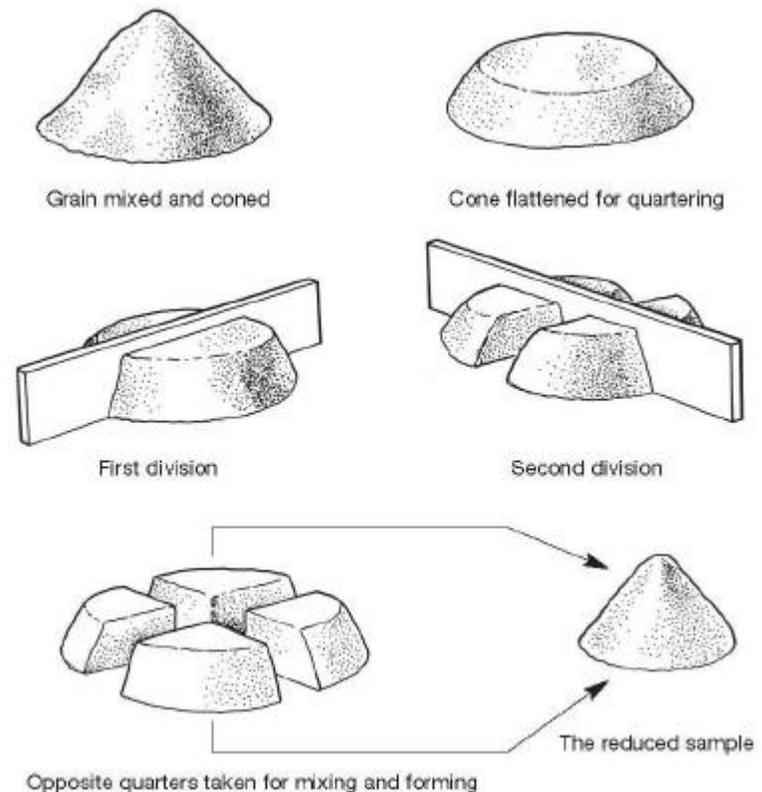
Technique: grab sampling

- Place spatula into powder, extract small amount for analysis
 - Easy, most used method
 - Maybe worse method
- May be acceptable for narrow distributions
- Problem: **segregation** of larger particles w/wide distribution
 - Large particles percolate upward
 - Small particles gravitate downward
- One solution: use a powder thief



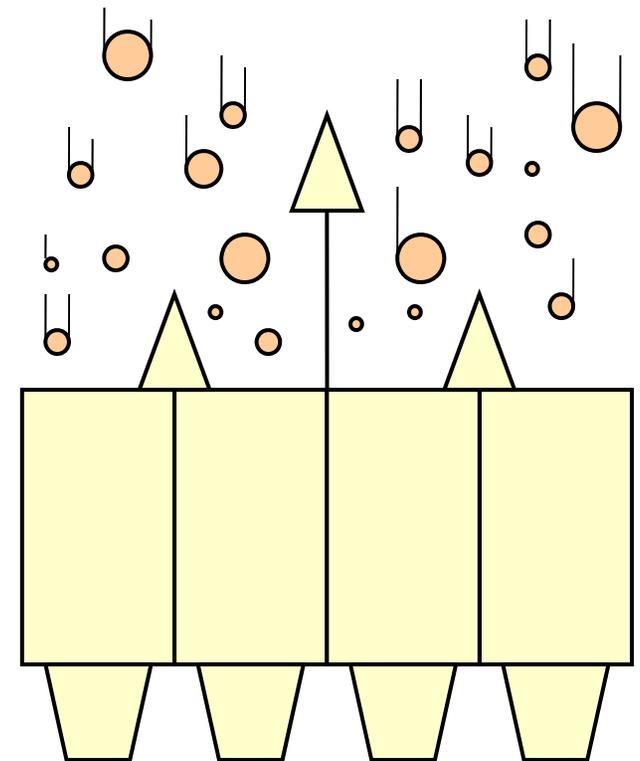
Technique: coning & quartering

- Pile of powder is divided into 4 sections.
- Two diagonal sections are discarded, and two are retained and mixed together.
- Mixture is again divided into 4 sections, and two diagonal sections are mixed.
- Process is repeated until remaining sample is correct amount for analysis.
- Can be carried out with very small sample amount or very large samples.



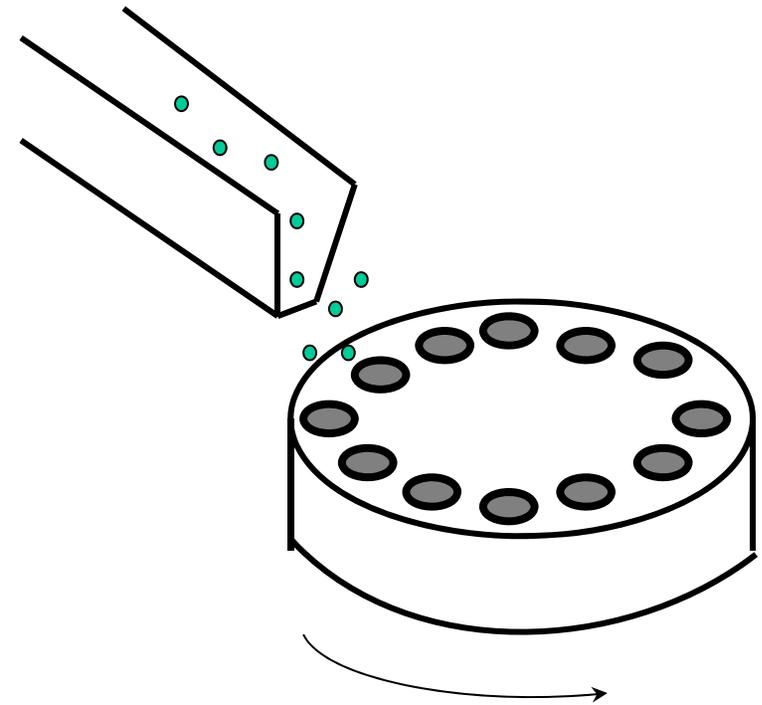
Technique: chute riffling

Chute splitting allows sample to vibrate down a chute to vanes which separate the mass into two portions. Each portion moves further where they each are divided into two parts, now giving four parts. This may be continued until usually 8 or 16 portions are obtained.



Technique: rotary riffling

The best method of representative splitting of powders is the ROTARY RIFFLER. The complete sample to be split is directed down a chute into open containers. Each container will receive a sample which is representative of the original bulk material because the distribution of material is averaged over time. The complete amount of the original bulk sample must be consumed.



These splitters are commercially available from companies that market various types of sample splitters.

See: www.retsch.com

www.quantachrome.com

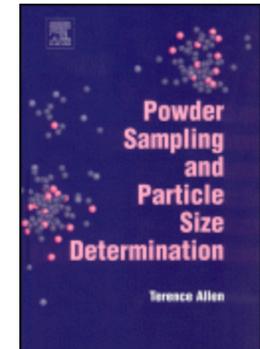
www.microscal.com



Importance of sampling technique

Standard Deviation (σ) in % Sugar-Sand Mixture

| | |
|-------------------------|-------------|
| SCOOP SAMPLING | 6.31 |
| TABLE SAMPLING | 2.11 |
| CHUTE RIFFLER | 1.10 |
| SPINNING RIFFLER | 0.27 |



Density of sand and sugar respectively 2.65 and 1.64 g/ml

Reference: Allen, T. and Khan, A.A. (1934), Chem Eng, 238, CE 108-112

| Method | Relative Standard Deviation (%) |
|-------------------|---------------------------------|
| Cone & Quartering | 6.81 |
| Scoop Sampling | 5.14 |
| Table Sampling | 2.09 |
| Chute Riffling | 1.01 |
| Spin Riffling | 0.125 |

Influence of spinning riffler

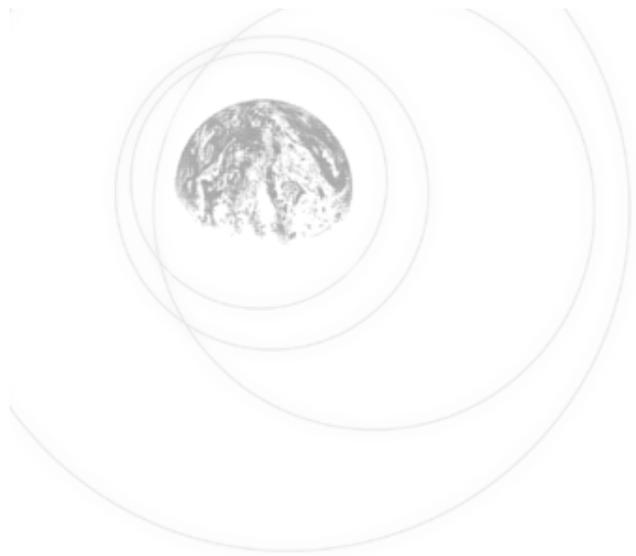
| LA-950 WET without Riffler | | | |
|----------------------------|--------------|---------------|----------------|
| Sample Name | D(v, 0.1) | D(v, 0.5) | D(v, 0.9) |
| Run #1 | 3.080 | 38.018 | 203.416 |
| Run #2 | 3.091 | 36.672 | 195.089 |
| Run #3 | 2.915 | 35.762 | 200.610 |
| Mean | 3.029 | 36.817 | 199.705 |
| Std. Dev. | 0.099 | 1.135 | 4.237 |
| COV (%) | 3.255 | 3.083 | 2.121 |



| LA-950 WET Analysis with Riffler | | | |
|----------------------------------|--------------|---------------|----------------|
| Sample Name | D(v, 0.1) | D(v, 0.5) | D(v, 0.9) |
| Run #1 | 2.796 | 36.848 | 202.660 |
| Run #2 | 2.828 | 37.260 | 205.074 |
| Run #3 | 2.895 | 35.998 | 200.843 |
| Mean | 2.840 | 36.702 | 202.859 |
| Std. Dev. | 0.051 | 0.644 | 2.123 |
| COV (%) | 1.779 | 1.753 | 1.046 |

Sample riffled
All of sub sample
dispersed and
measured as a
suspension

40+% improvement in COV



Data Interpretation

Webinars TR008, TR001, TR018, TR015, TR010



Explore the future

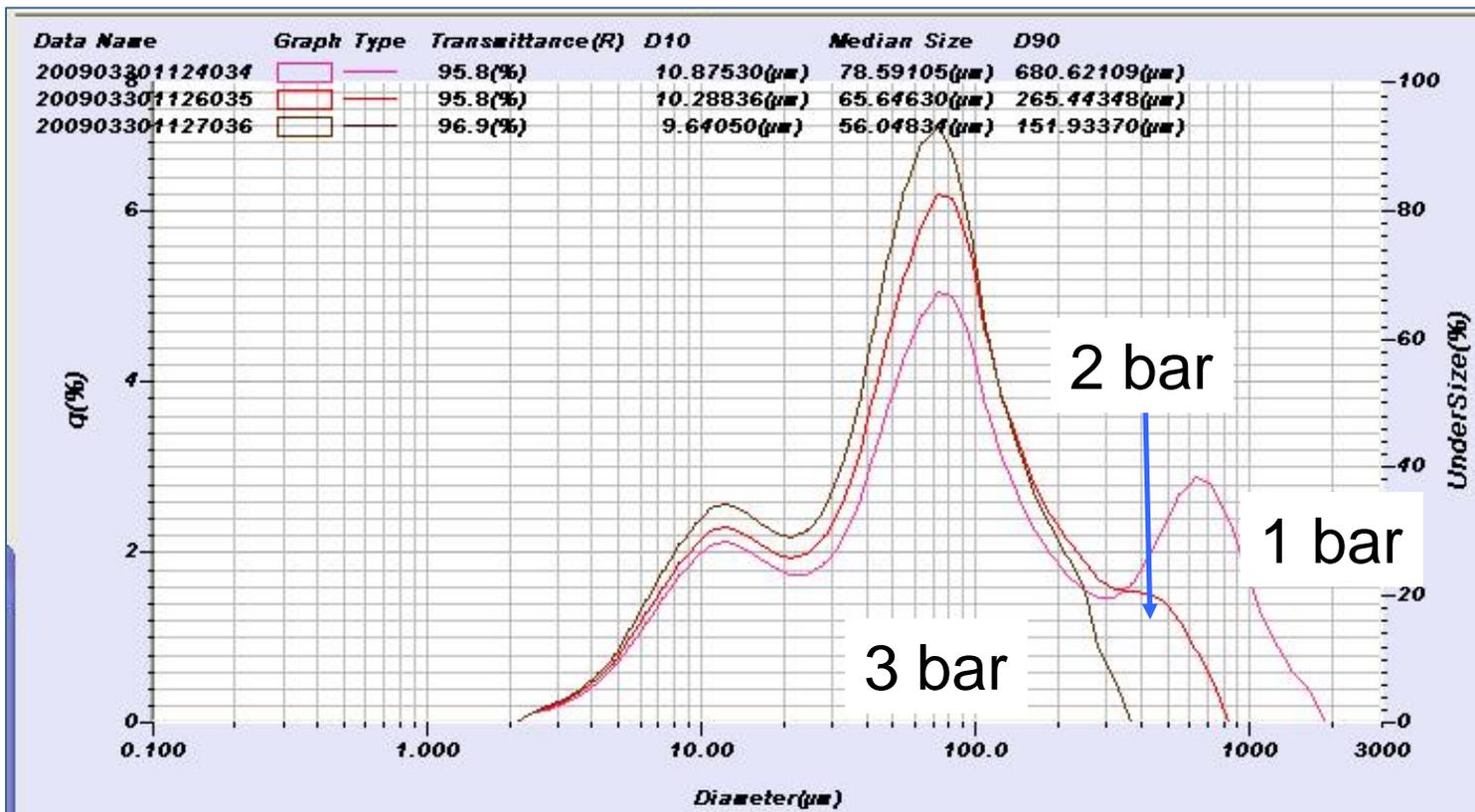
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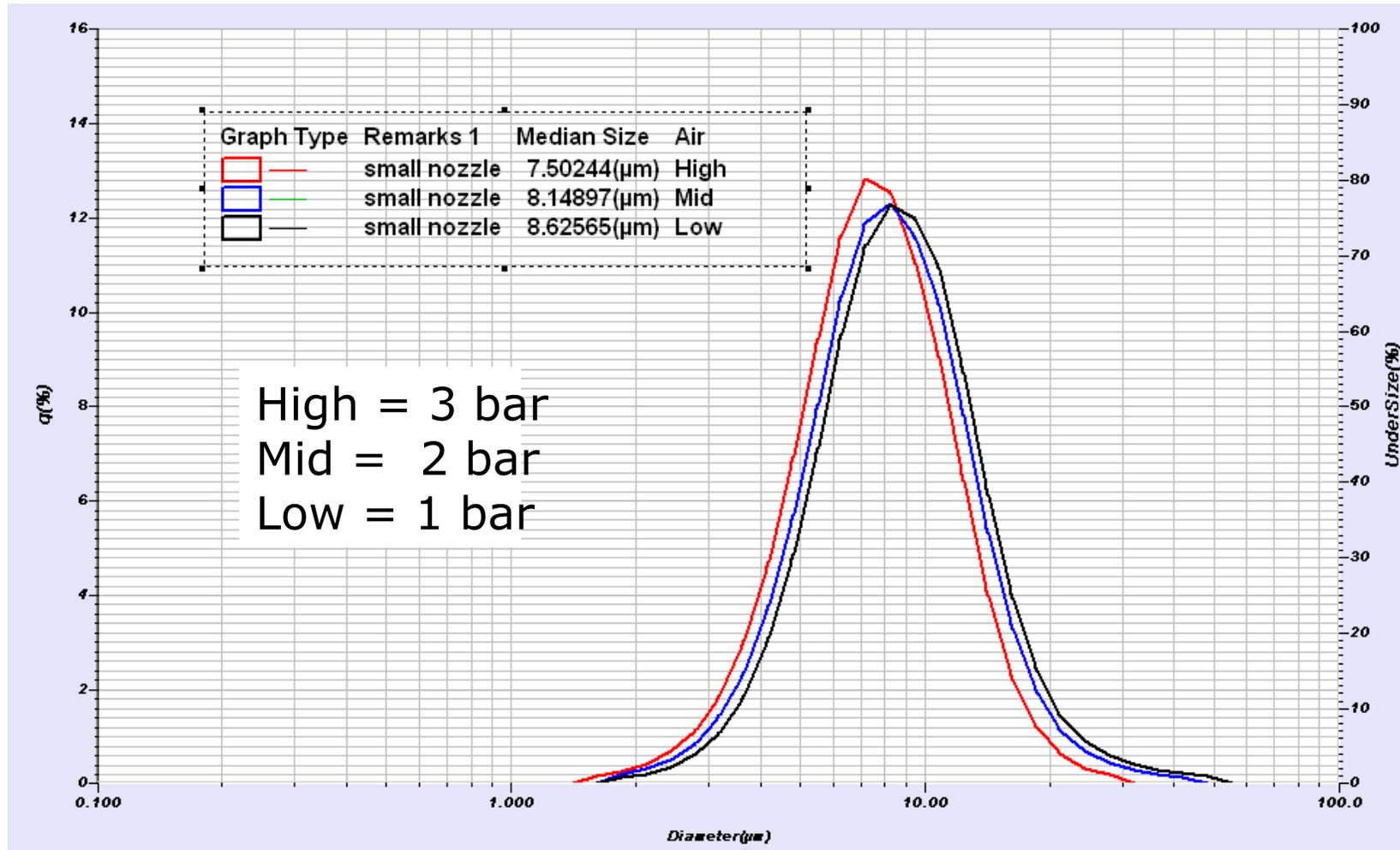
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Dispersing agglomerates

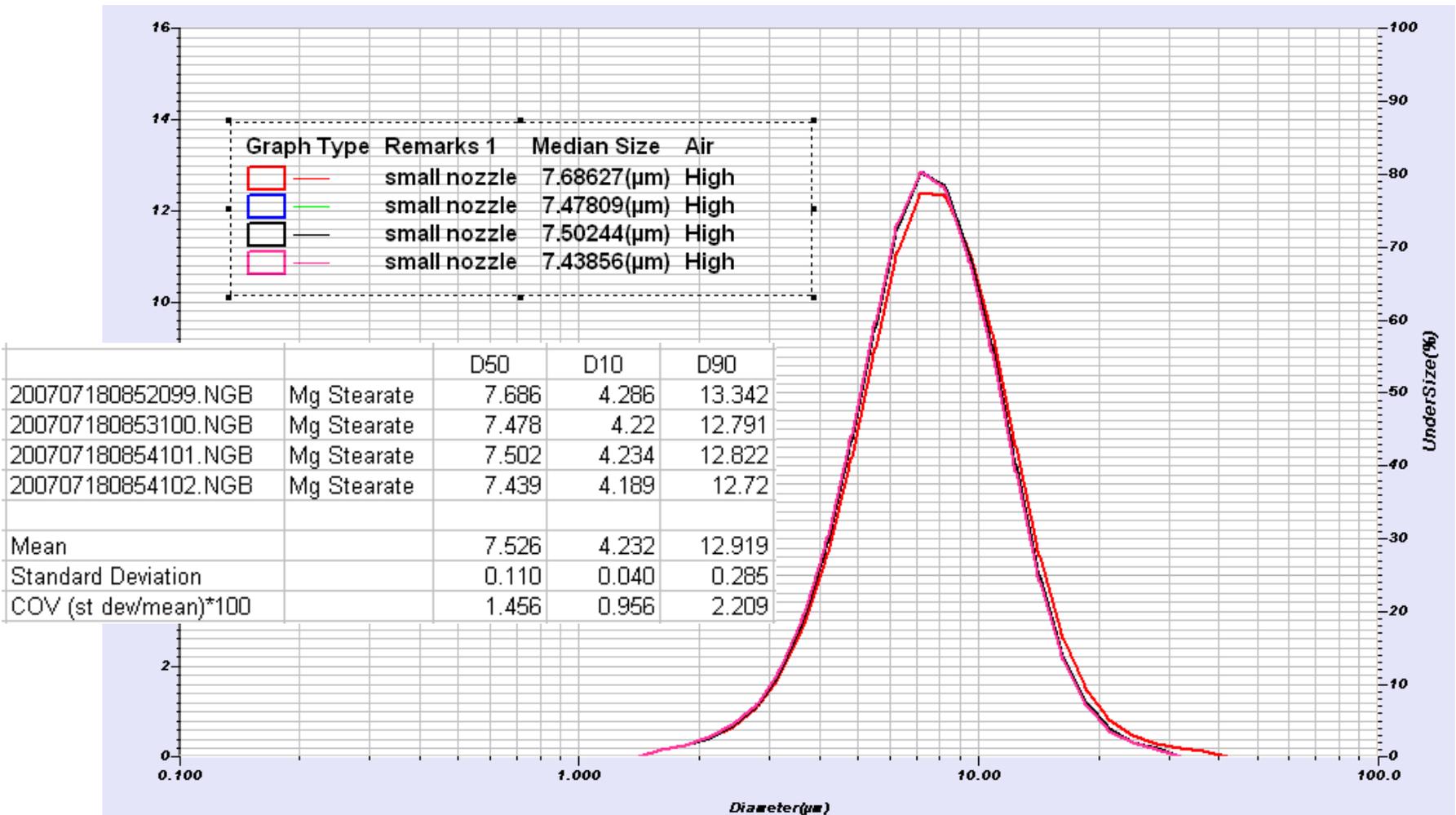
Watch for no change in coarsest particles with changing energy



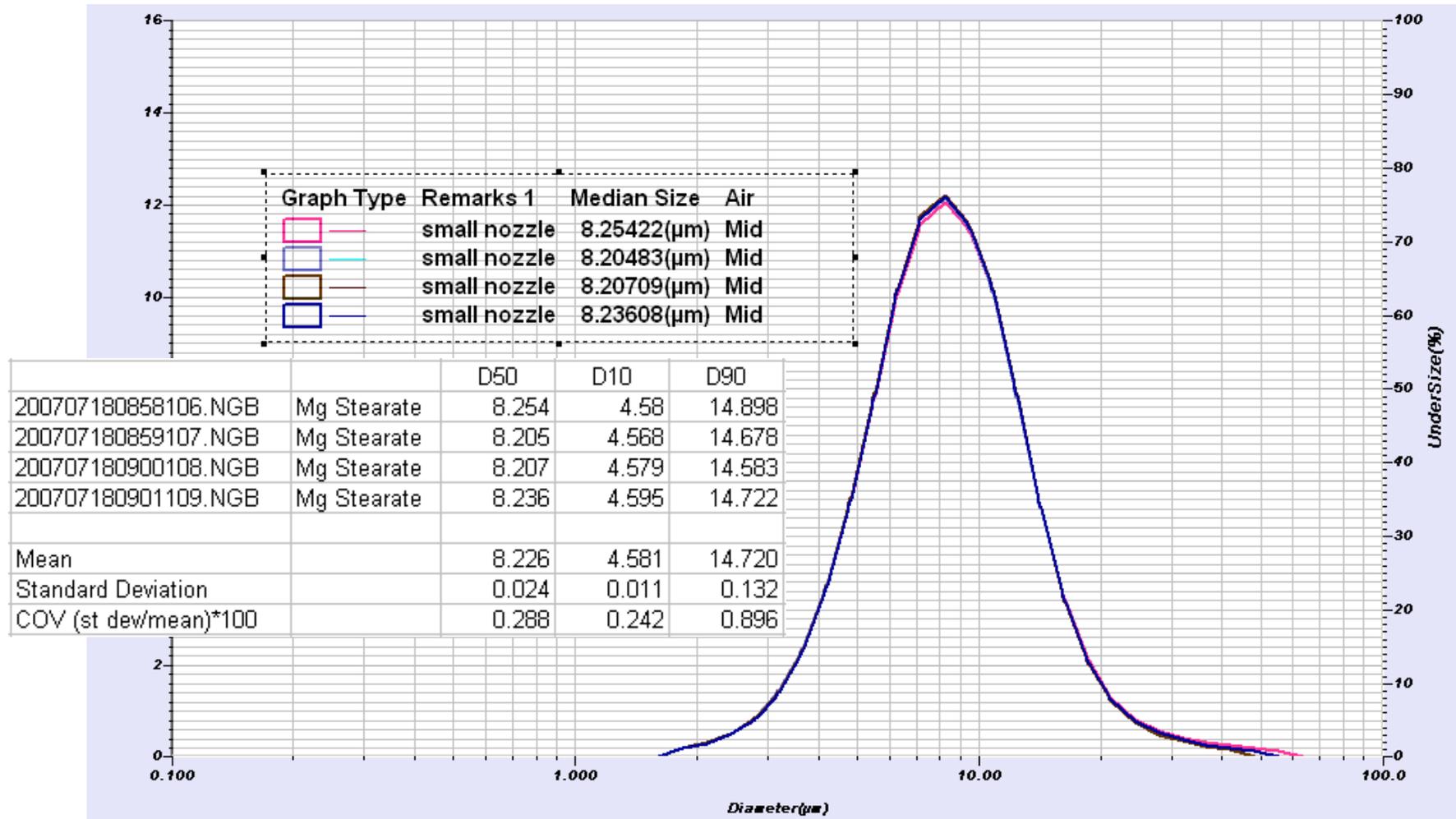
Effect of air pressure: Mg Stearate



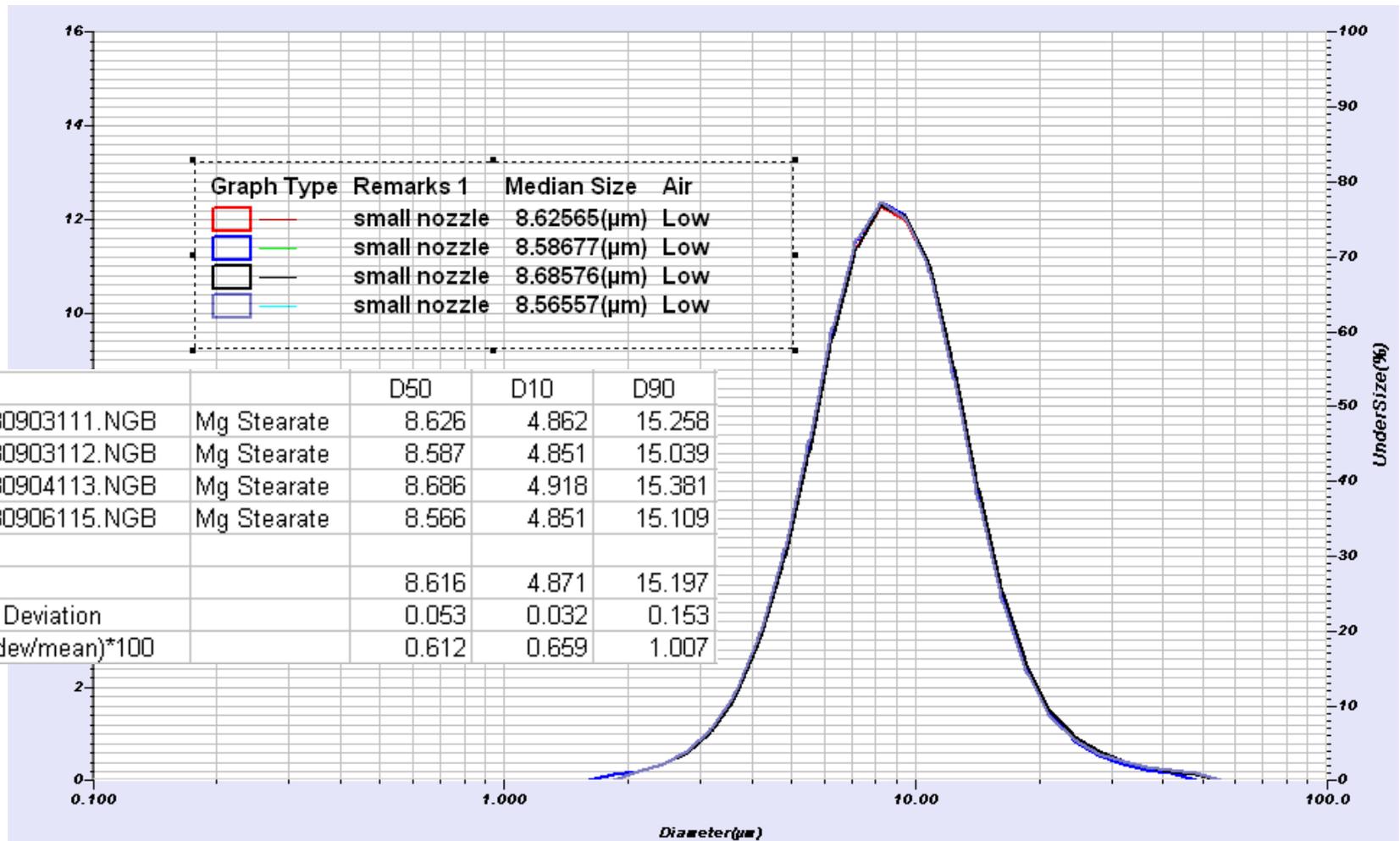
Reproducibility at 3 bar pressure



Reproducibility at 2 bar pressure

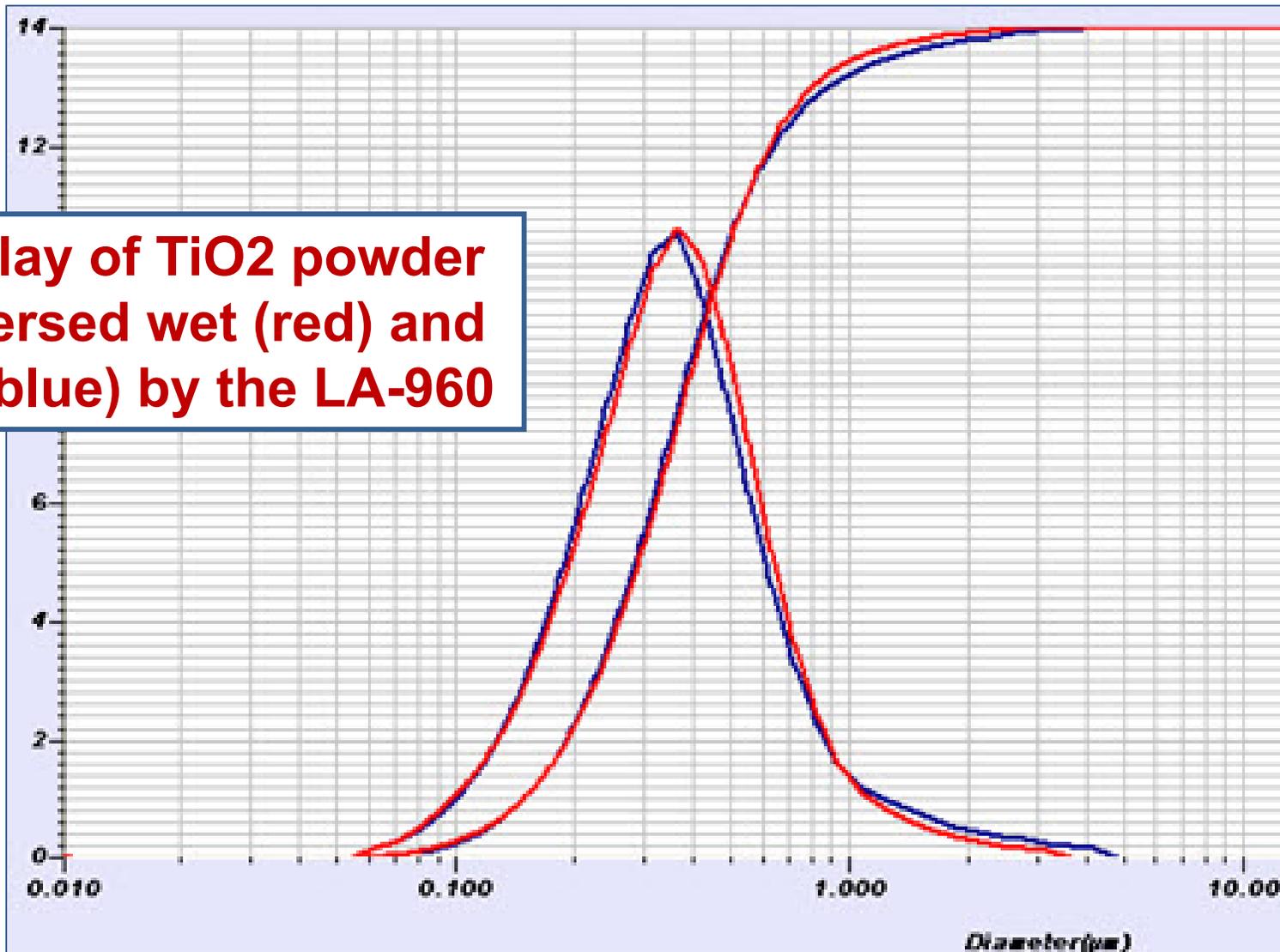


Reproducibility at 1 bar pressure



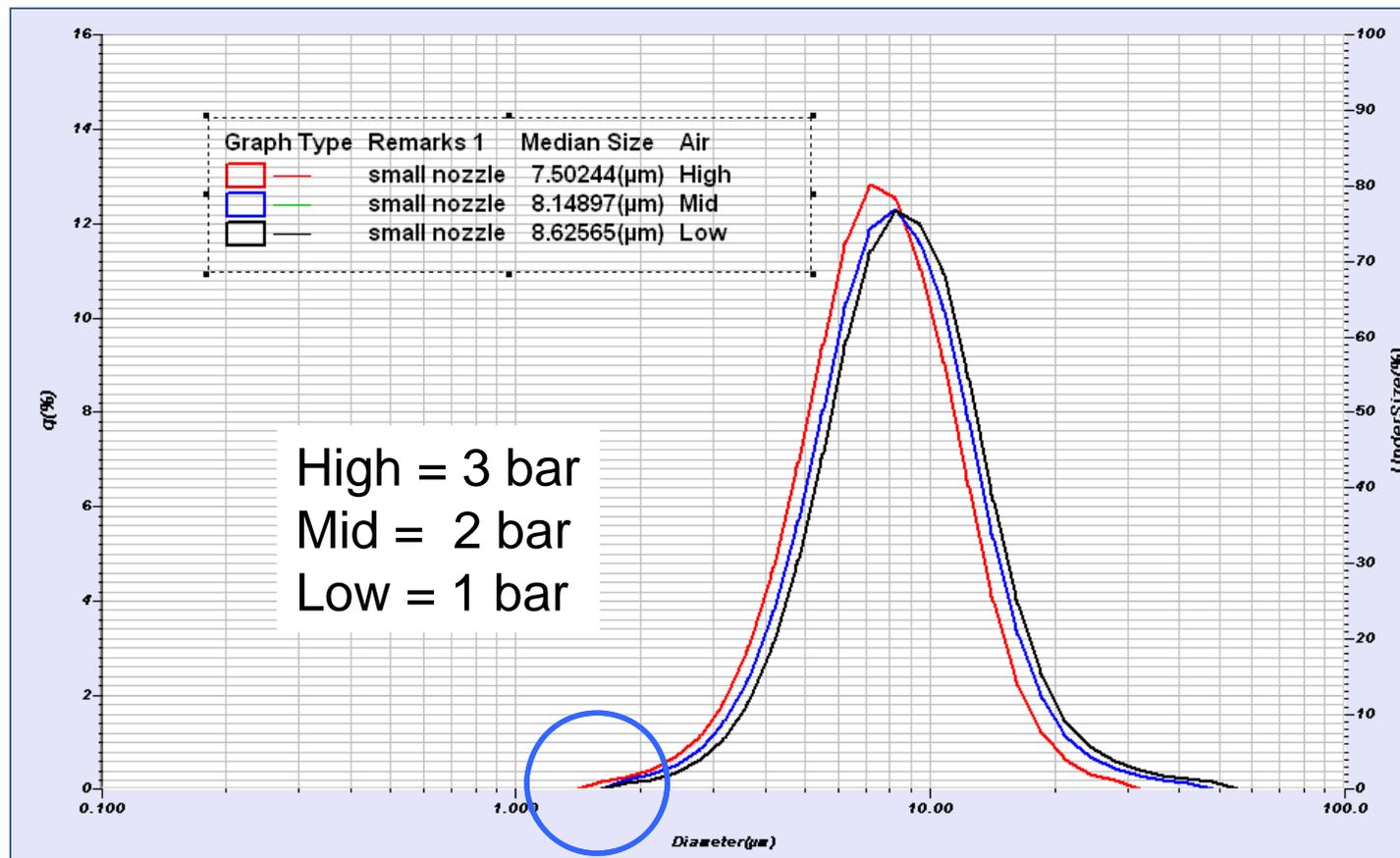
Wet and dry comparison

Overlay of TiO₂ powder dispersed wet (red) and dry (blue) by the LA-960



Breaking particles

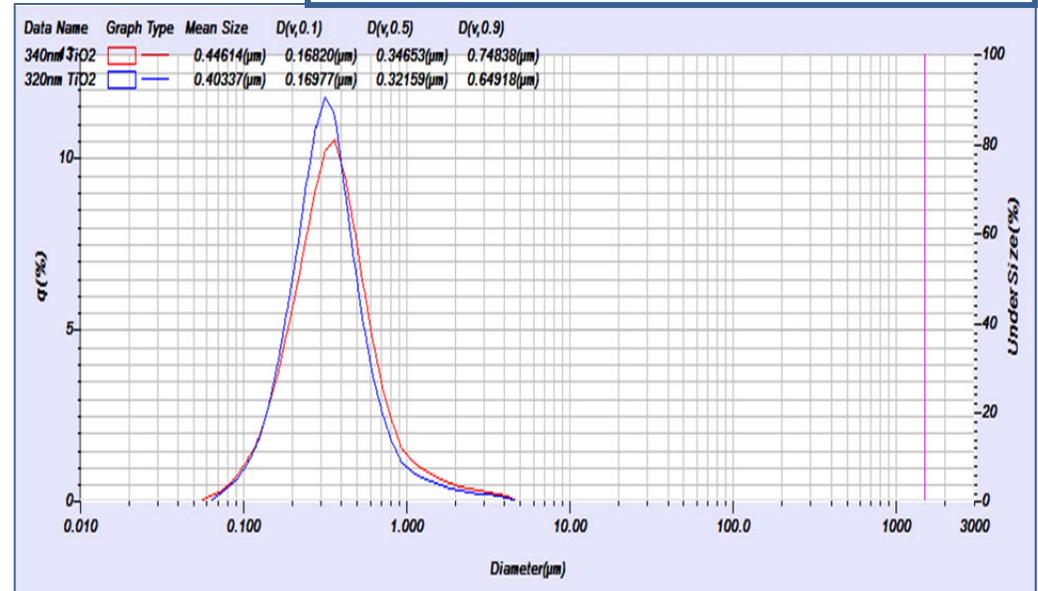
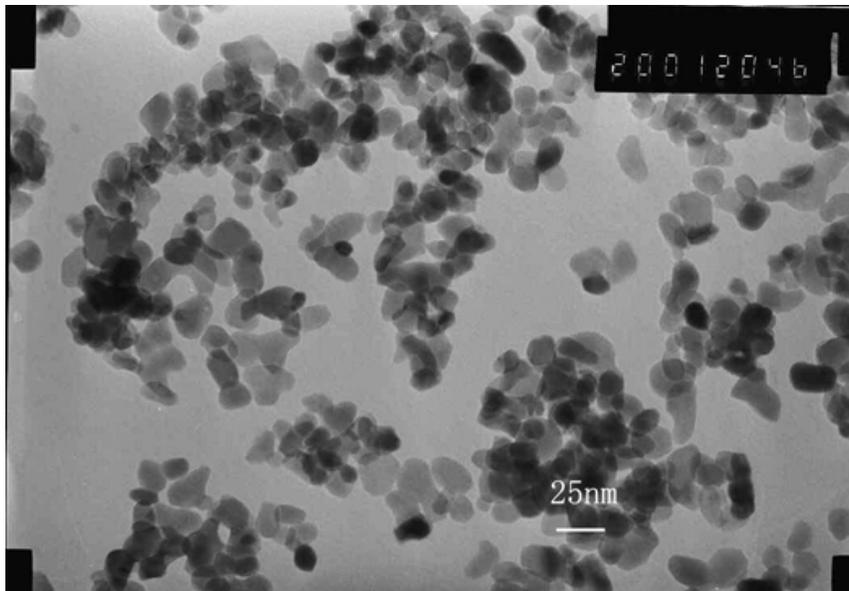
Watch for finer particles being created with increasing energy

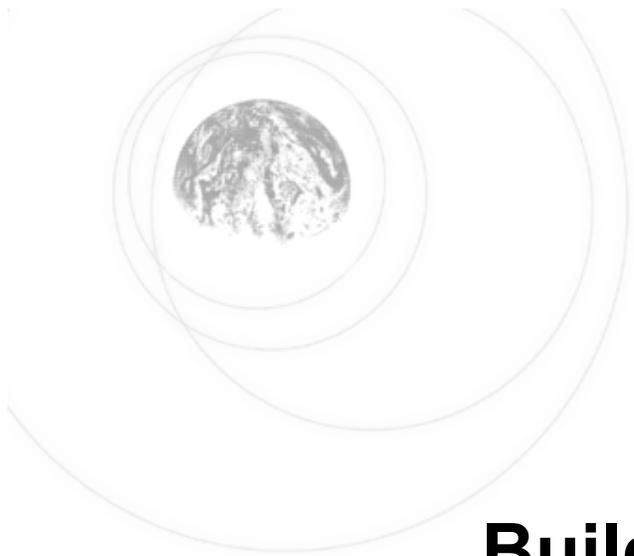


Matching expectations

- “Nanopowders” do not exist
- Know how the expectation was developed
- Classic example is TiO₂

PowderJet result with D50 of 320 nm does not compare to 20 nm!





Building Trust in Your Data

Webinar TR015, TR006, TR018



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First, trust your method

- Reproducible method that tracks product performance
- Use structured approach for any decision/choice that may influence result
- Have data to support selections made
- Document process so colleagues understand your choices
- Compare to accepted industry standards

ISO 13320

COV < 3% at Median (D50)
COV < 5% at D10 and D90

USP <429>

COV < 10% at Median (D50)
COV < 15% at D10 and D90

COV = 100*(StDev / Mean)

Note: All limits double when D50 < 10 μm

Note: Must acquire at least 3 measurements from unique samplings

A structured approach to method dev

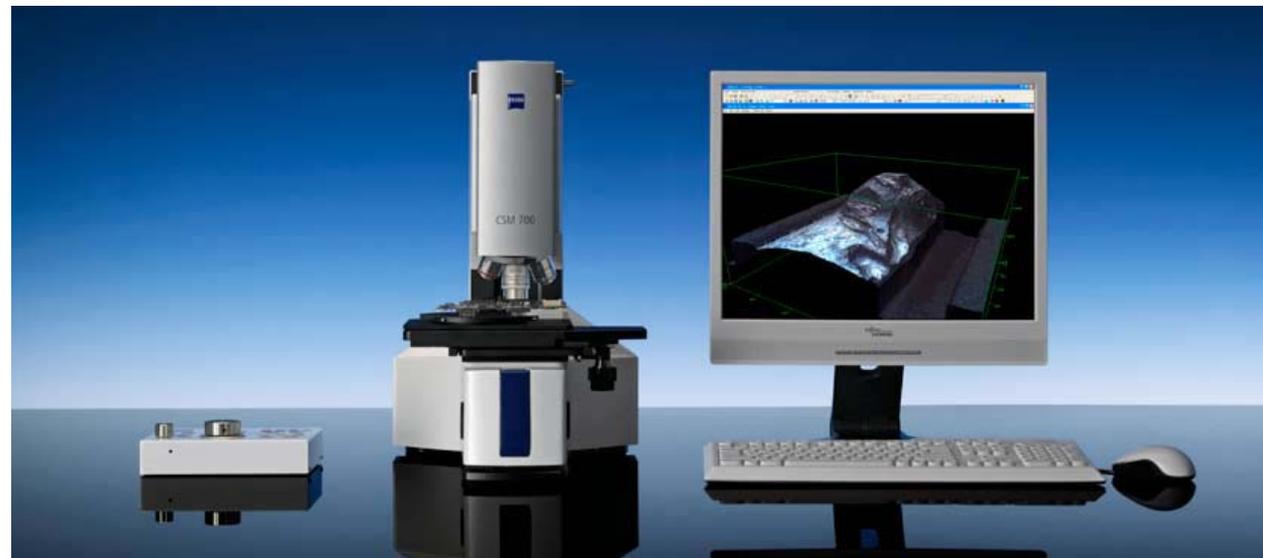
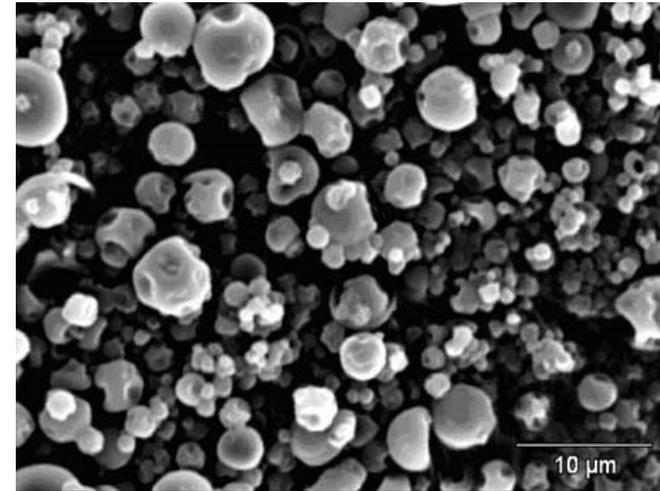
- First get sampling right & determine RI for diffraction
- Measure at 3 different pressures (low, medium, high)
- Determine optimum pressure based on good dispersion while not breaking particles
- Can also compare dry vs. wet measurements
- Adjust other settings to optimize mass flow & duration
- Ideally measure all of powder placed into the sampler
 - Segregation can occur on vibrating tray
 - Constant mass flow rate important for stable concentration during measurement
- Once settings chosen, test reproducibility, refine for maximum precision

Confirming dry particles < 1 micron

- Laser diffraction
- Ultramicroscopy
- Electron microscopy

Laser diffraction < 1 μm

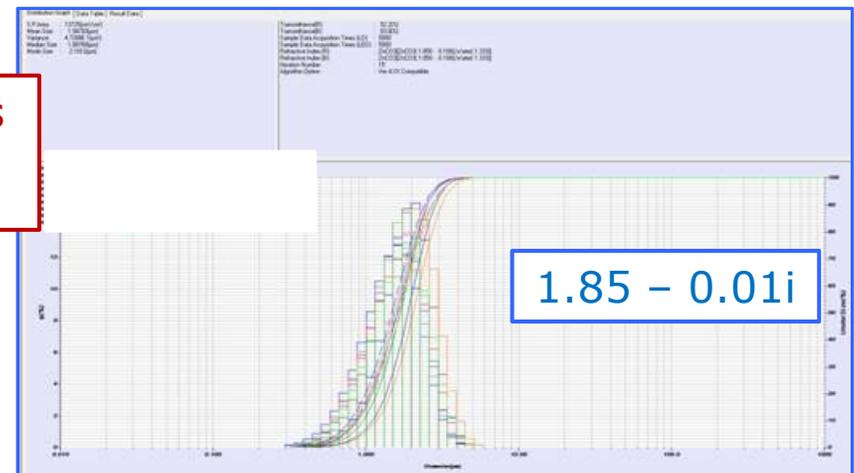
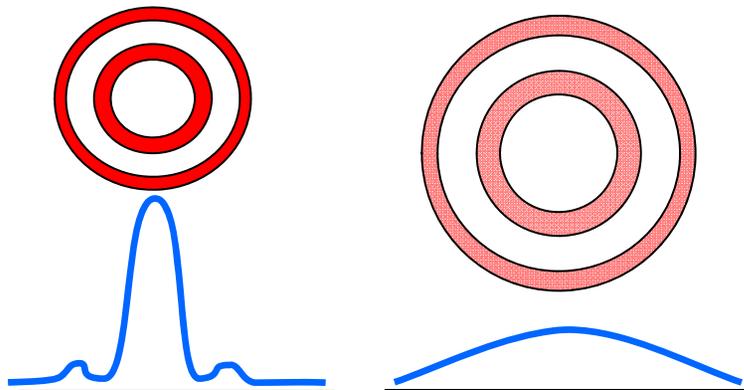
- Option: Electron Microscopy
 - Sampling is a concern
 - Can confuse primary particles and aggregates
 - Very high resolution



Laser diffraction < 1 μm

- Option: Change RI
 - Possible secondary scattering
 - Not as definitive as other options
 - Use Method Expert software to speed up

Large particles scatter intensely at low angles
 Small particles scatter weakly at high angles

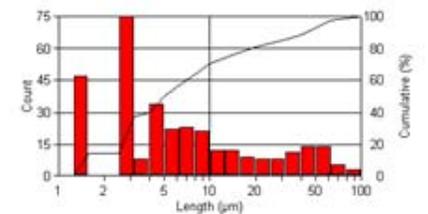
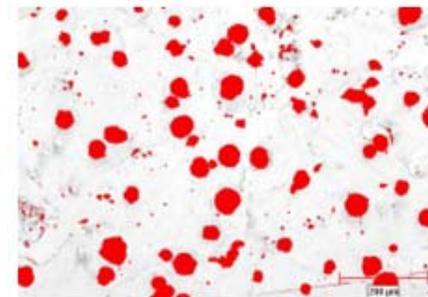
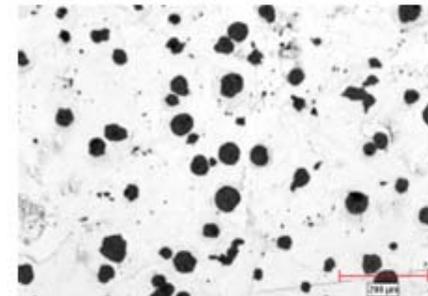


Confirming dry particles > 1 micron

- Laser diffraction
- Image analysis
- Sieves

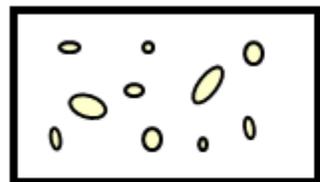
Laser diffraction > 1 μm

- Option: Image Analysis
 - Static or dynamic
 - Quickly verify large particles
 - Provide shape info
 - Automated or manual?
 - Reliable measurement?

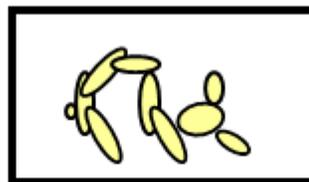


Laser diffraction $> 1 \mu\text{m}$

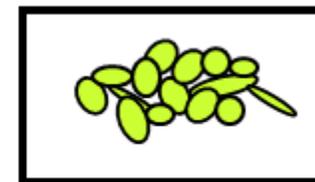
- Option: Sampling & dispersion
 - Large particles are more difficult to sample accurately
 - Try different sampling techniques like spin riffling (powders)
 - Large particles may actually be agglomerates
 - Try different air pressures
 - Try flow aids
 - See webinar TR005 on horiba.com



WELL DISPERSED



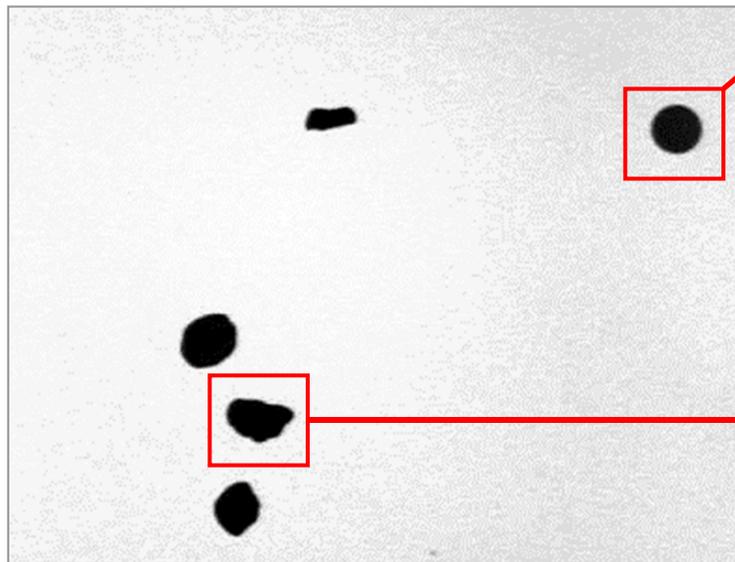
AGGLOMERATED



AGGREGATED

Image analysis > 1 μm

- Option: Save an image
 - Straightforward, convincing
 - Manual microscopy subjective
 - Automated IA software will save only those particles which meet certain size and shape criteria



x-values in mm

Nr=0 , d=2.148 ,

| | | |
|-----------------|-------------|-----------------|
| xFe_min=2.148 , | xFe=2.203 , | xFe_max=2.241 , |
| xMa_min=2.134 , | xMa=2.199 , | xMa_max=2.241 , |
| xc_min=2.148 , | xc=2.200 , | xc_max=2.241 , |

Symm=0.9827 , b/l=0.9480 ,

SPHT=0.9818 ,

Convex=0.9997 ,

OK

x-values in mm

Nr=0 , d=1.966 ,

| | | |
|-----------------|-------------|-----------------|
| xFe_min=1.970 , | xFe=2.546 , | xFe_max=3.063 , |
| xMa_min=1.889 , | xMa=2.419 , | xMa_max=3.047 , |
| xc_min=1.966 , | xc=2.419 , | xc_max=3.060 , |

Symm=0.9289 , b/l=0.6361 ,

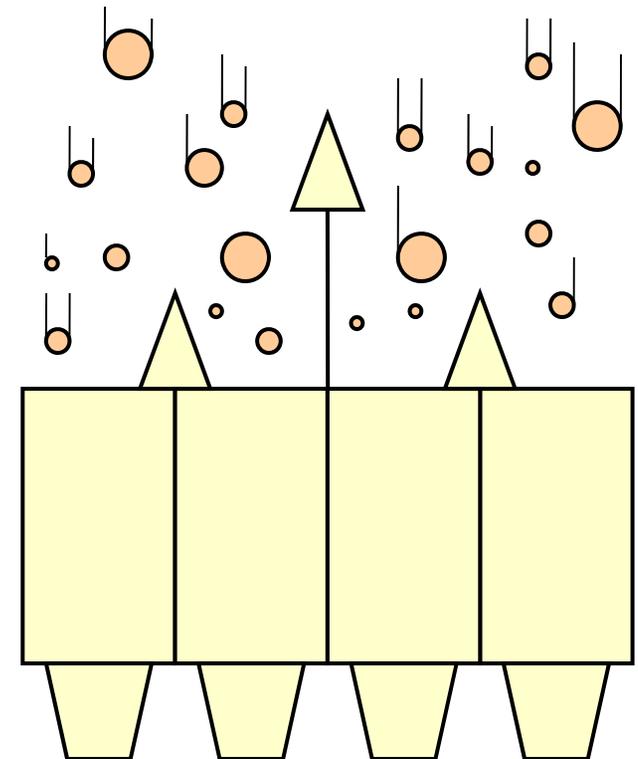
SPHT=0.9066 ,

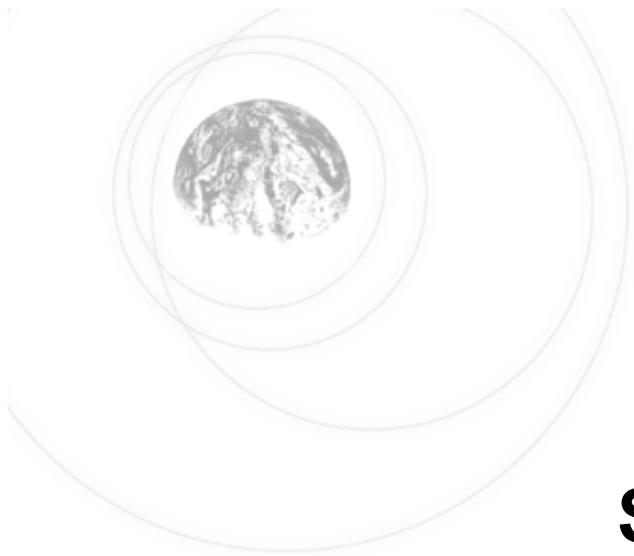
Convex=0.9995 ,

OK

Image analysis > 1 μm

- Option: Sampling & dispersion
 - Large particles are more difficult to sample accurately
 - Try different sampling techniques like spin riffling (powders)
 - Large particles may actually be agglomerates
 - Try different dispersing pressures
 - See webinar TR005 on horiba.com





System Verification

Webinar TR004
Verification web page



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System verification

- Look to standards for guidance
 - Laser diffraction – ISO 13320, USP <429>
 - Dynamic image analysis – ISO 13322-2
- Ask vendor for recommendations
- Are the materials reference standards or certified standards?
- Useful to develop internal reference material(s)

Polydisperse standards

- Now good range of sizes available
- Remember the typical error sources vs. size
- Can buy in proper quantities for given samplers
 - No sub-sampling concerns
- Ideal for dry powder systems
- No point in measuring more than one size range

| Nominal Size (µm) | Catalogue Number | Nom. Wt. Per Vial (g) | Sold in 10 bottle sets. Price per Set: | | |
|-------------------|------------------|-----------------------|--|-----|-----|
| | | | £ | €* | \$* |
| 0.1 - 1µm | PS180 | 0.01 | 206 | 315 | 415 |
| | PS181 | 0.02 | 240 | 365 | 485 |
| 1 - 10µm | PS190 | 0.025 | 69 | 105 | 140 |
| | PS191 | 0.05 | 92 | 140 | 185 |
| | PS192 | 0.10 | 115 | 175 | 235 |
| | PS193 | 0.25 | 156 | 240 | 315 |
| | PS194 | 0.50 | 206 | 315 | 415 |
| 3 - 30µm | PS200 | 0.025 | 59 | 90 | 120 |
| | PS201 | 0.05 | 69 | 105 | 140 |
| | PS202 | 0.10 | 92 | 140 | 185 |
| | PS203 | 0.25 | 115 | 175 | 235 |
| | PS204 | 0.50 | 156 | 240 | 315 |
| | PS205 | 1.0 | 206 | 315 | 415 |
| 10 - 100µm | PS211 | 0.05 | 59 | 90 | 120 |
| | PS212 | 0.10 | 80 | 125 | 165 |
| | PS213 | 0.25 | 102 | 155 | 205 |
| | PS214 | 0.50 | 146 | 225 | 295 |
| | PS215 | 1.0 | 194 | 295 | 390 |

www.whitehousescientific.com



Thank you

ありがとうございました

Dziękuję

ขอบคุณครับ

谢谢

Cảm ơn

Gracias

اشكر

Σας ευχαριστούμε

धन्यवाद

Grazie

Tacka

Danke

Merci

நன்றி

감사합니다

Большое спасибо

Obrigado

おもしろ おがしく

Omoshiro Okashiku

The screenshot shows the HORIBA Scientific website's Particle Characterization page. At the top, there's a navigation bar with categories like Automotive Test Systems, Process & Environmental, Medical, Semiconductor, Scientific, and All Segment Product Browser. Below this is a secondary navigation bar with links for Products, Markets & Industries, Service & Support, News & Events, Newsletter, About Us, Employment, and Feedback. The main content area is titled 'Particle Characterization' and includes a sidebar with links to Particle Size Analysis, Particle Shape Analysis, Zeta Potential Analysis, Surface Area Analysis, Applications, Technology, Bibliography, Request Information, and Download Center. The main text describes the company's commitment to innovation and lists various analytical techniques used in their instruments. A right sidebar contains sections for Request Information, Quick Request, Particle Size Essentials, Newsletter, and Download Center, each with a corresponding icon and a 'Sign Up' or 'More Info' button. At the bottom right, there is a Member login section with fields for E-Mail Address and Password, and a Login button.

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← View application & technical notes (170+), webinars (70+), white papers.