Optimizing Dry Powder Measurements

Featuring the LA-950 PowderJet

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What we'll talk about

- Why measure dry?
- Sampling & dispersion tips
- Unique PowderJet features
- Method development studies

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Why Measure Dry?

- Difficult to measure wet
  - Solubility
  - Density
  - Expensive
  - Swelling
- Final use is dry
- Native state

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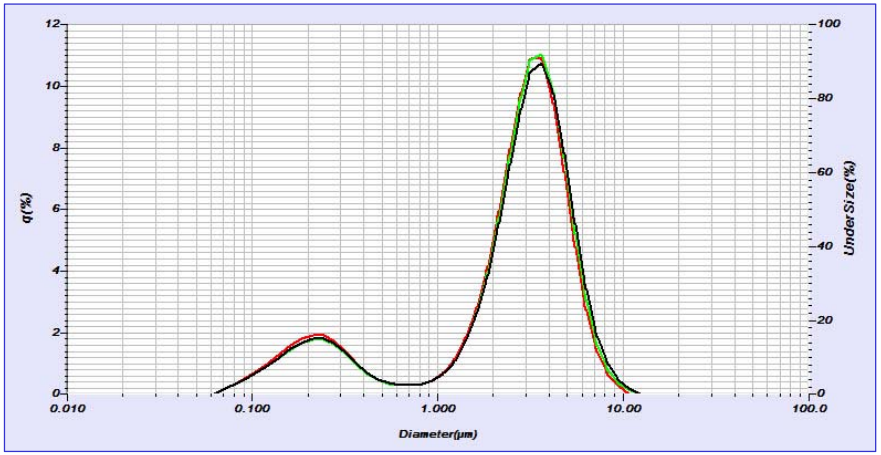
The Workflow

+

+

=



MAXIMUM PRECISION!

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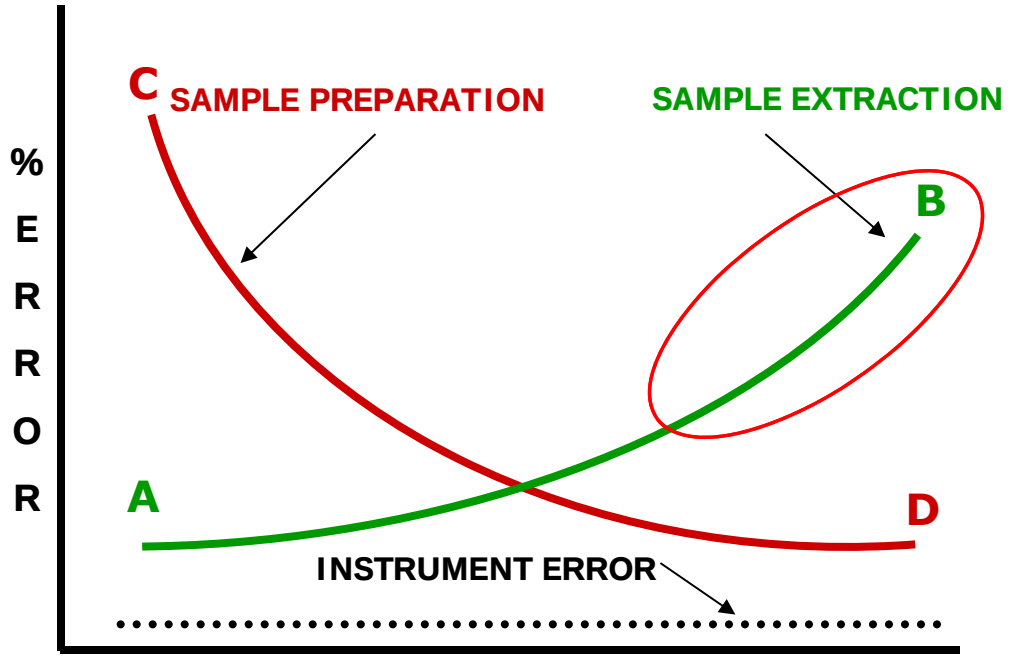
Measurement Error Sources

SMALL PARTICLES

- POTENTIALLY SMALL EXTRACTION ERRORS (A)
- POTENTIALLY LARGE SAMPLE PREP ERRORS (C)

LARGE PARTICLES

- POTENTIALLY LARGE EXTRACTION ERRORS (B)
- POTENTIALLY SMALL SAMPLE PREP ERRORS (D)



INSTRUMENT ERROR IS SMALL AND RELATIVELY CONSTANT

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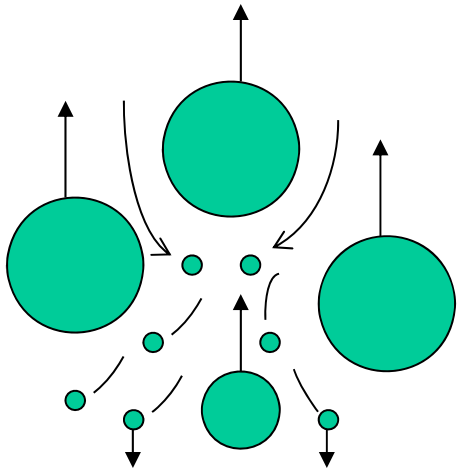
Technique: Grab Sampling

- **PLACE SPATULA INTO POWDER**

  EXTRACT SMALL AMOUNT FOR ANALYSIS

  ACCEPTABLE FOR NARROW DISTRIBUTIONS



SEGREGATE LARGE AND SMALL WHEN POLYDISPERSE

- LARGE PARTICLES PERCOLATE UPWARD
- SMALL PARTICLES GRAVITATE DOWNWARD

EASY METHOD

MOST USED METHOD

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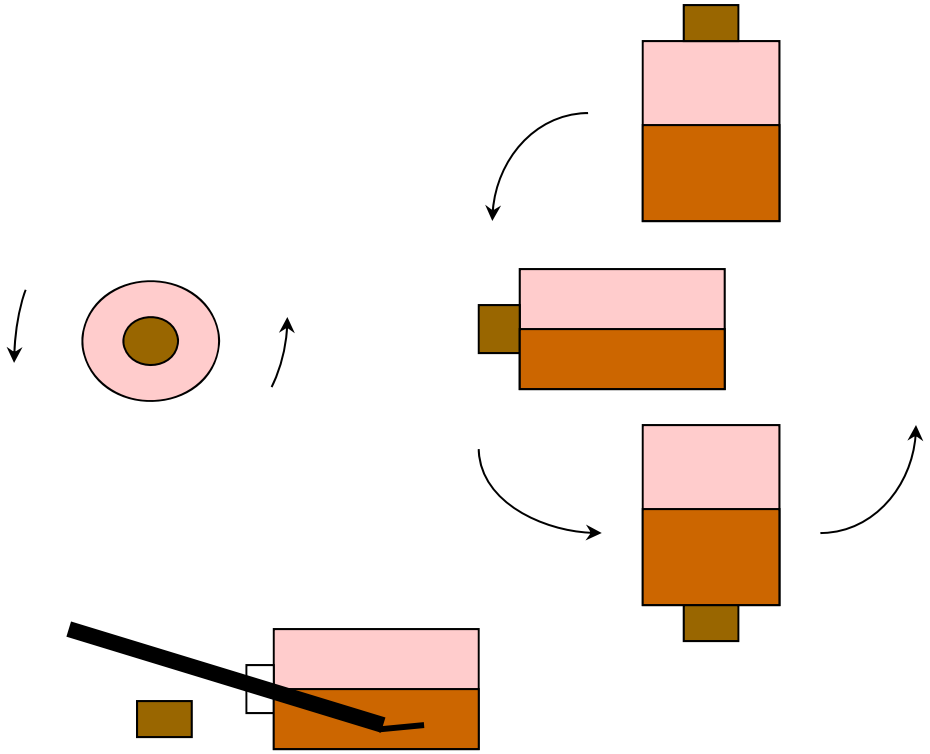
Grab Sampling from Bottle

When a powder is stored in a container, it can be mixed by rolling and tumbling the container. The container should not be more than half to two-thirds full. It is important to perform this action before "grabbing" a sample with a spatula.



Then pull sample with a spatula…..

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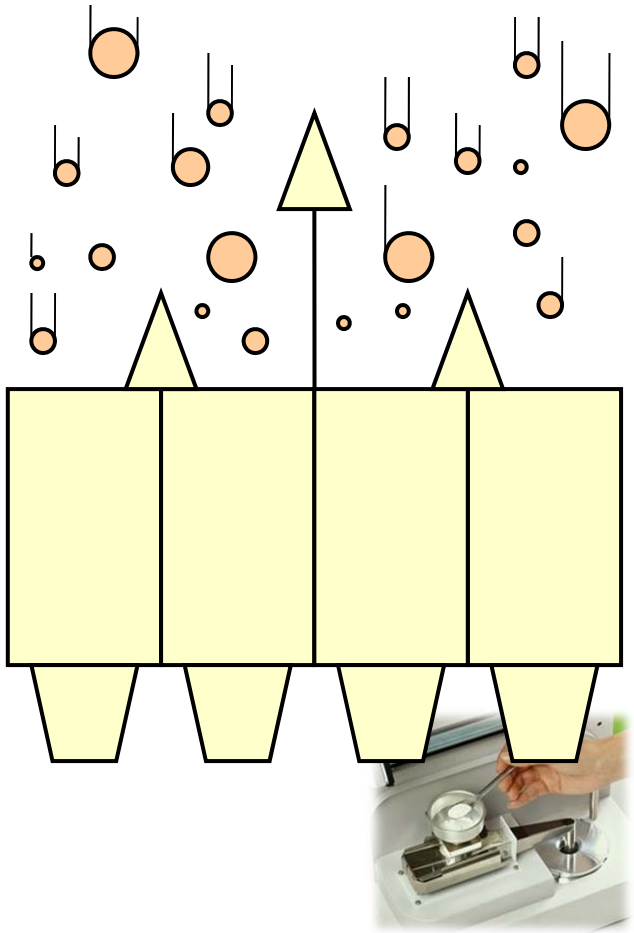
Technique: Chute Riffling

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.



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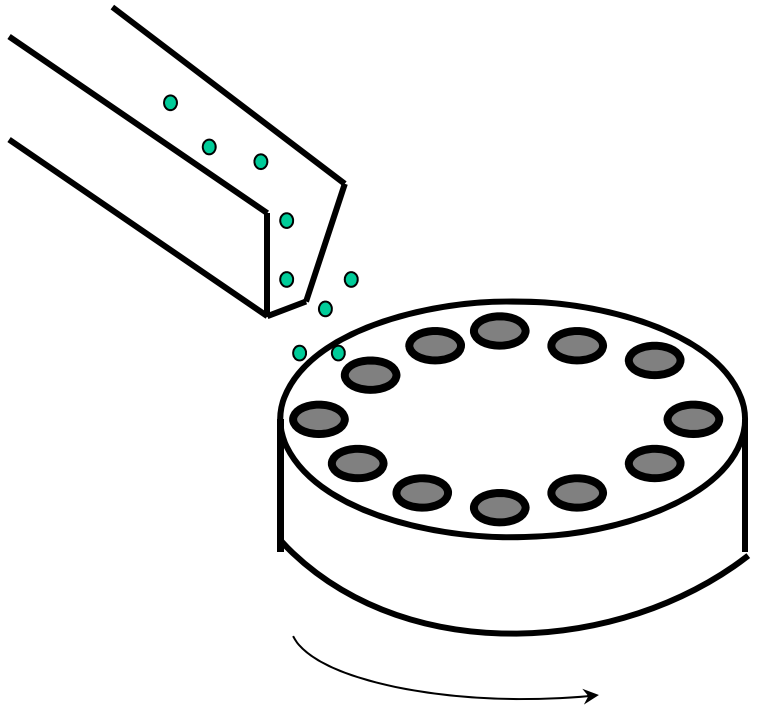
Technique: Rotary Riffling

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

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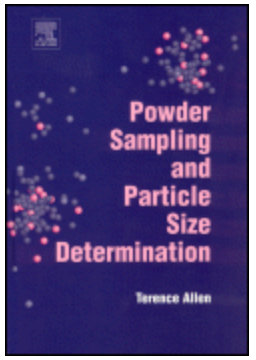
Sampling Technique Error Levels

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

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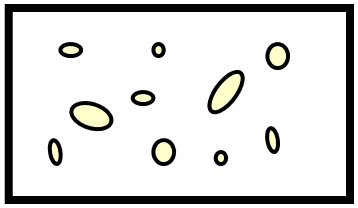
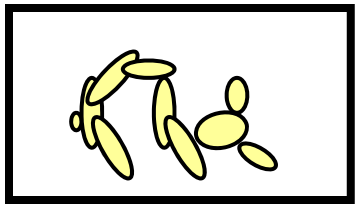
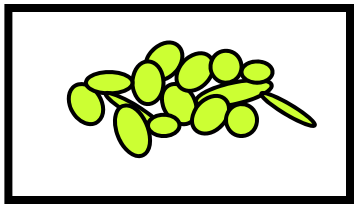
Dispersion Definitions



WELL DISPERSED



AGGLOMERATED



AGGREGATED

WELL DISPERSED particles can be easily detected under an optical microscope. They are separated from one another and show no tendency to cling together.

AGGLOMERATED particles appear in clumps that can be separated easily by the application of moderate amounts of energy, such as ultrasonics.

AGGREGATED particles are tightly bound and must be treated with higher levels of energy. Usually an ultrasonic probe applied directly to the sample slurry will disperse the particles. If they are very tightly bound, they may fracture before they can be separated.

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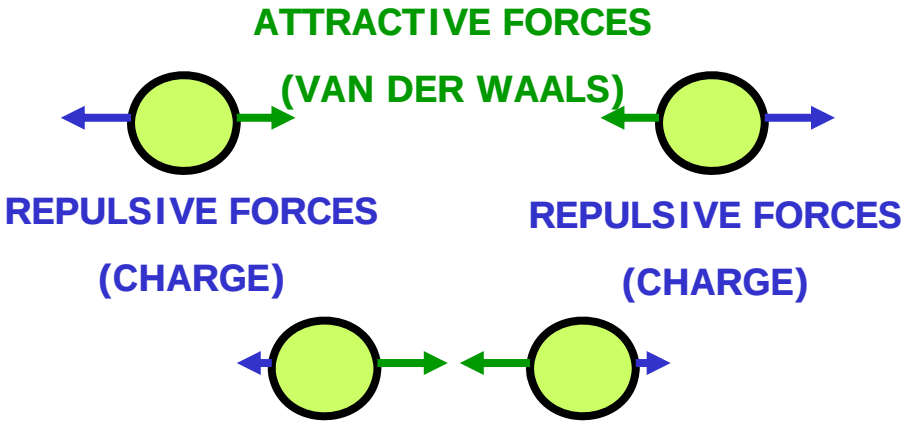
Particle Interactions



Particles are constantly moving with respect to one another. When they approach close enough to cross the potential barrier (when attractive forces exceed repulsive forces), they come together (agglomerate).

The object is to provide repulsive forces strong enough to keep particles apart, even during close approach. This can be accomplished by surfactant coating of particle surfaces for wet dispersions or sufficient compressed air for dry dispersions.

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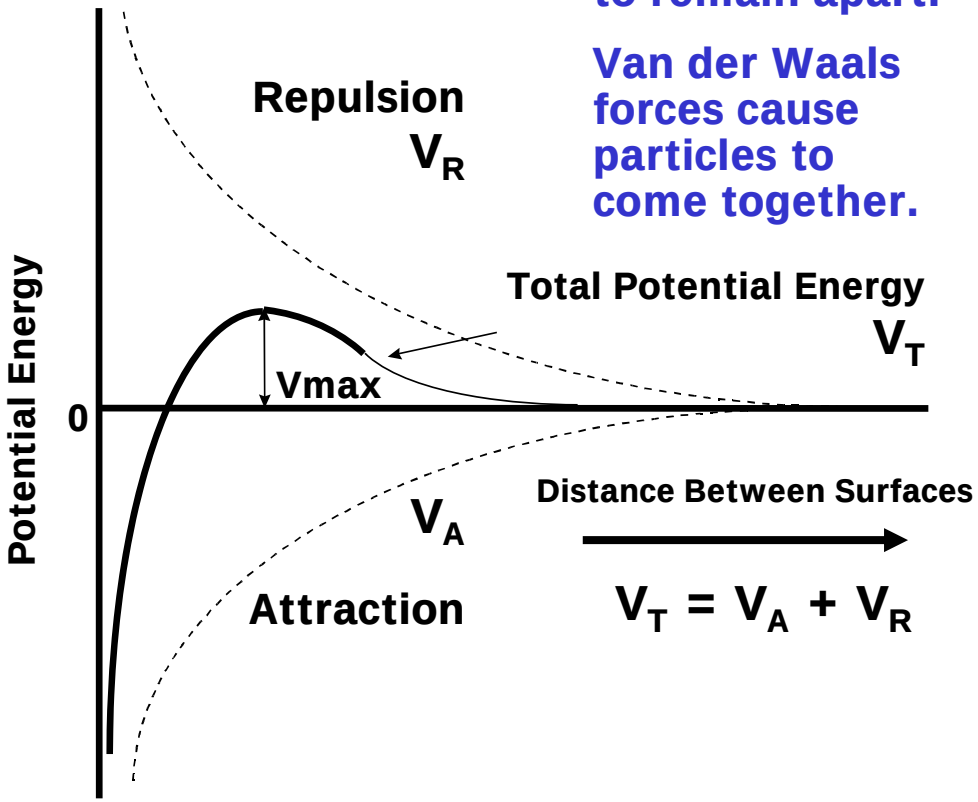
Energy of Interaction

- INTERACTION OF TWO CHARGED SURFACES



- **Stability of a system depends on forces between particles. Random motion brings them into close proximity. Whether two particles will combine depends on potential barrier between them. Potential energy consists of two forces, the ATTRACTIVE one due to Van der Waals, and the REPULSIVE one due to electrical double layers around particles.**
- **If height of the barrier, V_T, is lower than average thermal energy, K_T, then probability is high that two adjacent particles will eventually collide. They will probably remain attached to each other due to strong Van der Waals forces at very close distances.**

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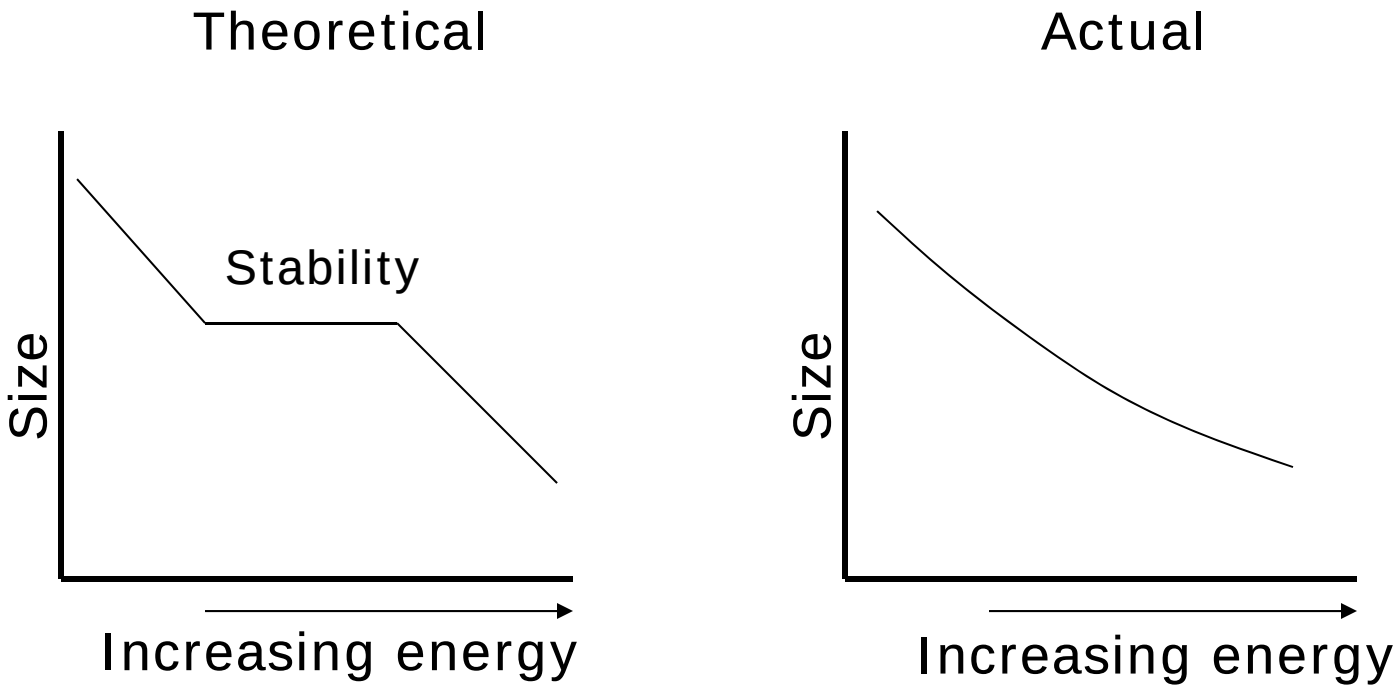
Dispersion vs. Breakage



Higher air pressure or longer ultrasound duration

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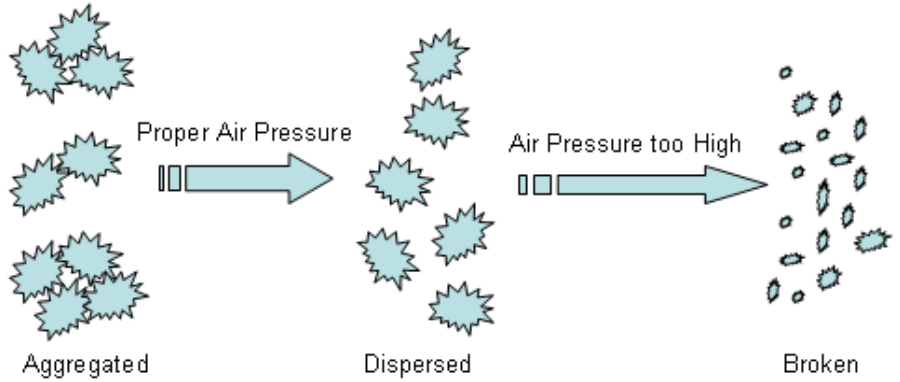
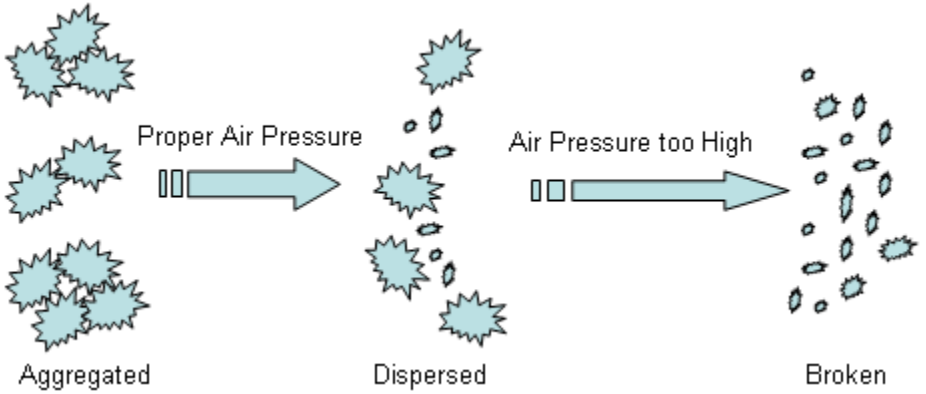
Dispersion vs. Breakage

- Dispersion and milling can be parallel rather than sequential processes

Theoretical



Actual



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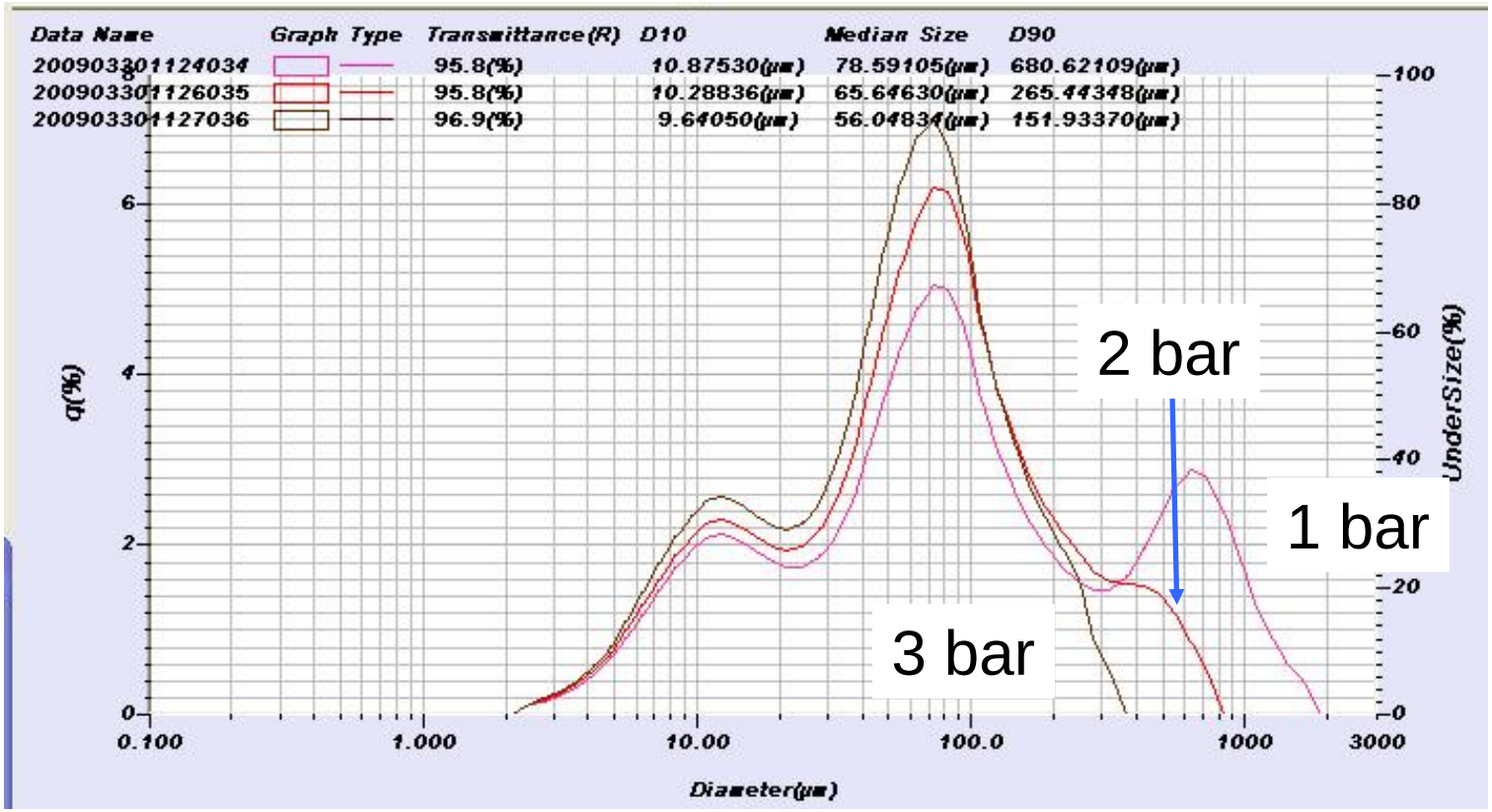
Dispersing Agglomerates

Watch for no change in coarsest particles with changing energy



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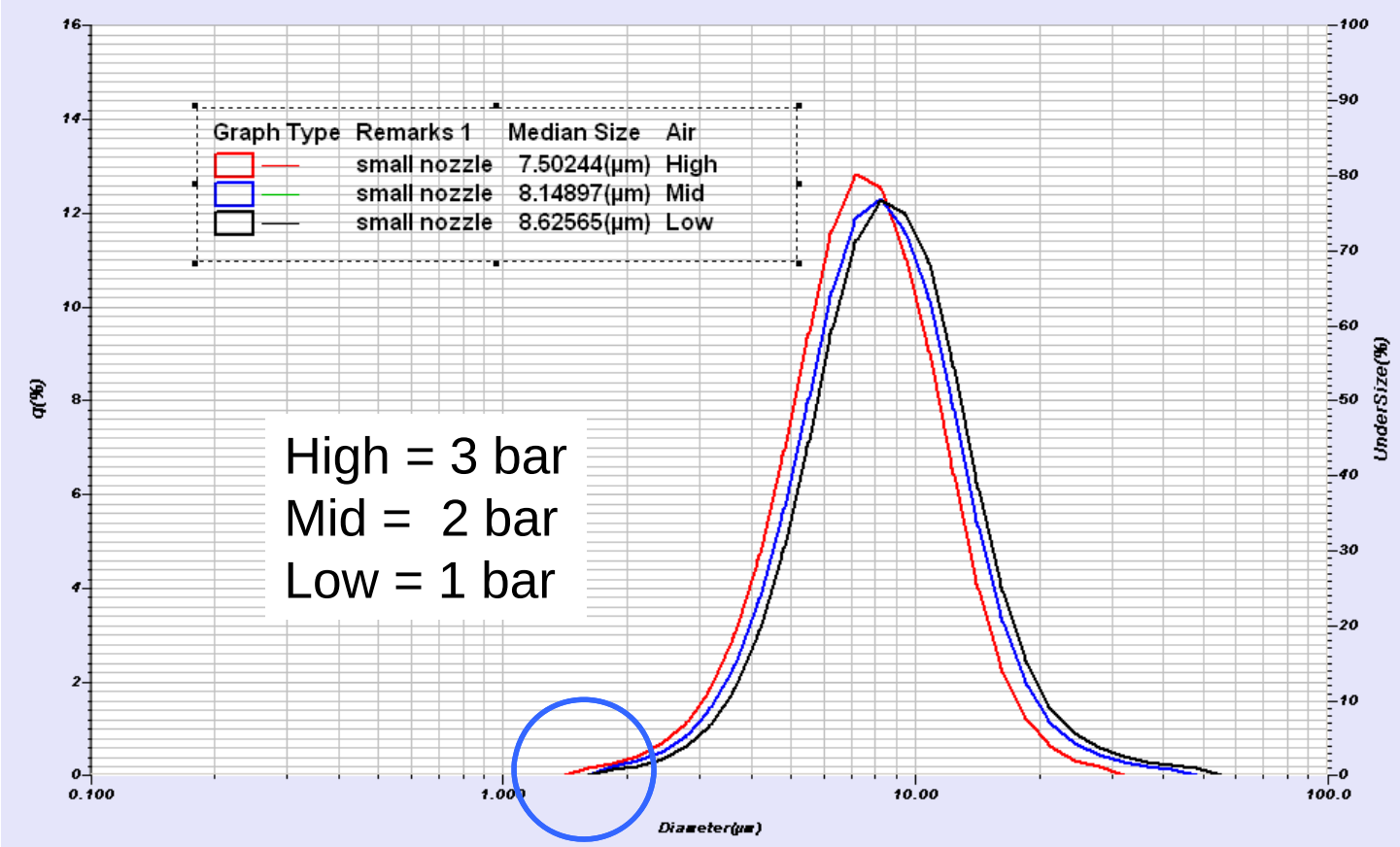
Breaking Particles

Watch for finer particles being created with increasing energy



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What we'll talk about

- Why measure dry?
- Sampling & dispersion tips
- Unique PowderJet features
- Method development studies

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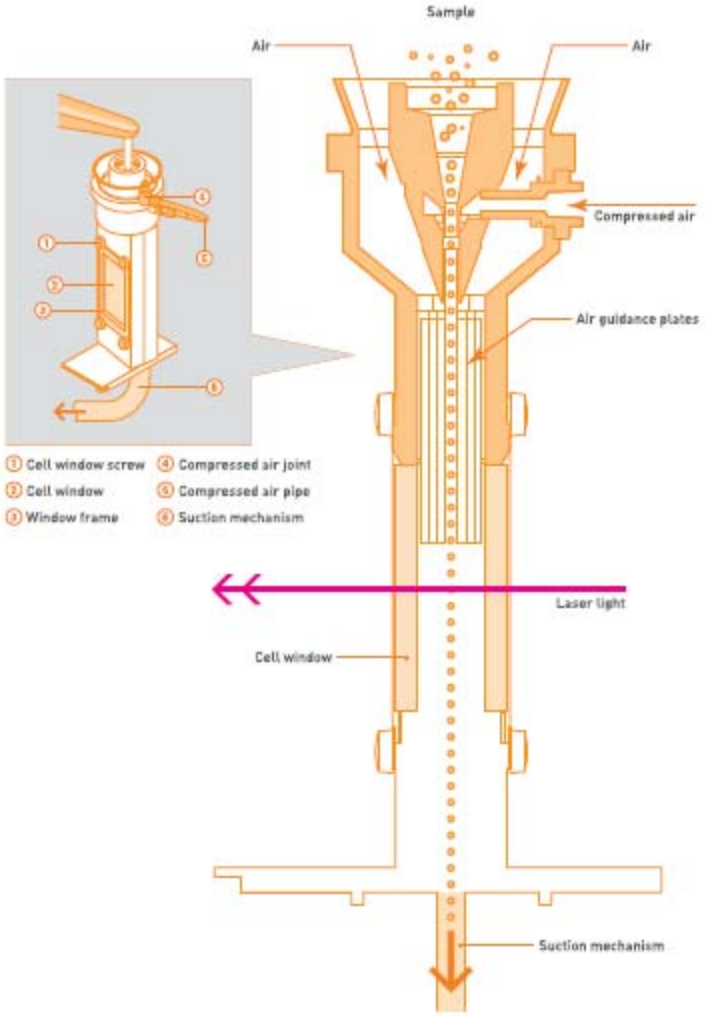
LA-950 PowderJet



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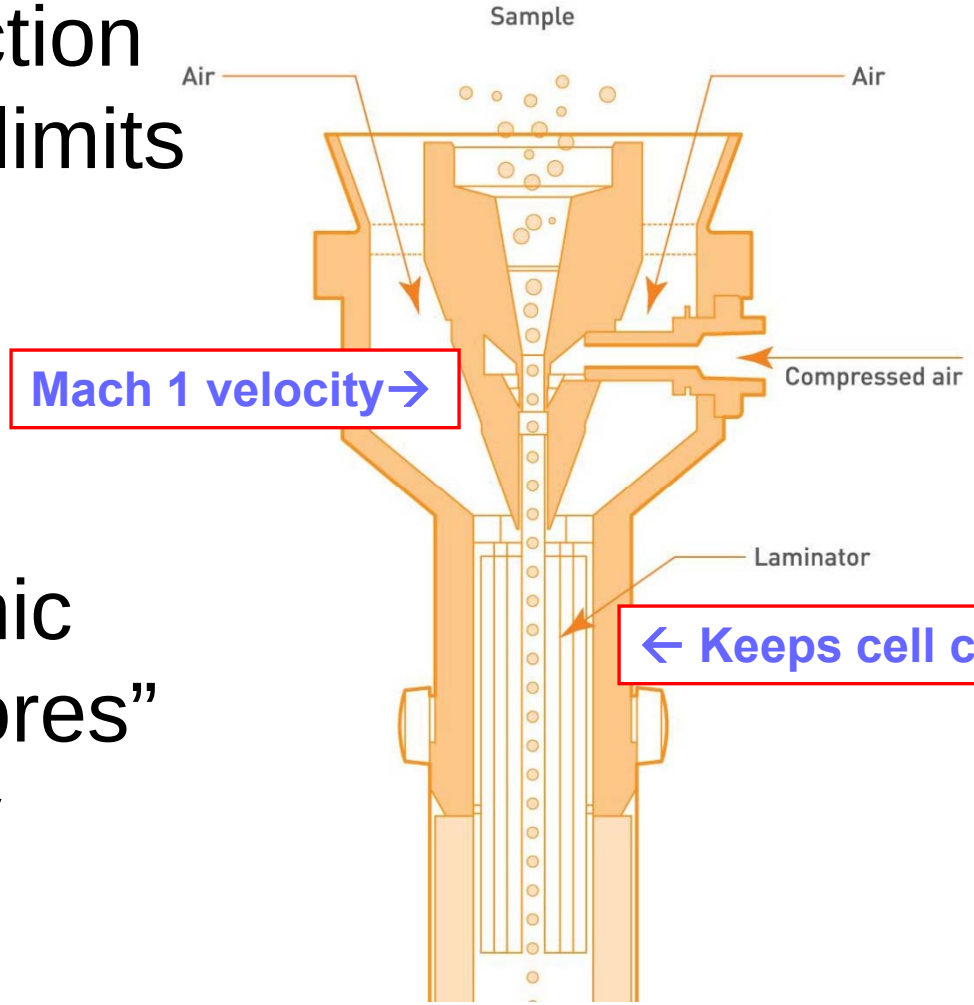
Rocket Science

- No impaction surfaces limits breakage



Mach 1 velocity→

- Supersonic flow “ignores” boundary layer

← Keeps cell cleaner, longer

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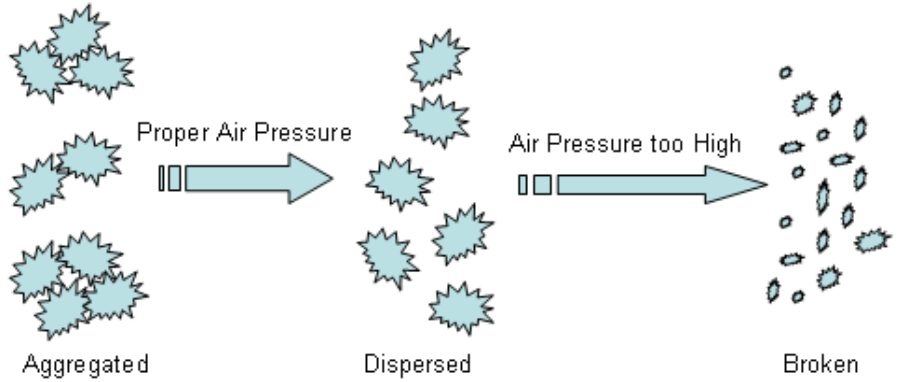
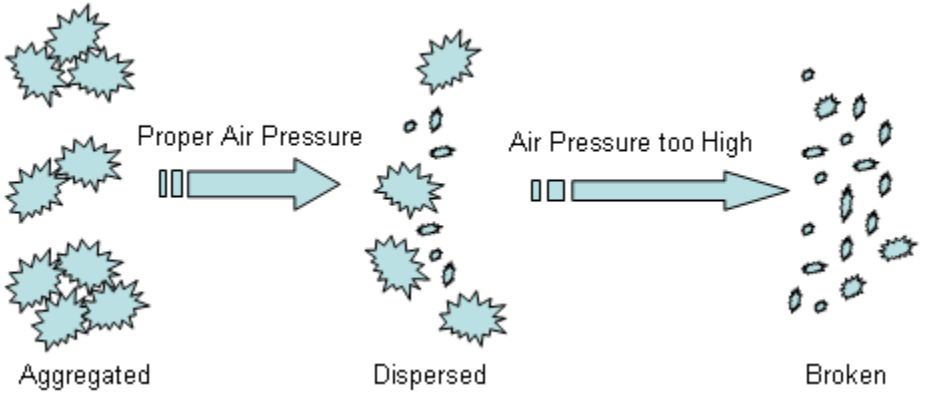
Dispersion vs. Breakage

- Dispersion and milling can be parallel rather than sequential processes

Theoretical



Actual



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Auto Measurement Setup

- Fastest way to get great data
- Need to make three choices
  - What starts the measurement?
  - What scans are good?
  - What stops the measurement?

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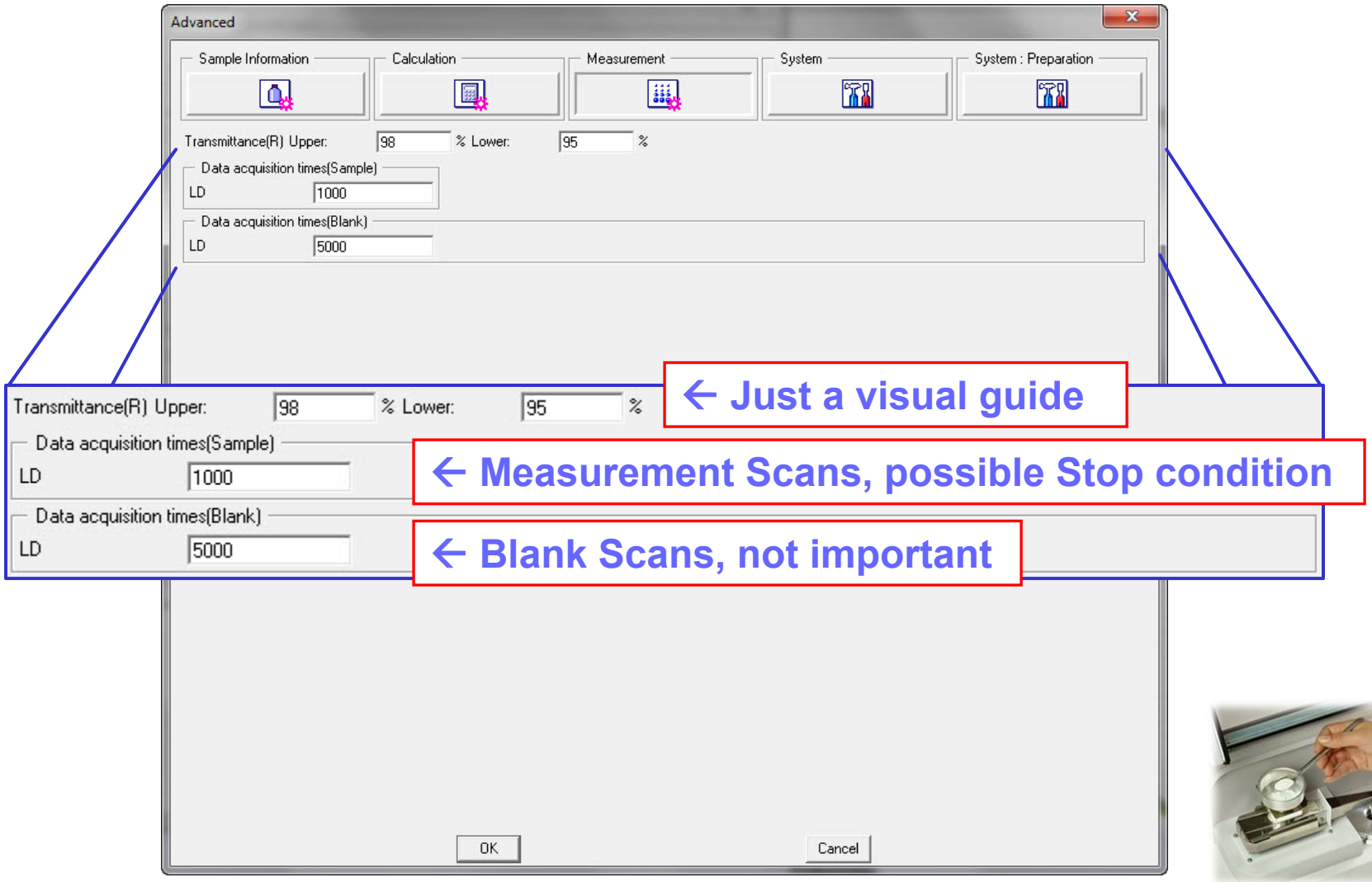
Auto Measurement Screens



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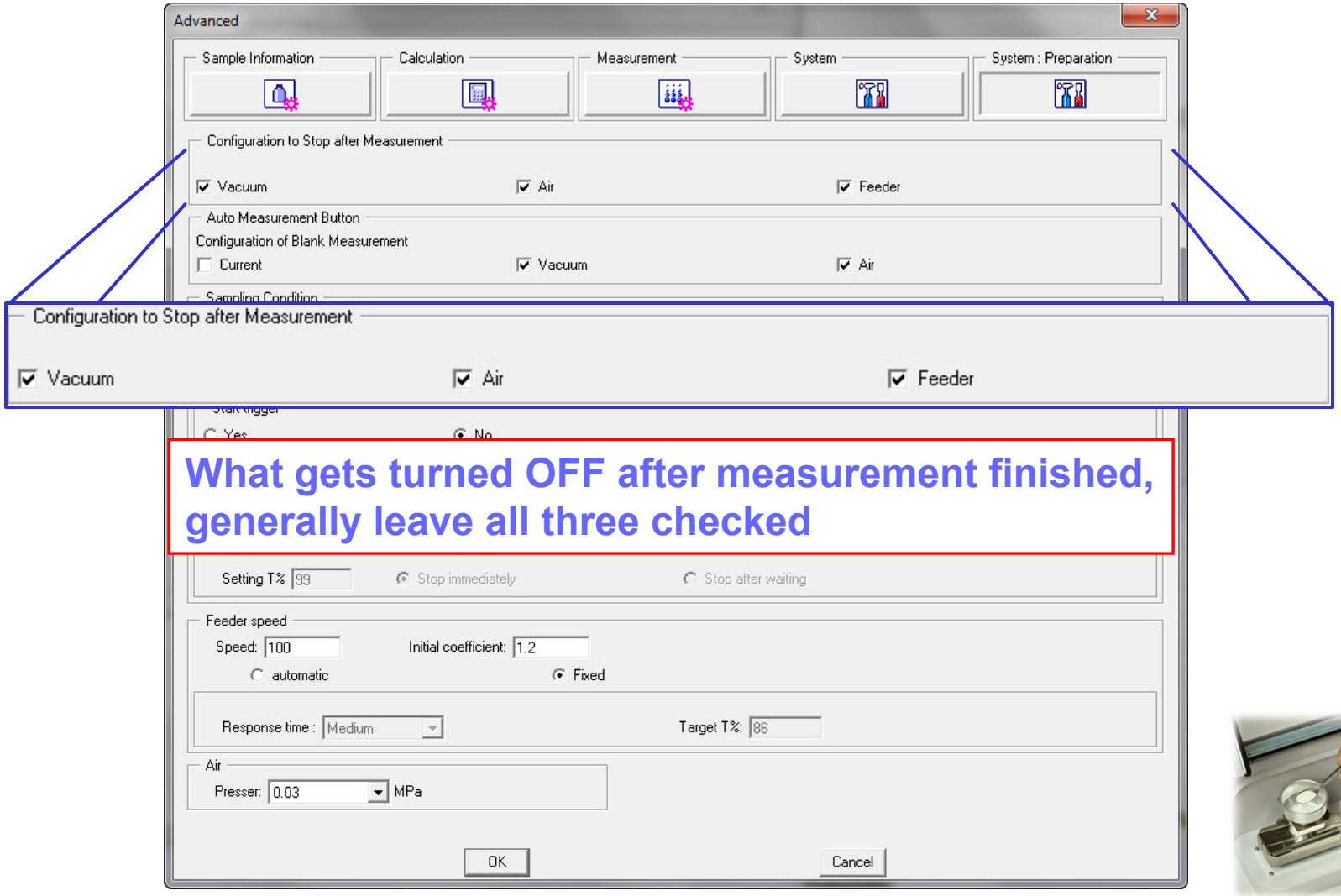
Auto Measurement Screens



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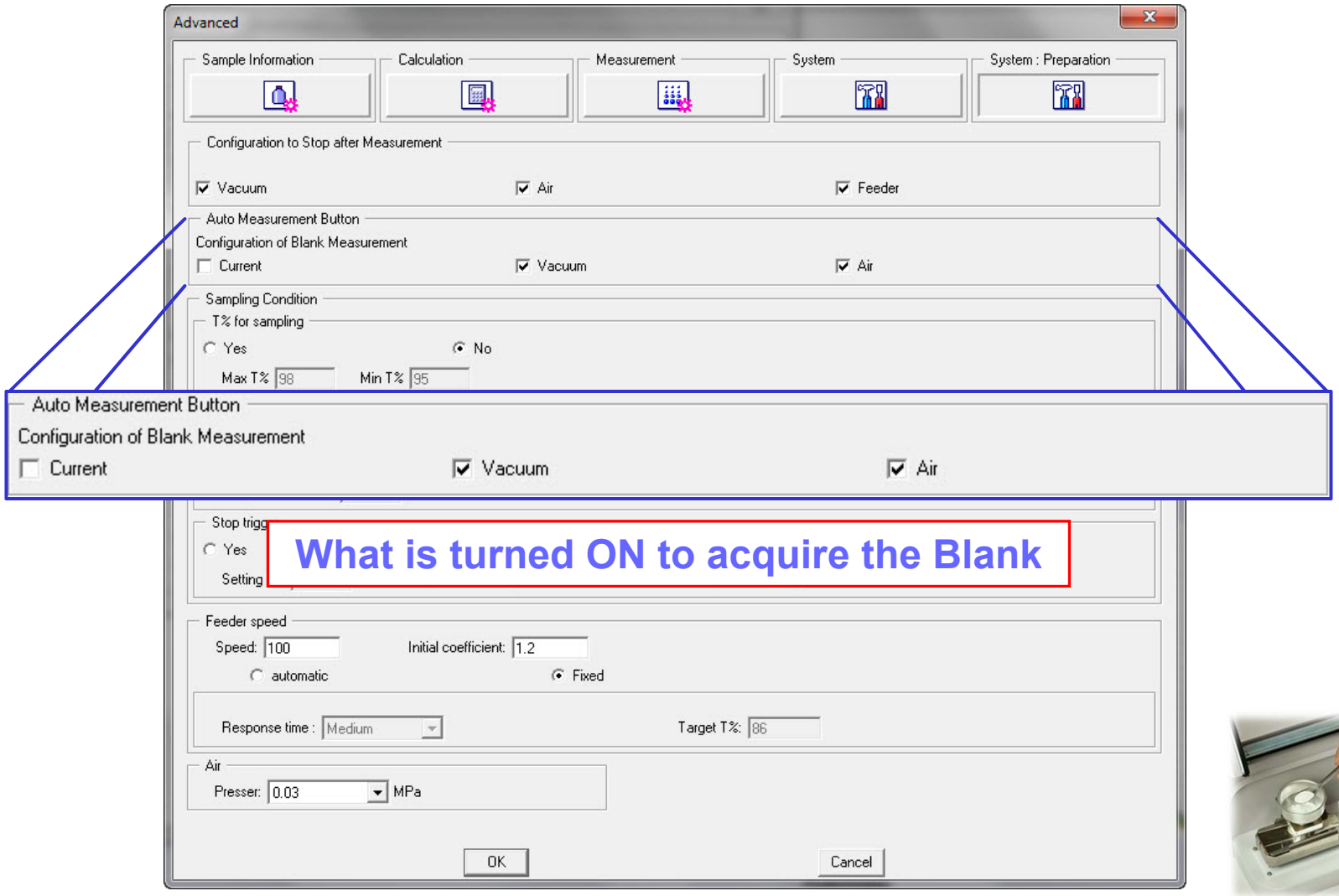
Auto Measurement Screens



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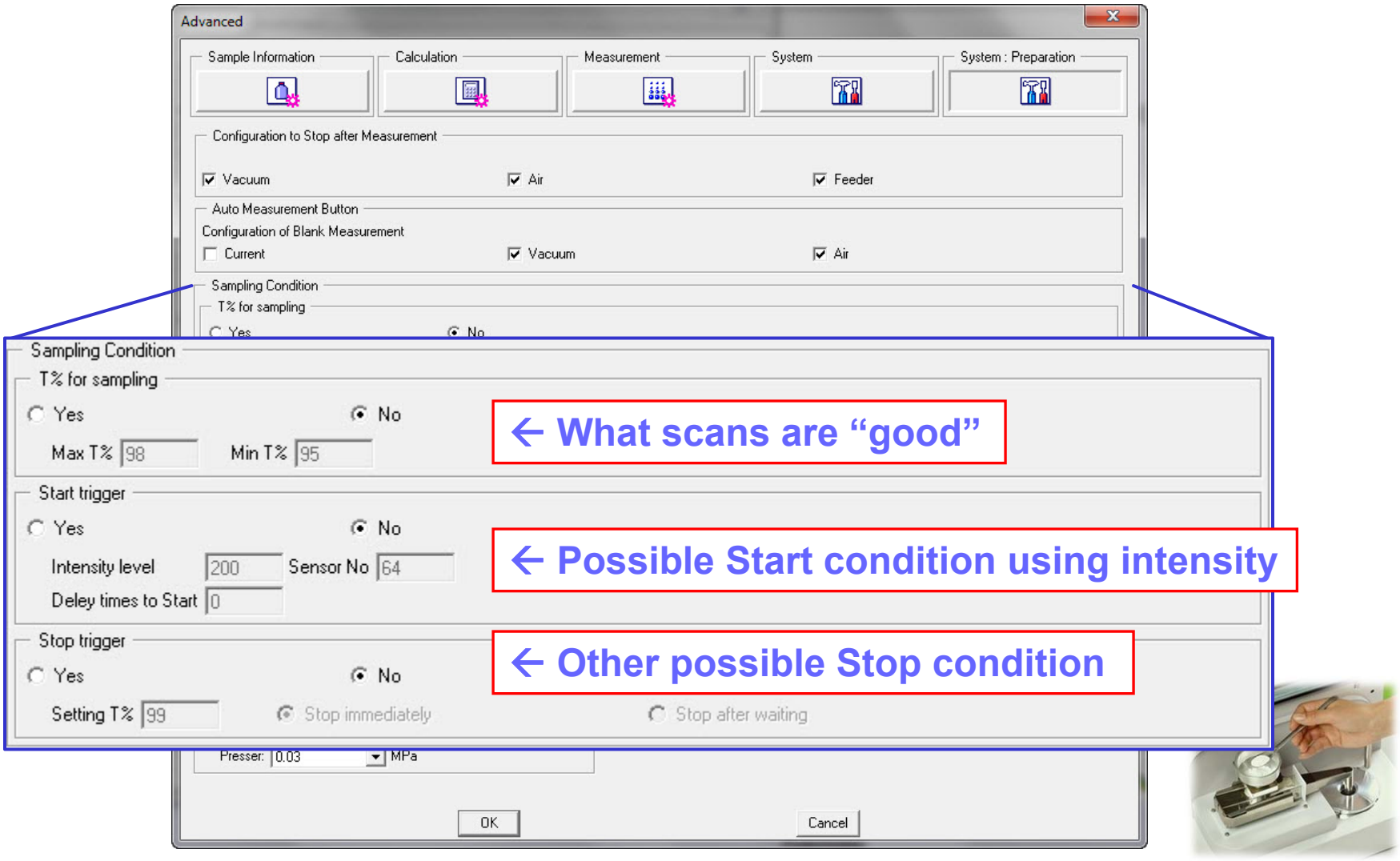
Auto Measurement Screens



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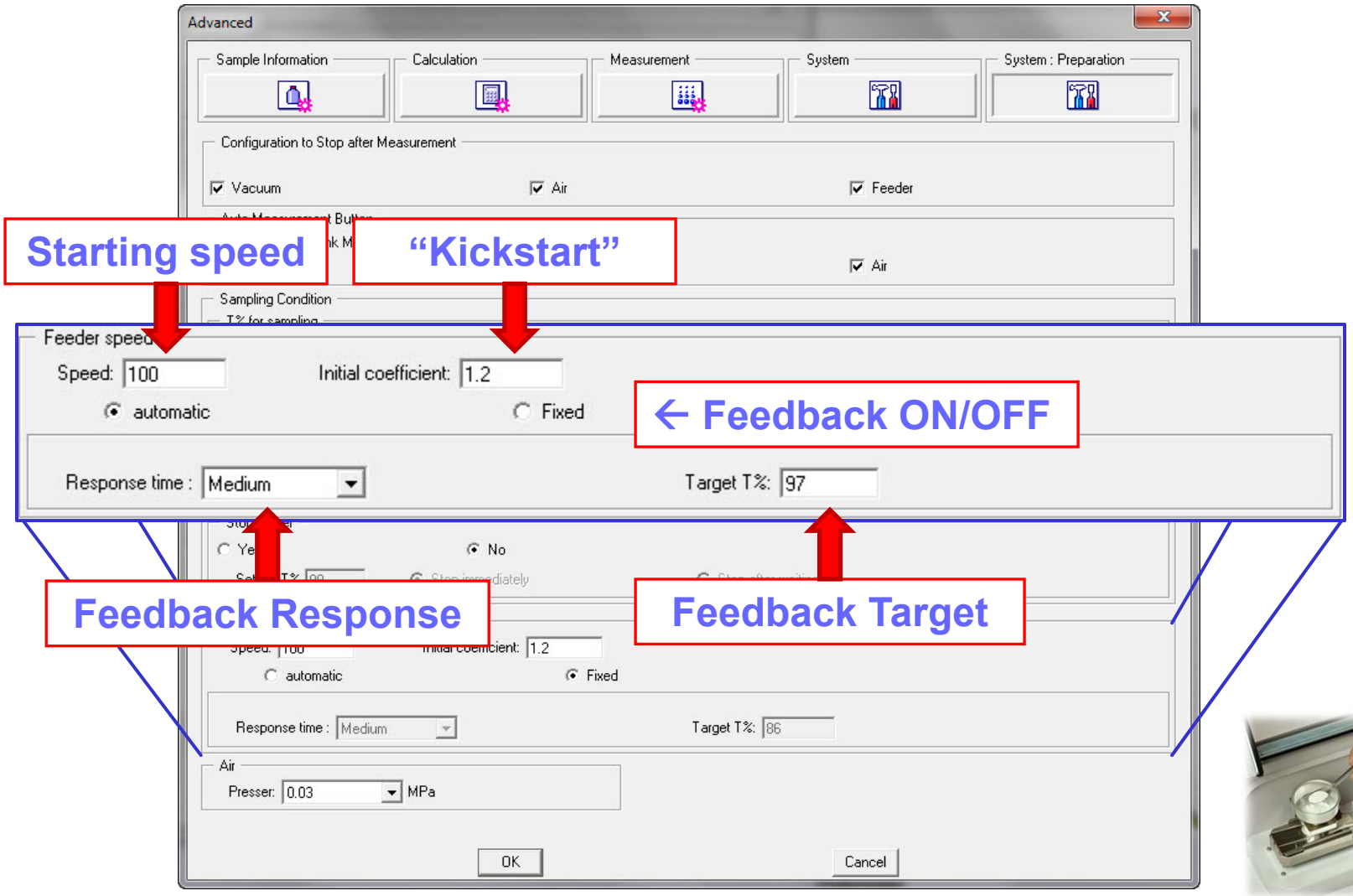
Auto Measurement Screens



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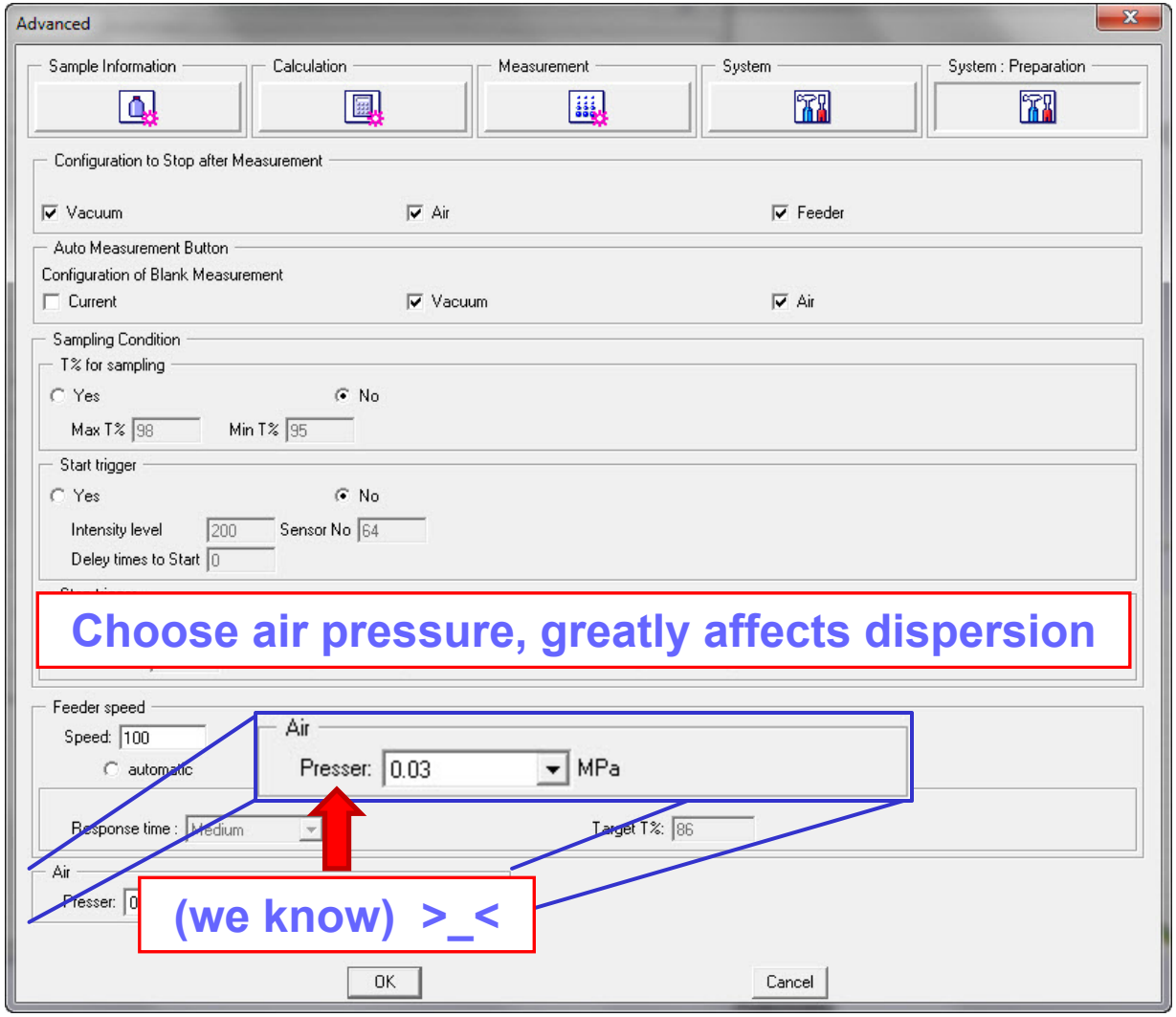
Auto Measurement Screens



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Starting a Measurement

- Two Options
  - Begin collecting scans immediately
  - Wait for Detector/Channel/Sensor to activate when powder flows (Start Trigger)
- Typically, we choose Option 1
- Take care with the Stop Trigger and powder loading on feeder tray

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Stopping a Measurement

- Two Options
  - Timed measurement (number of Scans)
  - Measure all powder (Stop Trigger)
- Typically, sampling determines choice
  - Choose timed measurement for easy
  - Measure entire tray for difficult sampling
- Take care to use wait period (Delay) with Stop Trigger

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During the Measurement

- Collect all scans or only “good”?
  - T% control improves precision
  - Tight range = best precision
  - Take care with very agglomerated powders
- To Feedback, or not to Feedback
  - We always use this
  - Take care that Target T% is inside T% range for “good” scans

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Superior Dry Powder Feeder

- Feedback control of sample flow rate
  - This is critical
    - Maximum precision
    - No ghost peaks or funny business
    - Fewer headaches!
  - Unique to HORIBA
- Supersonic dispersion
- Auto Measurement function

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Dry Method Workflow

- First get sampling right & determine RI
- 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 sample concentration & 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

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Goals for any Method

- Reproducible method that tracks product performance
- You might have other goals
  - Accuracy: tricky subject, is it the “real” particle size?
  - Repeatability: liquid suspension re-circulating in sampler
  - Reproducibility: prepare, measure, empty, repeat
  - Resolution: optimize to find second populations
  - Match historic data (sieves), but quicker, easier technique
- Use structured approach for any decision/choice that may influence result
- Have data to support selections made
- Document process so colleagues understand your choices

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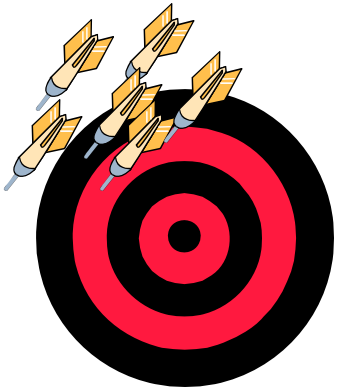
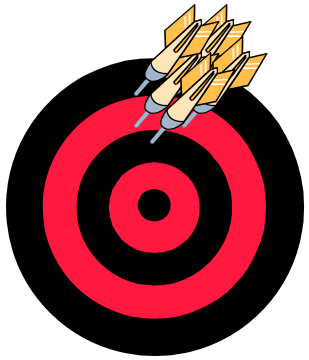
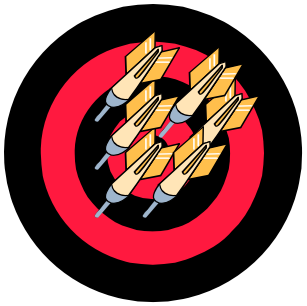
Accuracy vs. Precision



LOW ACCURACY
LOW PRECISION



LOW ACCURACY
HIGH PRECISION



HIGH ACCURACY
LOW PRECISION

HIGH ACCURACY
HIGH PRECISION

■(A) Low accuracy, low precision measurements form a diffuse, off-center cluster; (B) Low accuracy, high precision measurements form a tight off-center cluster; (C) High accuracy, low precision measurements form a cluster that is evenly distributed but distant from the center of the target; (D) High Accuracy, high precision measurements are clustered in the center of the target.

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The Basis for Reliable Data

HORIBA

Reproducibility!

Prepare, measure, empty, repeat

What would be good reproducibility?

Look at the accepted 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

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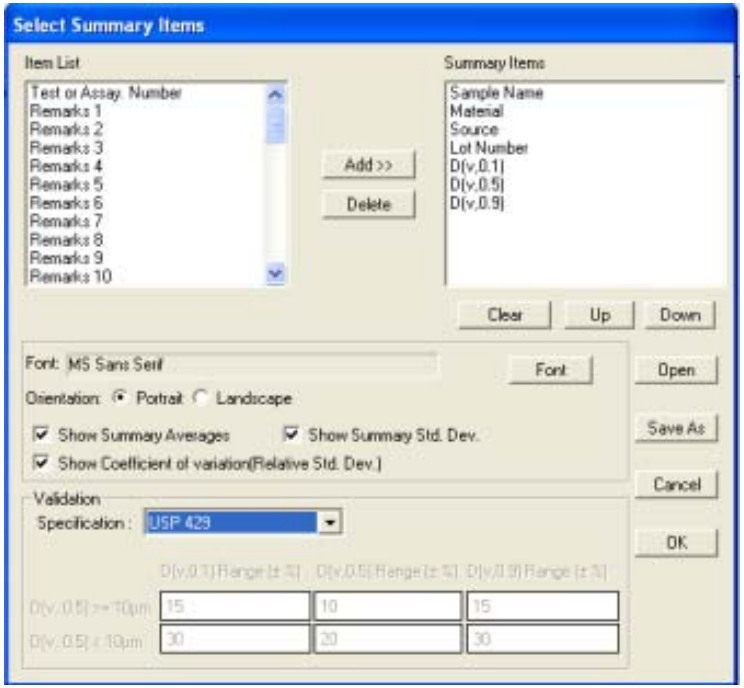
Calculation Automation



Summary Report

Export Summary | Print Summary | Edit Layout | Best Fit Columns | Hide Selected | Exit

File Name	Sample Name	D(v,0.1)	D(v,0.5)	D(v,0.9)
200811061138068.NGB	Zircoa Slurry	0.065	0.107	0.185
200811061140069.NGB	Zircoa Slurry	0.071	0.145	11.896
200811061144070.NGB	Zircoa Slurry	0.069	0.129	3.838
Average		0.068	0.127	5.306
Std. Dev.		0.003	0.019	5.992
CV (%)		4.471	15.023	112.921
ISO 13320-1		PASSED	FAILED	FAILED

Unique, automatic feature in LA-950 software
See Technical Note 169 in Download Center
for instructions to use these features

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Dry Method Development
Case Studies

Magnesium Stearate

Microcrystalline Cellulose

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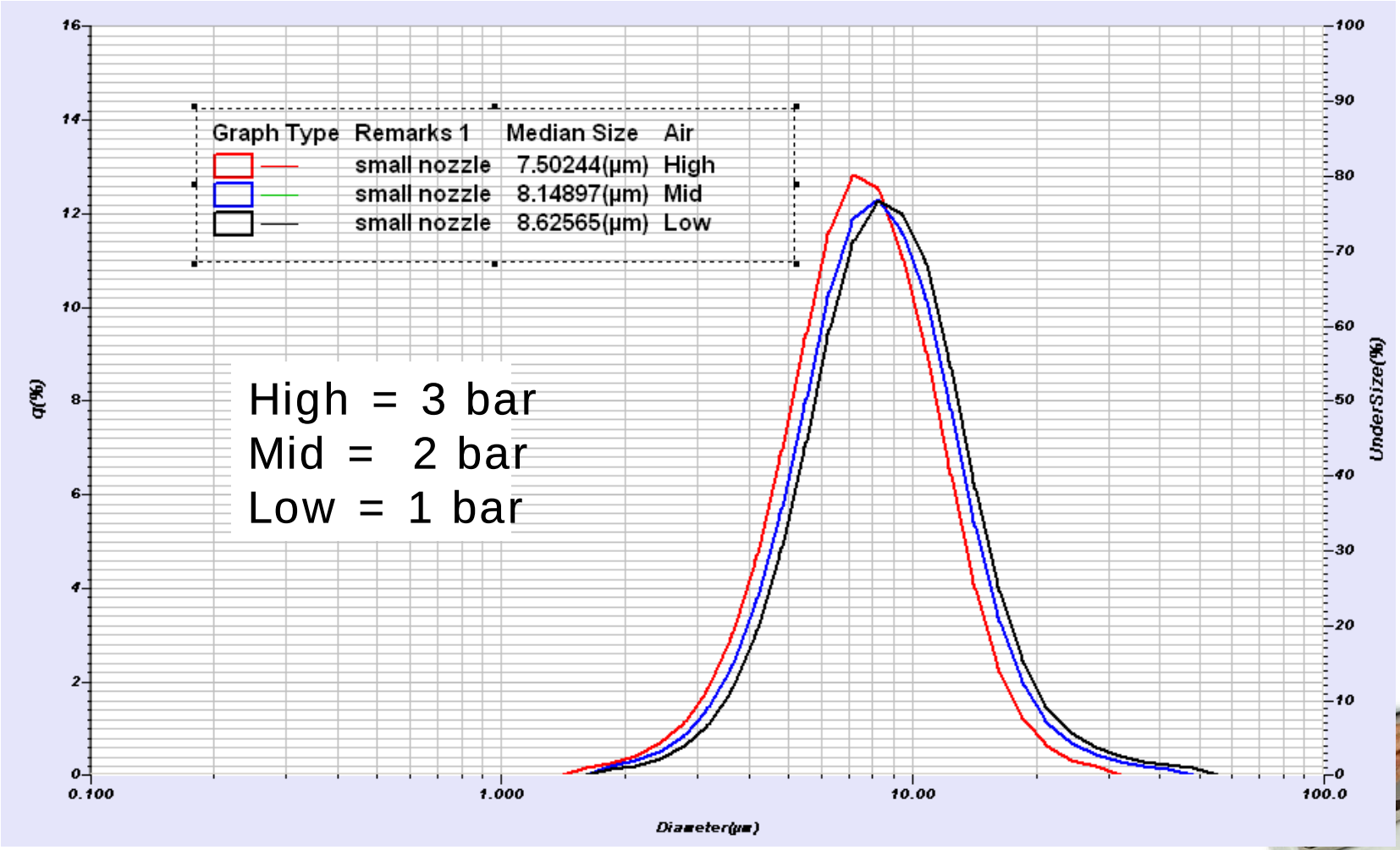
Effect of Air Pressure: Mg Stearate



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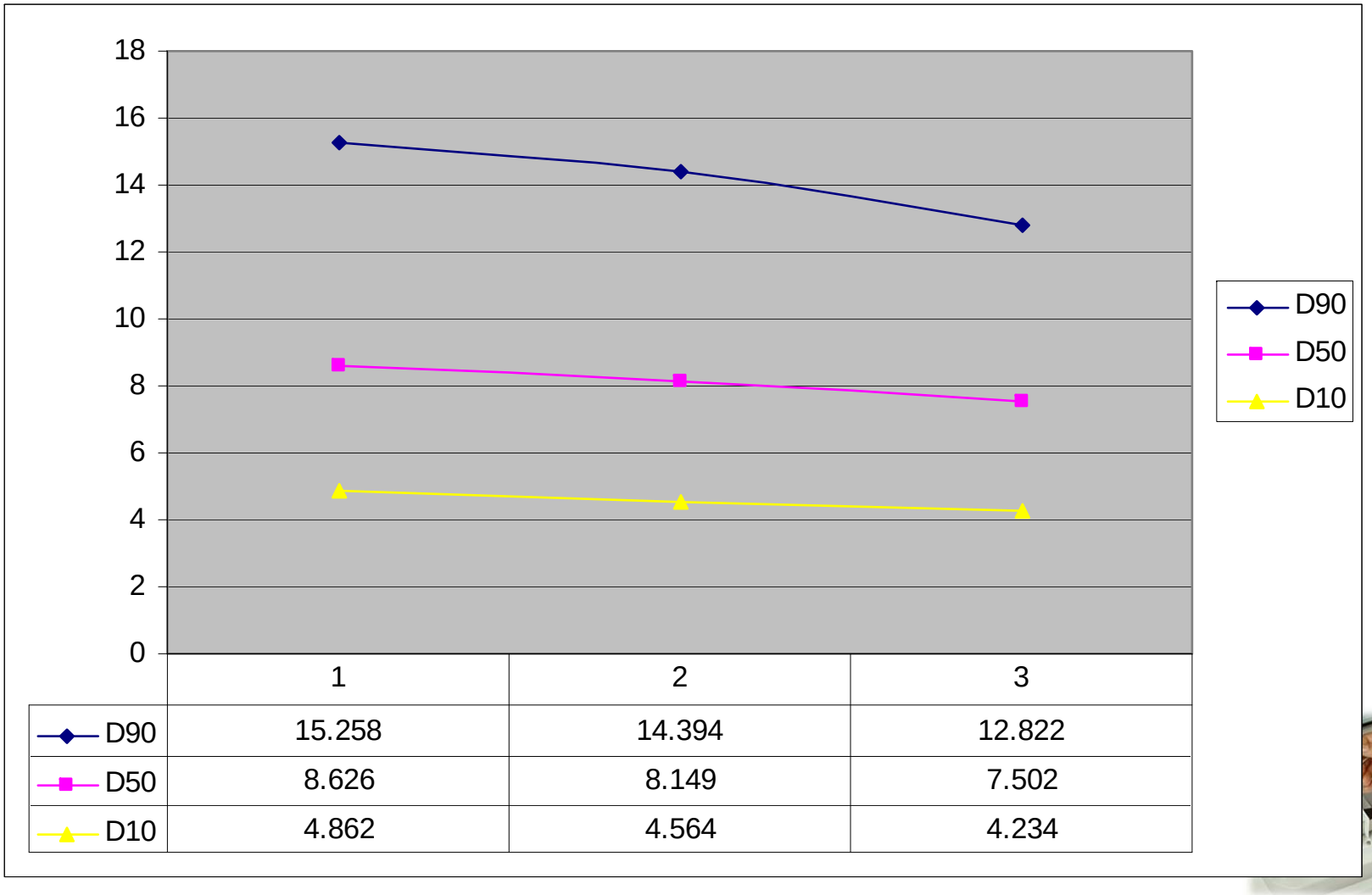
Effect of Air Pressure: Mg Stearate



	1	2	3
D90	15.258	14.394	12.822
D50	8.626	8.149	7.502
D10	4.862	4.564	4.234

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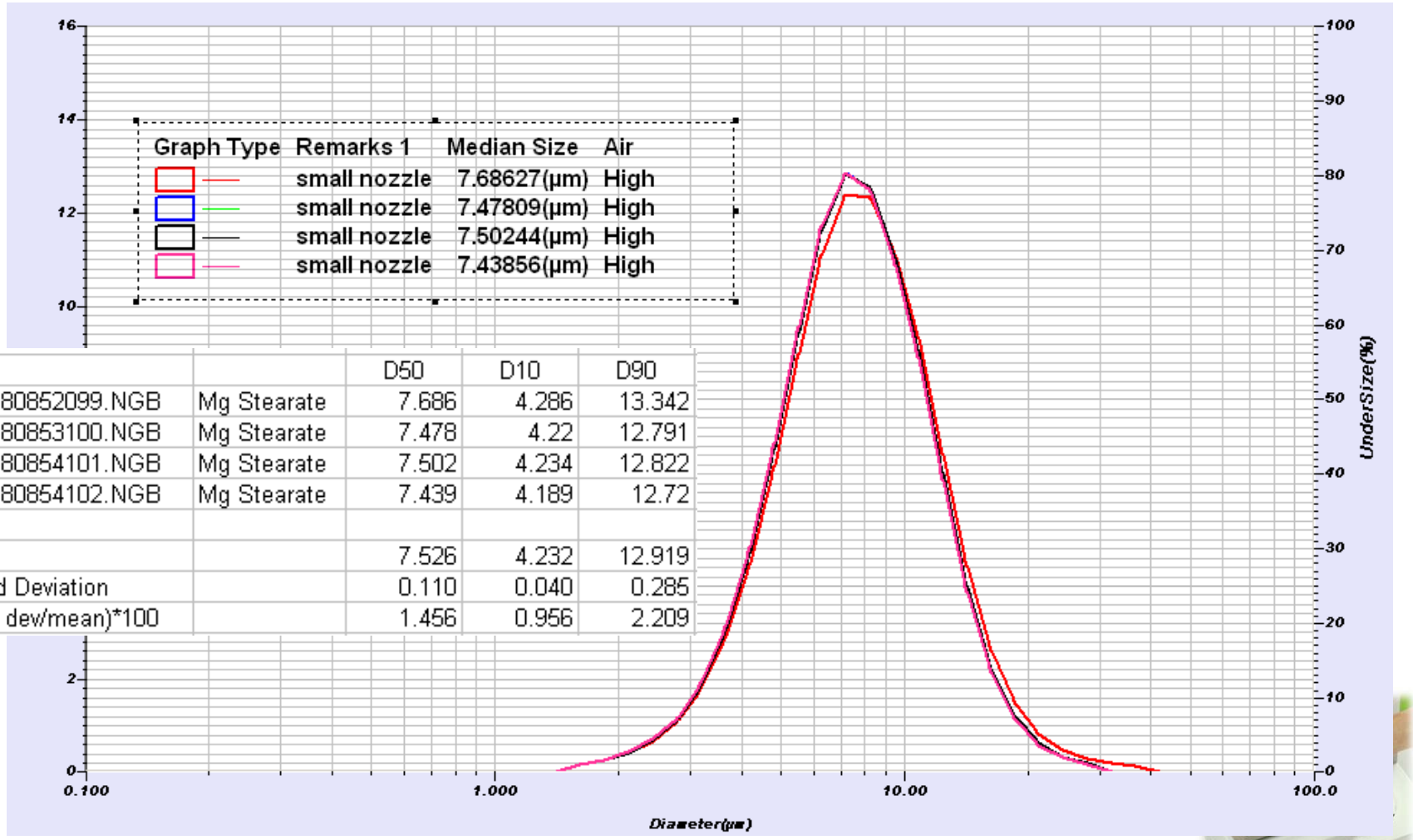
Reproducibility Test at 3 Bar



		D50	D10	D90
200707180852099.NGB	Mg Stearate	7.686	4.286	13.342
200707180853100.NGB	Mg Stearate	7.478	4.22	12.791
200707180854101.NGB	Mg Stearate	7.502	4.234	12.822
200707180854102.NGB	Mg Stearate	7.439	4.189	12.72
Mean		7.526	4.232	12.919
Standard Deviation		0.110	0.040	0.285
COV (st dev/mean)*100		1.456	0.956	2.209

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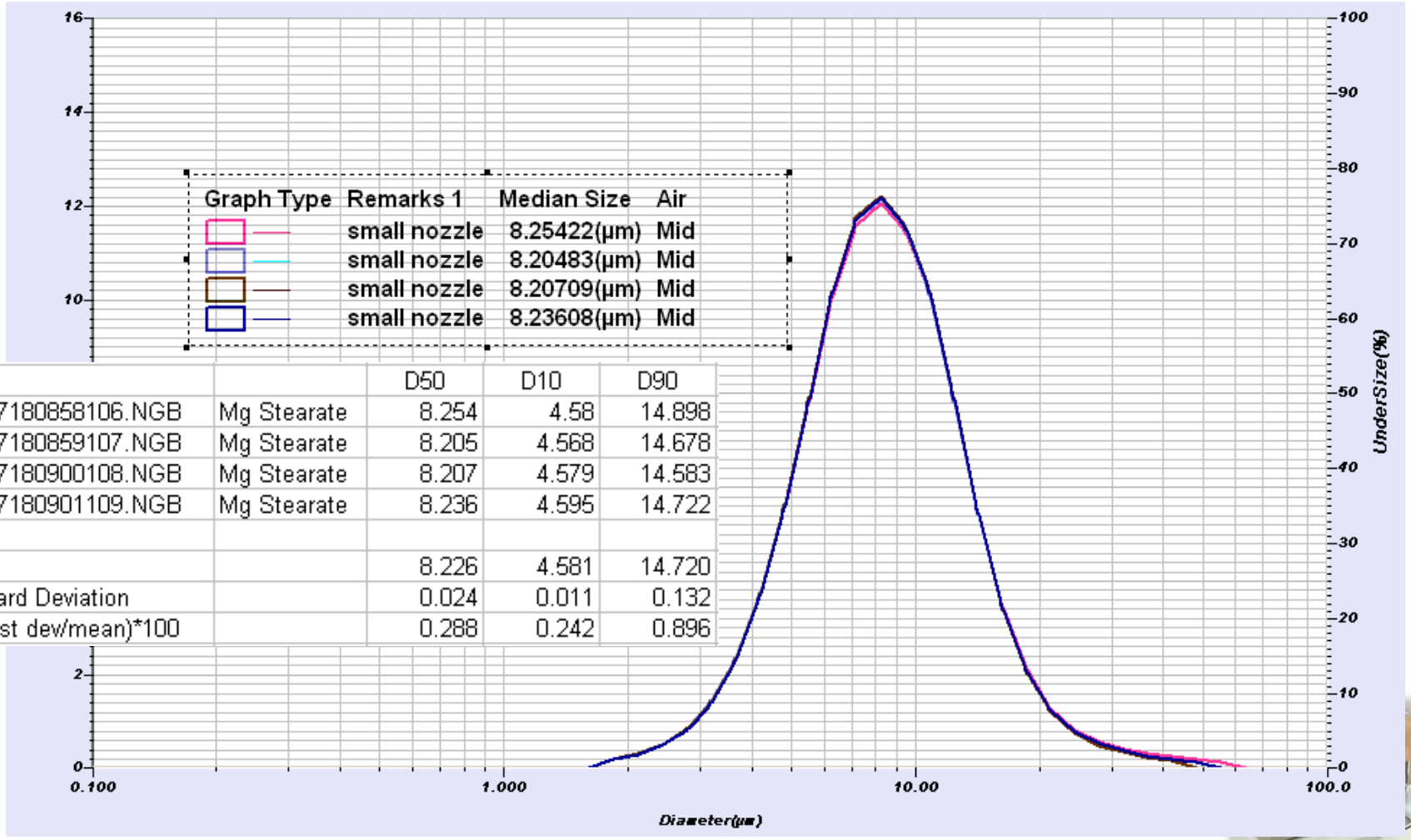
Reproducibility Test at 2 Bar



		D50	D10	D90
200707180858106.NGB	Mg Stearate	8.254	4.58	14.898
200707180859107.NGB	Mg Stearate	8.205	4.568	14.678
200707180900108.NGB	Mg Stearate	8.207	4.579	14.583
200707180901109.NGB	Mg Stearate	8.236	4.595	14.722
Mean		8.226	4.581	14.720
Standard Deviation		0.024	0.011	0.132
COV (st dev/mean)*100		0.288	0.242	0.896

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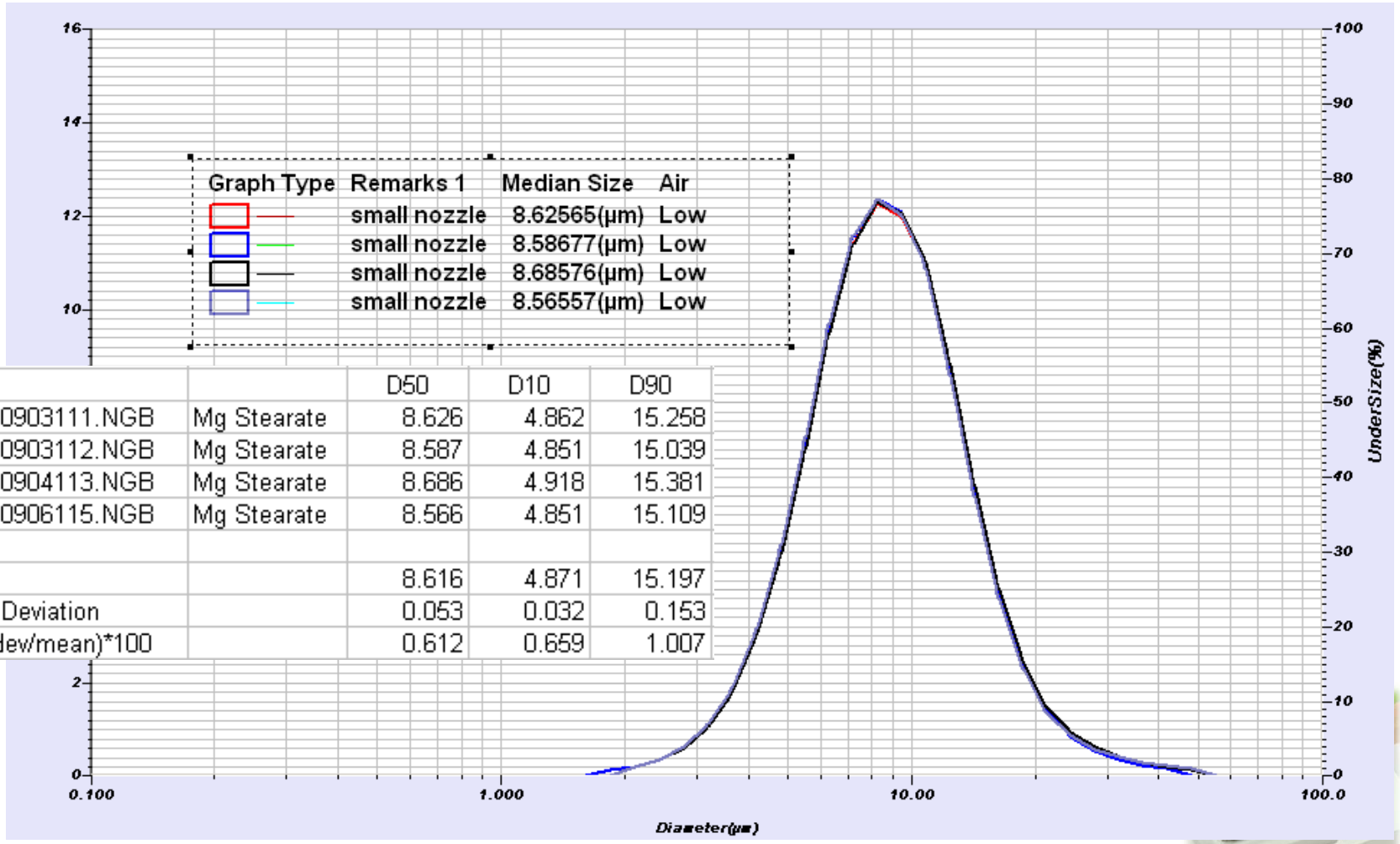
Reproducibility Test at 1 Bar



		D50	D10	D90
200707180903111.NGB	Mg Stearate	8.626	4.862	15.258
200707180903112.NGB	Mg Stearate	8.587	4.851	15.039
200707180904113.NGB	Mg Stearate	8.686	4.918	15.381
200707180906115.NGB	Mg Stearate	8.566	4.851	15.109
Mean		8.616	4.871	15.197
Standard Deviation		0.053	0.032	0.153
COV (st dev/mean)*100		0.612	0.659	1.007

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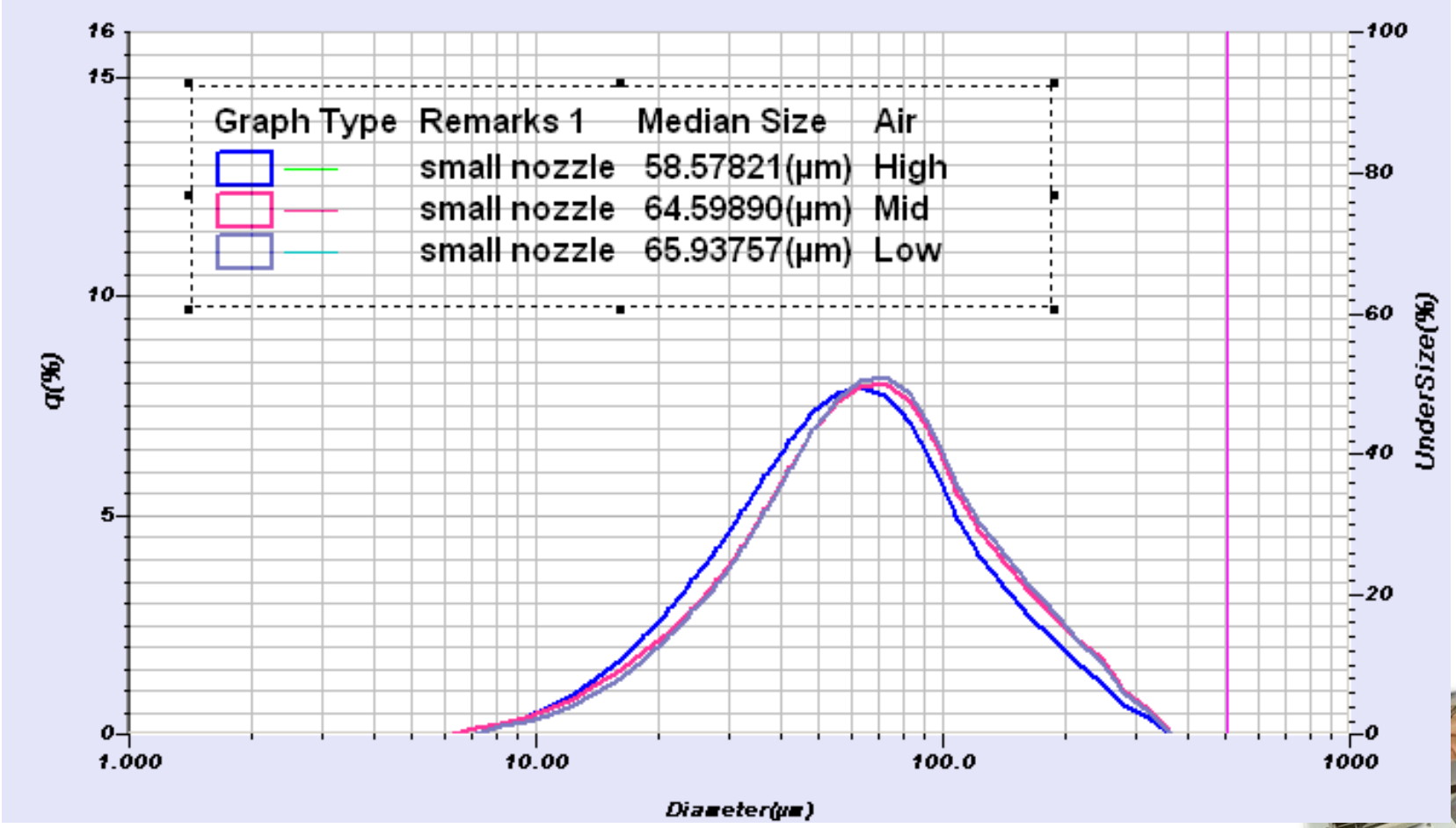
Effect of Air Pressure: MCC



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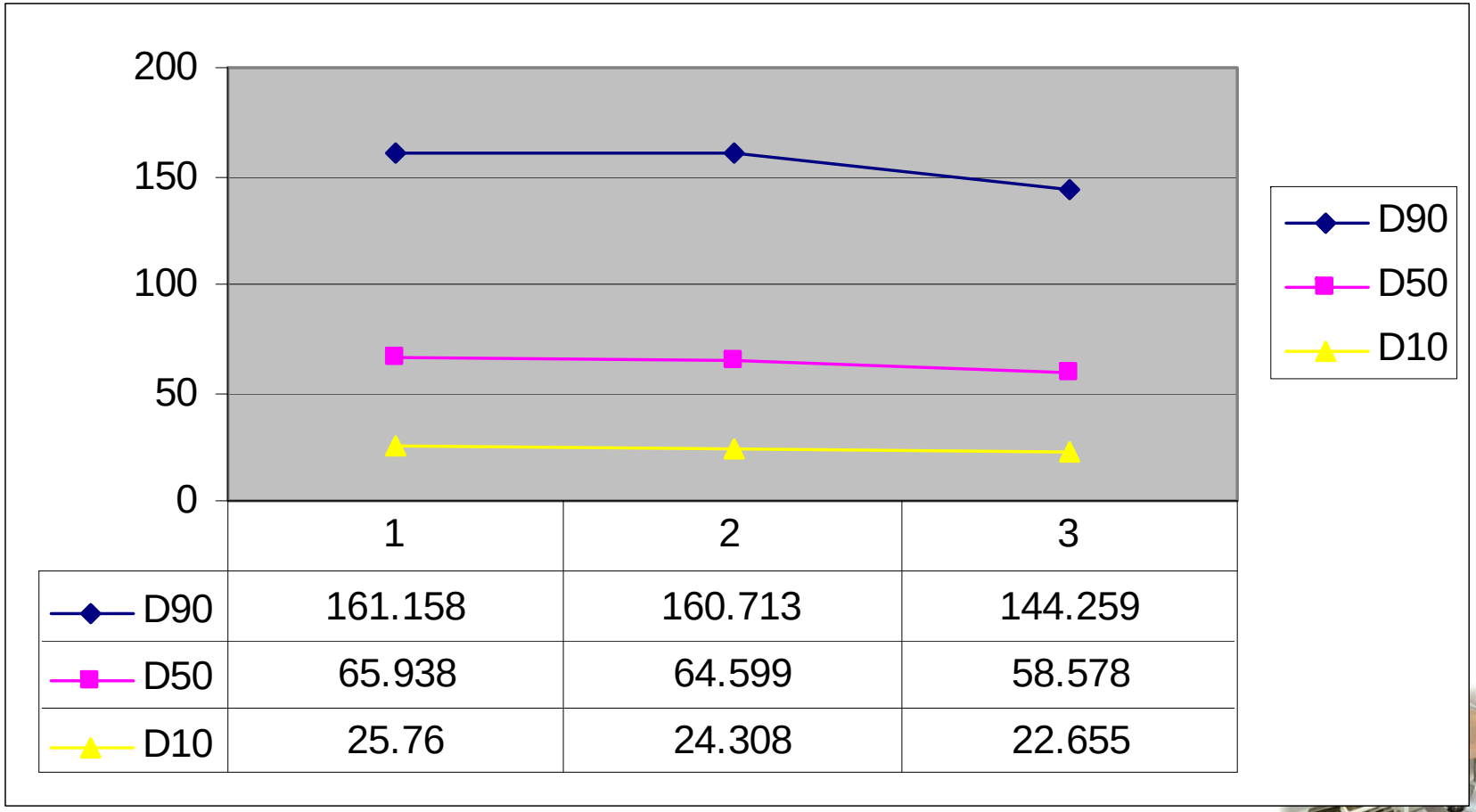
Effect of Air Pressure: MCC



	1	2	3
D90	161.158	160.713	144.259
D50	65.938	64.599	58.578
D10	25.76	24.308	22.655

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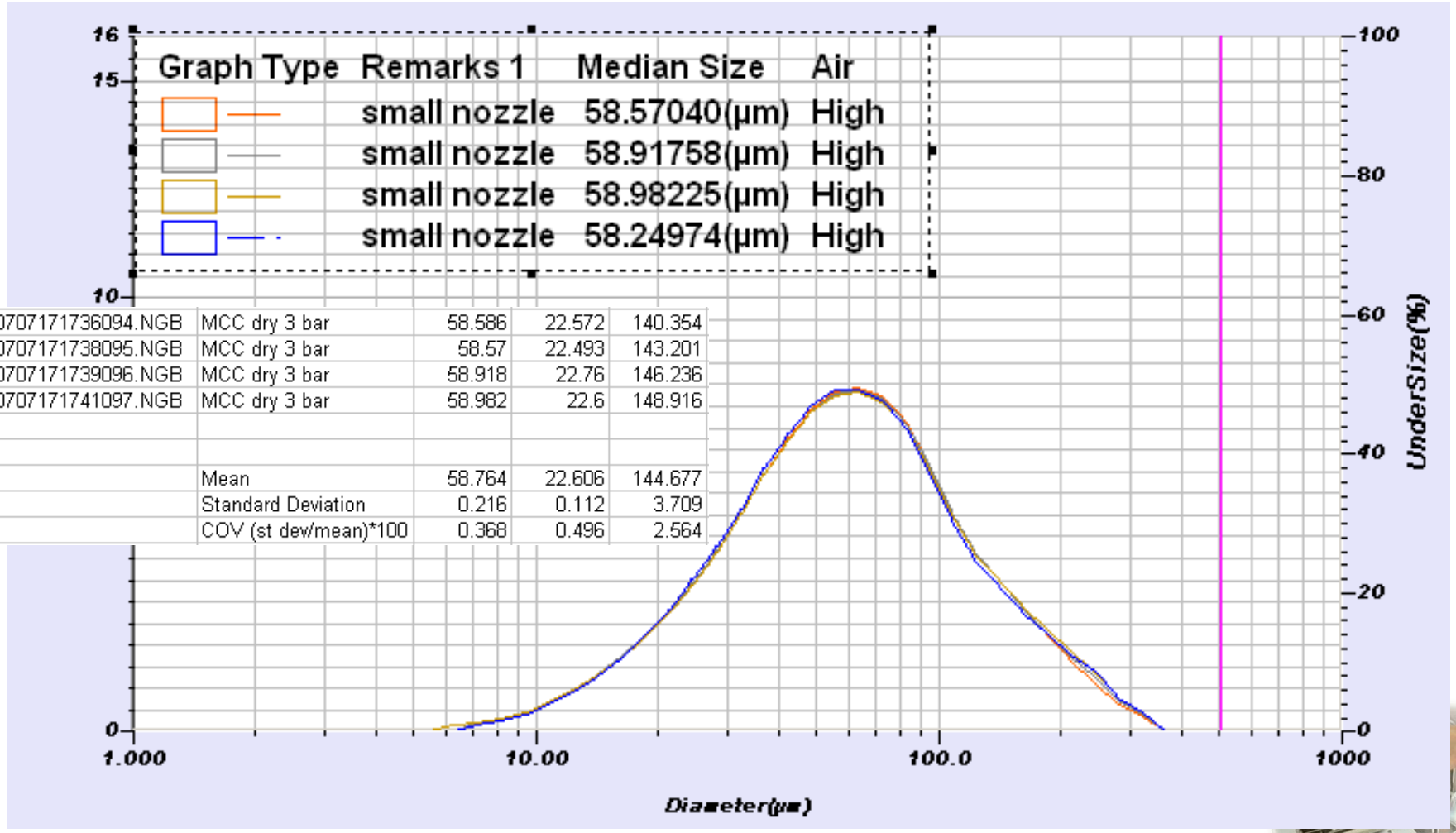
Reproducibility Test at 3 Bar



200707171736094.NGB	MCC dry 3 bar	58.586	22.572	140.354
200707171738095.NGB	MCC dry 3 bar	58.57	22.493	143.201
200707171739096.NGB	MCC dry 3 bar	58.918	22.76	146.236
200707171741097.NGB	MCC dry 3 bar	58.982	22.6	148.916
	Mean	58.764	22.606	144.677
	Standard Deviation	0.216	0.112	3.709
	COV (st dev/mean)*100	0.368	0.496	2.564

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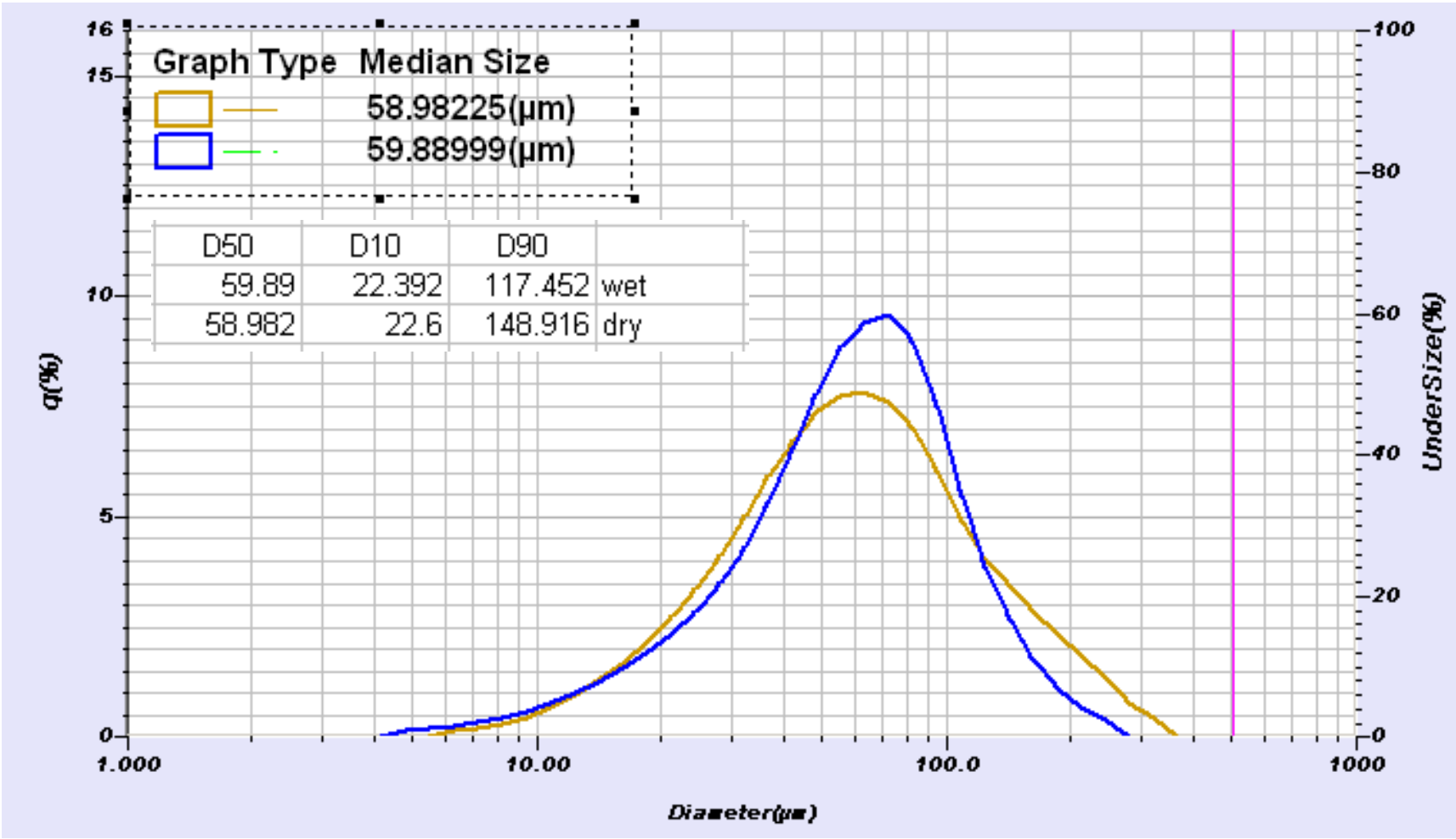
Wet and Dry Comparison



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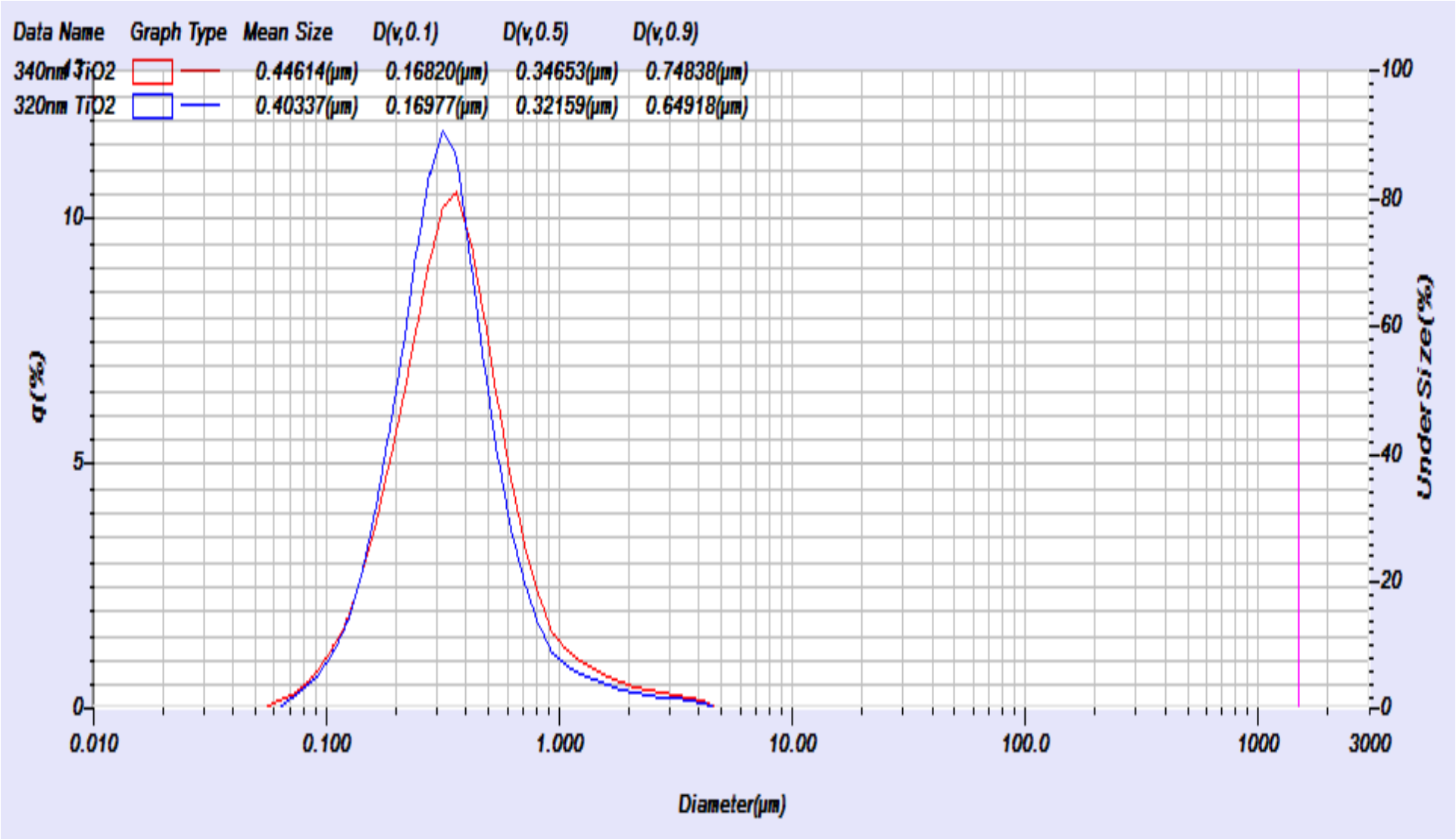
PowderJet Applications (TiO2)



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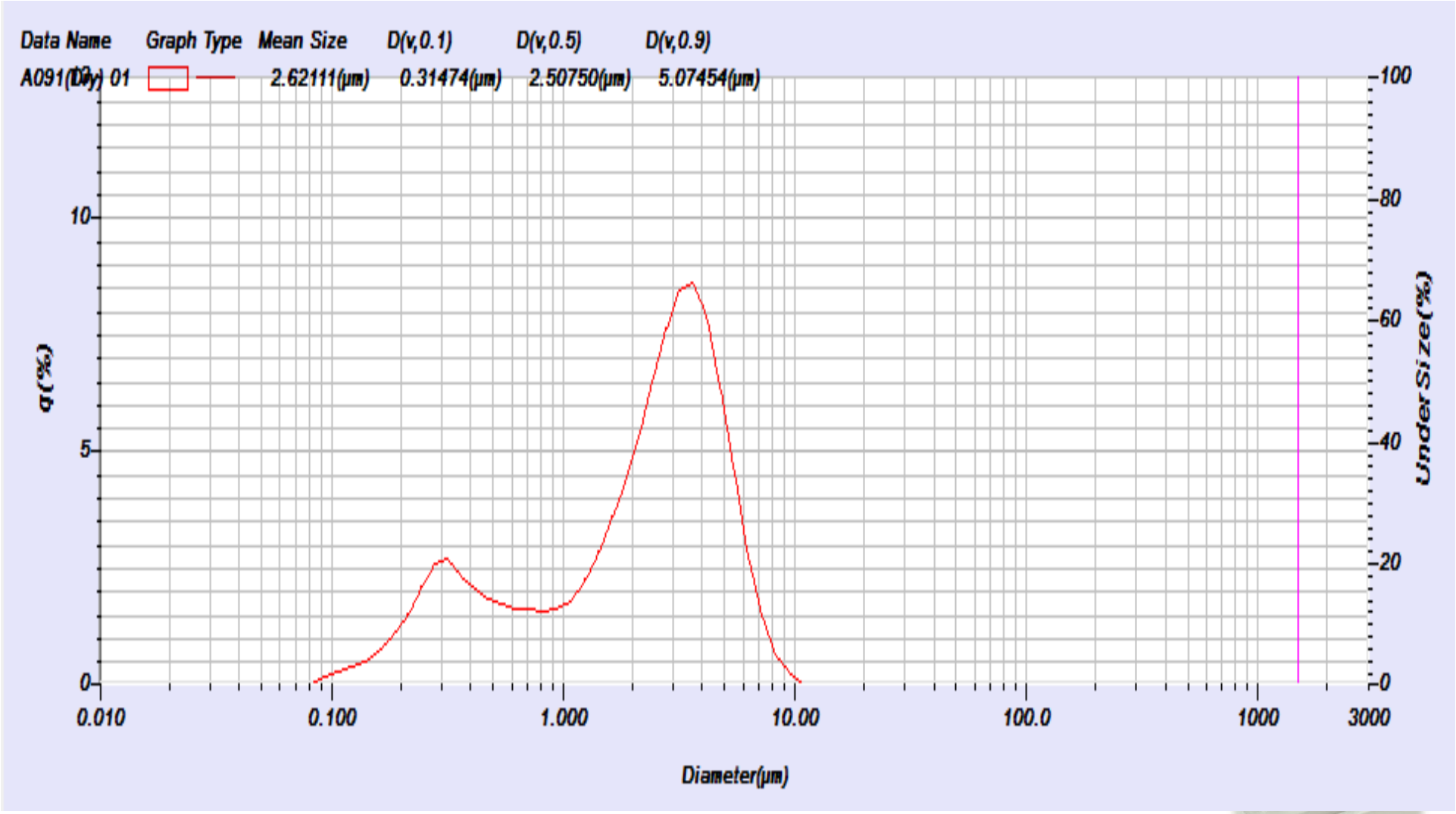
PowderJet Applications (Zirconia)



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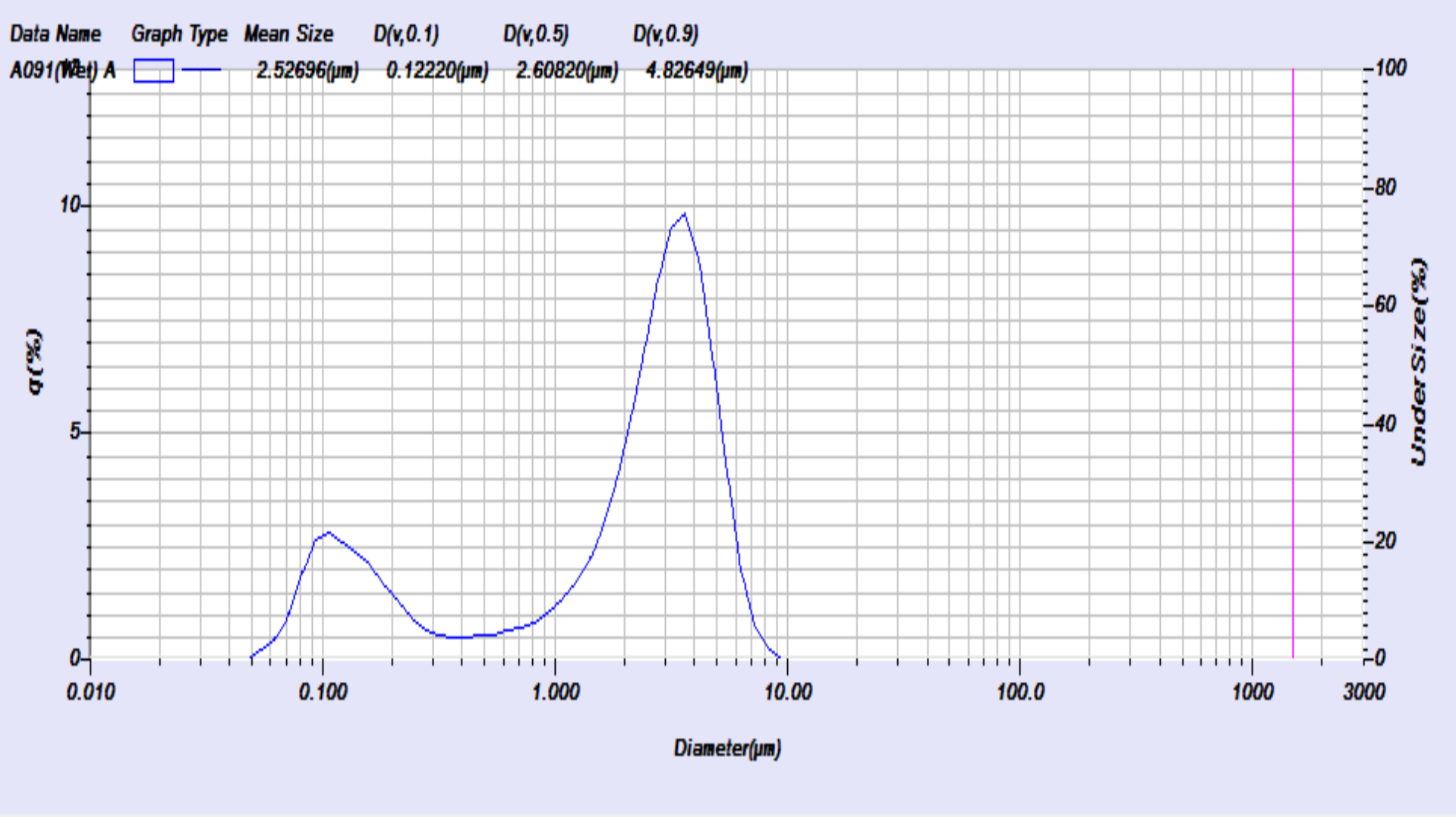
PowderJet Applications (Zirconia)



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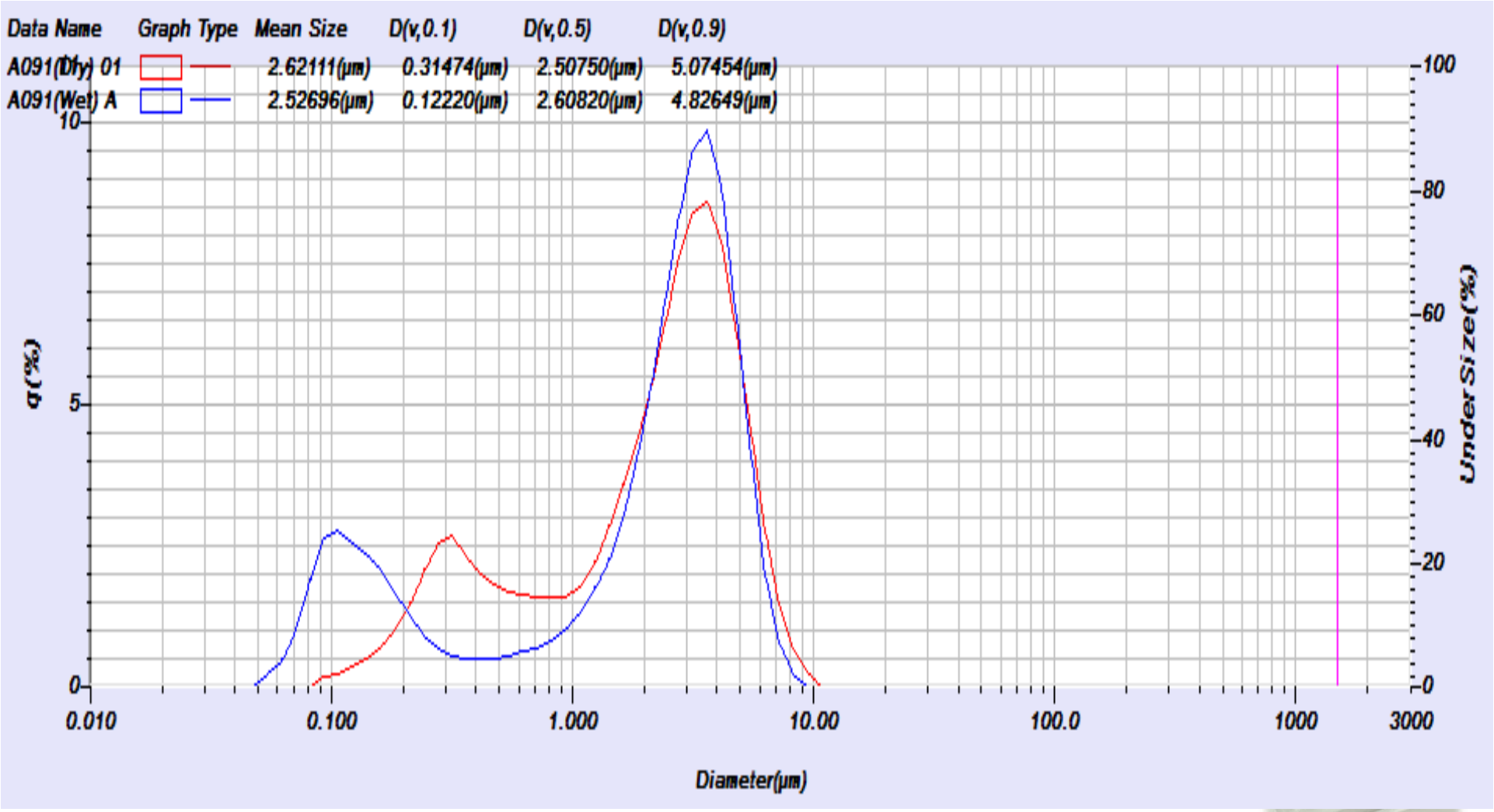
PowderJet Applications (Zirconia)



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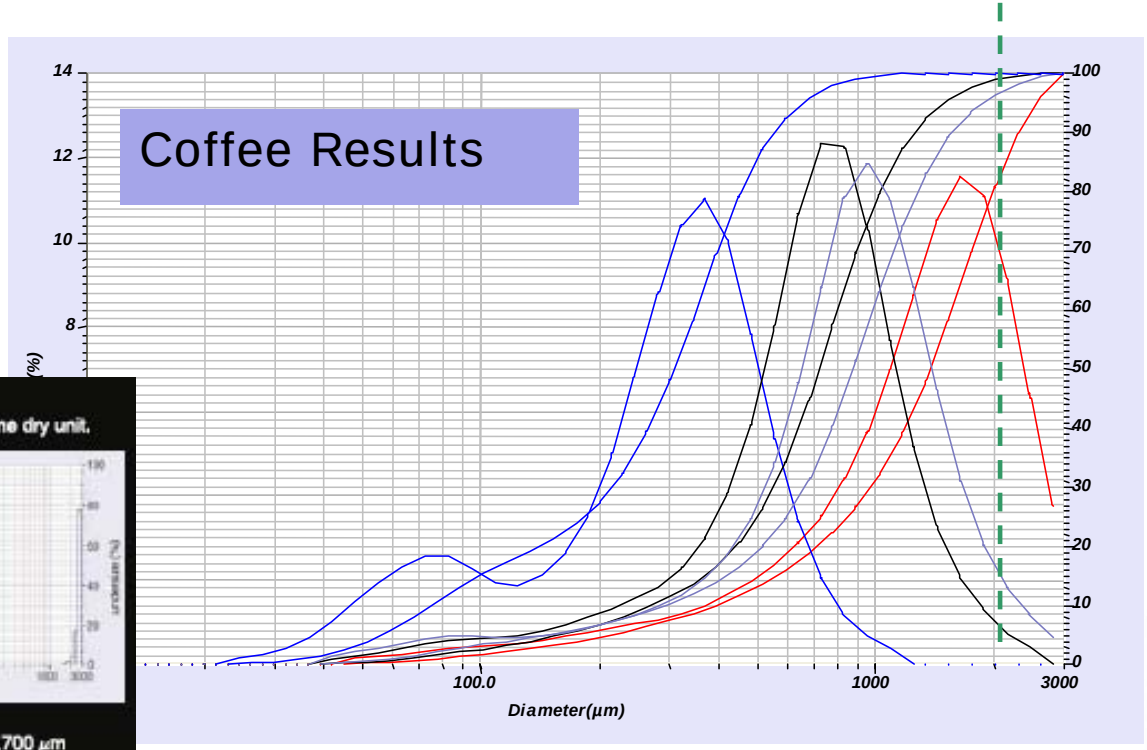
Large Particle Detection

- Need exceptionally stable optical bench
- Vertical design means no density limit for dry



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LA-950: Laser Diffraction

- Particle size performance leader
- Ninth generation
- Ultra durable
- Lowest total cost of ownership
- Suspension, emulsion, powder, paste, gel
- 10 nanometer – 3 mm

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Thank you

ありがとうございました

ขอบคุณครับ

谢谢

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Gracias

Grazie

Σας ευχαριστούμε

धन्यवाद

நன்றி

Tacka dig

Danke

Merci

Obrigado

감사합니다

Большое спасибо

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