HORIBA Explore the future



HORIBA Instruments Inc. Particle Characterization

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Sampling and Dispersion

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Particle Analysis Workflow





Outline

- 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



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)



PARTICLE SIZE

INSTRUMENT ERROR IS SMALL AND RELATIVELY CONSTANT

Sample Extraction: Good Sampling Practices

Learn to Love Your Riffler!





Sampling from Flowing Powder





Sampling from Drums

Powder Thief





www.samplingsystems.com



Sampling from Drums



www.samplingsystems.com



Sub-sampling for Measurement

bulk or process	gross	laboratory	test	measurement
stream	sample	sample	sample	sample
(10 ⁿ 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
- <u>SMALL PARTICLES GRAVITATE DOWNWARD</u>

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 <u>not be more than</u> <u>half to two-thirds full</u>. 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 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 <u>best method</u> 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 onethird of the way from the bottom when extracting sample.
- Alternative: When mixing powders into a slurry: make paste, pipette from paste





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Sample Preparation: Dispersions





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



Dispersion Definitions







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 ultrasonic baths.

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

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)



DROP OF LIQUID ON A SOLID



Particle Wetting

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





Screening for wetting agent

Set up vials or beakers with each candidate dispersant. Gently put a little bit of fine particle on the top of each.





Evaluate Wetting

Poor wetting: particles don't break surface tension



Good wetting: particles separate and stream through surface





Effect of Surfactant Addition

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



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

•	lgepal 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, strongly bonds to negatively charged surfaces





Sodium Hexametaphosphate

- Most common stabilizer
- Abbreviated NaHMP
- Keeps particles from reagglomerating
- Disperse sample in 0.01 –
 1.0% (NaPO₃)₆ rather than
 DI water
- Tetrasodium pyrophosphate also used (sodium pyrophosphate,







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



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 outside of the Stern layer is designated the ZETA Potential.

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





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 by 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.

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Dispersion vs. Breakage

 Dispersion and breakage can both occur





Summary

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



Thank you



