Explore the future

HORIBA Scientific

HORIBA Instruments Incorporated

Particle Characterization

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How and Why to Analyze Ceramic Powder Particles

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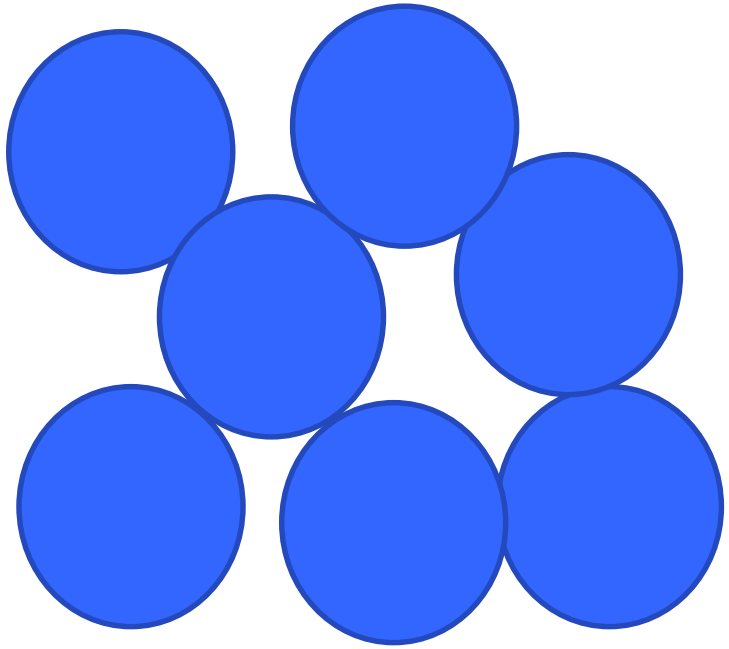
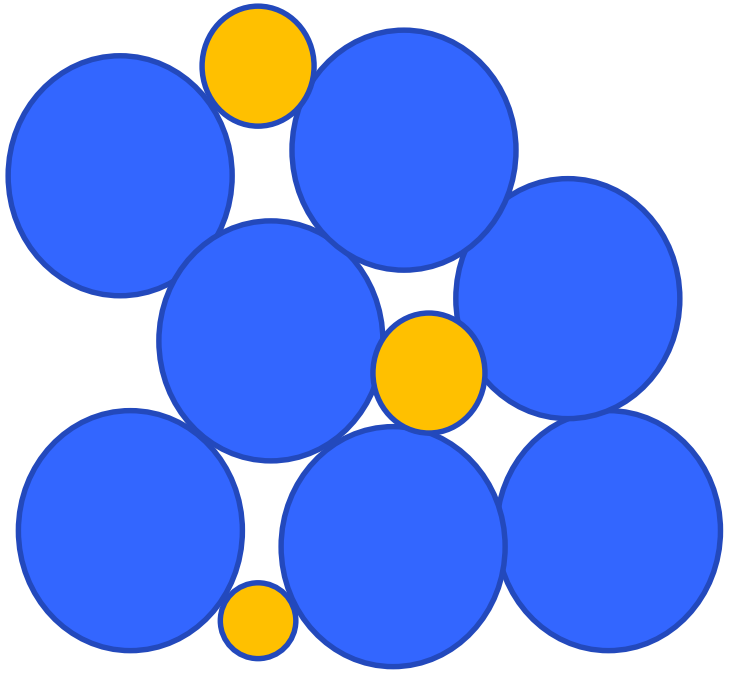
Particle size distribution affects:

- Packing density (wider distribution tends to give a higher density)
- Slurry viscosity
- Die filling/compression (fill speed)
- Green strength
- Extrusion performance (scratch in line from large particles)
- Defects in finished parts

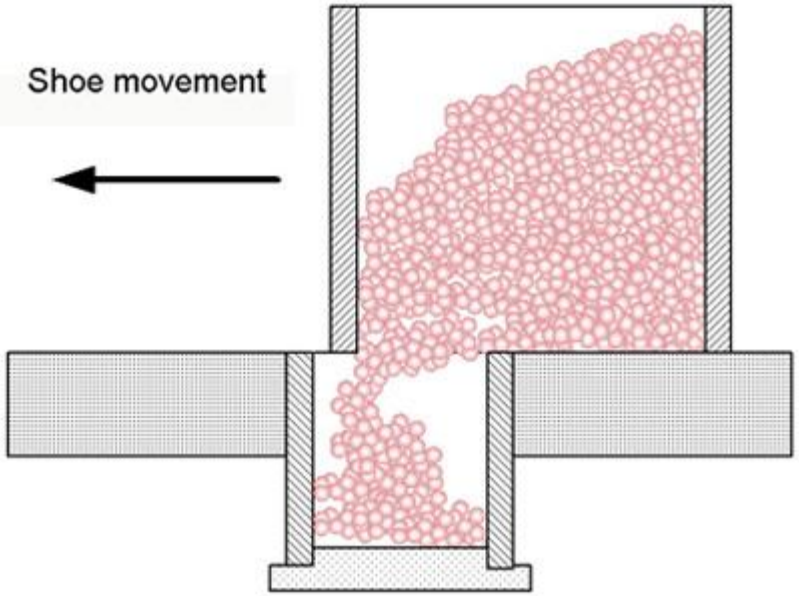
Packing Density





Affects strength and defects of green and finished parts

Die Filling



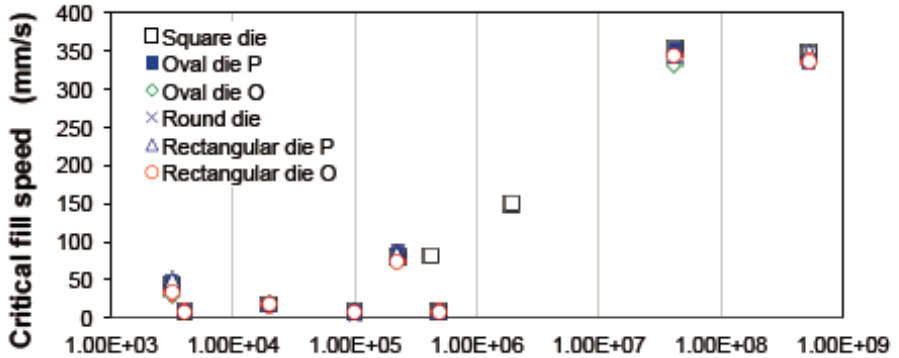


Fig. 10 Critical fill speeds for all cases considered

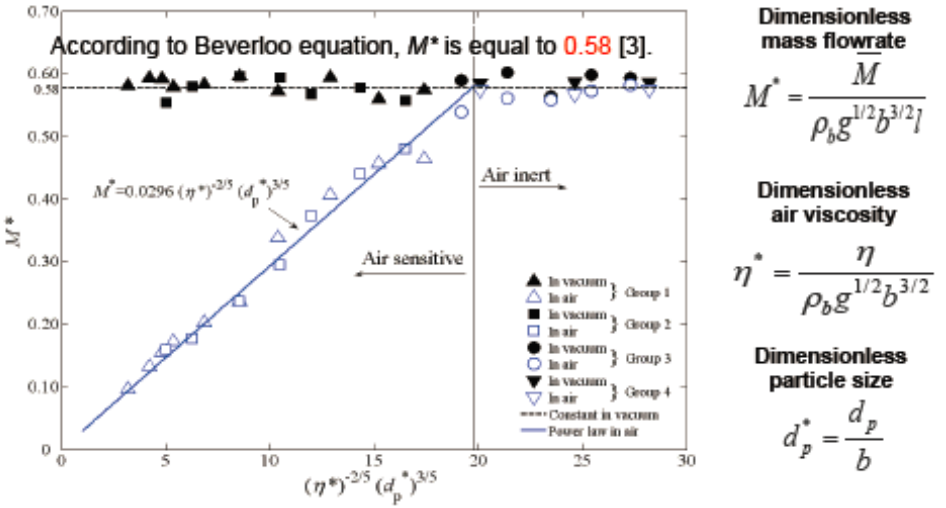
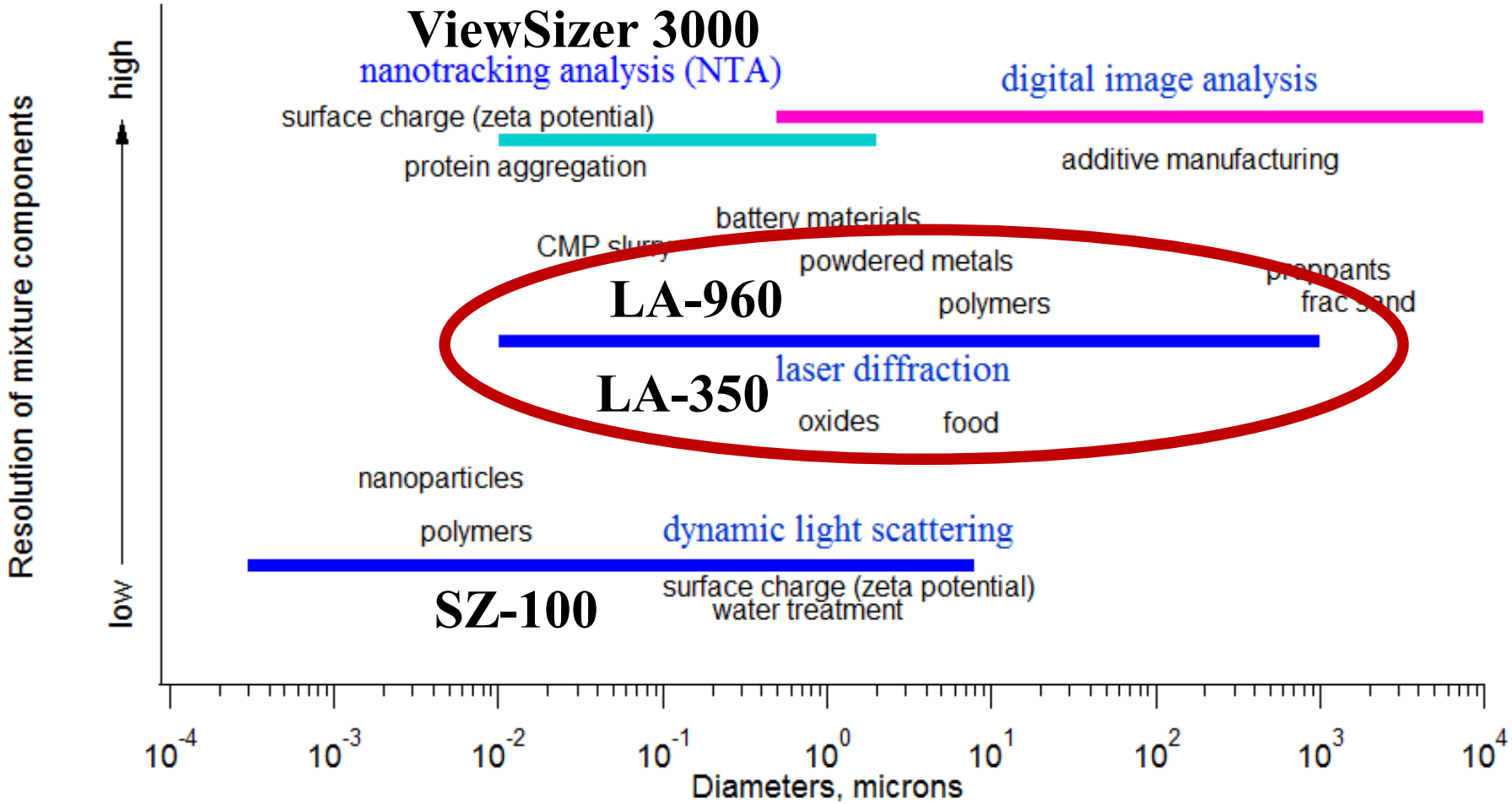


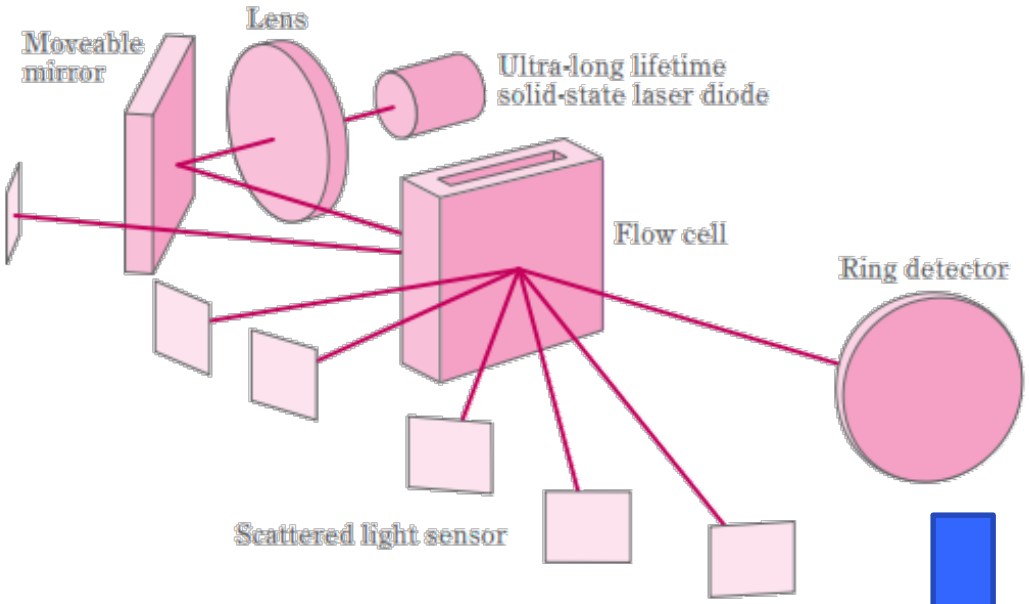
Fig. 11 Dimensionless mass flowrate for die filling in air and in a vacuum (Guo et al. 2009).

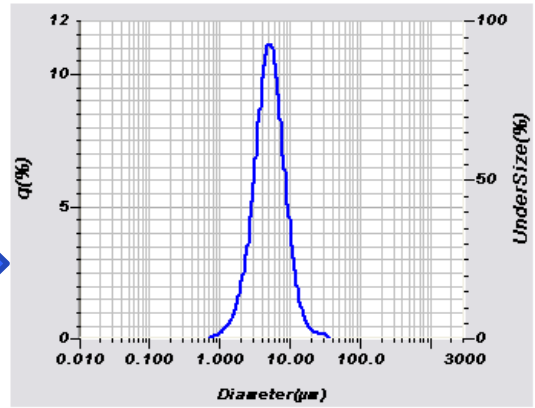
Size range



Laser diffraction

Investigate a particle with light and determine its size

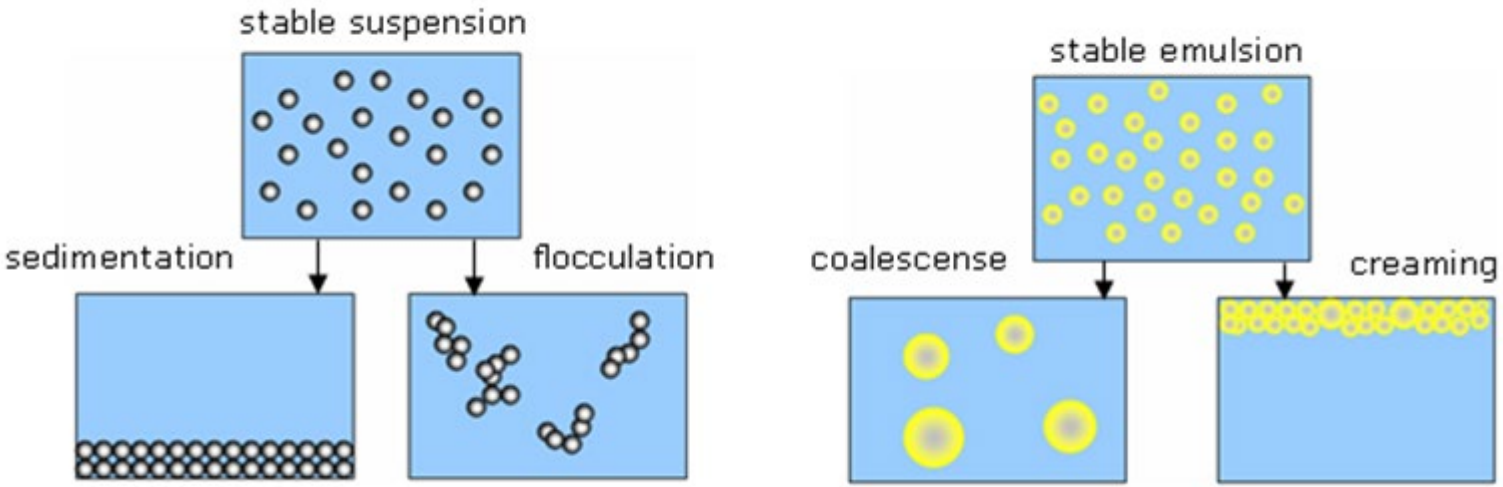




Measurement Workflow

Prepare the sample

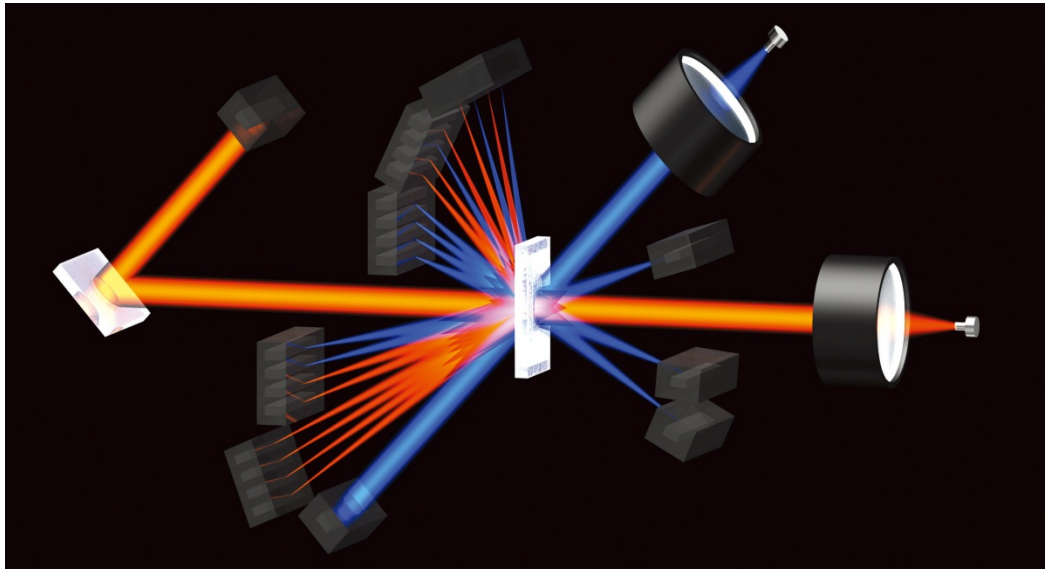
- Good sampling and dispersion a must!
- May need to use surfactant or admixture



Measurement Workflow

Prepare the system

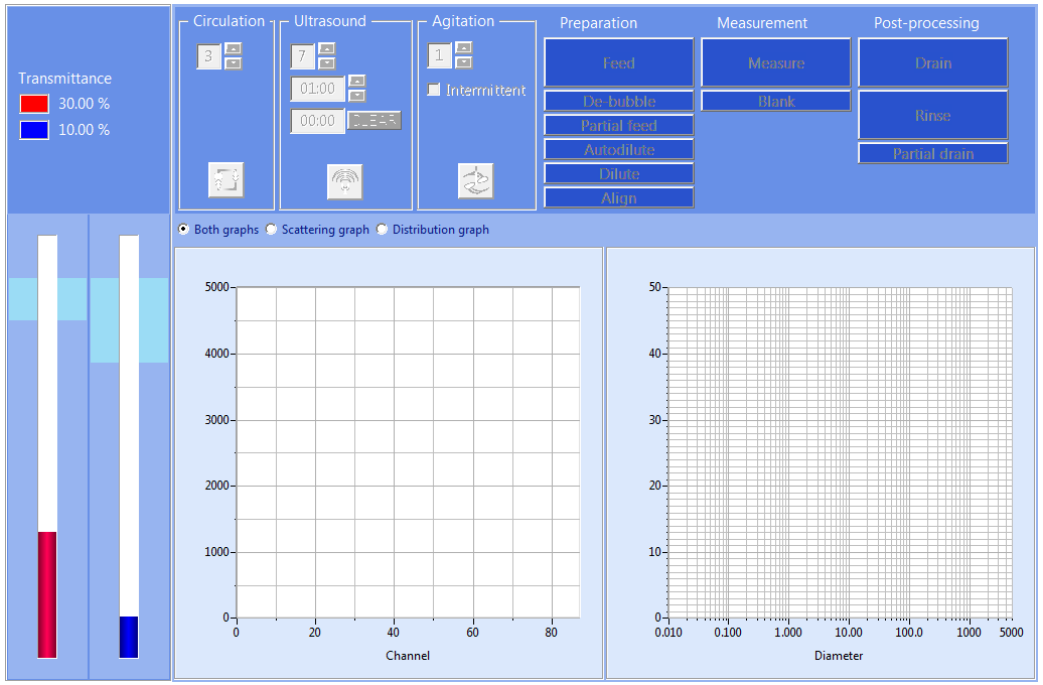
- Align laser to maximize signal-to-noise
- Acquire blank/background to reduce noise



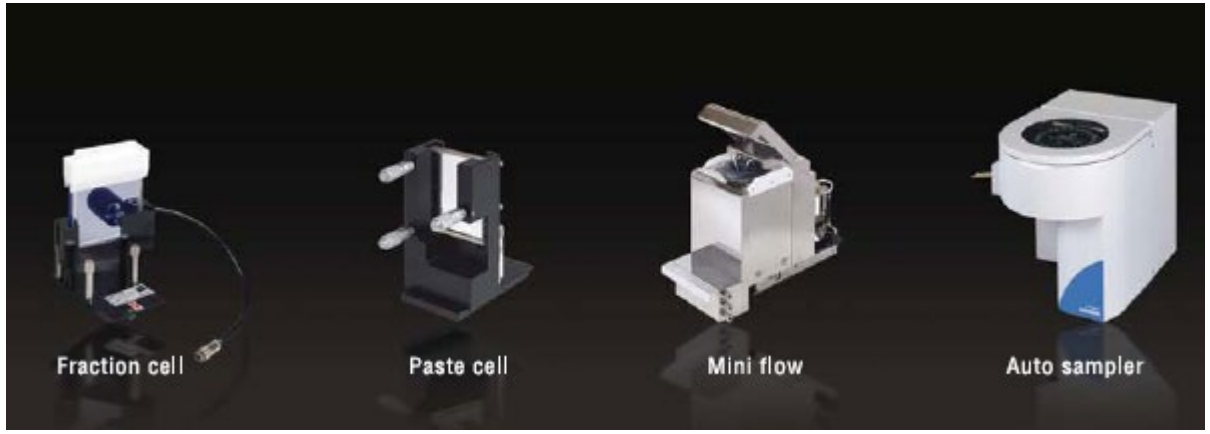
Measurement Workflow

Introduce sample

- Add sample to specific concentration range
- Pump sample through measurement zone
- Final dispersion (ultrasonic)



Flexible Sample Handlers



10 ml 35 ml 200 ml powders

- Wide range of sample cells depending on application
- High sensitivity keeps sample requirements at minimum
- Technology has advanced to remove trade-offs

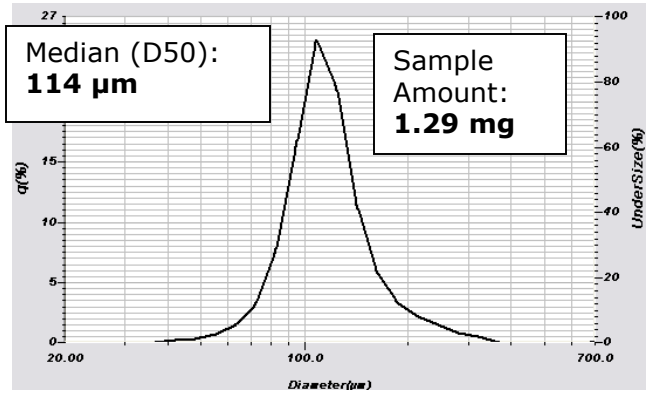
How much sample (wet)?

It depends on sample, but here are some examples.

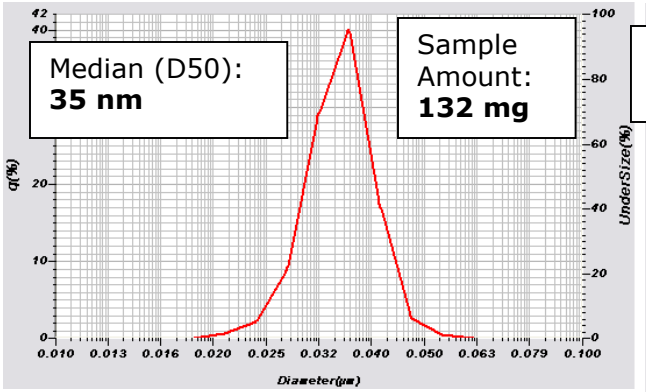
- Larger, broad distributions require larger sample volume
- Lower volume samplers for precious materials or solvents

Sample Handlers	Dispersing Volume (mL)
Aqua/Solvo Flow	**180 - 330**
MiniFlow	**35 - 50**
Fraction Cell	**15**
Small Volume Fraction Cell	**10**

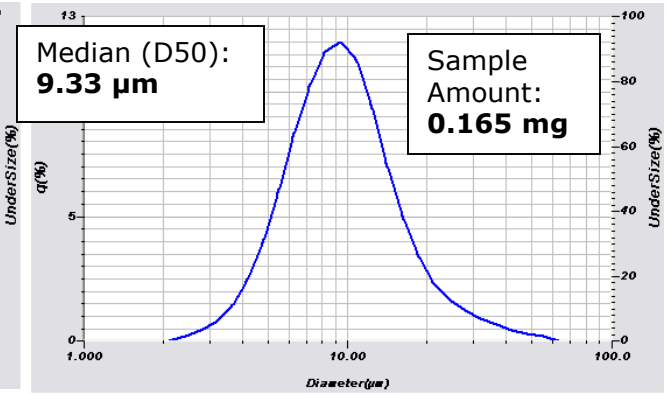
Note: Fraction cell has only magnetic stir bar, not for large or heavy particles



Bio polymer



Colloidal silica



Magnesium stearate

How much sample (dry)?

It depends on sample …..

- Larger, broad distributions require larger sample quantity
- Can measure less than 5 mg (over a number of particle sizes).

Method Workflow

- Determine particle refractive index (RI)
- Choose diluent (water, surfactants, hexane, etc.)
- Sampler selection: sample volume
- Pump & stirrer settings
- Concentration
- Measurement duration
- Does the sample need ultrasound?
  - Document size-time plot
  - Disperse sample, but don’t break particles
  - Check for reproducibility

Instrument to instrument variation

20 instruments, 5 standards

Sample	CV D10	CV D50	CV D90
PS202 (3-30µm)	2%	1%	2%
PS213 (10-100µm)	2%	2%	2%
PS225 (50-350µm)	1%	1%	1%
PS235 (150-650µm)	1%	1%	2%
PS240 (500-2000µm)	3%	2%	2%
These are results from running polydisperse standards on 20 different instruments			

Instrument to instrument variation

Industrial Samples

4 instruments, real sample

	Dmean	D5	D10	D50	D90	D95
Average (nm)	155	112	119	152	193	208
Std. Dev. (nm)	0.8	0.8	0.7	1.0	1.1	0.7
CV (%)	0.5	0.7	0.6	0.6	0.6	0.3

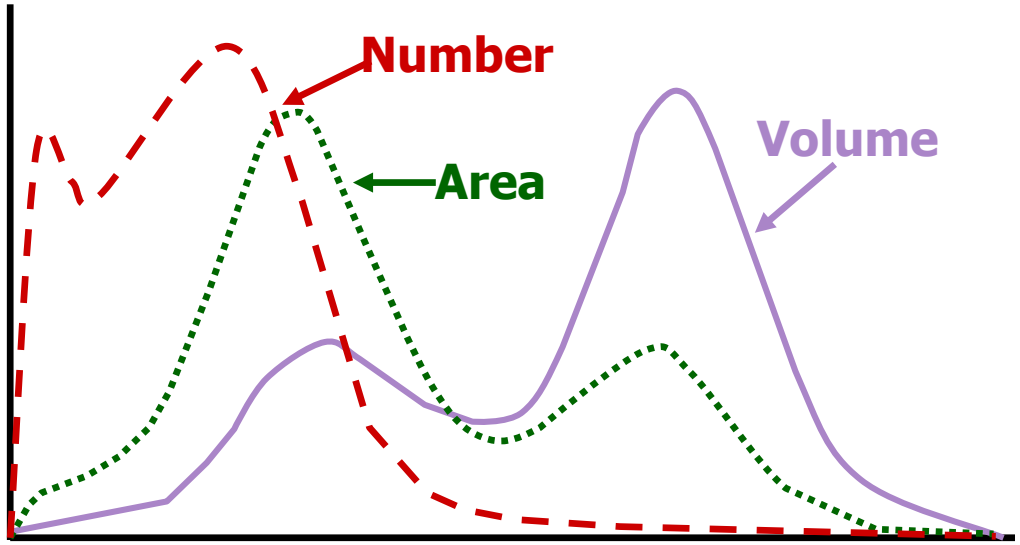
Figure 8: Instrument to instrument variation across four LA-950 systems for Formulation 1.

	Dmean	D5	D10	D50	D90	D95
Average (nm)	193	136	147	187	247	264
Std. Dev (nm)	1.5	0.5	0.4	0.6	0.4	1.1
CV (%)	0.8	0.4	0.3	0.3	0.2	0.4

Figure 9: Instrument to instrument variation across four LA-950 systems for Formulation 2.

Diffraction Drawbacks

- Volume basis by default
  - Although excellent for mass balancing, cannot calculate number basis without significant error
- No shape information

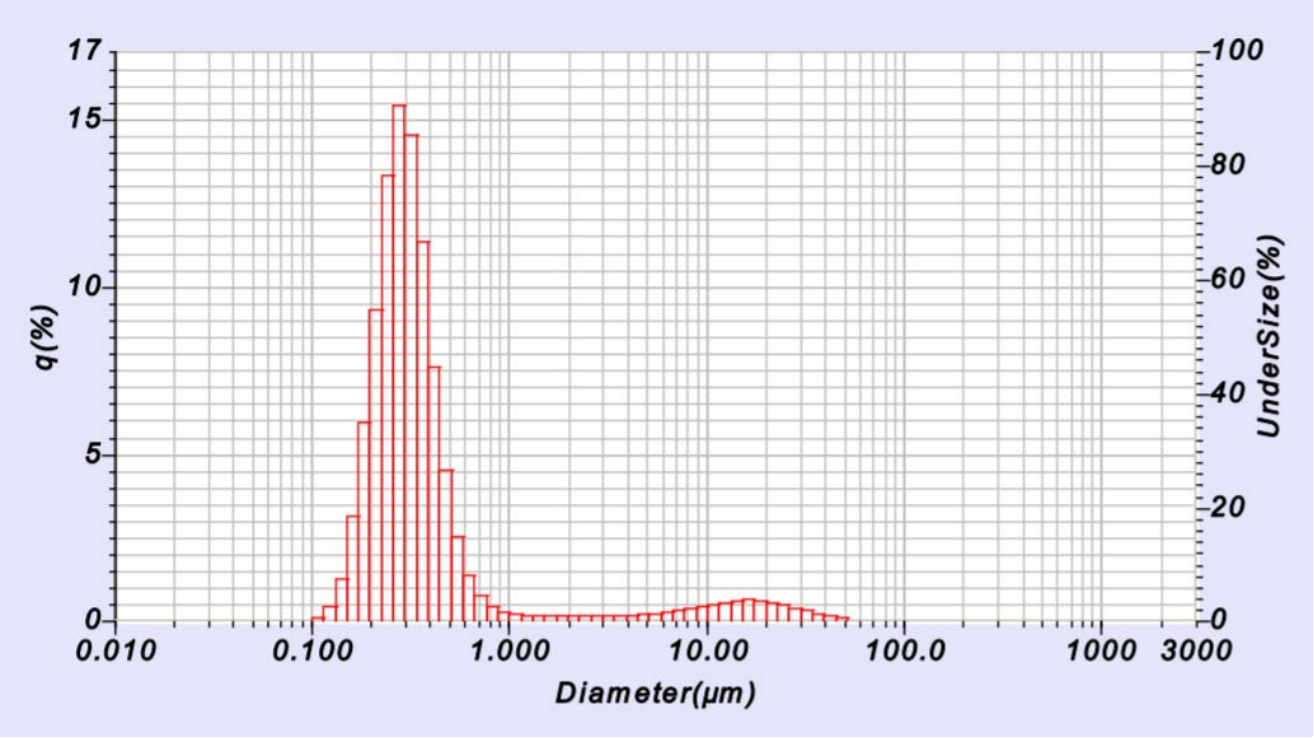


Benefits

- Wide size range
  - Most advanced analyzer measures from 10 *nano* to 5 *milli*
- Flexible sample handlers
  - Powders, suspensions, emulsions, pastes, creams
- Very fast
  - Allows for high throughput, 100's of samples/day
- Easy to use
  - Many instruments are highly automated with self-guided software
- Good design = Excellent precision
  - Reduces unnecessary investigation/downtime
- First principle measurement
  - No calibration necessary
- Massive global install base/history

Alumina

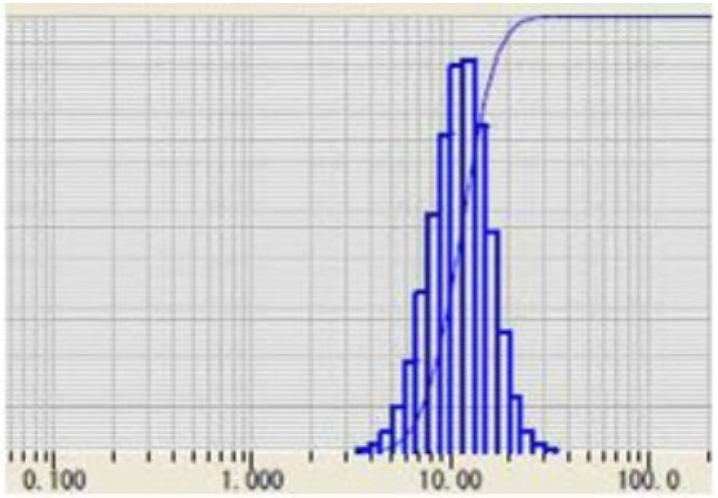
Refractive Index (particle): 2.66
Dispersant fluid: Water, 0.1% Igepal 630 surfactant
Sonication: 15 minutes, power 4

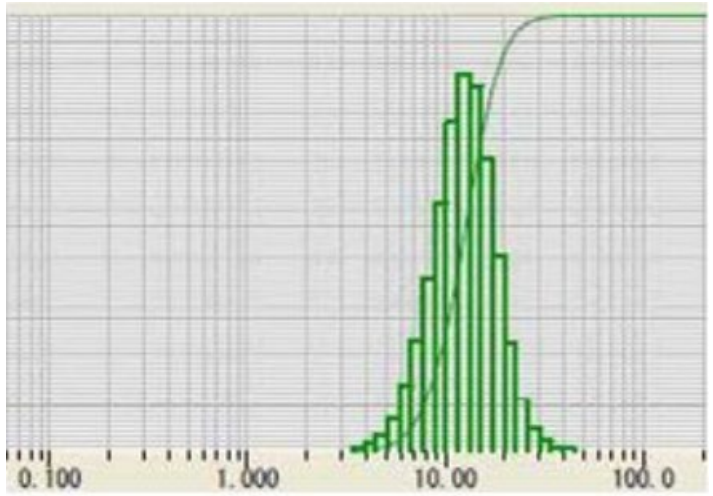


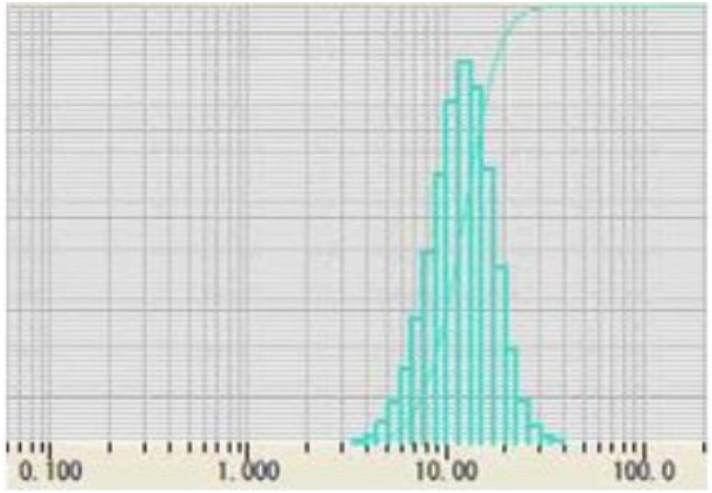
Large particles confirmed by microscopy

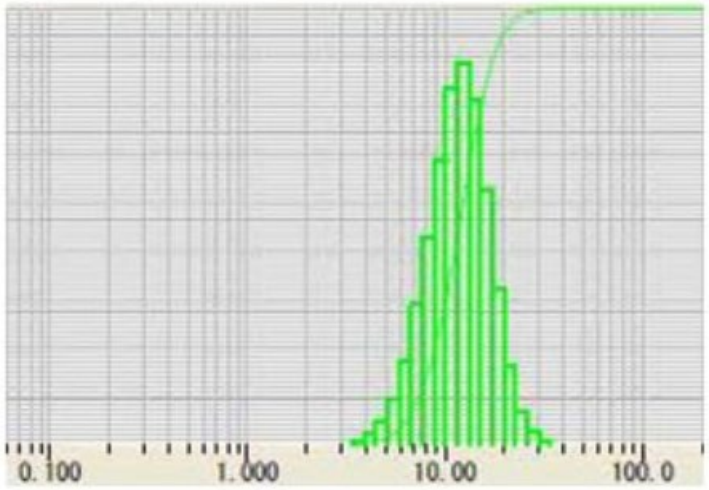
LiCoO2

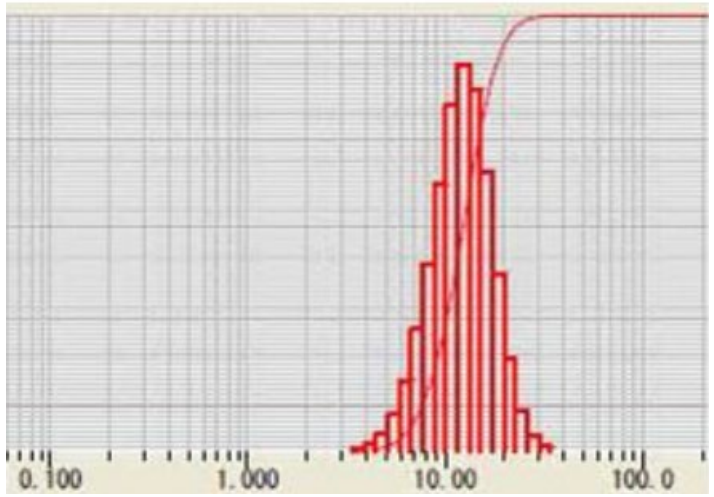
0.2% sodium hexametaphosphate (aq)









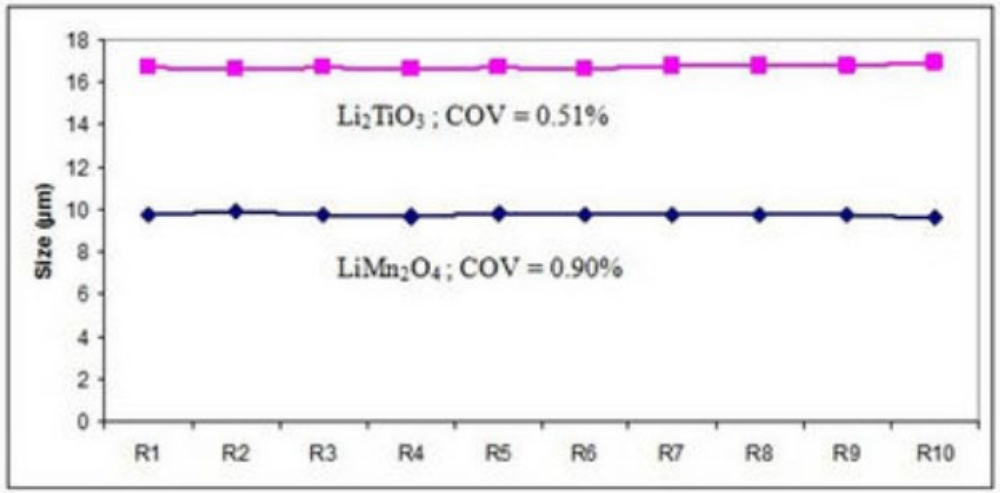


Lot	Median (micron)
No. 1	11.3
No. 2	11.8
No. 3	12.2
No. 4	12.5
No. 5	11.9

Reproducibility

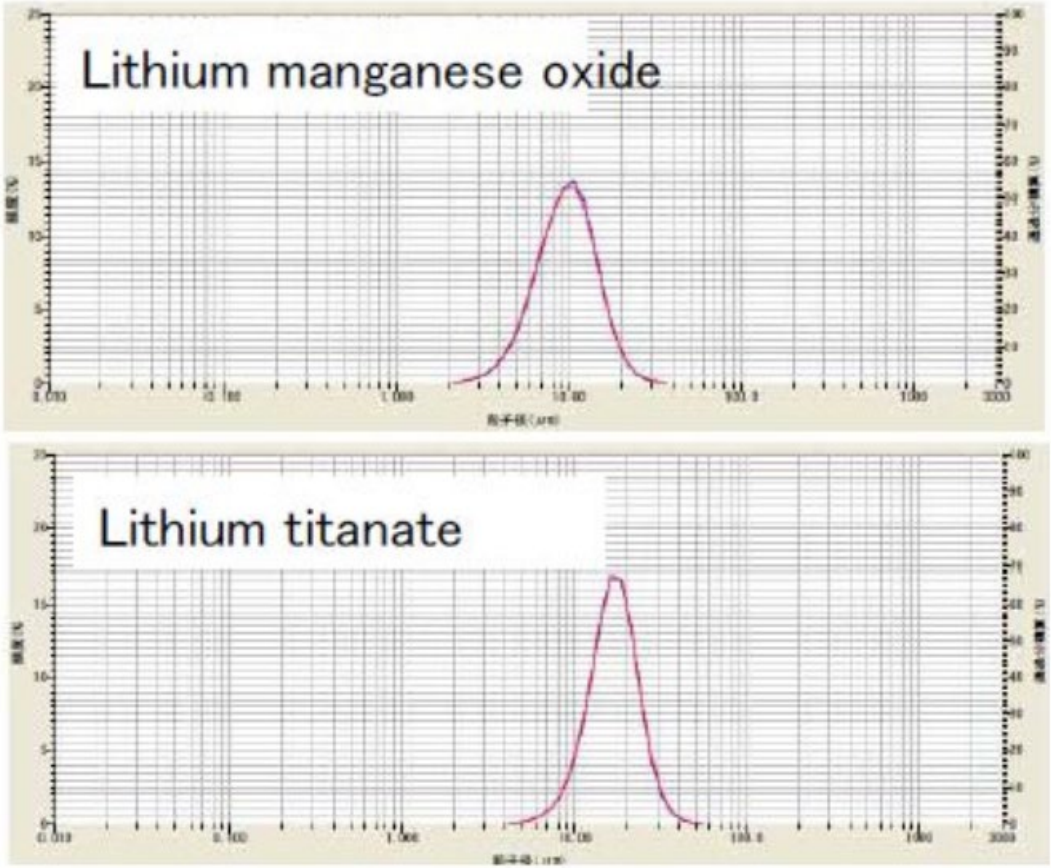
Lithium Manganese Oxide/Lithium Titanate

Two samples ($LiMn_2O_4$ and Li_2TiO_3) were analyzed ten times to quantify the reproducibility of the LA-960. The results are shown below



Run	$LiMn_2O_4$	Li_2TiO_3
1	9.75	16.7
2	9.93	16.6
3	9.75	16.7
4	9.66	16.6
5	9.83	16.7
6	9.78	16.6
7	9.76	16.8
8	9.75	16.8
9	9.79	16.8
10	9.6	16.9
Mean	9.76	16.7
COV	0.90%	0.51%

Instrument to Instrument Agreement



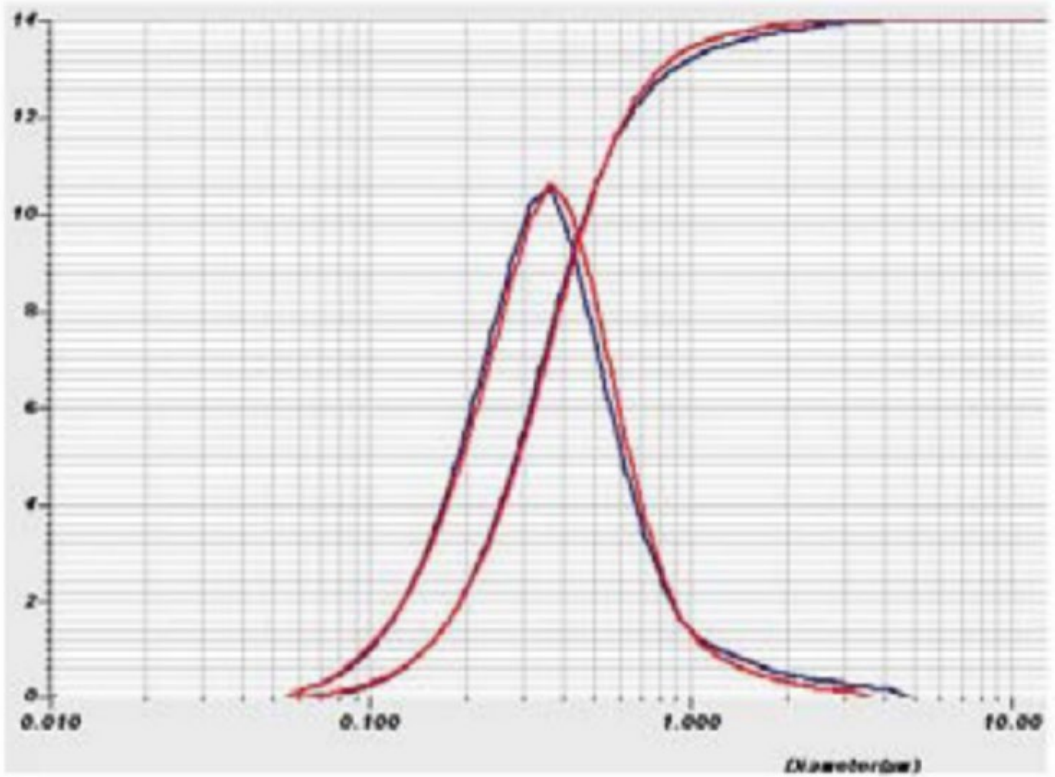
	LA-960 #1	LA-960 #2	Delta
LiMn2O4	9.75	9.64	0.1
Li2TiO3	16.7	16.9	0.2

Titanium Dioxide

Wet vs dry

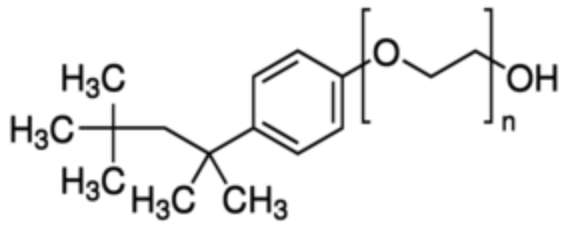
Predisperse, then add to the LA-960

The LA-960 is filled with the SHMP dispersant.

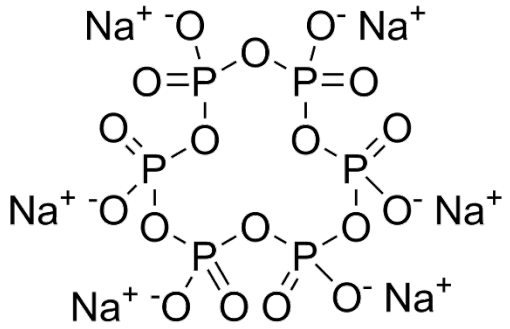


Surfactants

0.1 % Igepal 630 – nonionic



0.2 % sodium hexametaphosphate (SHMP)



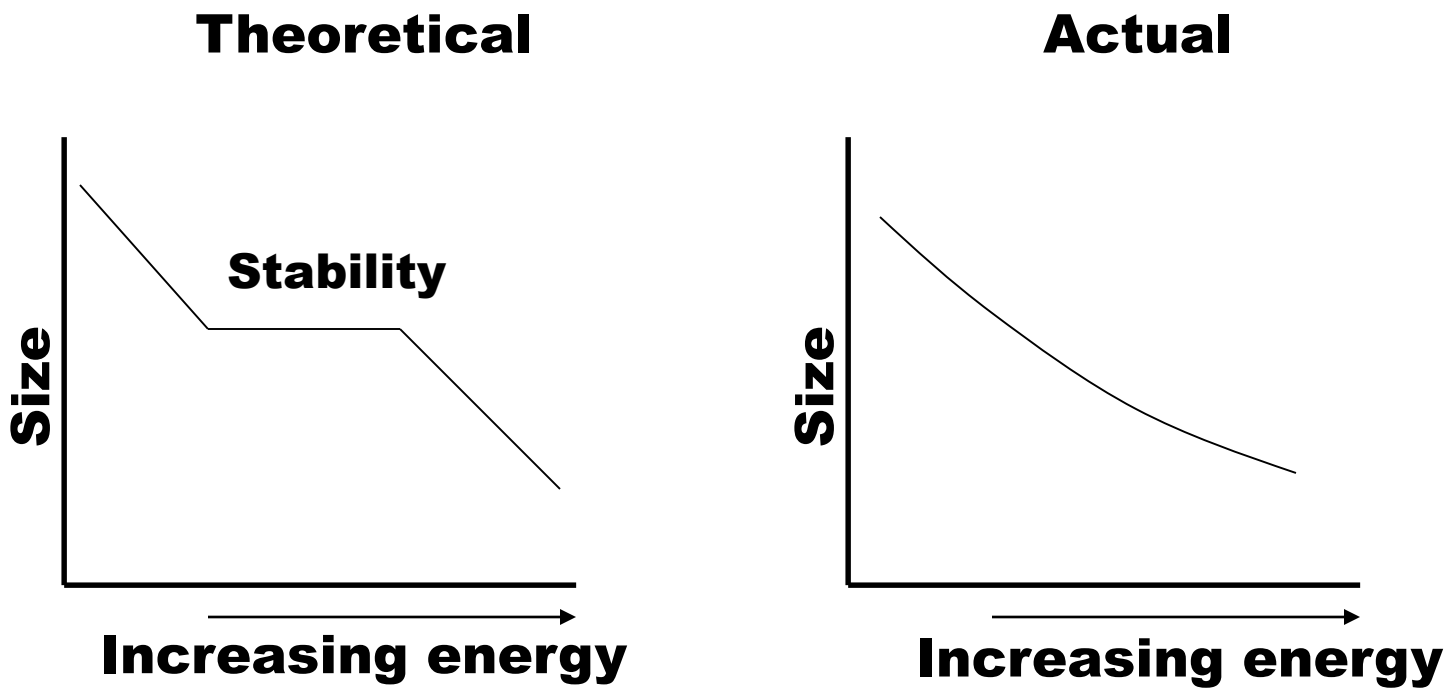
Sometimes you need to fill the analyzer with surfactant solution to avoid stripping surfactant off the particles.

Phosphate is your friend. So is 0.1~0.2%

Ultrasonic Dispersion

- Adding energy to break up agglomerates – disperse to primary particles, without breaking particles
- Similar to changing air pressure on dry powder feeder
- Typically set to 100% energy, vary time (sec) on
- Investigate tails of distribution
  - High end to see if agglomerates removed
  - Small end to see if new, smaller particles appear (breakage)
- Test reproducibility, consider robustness
- Note:
  - Do not use on emulsions
  - Can cause thermal mixing trouble w/solvents - wait
  - Use external probe if t> 2-5 minutes

Dispersion vs. Breakage



Higher air pressure or longer ultrasound duration

Conclusions

- Particle size distribution is important to ceramic performance.
- Laser diffraction is an excellent tool for this size range and material due to its speed and reproducibility.
- Often, especially with smaller sizes, surfactants and ultrasound are required to prepare a sample dispersion.

LA-960

This is what you want for your birthday present!

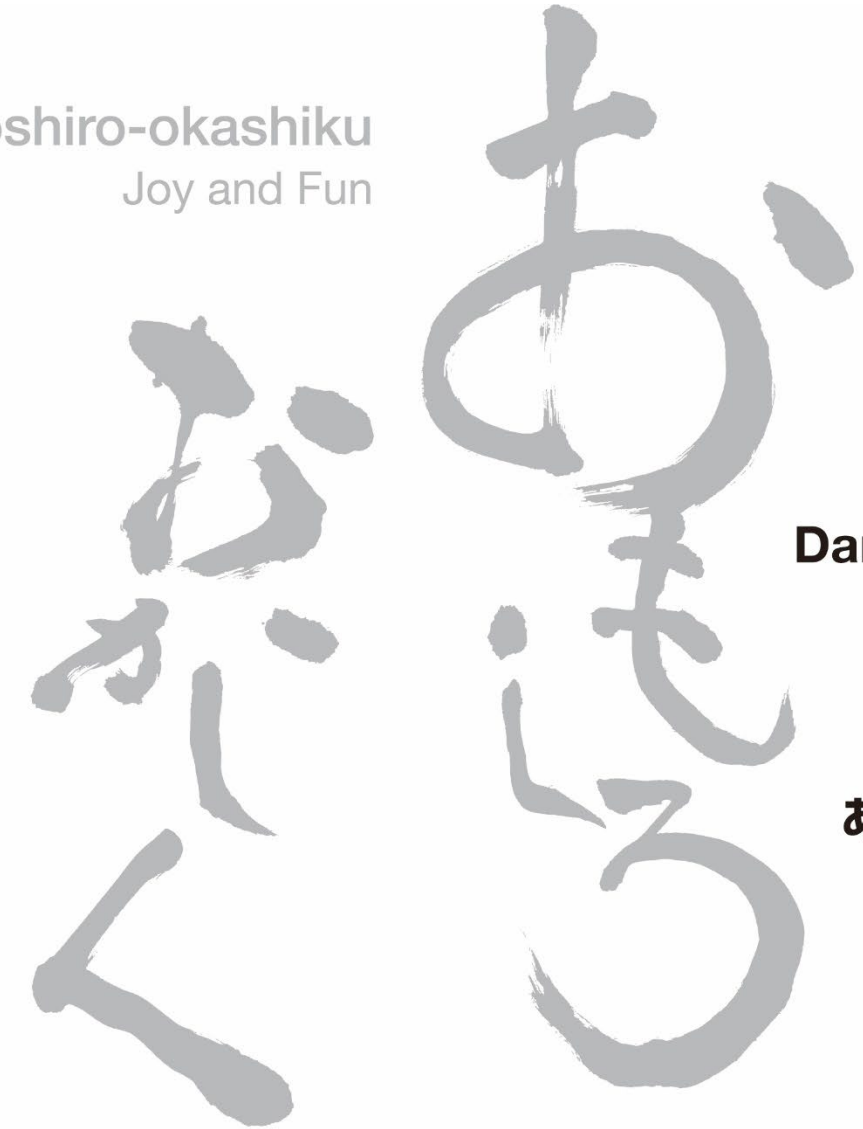
Questions? Contact us at labinfo@horiba.com

HORIBA Scientific

Thank you

Omoshiro-okashiku

Joy and Fun



Terima kasih

Gracias 谢谢

Σας ευχαριστώ πάρα πολύ

Danke Tack ska du ha Grazie

THANK YOU

ขอบคุณครับ Obrigado Большое спасибо

ありがとうございました Cảm ơn Merci 감사합니다

Dziękuję