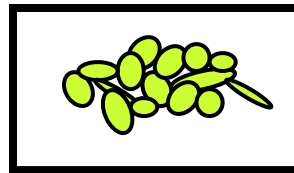
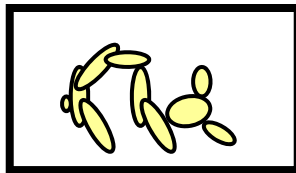
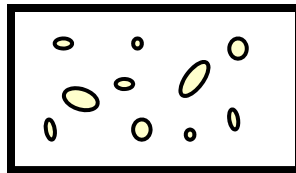


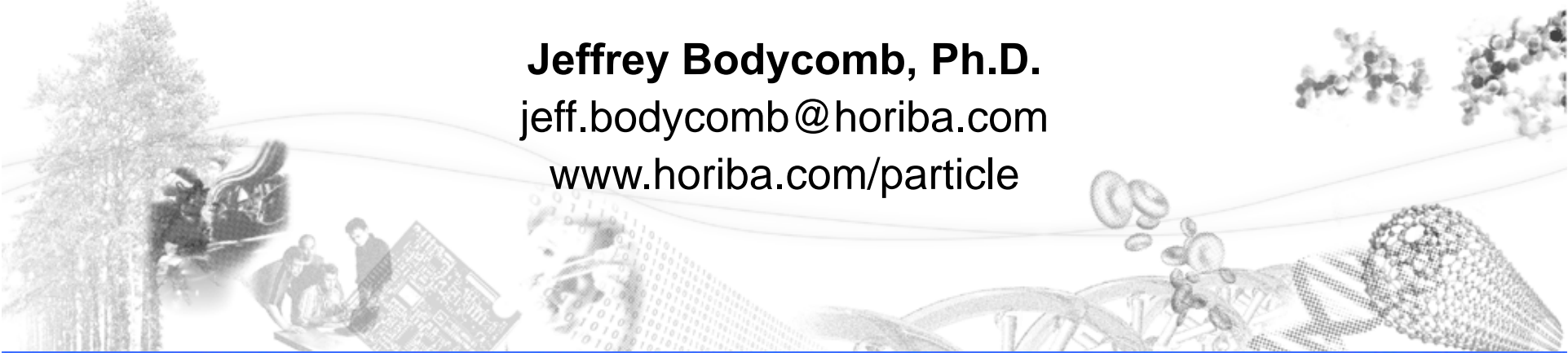


Sampling and Dispersion

The Key to Precision



Jeffrey Bodycomb, Ph.D.
jeff.bodycomb@horiba.com
www.horiba.com/particle



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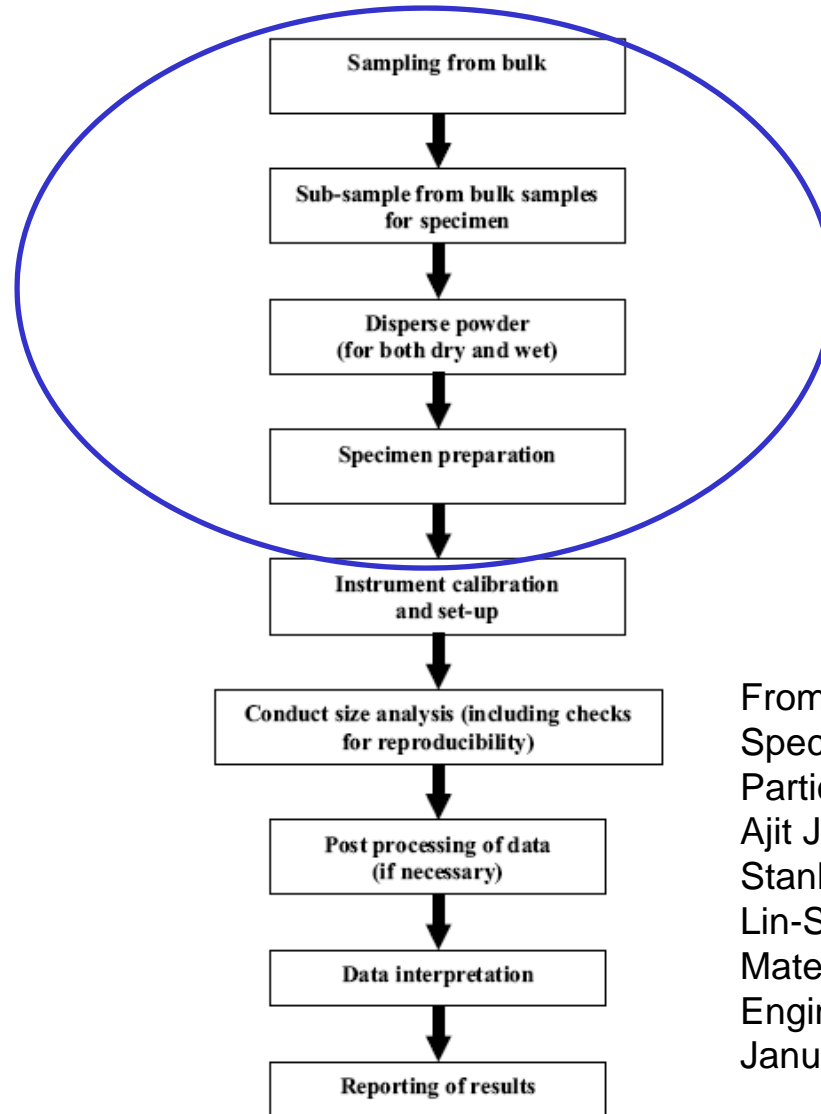
HORIBA

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What we'll talk about

- **Sampling techniques**
- **Particle wetting, surfactant use**
- **Dispersing agglomerates**
- **Tips for HORIBA size analyzers**

Particle Sizing Workflow



Today's subject area

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

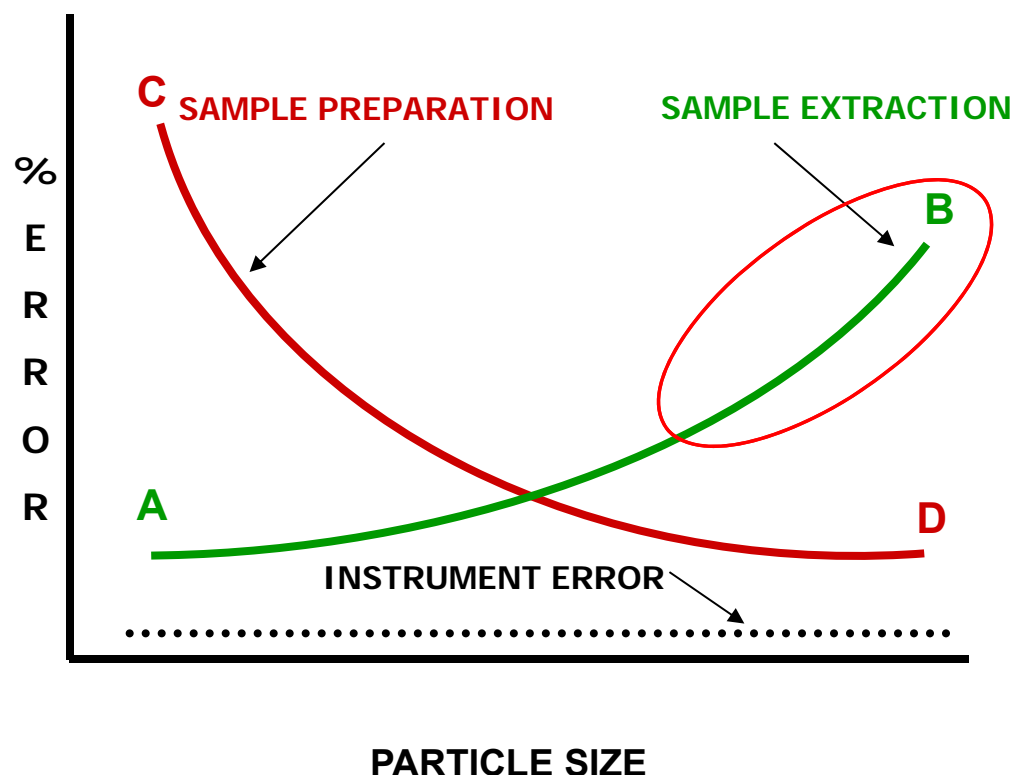
Measurement Error Sources

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

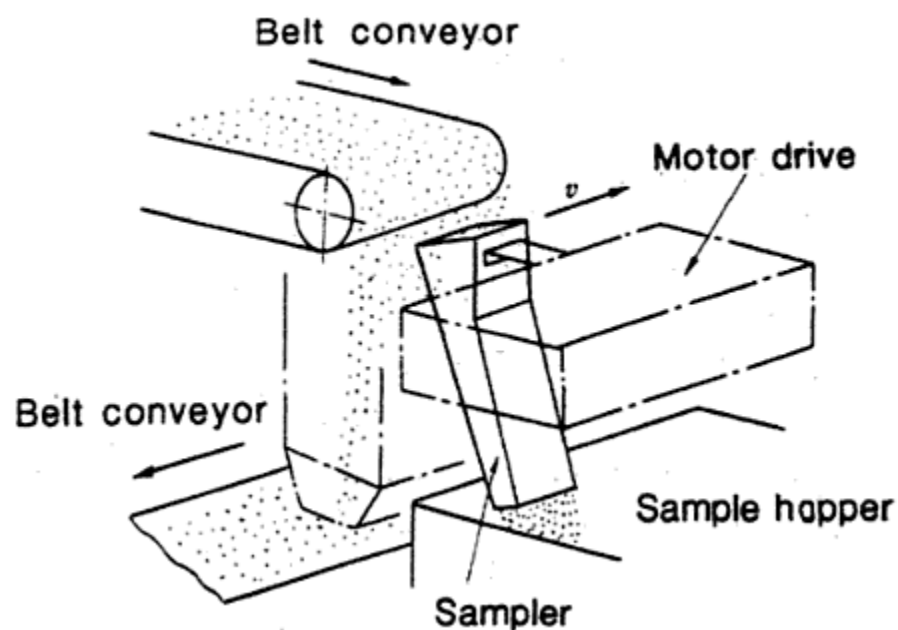
Question?

- What size particles do you analyze?

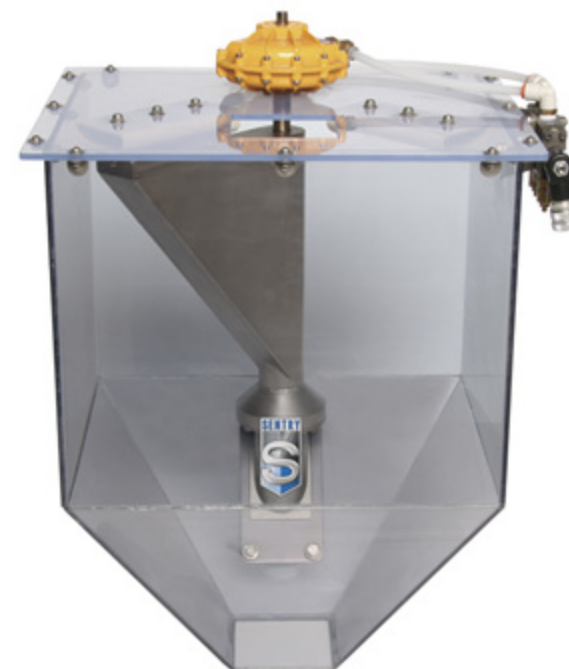
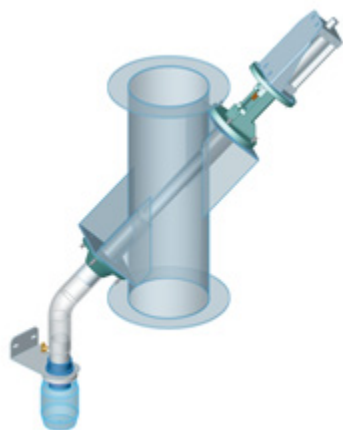
Section Overview

- Sampling from bulk
- Sub-sample for measurement
- Disperse sample
 - Wet powders, apply air pressure or ultrasound
- Sometimes second sub-sampling
 - From beaker to instrument
- Perform measurement

Sampling from Flowing Powder



Sampling from Flowing Powder



Cross-cut sampler

Cross-cut sampling: $w = \frac{L}{v} \frac{W}{L} b = \frac{Wb}{v}$

v = sampling speed (m/s)

W = sample mass

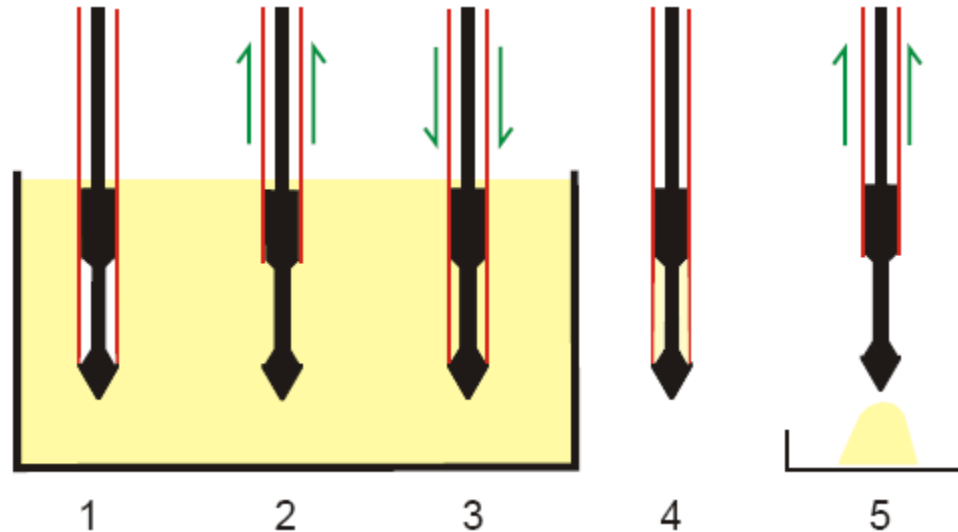
L = width of powder stream

b = sample cutter width*

*Masuda, H, Powder Technology Handbook, CRC Press, p 771

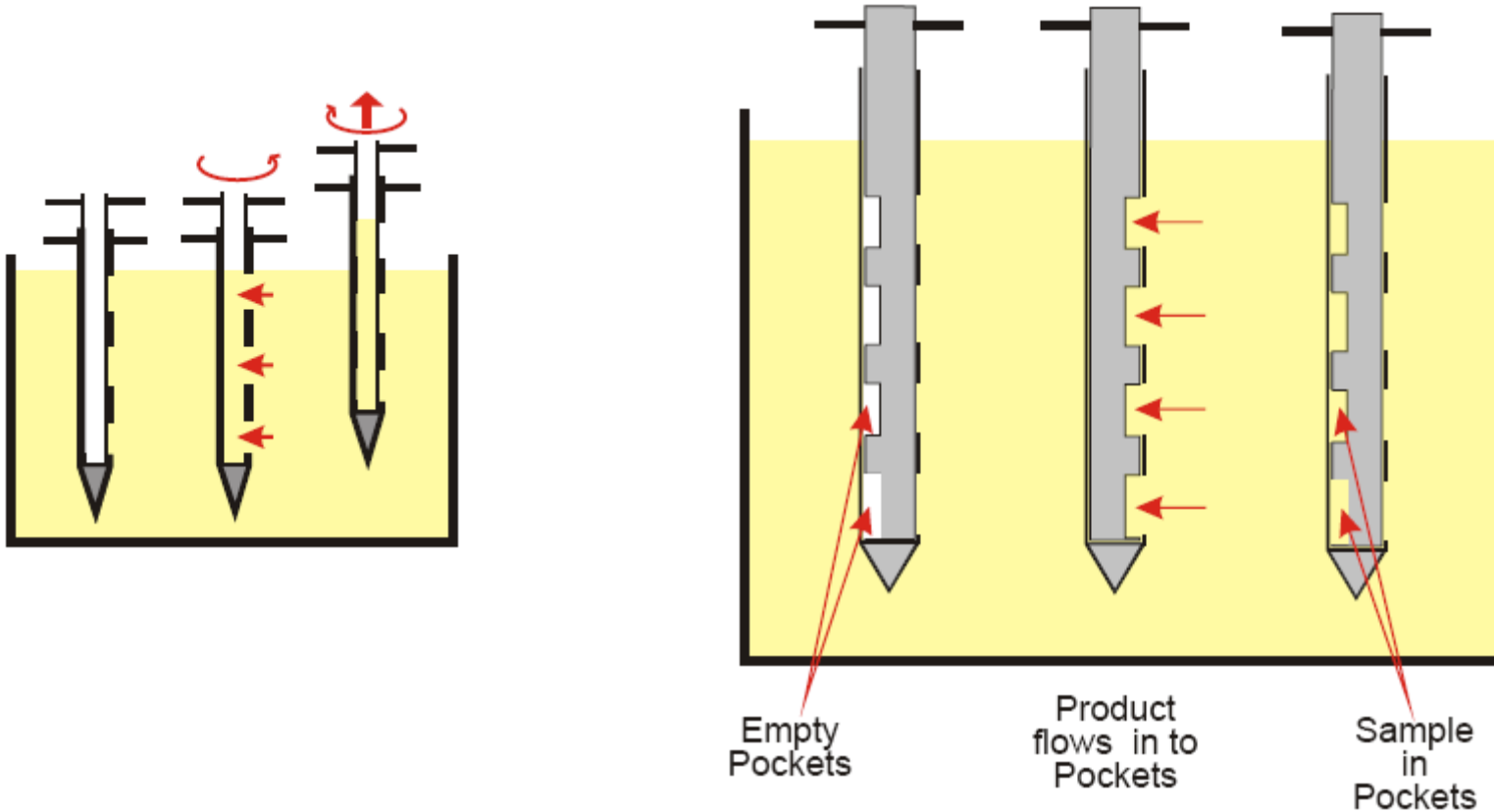
Sampling from Drums

Powder Thief



www.samplingsystems.com

Sampling from Drums



www.samplingsystems.com

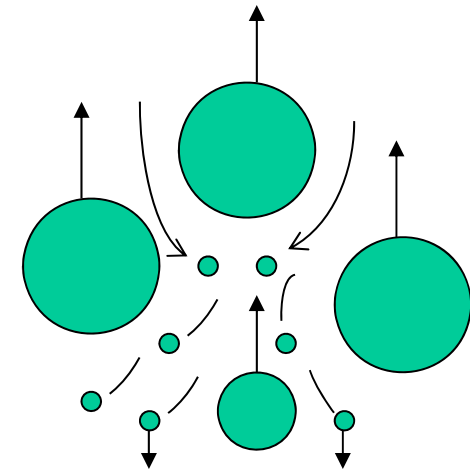
Sub-sampling for Measurement

bulk or process stream	gross sample	laboratory sample	test sample	measurement sample
(10 ⁴ kg)	(> kg)	(< kg)	(g)	(mg)

- Not all of sample brought to lab is analyzed
- Must sub-divide sample
- How to introduce representative sample into instrument

Technique: Grab Sampling

- PLACE SPATULA INTO POWDER
- EXTRACT SMALL AMOUNT FOR ANALYSIS
- ACCEPTABLE FOR NARROW DISTRIBUTIONS



SEGREGATE LARGE AND SMALL WHEN POLYDISPERSE

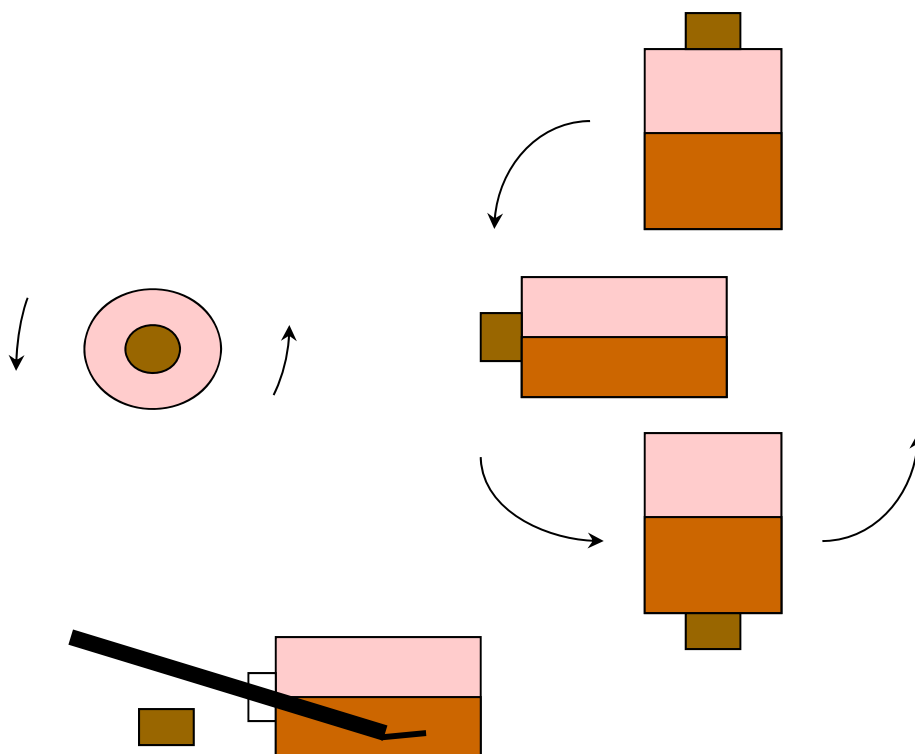
- LARGE PARTICLES PERCOLATE UPWARD
- SMALL PARTICLES GRAVITATE DOWNWARD

EASY METHOD

MOST USED METHOD

Grab Sampling from Bottle

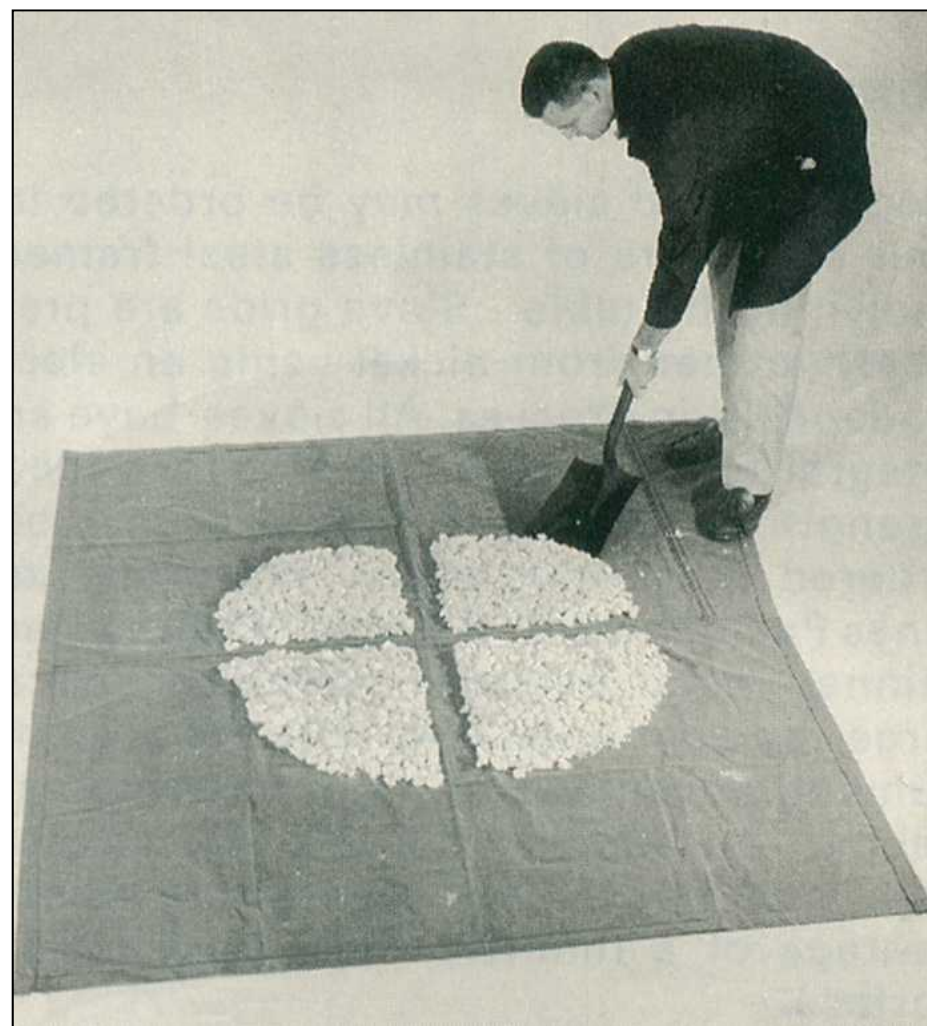
When a powder is stored in a container, it can be mixed by rolling and tumbling the container. The container should not be more than half to two-thirds full. It is important to perform this action before “grabbing” a sample with a spatula.



Then pull sample with a spatula.....

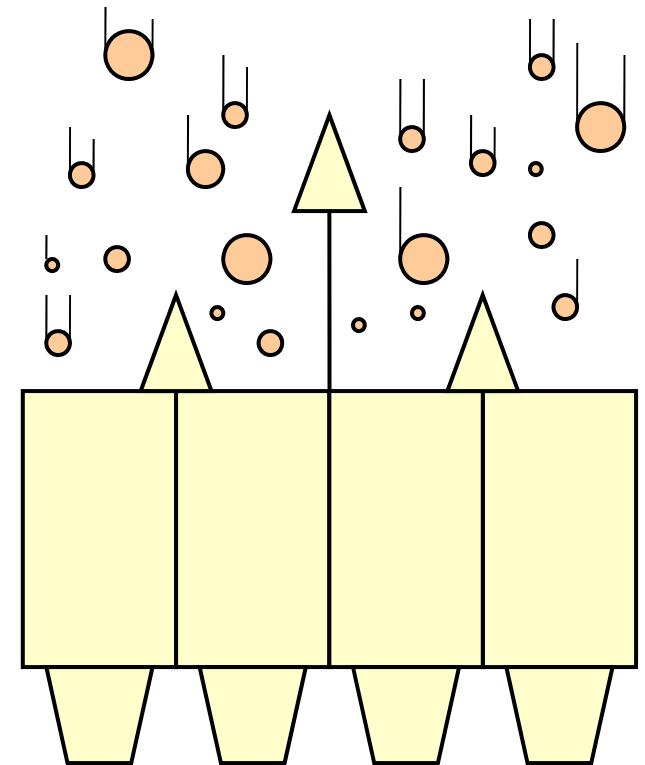
Technique: Coning & Quartering

- 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.



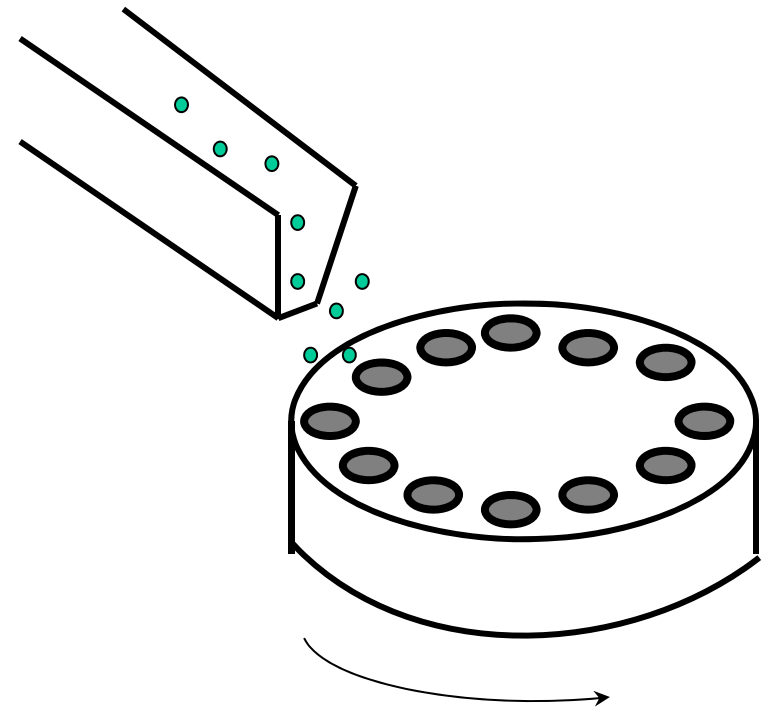
Technique: Chute Riffing

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 Riffing

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



Sample Dividers



Laboratory sample divider PT 100

- *for pourable powders and granules*
- *feed size up to 10 mm*
- *division into 6, 8 or 10 representative samples*



Laboratory rotary tube sample divider PKZ 1000

- *for pourable powders and granules*
- *feed size up to 10 mm*
- *various division ratios*



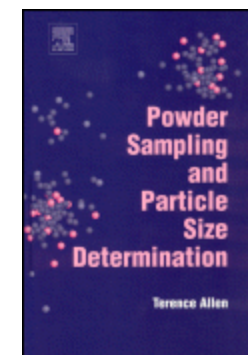
Sample splitter RT

- *for bulk materials*
- *feed size up to max. 50 mm*
- *division into 2 samples*

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

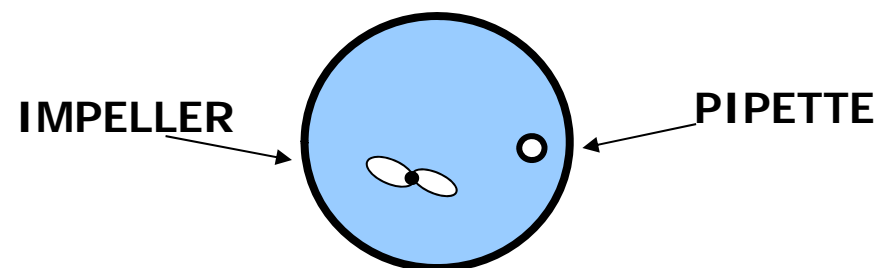
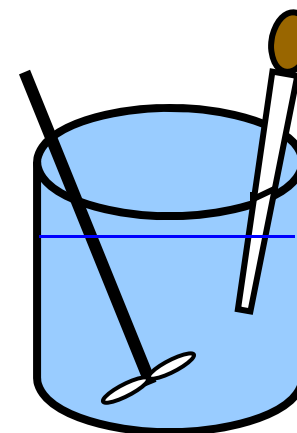
Method	Relative Standard Deviation (%)
Cone & Quartering	6.81
Scoop Sampling	5.14
Table Sampling	2.09
Chute Riffling	1.01
Spin Riffling	0.125

Technique: Sampling from Beaker

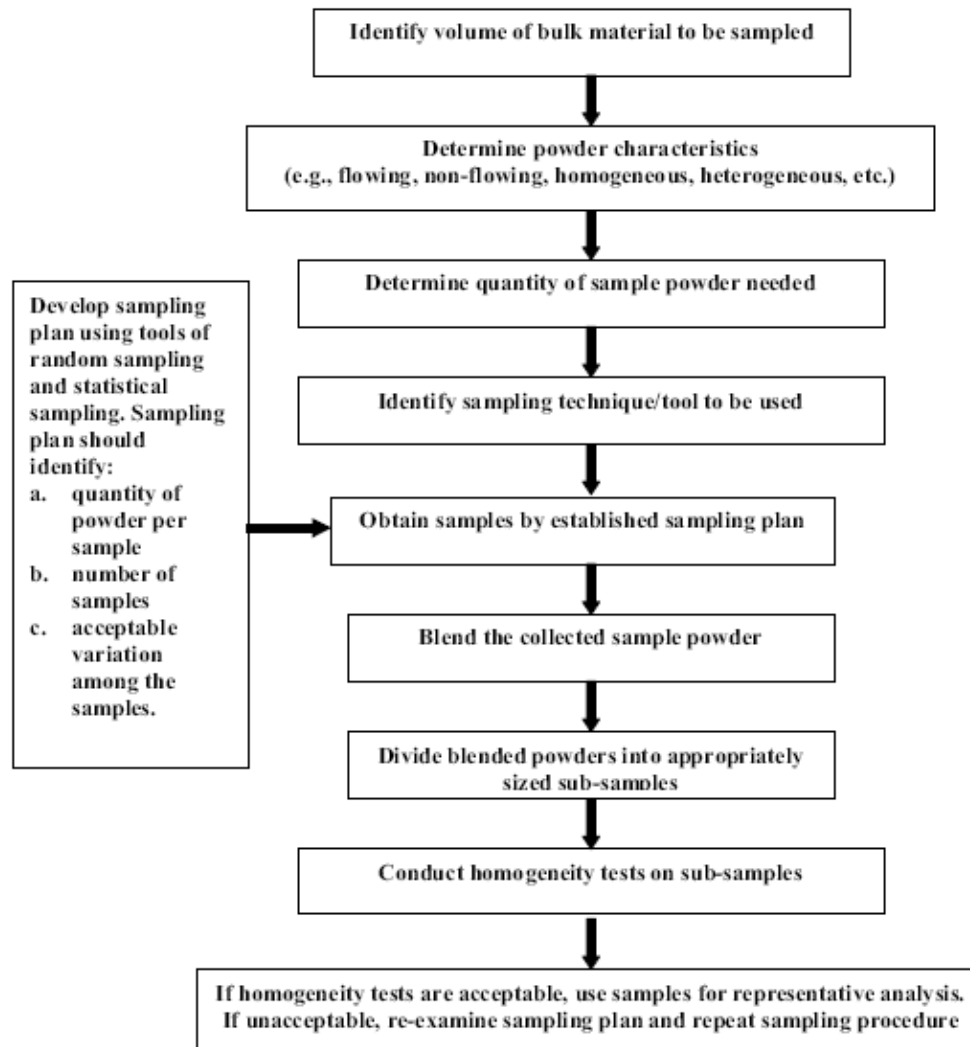
Liquid should be in motion vertically and horizontally to insure good mixing.

Pipette should be about one-third of the way from the bottom when extracting sample.

Alternative: When mixing powders into a slurry: make paste, pipette from paste



Summary



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

What we'll talk about

- **Sampling techniques**
- **Particle wetting, surfactant use**
- **Dispersing agglomerates**
- **Tips for HORIBA size analyzers**

Dispersion Strategies

■ Powders

- When measuring powder as suspension
- Choose solvent (avoid dissolution)
- Wet powder (surfactant)
- Dispersing aid to avoid re-agglomeration
- Energy to break agglomerates into primary particles
 - Pump & stirrer or ultrasound

■ Suspensions

- Dilute
- Energy

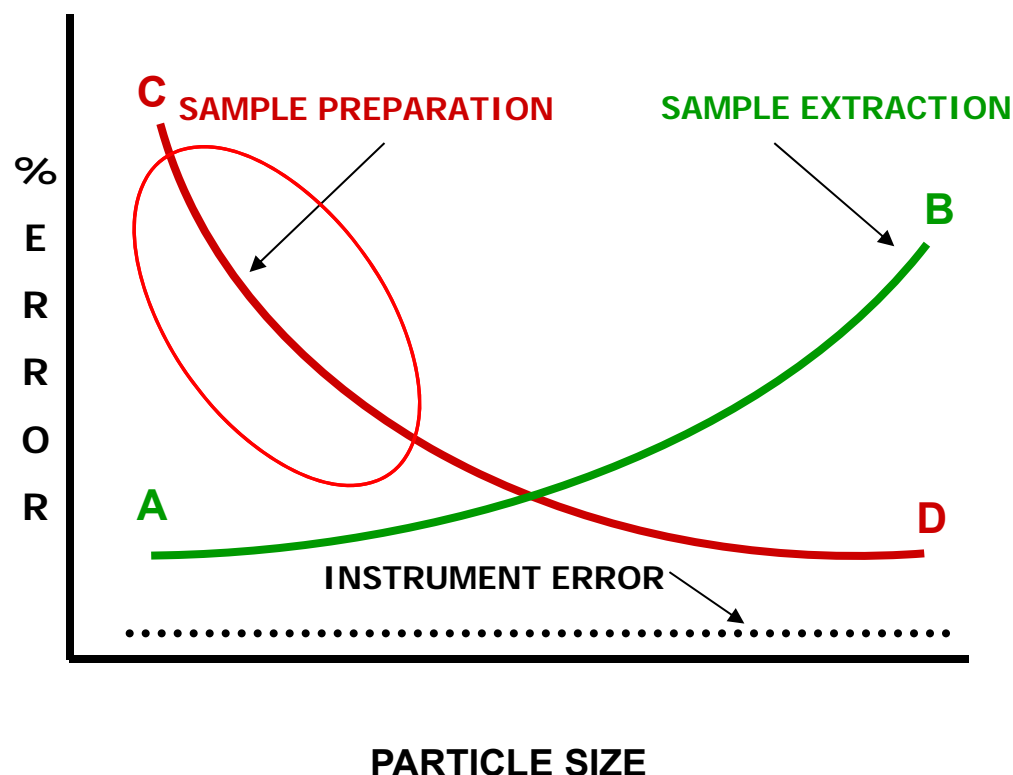
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SMALL PARTICLES

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

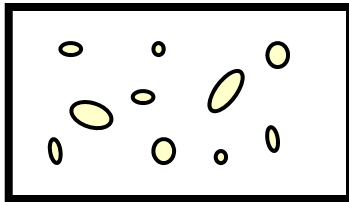
LARGE PARTICLES

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



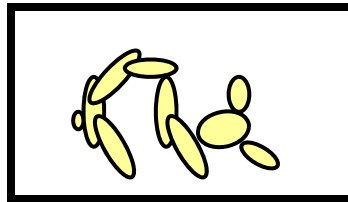
INSTRUMENT ERROR IS SMALL AND RELATIVELY CONSTANT

Dispersion Definitions



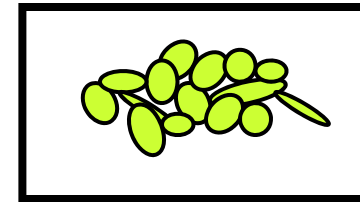
WELL DISPERSED

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



AGGLOMERATED

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



AGGREGATED

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.

Particle Wetting

MEASUREMENT OF CONTACT ANGLE (θ)

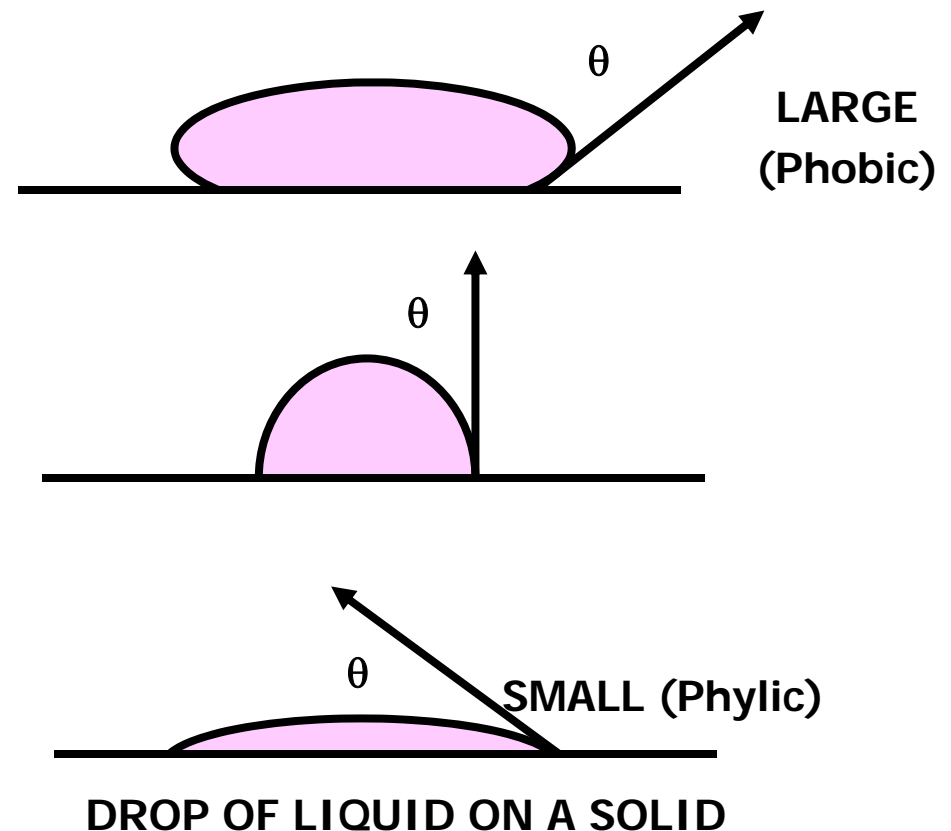
The contact angle is a measure of how well the liquid drop adheres to the surface of a solid

Large angles indicate poor wetting ability.

Small angles indicate good wetting ability.

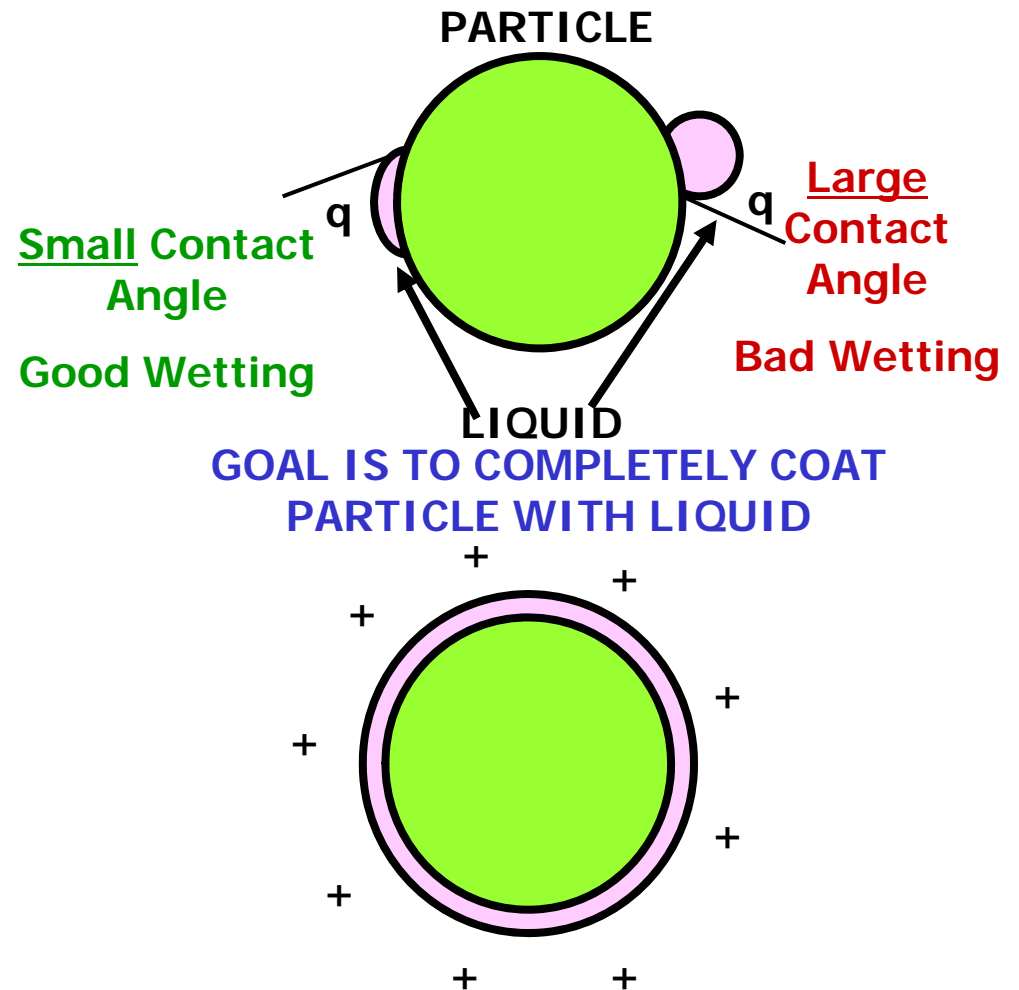
Surfactants reduce surface tension and thereby are conducive to good wetting.

(Instruments are available for measuring contact angle)



Particle Wetting

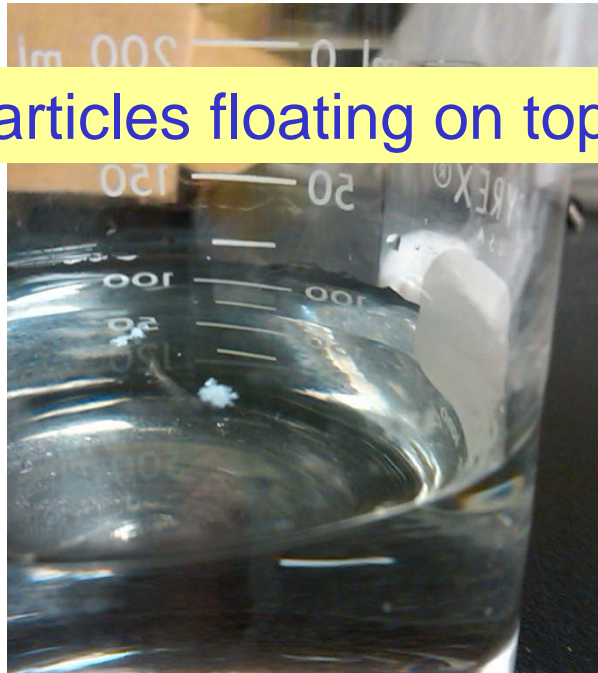
Surface Tension must be lowered so liquid will adhere to particles.



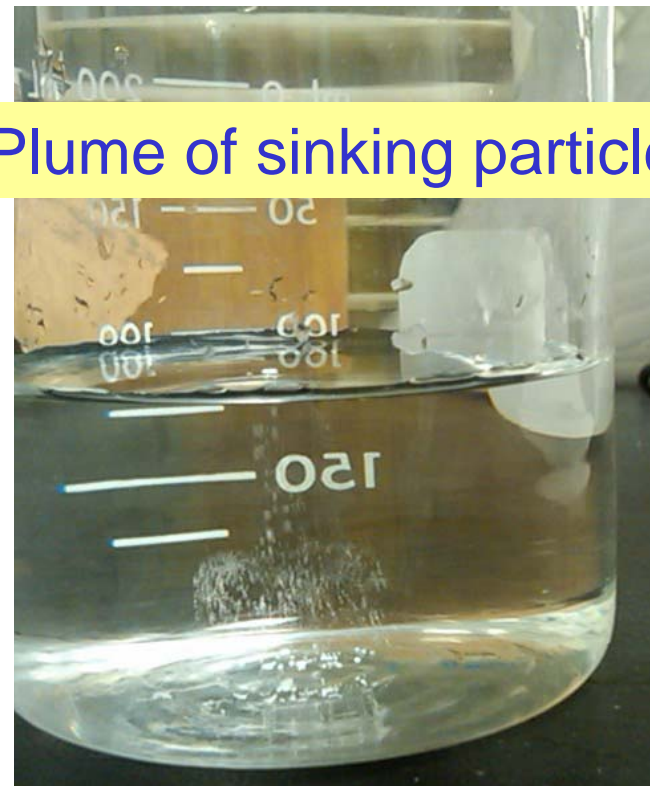
How to check for wetting

- Sprinkle particles on of target dispersant. If the particles float on top and do not penetrate the water surface, they are not wetted. This is usually a bad sign.
- If the particles break through surface and sink, they are a) wetted or b) so big that gravity is more important than surface tension. If it is case a, you are in luck.

Particles floating on top



Plume of sinking particles

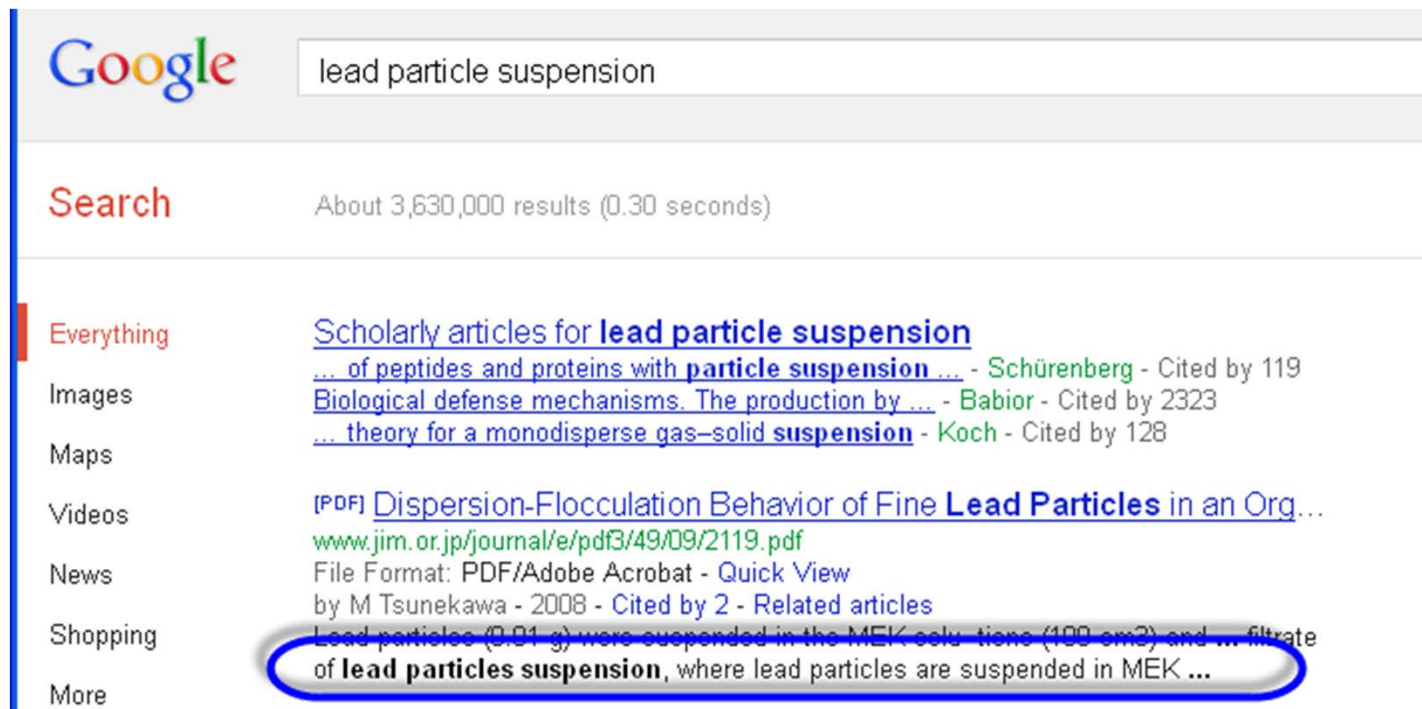


Don't forget changing solvents

- Working with aqueous systems is usually easier for many reasons.
- But don't forget to try a less polar solvent such as isopropyl alcohol.
- And, don't forget that organic solvents are more difficult to handle due to fire and health hazards.

If the going gets tough...

- Check the literature and the web and see what other people use.
- Here I use Google to get the idea to use MEK with lead.



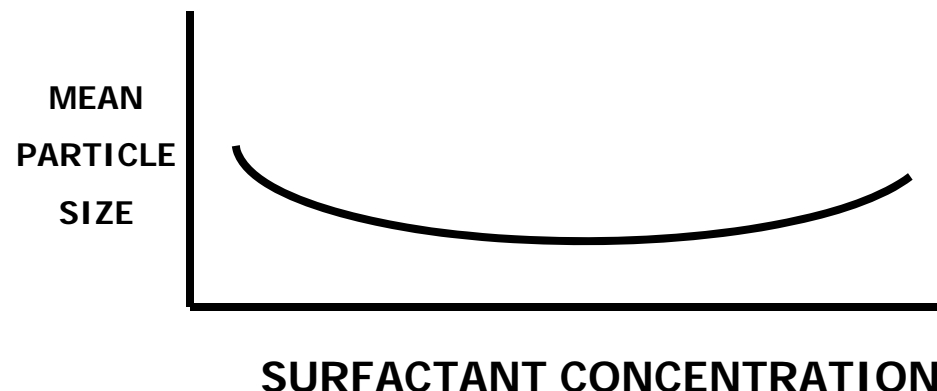
If the going gets tough...

- Try a series of options.
- Here I make a series of suspensions and check them by eye, then measure.



Effect of Surfactant Addition

Addition of surfactant to a sample will disperse the particles so a proper measurement may be made. However, addition of too much surfactant will cause agglomeration.



The graph illustrates that there is an optimum amount of surfactant to effect optimum dispersion. The Particle Size Analyzer can determine when the amount of surfactant exceeds the proper concentration.

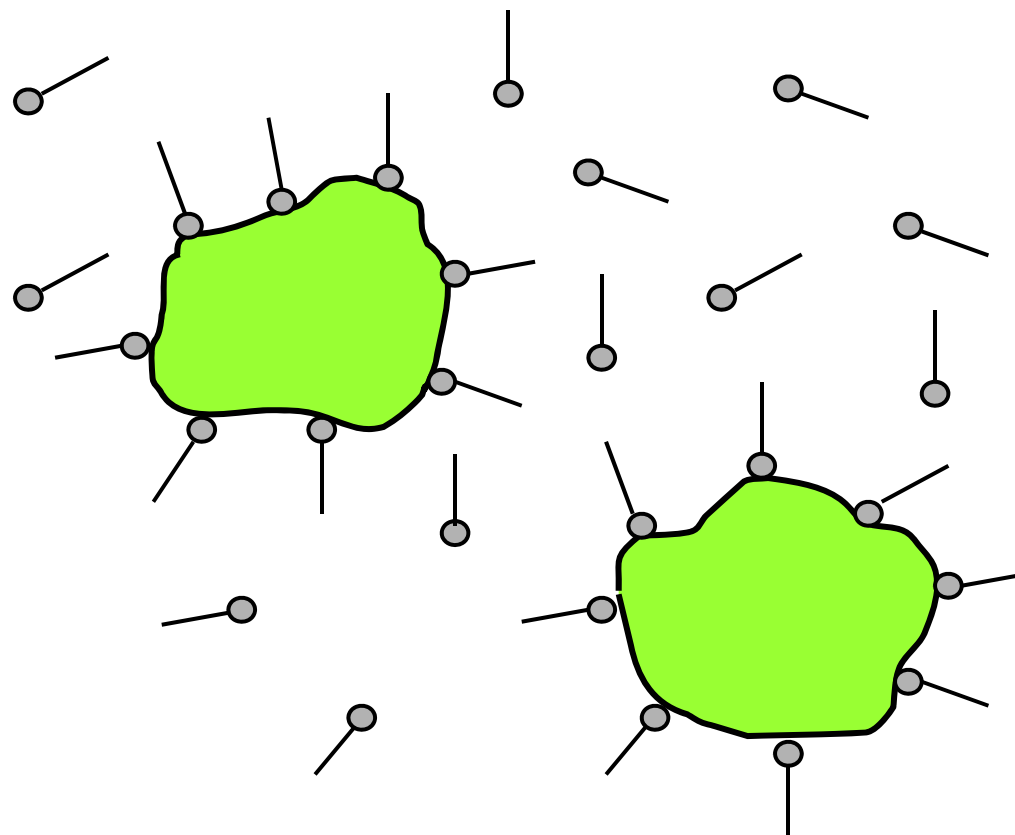
As initial surfactant is added, the mean particle size will decrease. It will reach a minimum as the proper surfactant concentration is reached.

As additional surfactant is added, the apparent mean particle size will increase, indicating agglomeration of particles.

Common concentration: 0.01-0.1%

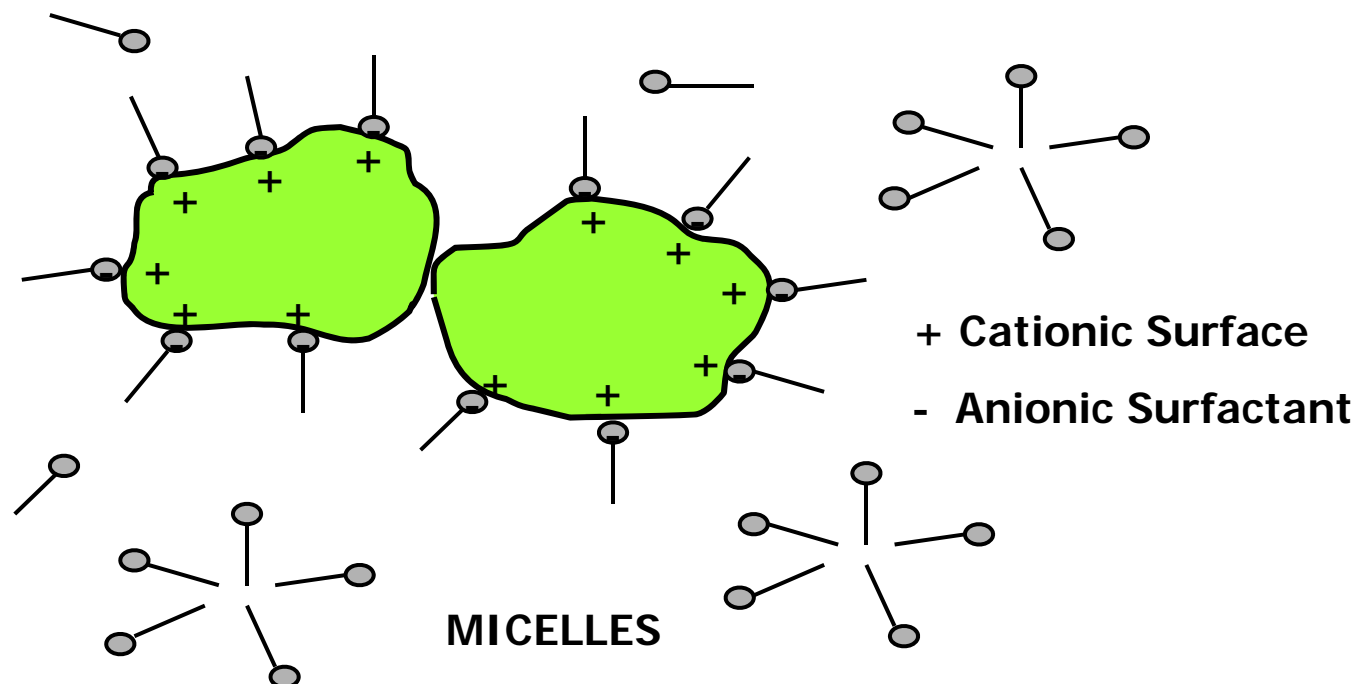
Surfactant Mechanism

■ **EQUILIBRIUM**
established between
SURFACTANT ON
PARTICLES and
SURFACTANT IN
SOLUTION.



— **NON-POLAR HYDROCARBON**
● **POLAR IONIC DIPOLE**

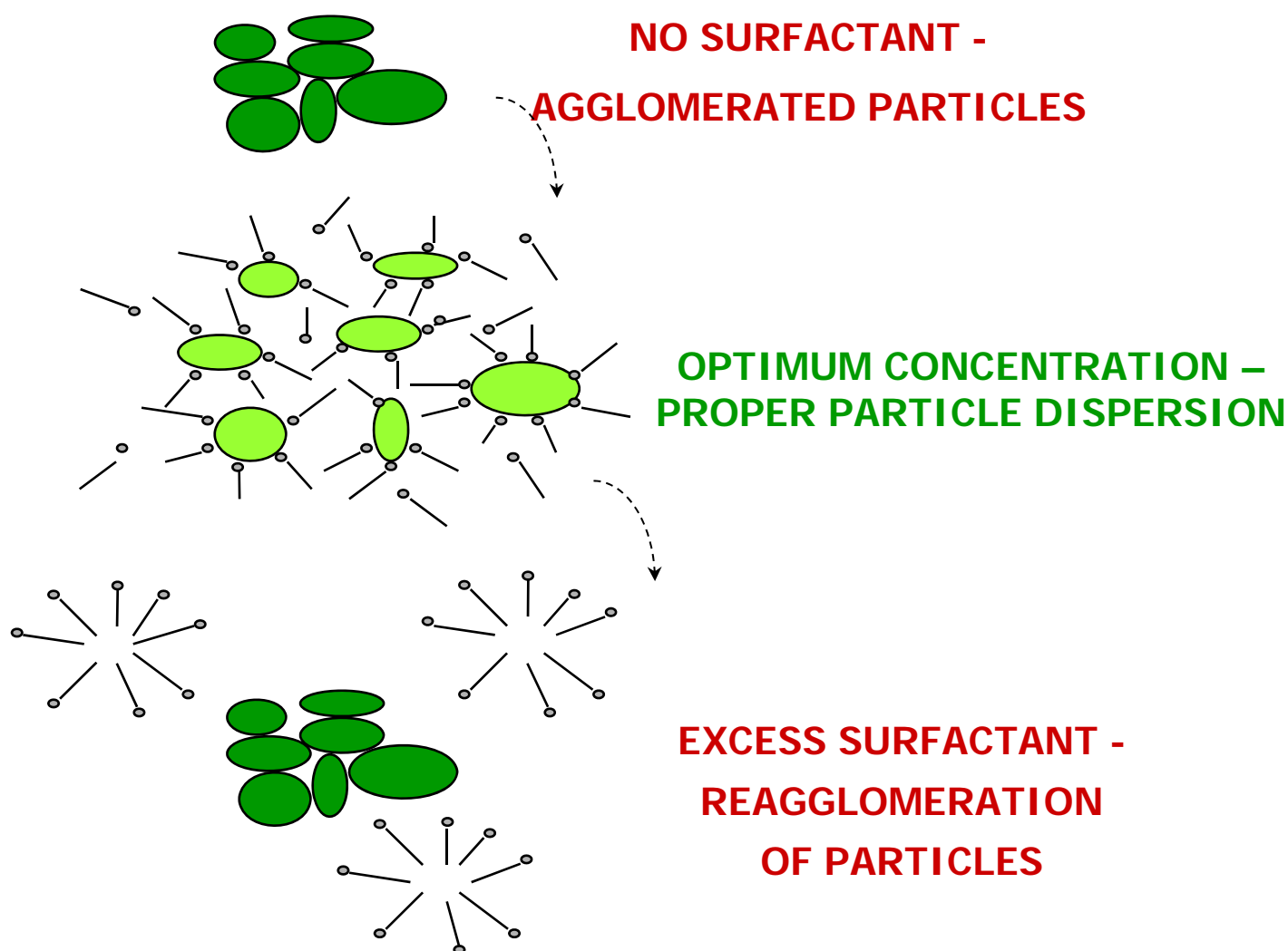
Critical Micelle Concentration



As more surfactant is added, equilibrium shifts. Surfactant leaves surfaces to start formation of MICELLES. This is called CRITICAL MICELLE CONCENTRATION (CMC).

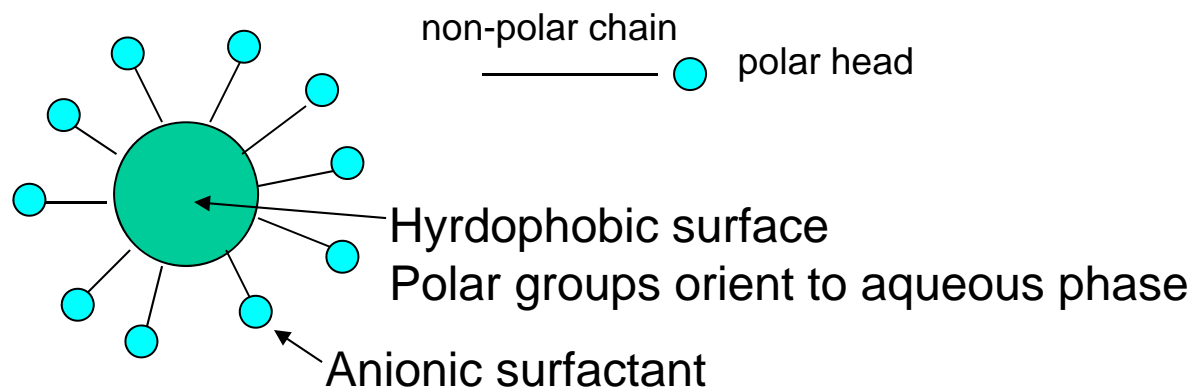
Particle surfaces are no longer repulsed, and energy of the system favors REAGGLOMORATION.

Effect of Surfactant Addition



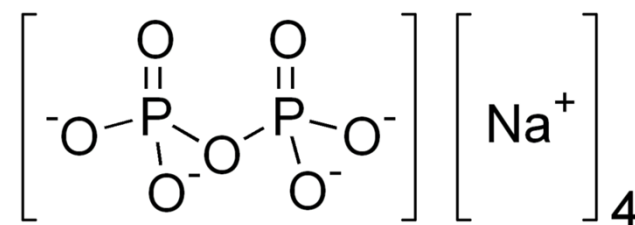
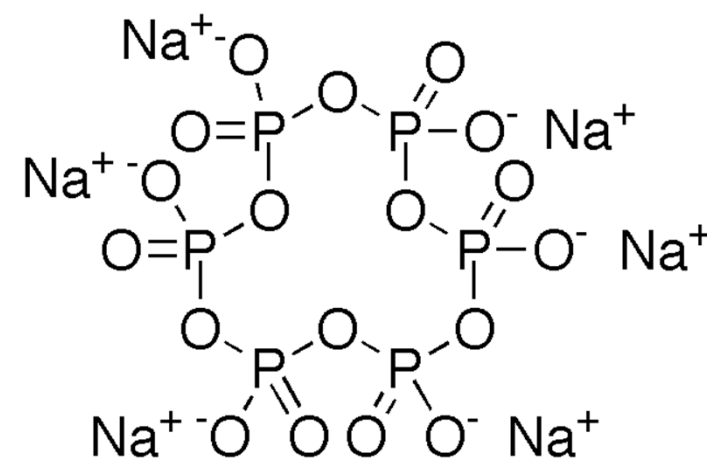
Common Surfactants

- Nonionic surfactants adsorb to charged and neutral surfaces, create steric barrier
- Igepal CA630 Ethoxylated octyl phenol Nonionic
- Triton X100 Octylphenoxypolyethoxy ethanol Nonionic
- Tween 20 Polyoxyethylene sorbitan Nonionic
- Aerosol-OT Dioctyl ester Na Sulfo succinic acid Anionic
- Cationic surfactants often used for biological samples, stringly bonds to negatively charged surfaces



Sodium Hexametaphosphate

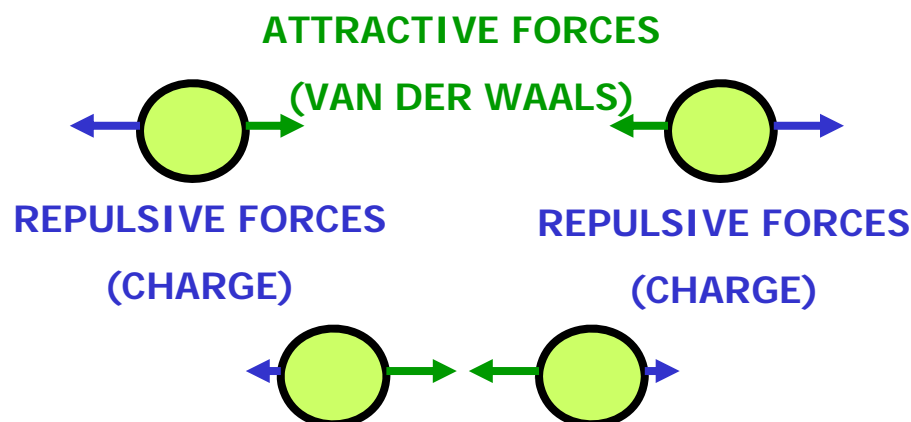
- Most common stabilizer
- Abbreviated NaHMP
- Keeps particles from re-agglomerating
- Disperse sample in 0.01 – 1.0% $(\text{NaPO}_3)_6$ rather than DI water
- Tetrasodium pyrophosphate also used (sodium pyrophosphate, NaPP)



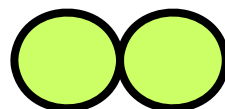
What we'll talk about

- **Sampling techniques**
- **Particle wetting, surfactant use**
- **Dispersing agglomerates**
- **Tips for HORIBA size analyzers**

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).



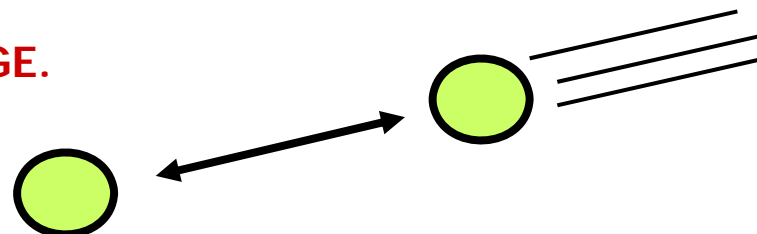
The object is to provide repulsive forces strong enough to keep particles apart, even during close approach. This can be accomplished by surfactant coating of particle surfaces.



Particle Interactions

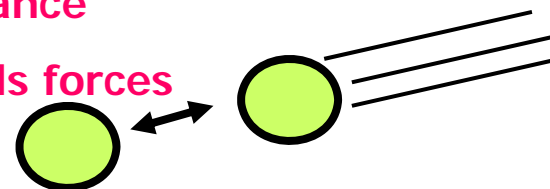
Inter-particle distance is **LARGE**.

Van der Waals forces **WEAK**



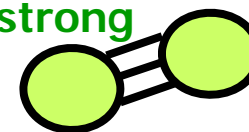
Decreasing particle distance

Increasing Van der Waals forces

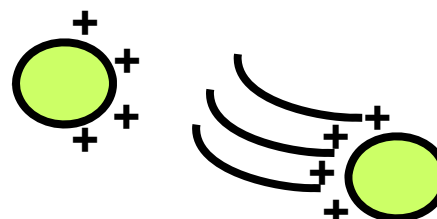


Particle distance very small

Van der Waals forces **strong**



If surfactant charge is sufficiently high, it will overcome Van der Waals forces before the particles approach closely.

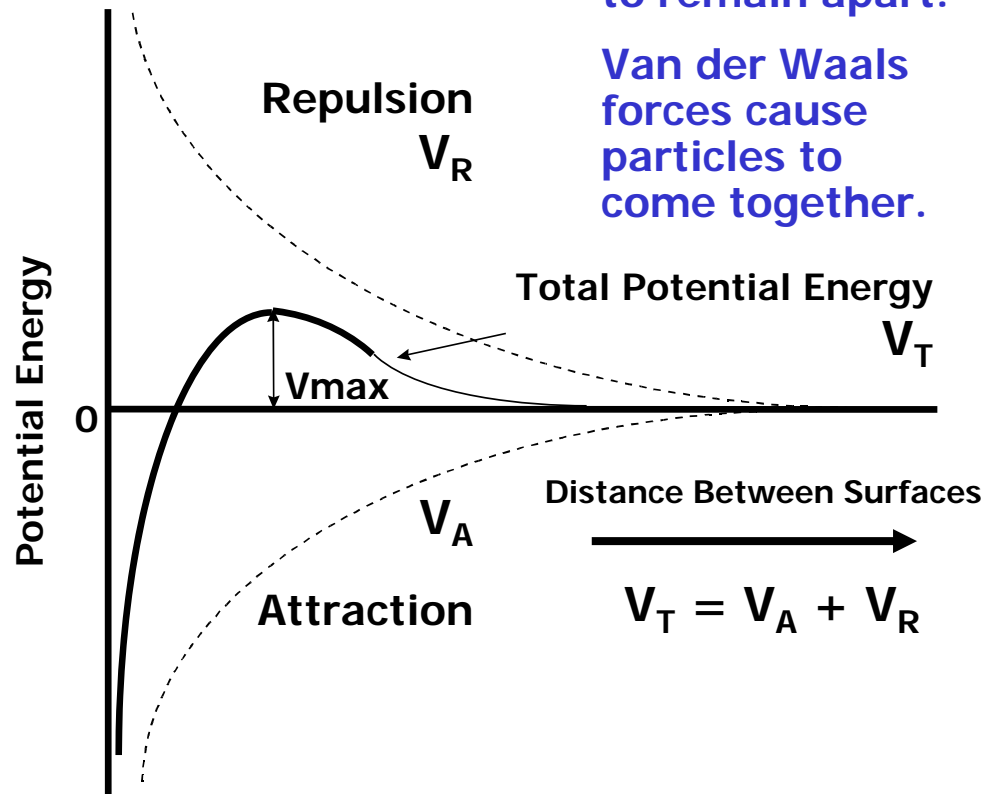


Energy of Interaction

■ INTERACTION OF TWO CHARGED SURFACES

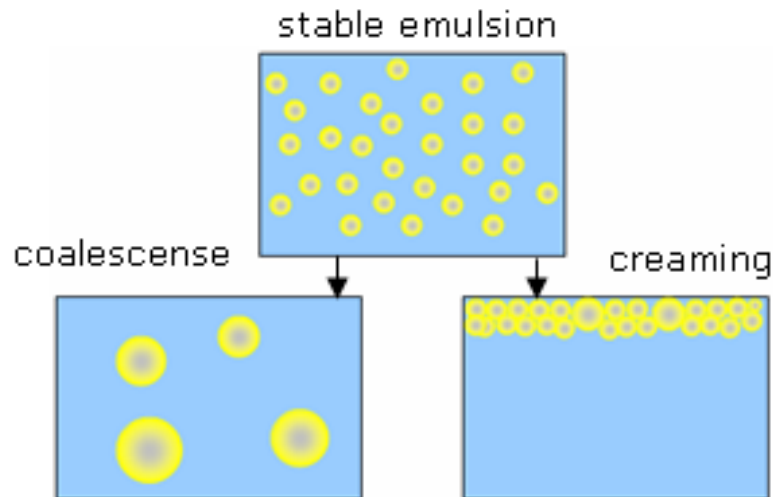
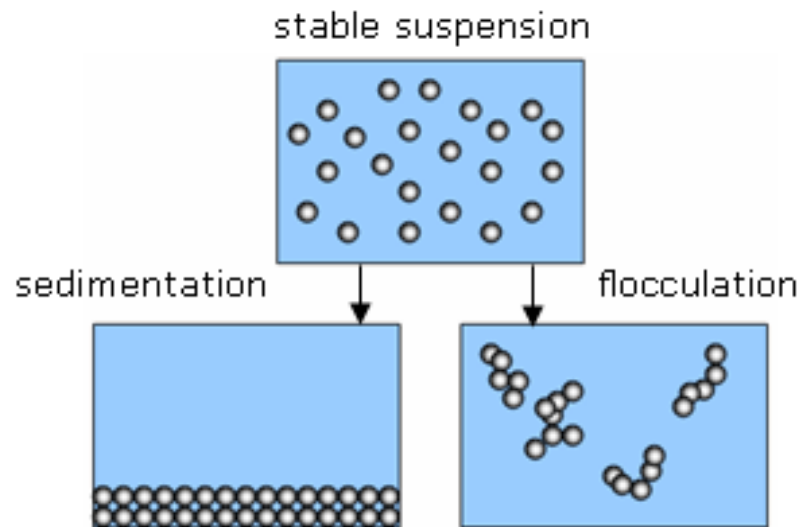
Electrical forces cause particles to remain apart.

Van der Waals forces cause particles to come together.

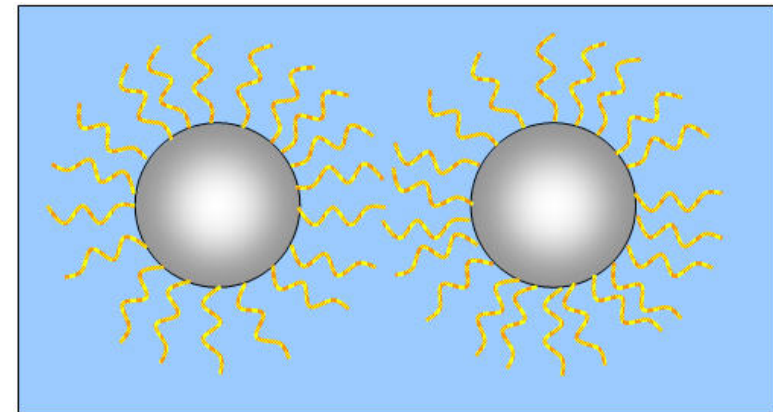


- Stability of a system depends on forces between particles. Random motion brings them into close proximity. Whether two particles will combine depends on potential barrier between them. Potential energy consists of two forces, the ATTRACTIVE one due to Van der Waals, and the REPULSIVE one due to electrical 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.

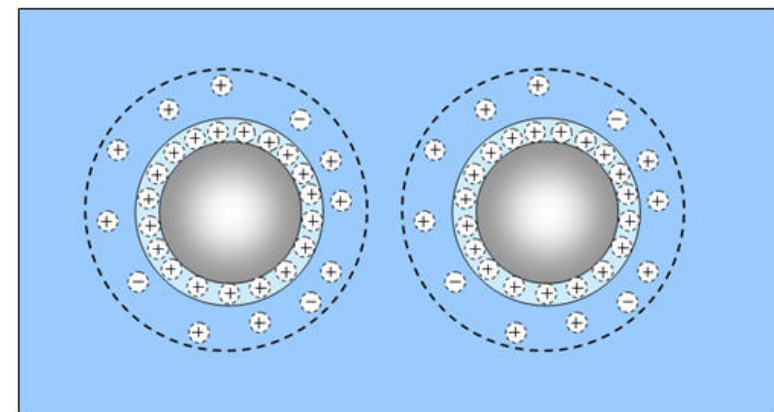
Dispersion Stability



steric stabilization



electrostatic stabilization

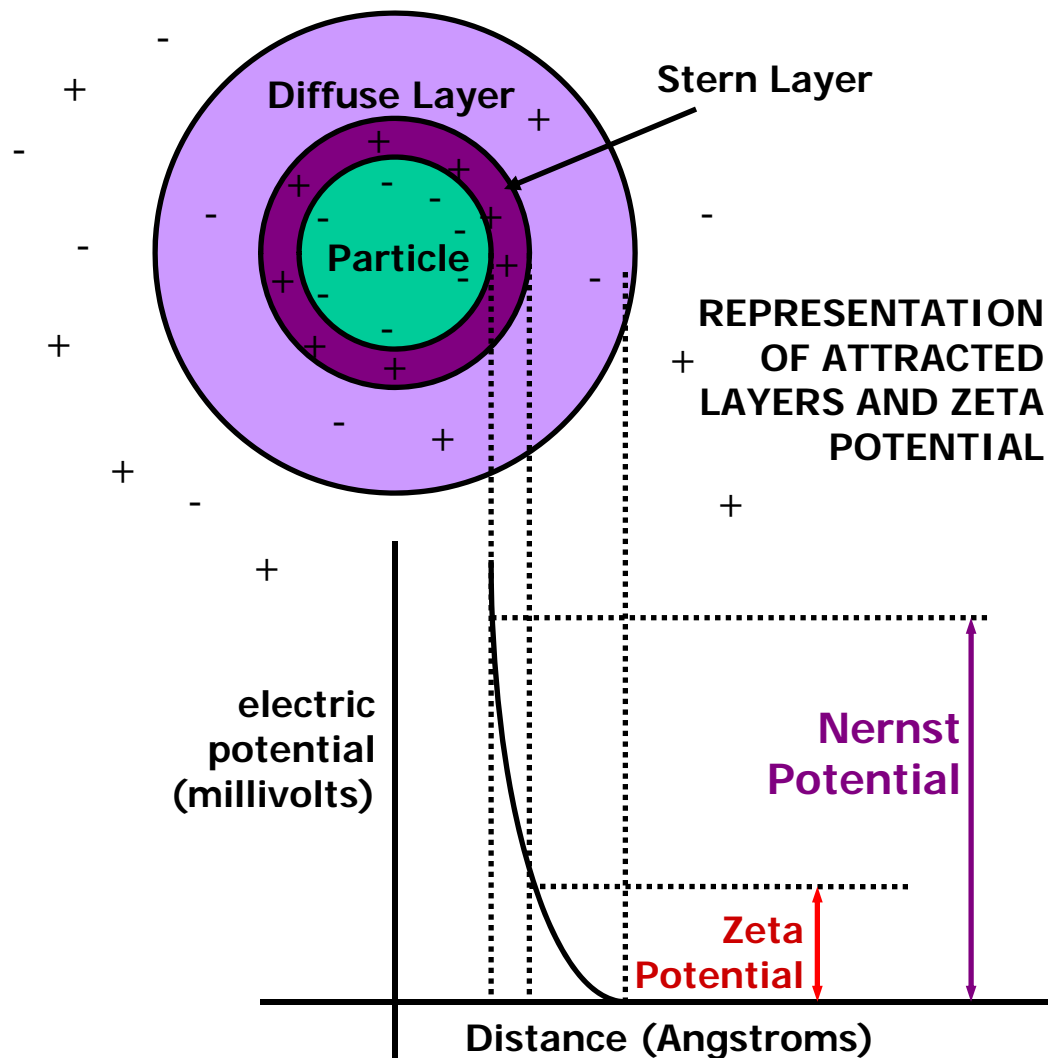


Zeta Potential

■ A double layer exists around each particle. If a particle is negatively charged, a thin layer of positive charge forms around the particle (the Stern Layer). Beyond the Stern Layer, there is a wider layer of mostly opposite charge known as the DIFFUSE Layer.

■ The potential at the surface of the particle is designated the NERNST Potential, and the potential at the shear plane is designated the ZETA Potential.

■ ZETA Potential is a useful measurement quantity because it is a measure of surface activity in colloidal particles.



Pop Quiz

- As particle size distribution becomes wider....

What we'll talk about

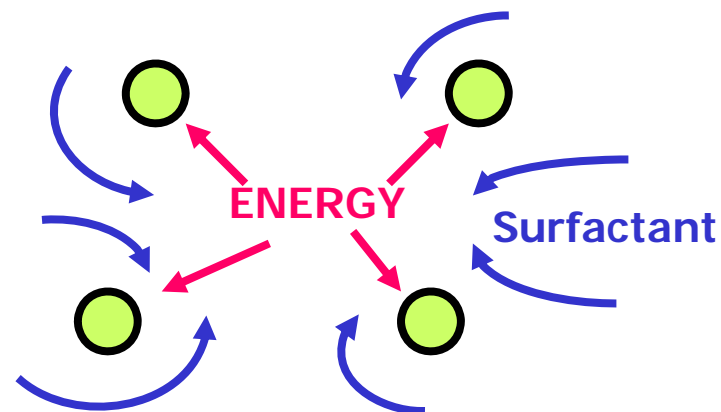
- **Sampling techniques**
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Dispersion: Mechanical Energy

The purpose of applying energy is to separate particles for a sufficient period to allow surfactants to develop a coating.

TYPES OF ENERGY DEVICES

- Blenders
- Stirrers
- Ultrasonic Devices
 - Ultrasonic Bath
 - Ultrasonic Probe

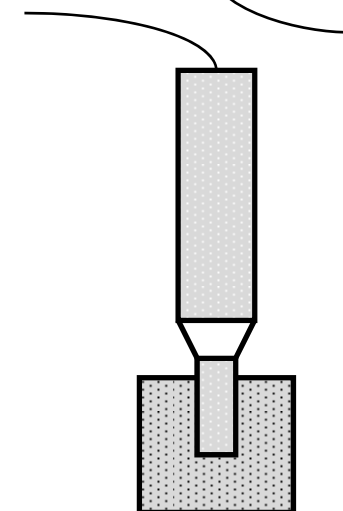
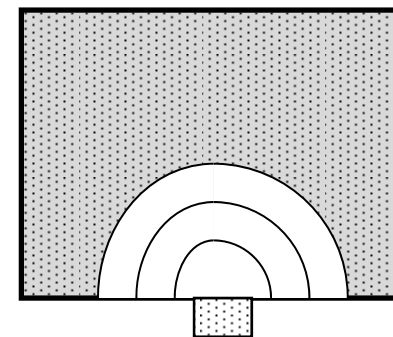


Dilute surfactant is mixed with suspending liquid before particulate sample is added. As energy is applied, the surfactant is able to attach to the particles, providing sufficient charge to keep individual particles apart.

Dispersion: Ultrasonic Energy

- Ultrasonic waves generate microscopic bubbles or cavities (cavitation) which produce shearing action causing the liquid and suspended particles to become intensely agitated.
- Agglomerates are broken apart.
- In some cases fragile particles are shattered.
- The selection of appropriate type and level of ultrasonic energy must be made carefully.

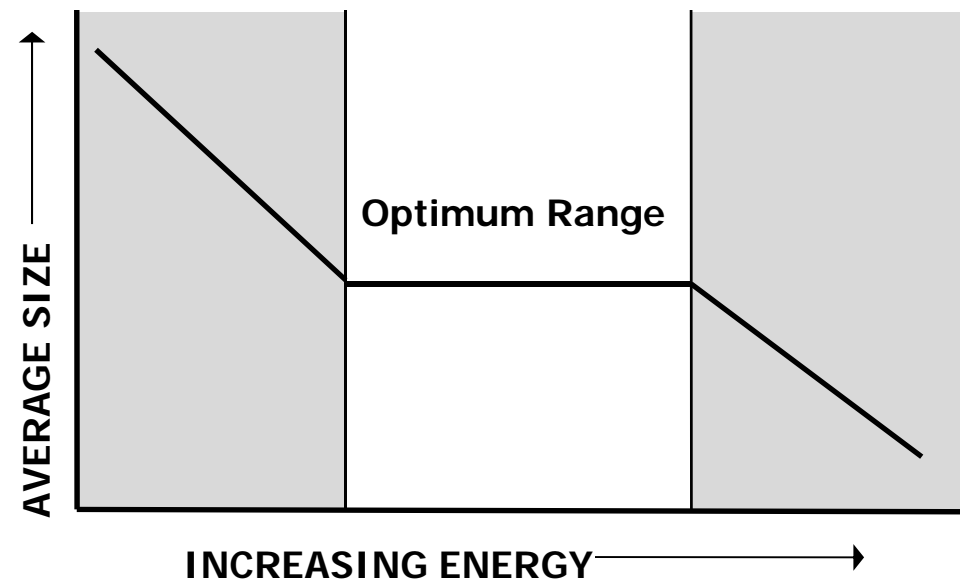
Ultrasonic Bath



Ultrasonic Probe

Effect of Applied Energy

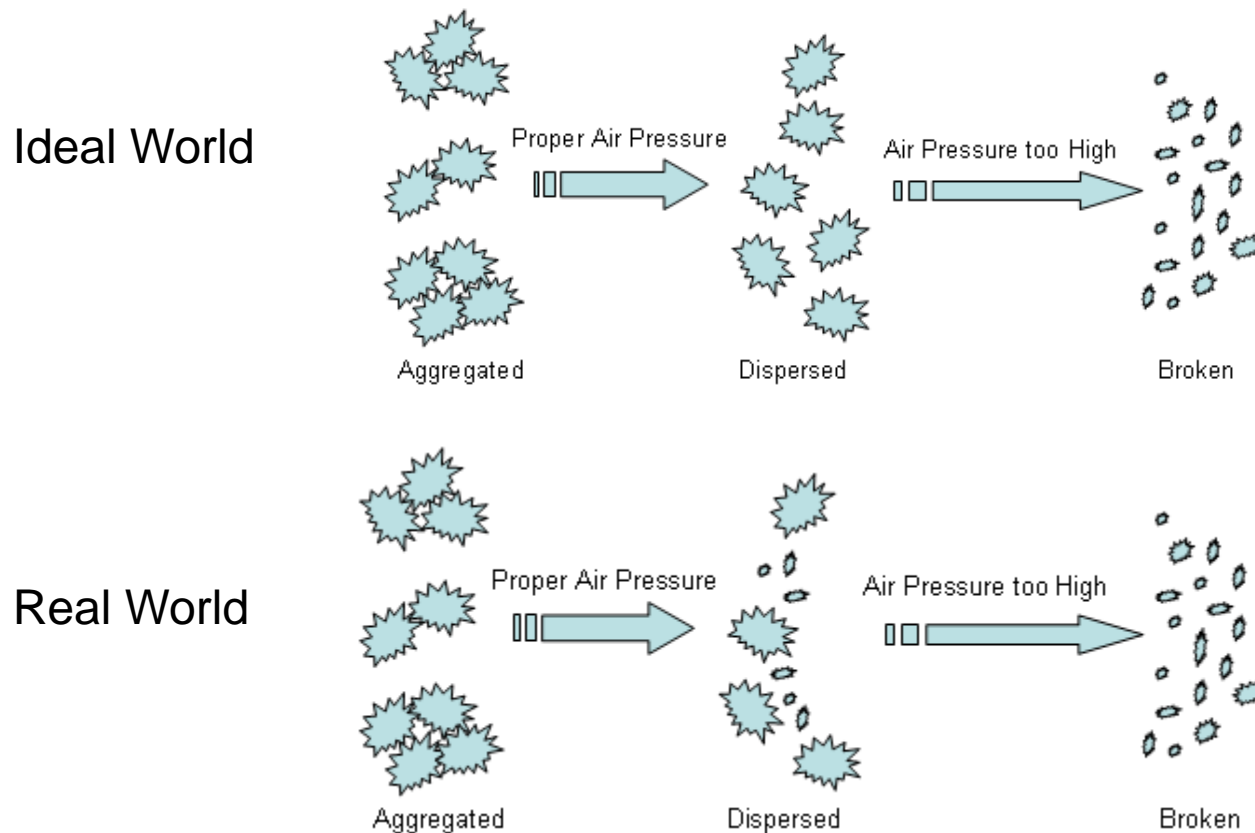
- The effect of applied energy is to break up agglomerates into individual particles for size measurement. However, if too much energy is applied, particles may be broken into fragments. The desired result is to apply just enough energy to disperse material into basic particles for measurement without damaging friable materials.



- The graph illustrates how this can be accomplished. Effects of applied energy on particulate samples can be tested by using results from measurements made on the instrument. By treating the sample with varying levels of ultrasonic power, performing analyses, and noting the average particle size (mean, median) as a function of power level, one can choose a range of applied energy that is optimum for that material.

Dispersion vs. Breakage

- Dispersion and breakage can both occur



What we'll talk about

- **Sampling techniques**
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- **Dispersing agglomerates**
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Laser Diffraction

- Starting from a powder...
 - Solubility issues? Can measure dry!
 - Sampling critical
 - Air pressure only dispersion choice
 - Take a look at webinar TE016: Optimizing Dry Powder Measurements
 - Solubility OK? Many options
 - Make paste w/ surfactant to wet
 - Sample from paste

Laser Diffraction

- Starting from an emulsion...
 - Sampling typically less critical
 - Dispersion stable upon dilution?
 - pH, shear forces, temperature, surfactant conc.
 - Avoid high pumping speeds, avoid high ultrasonic

Dynamic Light Scattering

- Starting from a powder...
 - Very few nanopowders ☹
 - Dispersion very critical
 - Use filters to remove agglomerates/dust
 - Dispersion conditions directly affect zeta potential
- Starting from a suspension/emulsion...
 - Visually inspect for “crud”
 - Use filters to remove agglomerates/dust

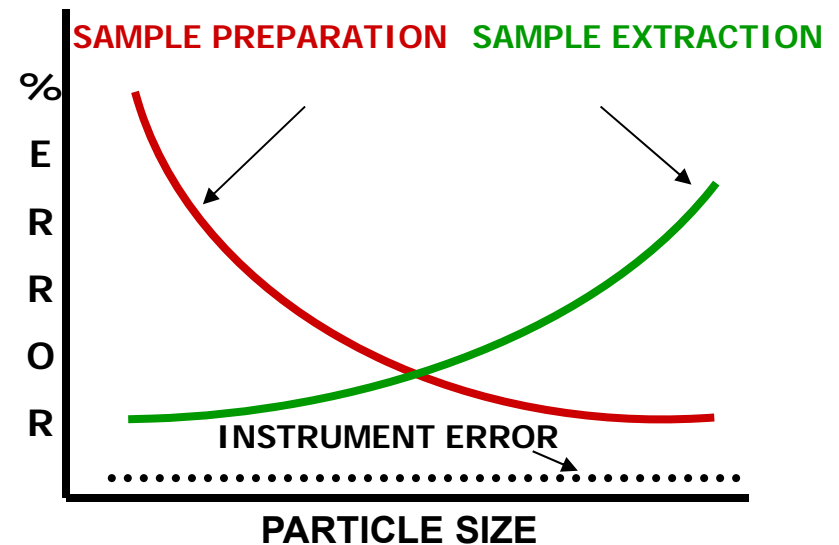
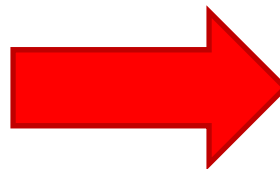
Dynamic Image Analysis

- Vast majority are powder applications
 - Sampling critical
 - Recommend Retsch PT100 rotary splitter for CAMSIZER
 - Recommend Retsch chute rifflers for CAMSIZER XT
 - Measure every particle on the chute
 - If comparing with sieving, then same good sampling practices need to be applied to sieves
- Suspensions (XT only) follow diffraction

Summary

- Surfactants wet powders
- Use admixture to alter surface chemistry
 - Sodium hexametaphosphate
 - Sodium pyrophosphate
- Ultrasound reduces size
 - De-agglomeration and/or breakage

■ REMEMBER!



For More Details

Visit www.horiba.com/particle

Contact us directly at labinfo@horiba.com

Visit the [Download Center](#) to find this recorded presentation and many more on other topics

Thank-you

Thank you

ありがとうございました

ขอบคุณครับ

谢谢

اشكر

Gracias

Grazie

Σας ευχαριστούμε

धन्यवाद

நன்றி

Tacka dig

Danke

Merci

Obrigado

감사합니다

Большое спасибо

おかしき

Omoshiro Okashiku