JMBC course : Particle Technology
April 29 – May 03, 2019 U-Parkhotel, UTwente, NL

Particle Characterisation

1

UNIVERSITY of GREENWICH

JMBC course 2019
Dr Pablo Garcia-Trinanes

1

Powders




- Powders are an abundant and diverse class of products that underpin the health and comfort of day-to-day life.
- From the fluid catalytic cracking catalysts used for oil refining, and metal powders that make up aerospace components, 3D printing, pharmaceutical formulations, detergents, cosmetics and food powders.

2

JMBC course 2019
Pablo Garcia-Trinanes

2

Particle Characterisation

Courtesy of Malvern Panalytical Courtesy of Mountech Co. Ltd. Courtesy of Sympatec GmbH

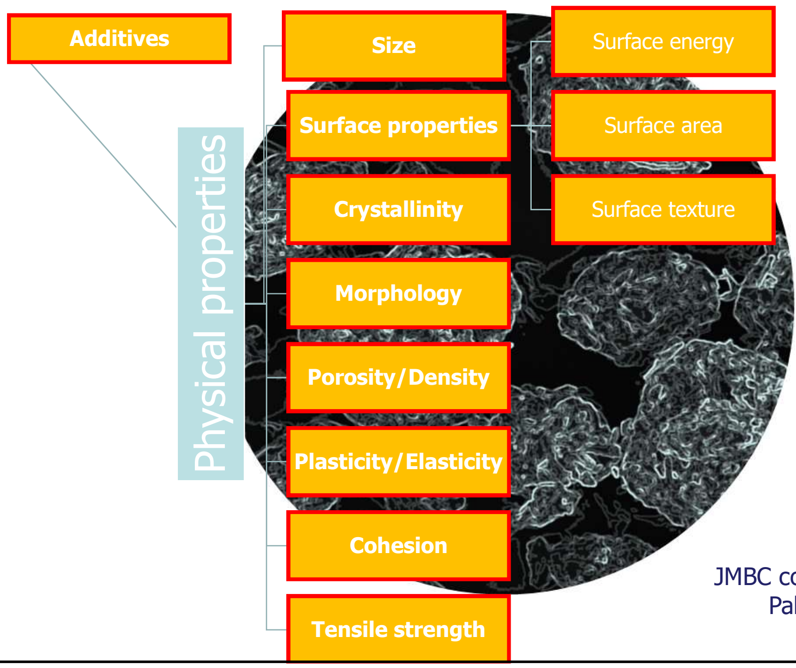
- Developing powders fit for every purpose relies on engineering materials from the particle scale through to bulk powder performance.
- Size, shape, and density are important defining physical parameters as well as chemistry!
- Due to the complexity a group or portfolio of analytical solutions are needed.

3

JMBC course 2019
Pablo Garcia-Trinanes

3

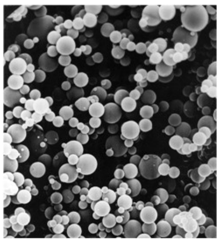
Particle Characterisation



JMBC course 2019
Pablo Garcia-Trinanes

4

Particle Characterisation is much more than just size



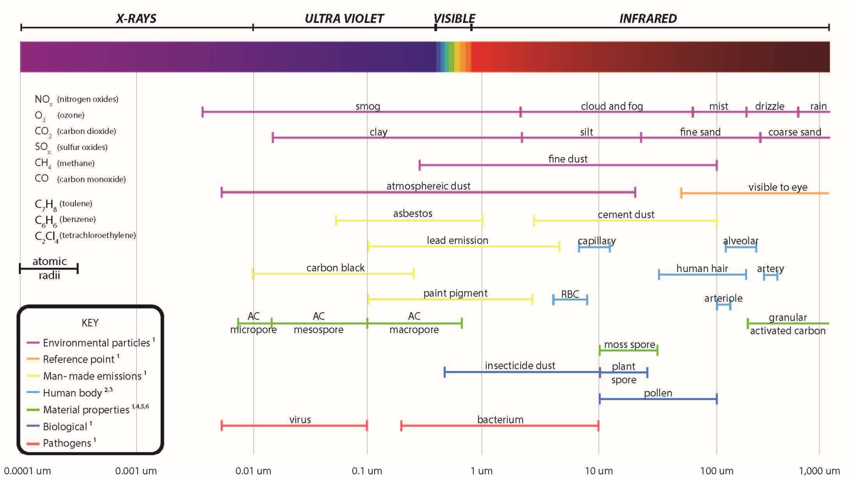
- **Particle structure via:**
  - Surface area
  - Porosity
  - Density
- **Particle morphology, via:**
  - Particle size distributions (PSD); pure or blended materials
  - Particle shape parameters that define form, regularity, opacity
  - Surface topography
- **Bulk powder behaviour, via:**
  - Shear parameters such as unconfined yield strength
  - Dynamic flow properties
  - Bulk powder properties including bulk density, compressibility and permeability

5

JMBC course 2019
Pablo Garcia-Trinanes

5

Particle size matters



6

1. http://www.h2odistributors.com/chart-particle-sizes.asp
2. http://www.coheadquarters.com/PennLibr/MyPhysiology/lect0p/lect0.03.htm
3. http://www.circulatory-system.com/blood-vascular-system/
4. http://www.tigg.com/activated-carbon-properties.html
5. http://www.whatman.com/PRODTeflonPTFEMembranes.aspx
6. http://www.pottiaceae.com/imagenes/pdf/P6.pdf
7. http://www.gulflink.osd.mil/appendix_d.pdf
8. http://www.tsi.com/uploadedFiles/Product_Information/Literature/Application_Notes/ITI-050.pdf

6

Particle description

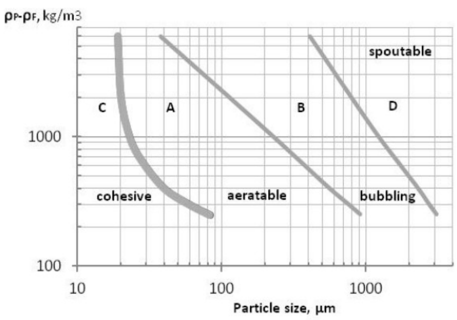
- EXAMPLE: Particle size
- GOAL: Describe the particle size

  (but use only ONE number)

- FACTORS TO CONSIDER:
  - What will be done with the particle?
  - What devices are available?

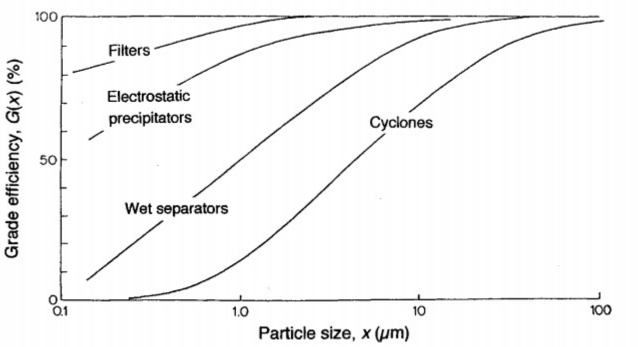
Relation with process properties

- Geldart diagram



Relation with process properties

- Typical grade efficiency curves

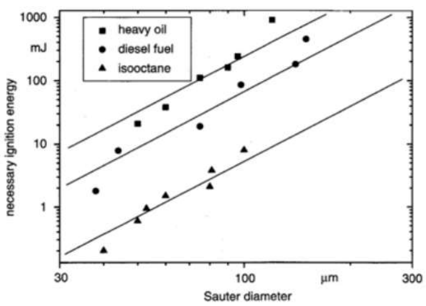


9

9

Relation with process properties

- Effect of particle size on Minimum Ignition Energy (MIE) for three mists



d_{32} or D[3, 2]

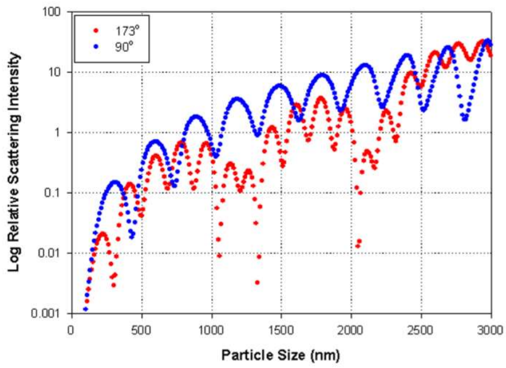
$$d_v = \left(\frac{6V_p}{\pi}\right)^{1/3}, \quad d_s = \sqrt{\frac{A_p}{\pi}}, \quad SD = D[3,2] = d_{32} = \frac{d_v^3}{d_s^2}.$$

10

10

Relation with process properties

- Scattered light intensity single particles

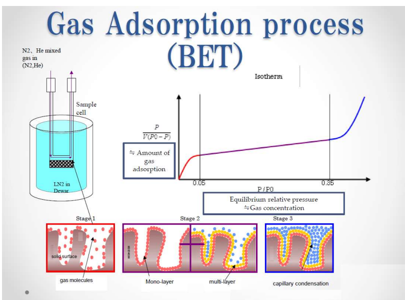


MIE Theory: When the size of the particles becomes roughly equivalent to the wavelength of the illuminating light, then a complex function of maxima and minima with respect to angle is observed.

Dynamic Light Scattering: An Introduction in 30 Minutes. Malvern Technical Note.

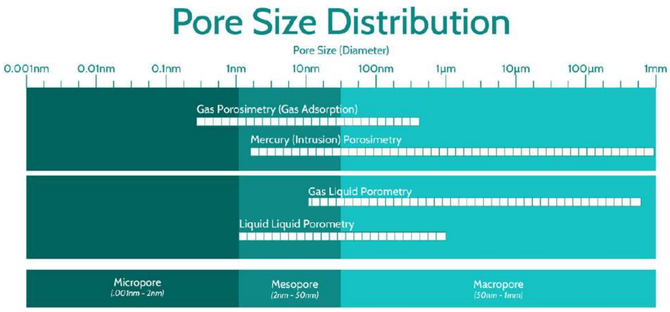
Gas absorption (Physical adsorption)

Physical gas adsorption is the classical technique for quantification of the **surface area** of a solid and can also be used to characterize porosity.
Parameters generated include specific surface area, total pore volume and pore volume distribution by pore size.



Mercury Intrusion Porosimetry

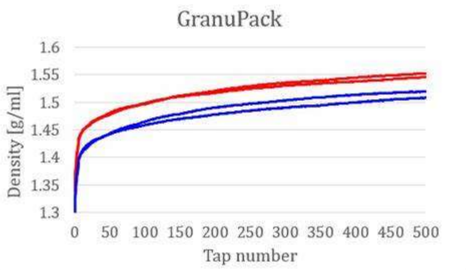
Mercury intrusion porosimetry, or more usually mercury porosimetry, quantifies porosity generating parameters including **pore size distribution**, total pore volume, total pore surface area and median pore diameter. It can also measure bulk and skeletal (or apparent) density.



13

Bulk density and Compressibility

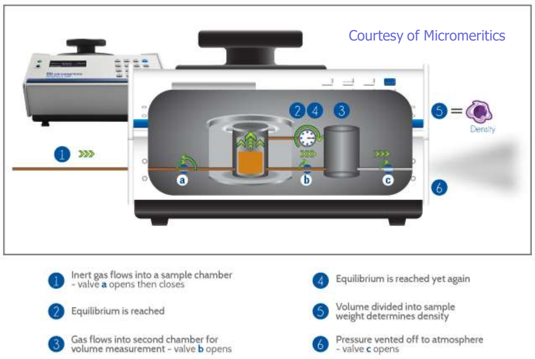
- The behaviour of the powder submitted to successive taps is analysed with an automatized device.
- The Hausner ratio HR, the initial density and the tapped density are measured precisely (typically 0.5% of accuracy).



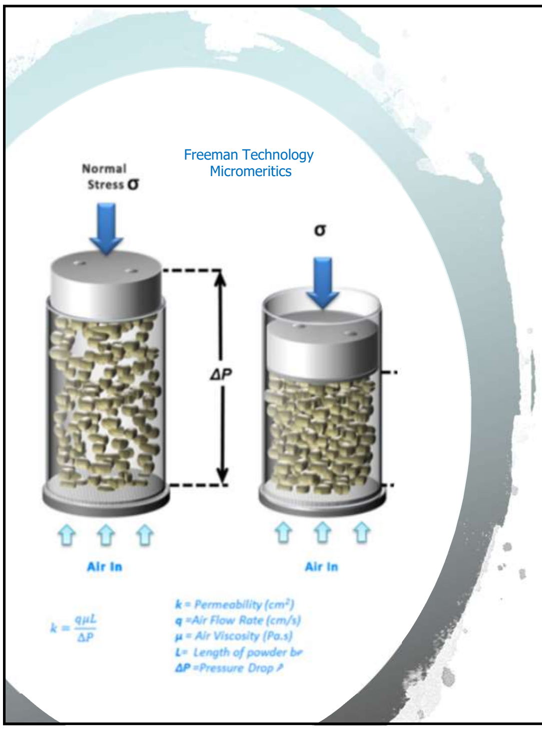
https://youtu.be/asqmkHD-x1M

Pycnometry

Pycnometry measures the volume of particles, to determine true (absolute) and skeletal (apparent) density. Solid phase gas pycnometry can be used to measure the envelope density of objects or larger samples.



15



Permeability

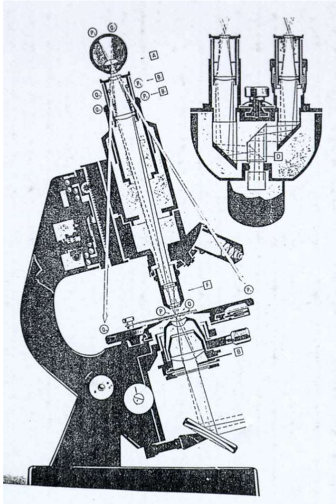
Permeability is a measure of the powder's resistance to air flow.

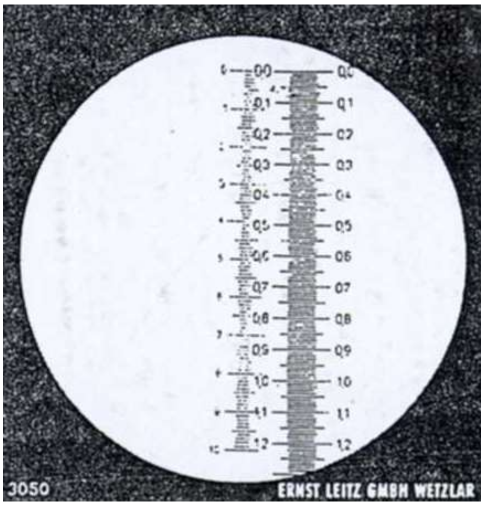
The relative difference in air pressure between the bottom and the top of the powder column is a function of the powder's permeability.

Tests can be completed under a range of normal stresses and air flow rates.

16

Microscope





Ernst Leitz I. (1843–1920)

17

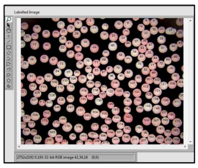
JMBC course 2019
Pablo Garcia-Trinanes

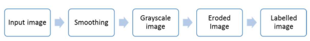
17

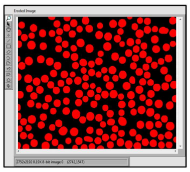
Image Analysis

+ Low cost
+ Large sample size can be evaluated
+ Rapid measurement
- Limited in particle size for analysis

Morphology G3
Courtesy of Malvern Panalytical

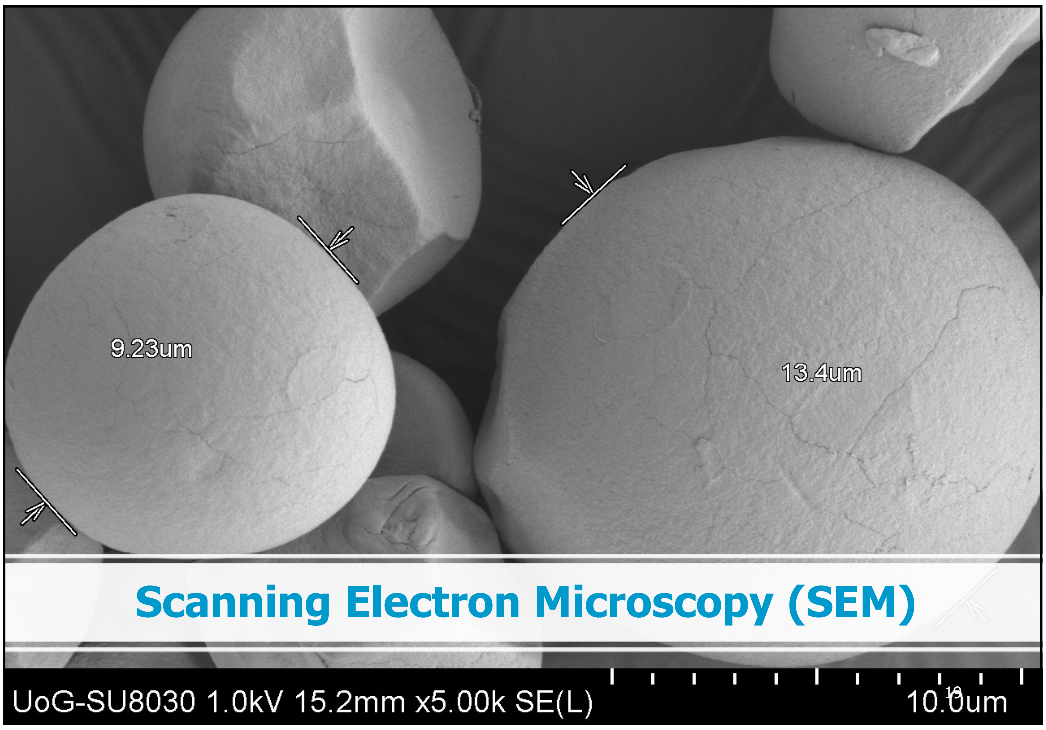






18

18

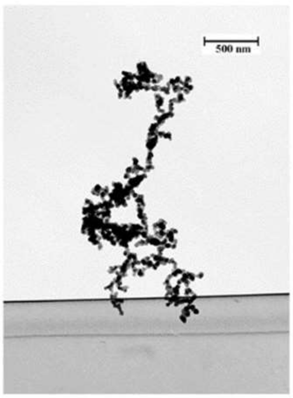


Scanning Electron Microscopy (SEM)

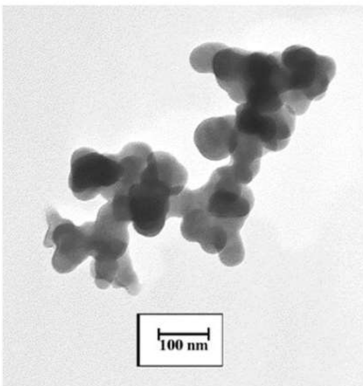
19

Transmission Electron Microscopy (TEM)

Examples of non spherical particles



Kerosene lamp (soot agglomerate)

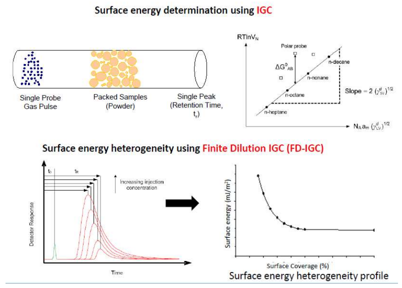


Particle from tire wear

20

iGC-SEA Surface Energy Analyser

Courtesy of Surface Measurement Systems



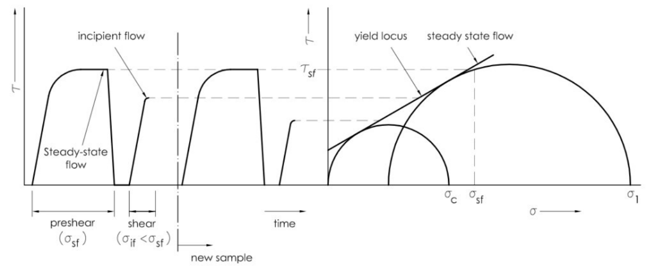
- There are some chemical and structural properties that could affect the surface energy of a solid material, especially its surface energy heterogeneity.
- Such properties are, for example, the crystallinity degree, crystal imperfections, surface irregularities, the particle size distribution, the impurities and so on.

21

https://youtu.be/Xas3C3RvDTg

21

Shear cell analysis



Jenike

Brookfield PFT

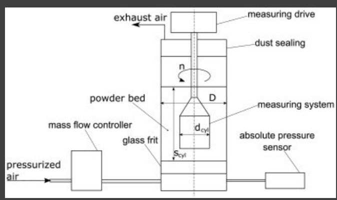
Schulze

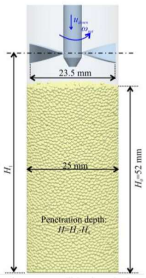
22

22

Dynamic flow properties

- Widely used nowadays in industry for characterisation of particle flow under dynamic conditions of shear strain rate.
- Measuring the apparent viscosity of granular materials.





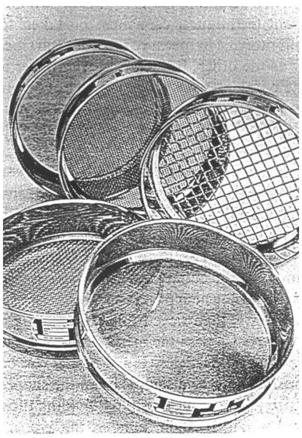
Freeman FT4 - Micromeritics

Anton Paar – Powder rheometer

23

23

Traditional sieves



Courtesy of Russell Finex

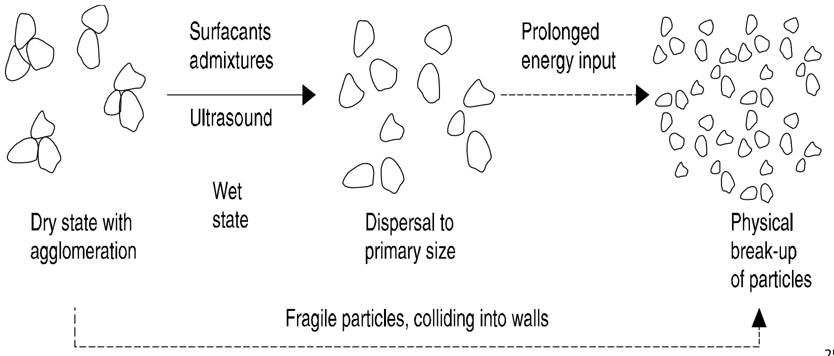
24

JMBC course 2019
Pablo Garcia-Trinanes

24

How do we know whether there are agglomerates in the system?

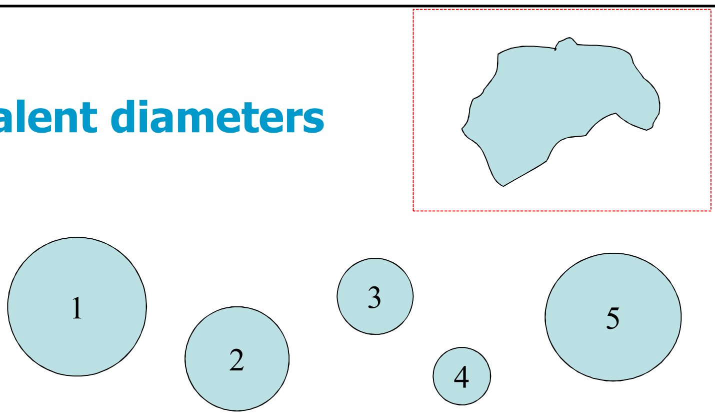
Subject the system to (controlled) energy input…



25

25

Equivalent diameters



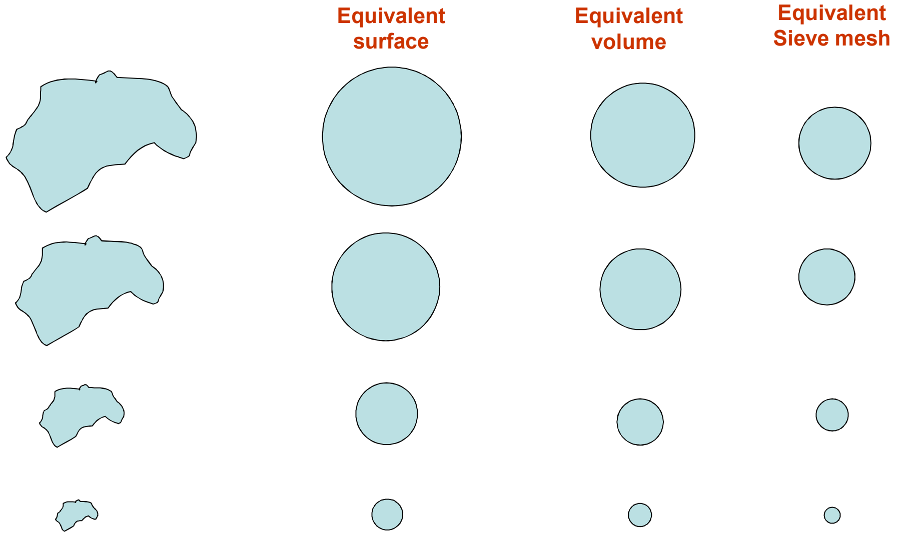
1. Sphere of equivalent surface
2. Sphere of equivalent volume
3. Sphere of equivalent settling velocity, low Re
4. Sphere of equivalent settling velocity, high Re
5. Sphere of equivalent sieve mesh

26

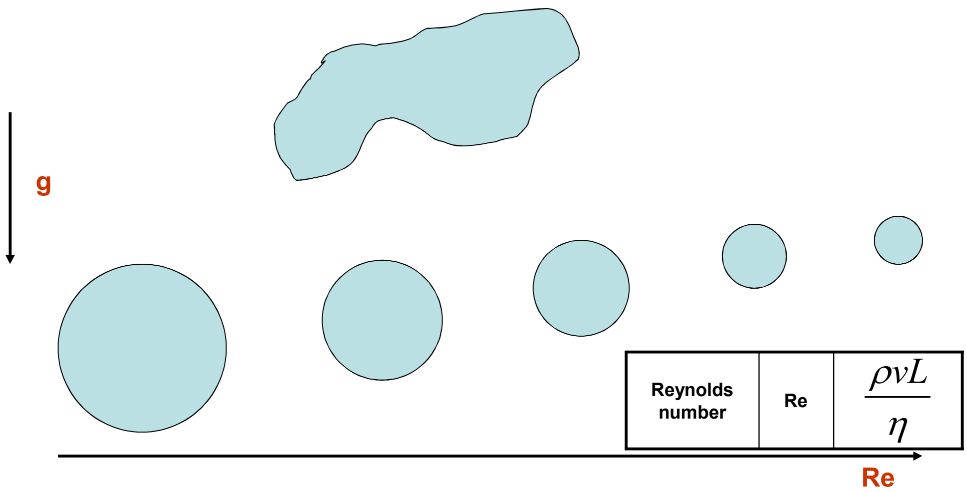
JMBC course 2019
Pablo Garcia-Trinanes

26

Equivalent diameters

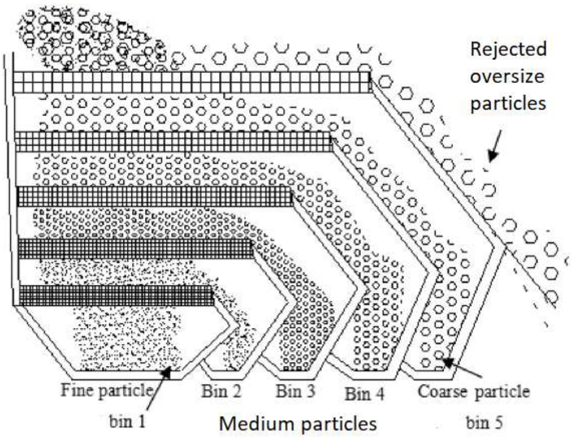


Equivalent settling diameter



Reynolds number	Re	$\frac{\rho v L}{\eta}$

Schematic view of the sieving process



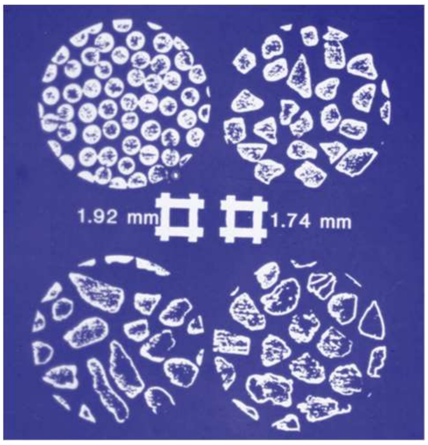
29

JMBC course 2019
Pablo Garcia-Trinanes

29

Near mesh particles

"Square peg in a round hole"



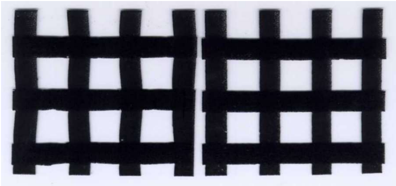
Sieve Number	Sieve opening (µm)
20	850
40	425
60	250
80	180
120	125
.	.
..	..
…	…
400	38

30

JMBC course 2019
Pablo Garcia-Trinanes

30

Sieving errors can arise from:

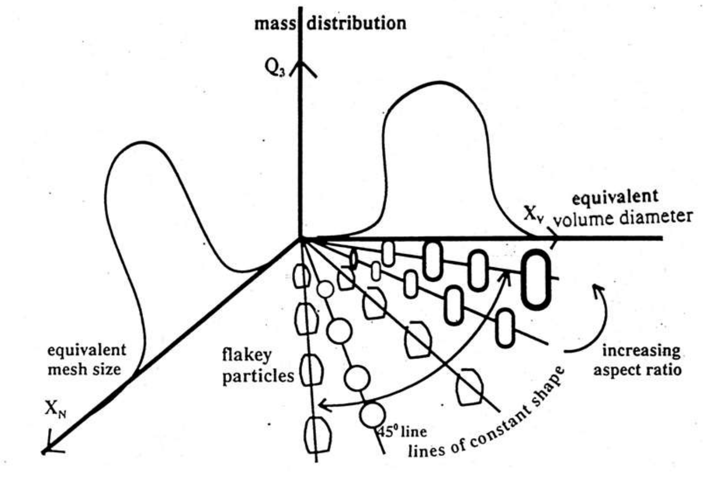


- Overloading of the sieve
- Forcing the powder through the sieve
- Insufficient time of agitation
- Inadequate intensity of agitation
- Improper cleaning and care of equipment, especially sieves
- When it comes to finer materials smaller than #100 mesh, sieve analysis becomes less accurate

31

JMBC course 2019
Pablo Garcia-Trinanes

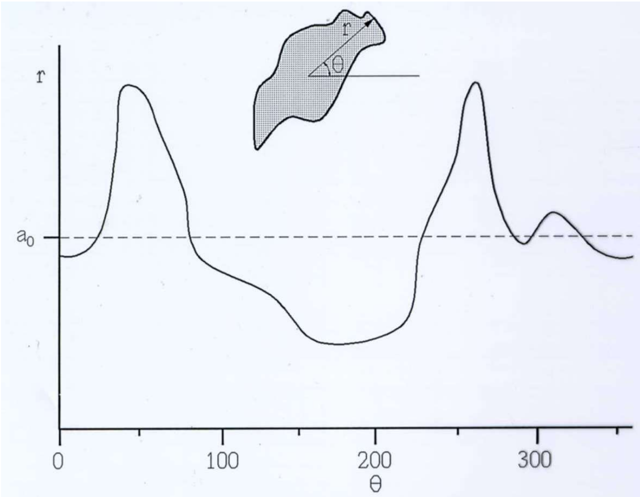
Scarlett Plot



32

JMBC course 2019
Pablo Garcia-Trinanes

Polar Coordinates



33

JMBC course 2019
Pablo Garcia-Trinanes

33

Fourier Transform

$$r(\theta) = a_0 + \sum_{n=1}^{a} \left(a_n \cos n\theta + b_n \sin n\theta \right)$$

34

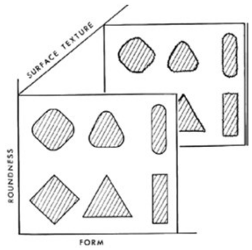
JMBC course 2019
Pablo Garcia-Trinanes

34

Particle geometry

Particle geometry can be fully expressed in terms of three independent properties: form, angularity (or roundness), and surface texture (i.e. one can vary widely without necessarily affecting the other two properties).

- Sphericity
- Roundness
- Angularity
- Convexity



The Hierarchical View of Form, Roundness, and Surface Texture (Barrett, 1980)

35

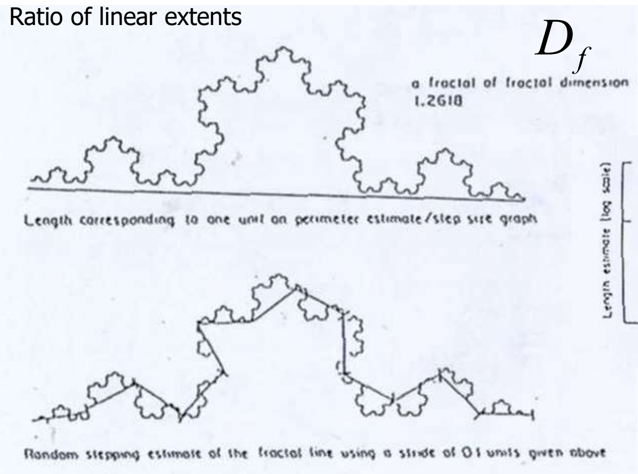
JMBC course 2019
Pablo Garcia-Trinanes

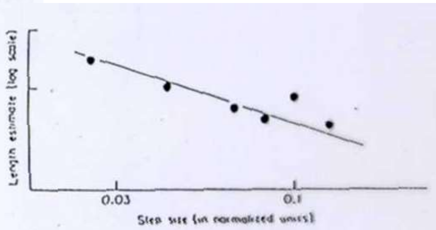
35

Particle fractal dimension

Fractal theory uses the concept of fractal dimension, D_R, as a way to describe the shape of particles.

Ratio of linear extents





Mass: $m \propto x^{D_f}$

Perimeter: $P = c\lambda^{1-D_f} \propto \lambda^{1-D_f}$

36

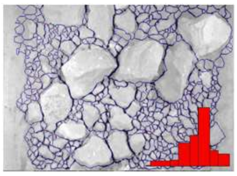
JMBC course 2019
Pablo Garcia-Trinanes

36

Particle Size Analyzers

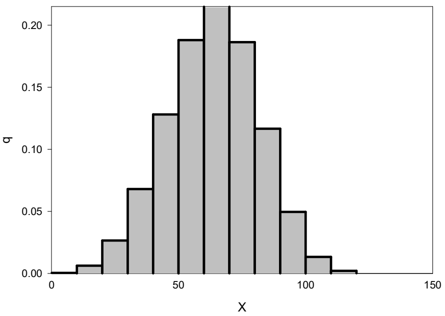
Centrifuge	Sedimentation	0.01-40 μm
Electrical Sensing	Suspension in electrolyte	1-240 μm
Laser diffraction	Angular light scattering	0.04-2000 μm
Light scattering	(monodisperse spheres)	0.003-3 μm
Optical	Microscope	0.5-several μm
Scanning Electron	Microscope	resol. 10 nm

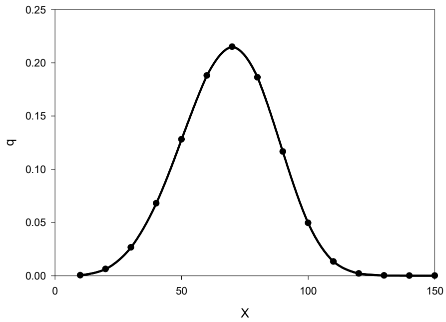
Distribution by histogram



Quantity = q_N **(numbers)**
= q_0 **(normalized)**

Particle Size = x





Normalization

Any distribution (e.g. by numbers/counts)

$$q_N(x) \qquad \int q_N(x)\,dx = N$$

can be normalized

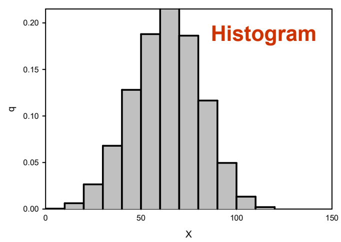
$$q_0(x) = \frac{q_N(x)}{\int_0^{\infty} q_N(x)\,dx} \qquad \int q_0(x)\,dx = 1$$

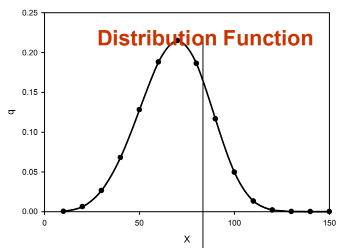
(integration boundaries are dropped if 0…∞)

39

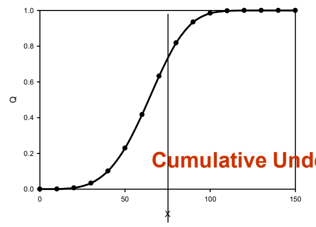
JMBC course 2019
Pablo Garcia-Trinanes

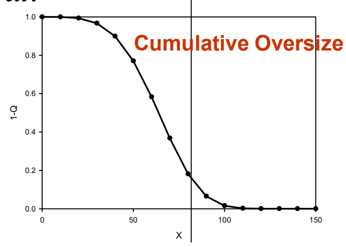
Graphical presentation of distributions





$$Q(x) = \int_0^{x} q_0(x')\,dx'$$





JMBC course 2019
Pablo Garcia-Trinanes

Particle size distribution

Modal Size

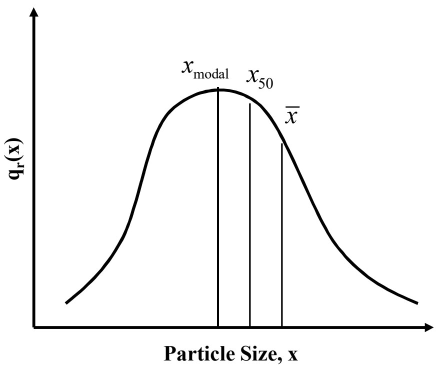
$$x_{\text{modal}} = \text{value at which } q_0(x) = \max$$

Median Size

$$x_{50} = 50\% \text{ value i.e. } \begin{matrix} \tfrac{1}{2} \text{ greater in size} \\ \tfrac{1}{2} \text{ less in size} \end{matrix}$$

Mean Size

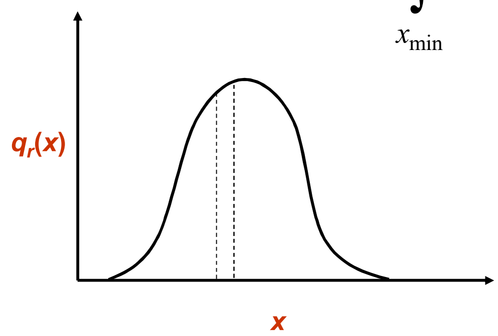
$$\bar{x} = \frac{\int q(x)\,x\,dx}{\int q(x)\,dx} = \int q_0(x)\,x\,dx$$



41

Moments of a distribution

$$M_k = \int_{x_{\min}}^{x_{\max}} q_0(x)\,x^k\,dx$$



$$M_1 = \int_{x_{\min}}^{x_{\max}} q_0(x)\;x\;dx = \bar{x}$$

$$M_2 = \int_{x_{\min}}^{x_{\max}} q_0(x)\;x^2\;dx$$

$$M_3 = \int_{x_{\min}}^{x_{\max}} q_0(x)\;x^3\;dx$$

42

Distribution functions

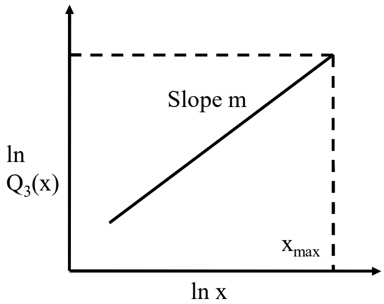
Gaudin-Schuman

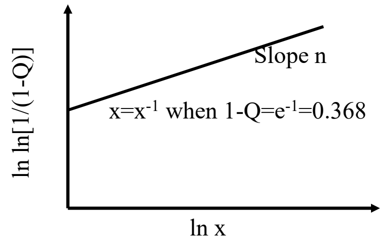
$$Q_3(x) = \left(\frac{x}{x_{\max}}\right)^m$$

Rosin-Rammler

$$1 - Q_3(x) = \exp\left[-\left(\frac{x}{x'}\right)^n\right]$$

$$\ln\ln\left(\frac{1}{1-Q_3(x)}\right) = n\ln x - n\ln x'$$





43

JMBC course 2019
Pablo Garcia-Trinanes

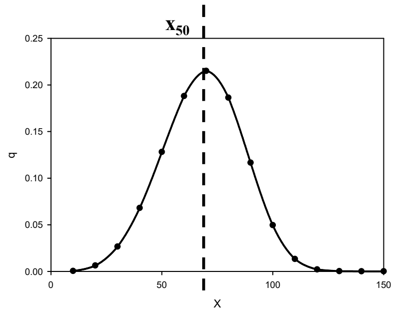
43

Gaussian Normal distribution

Put $z = \dfrac{x - x_{50}}{s}$

where $s = \sqrt{\overline{(x - x_{50})^2}}$

then $s\,dz = dx$



Thus $q(x) = \dfrac{1}{s\sqrt{2\pi}}\exp\left[-\dfrac{(x - x_{50})^2}{2s^2}\right]$

44

JMBC course 2019
Pablo Garcia-Trinanes

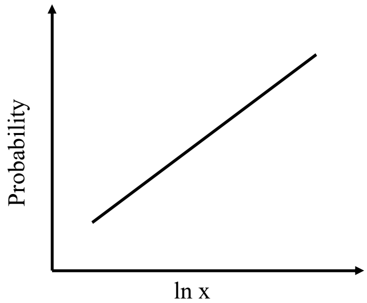
44

Logarithmic Normal Distribution

Put:

$$z = \frac{\ln x - \ln x_{50}}{s_z}$$

$$s_z = \sqrt{(\ln x - \ln x_{50})^2}$$



Then

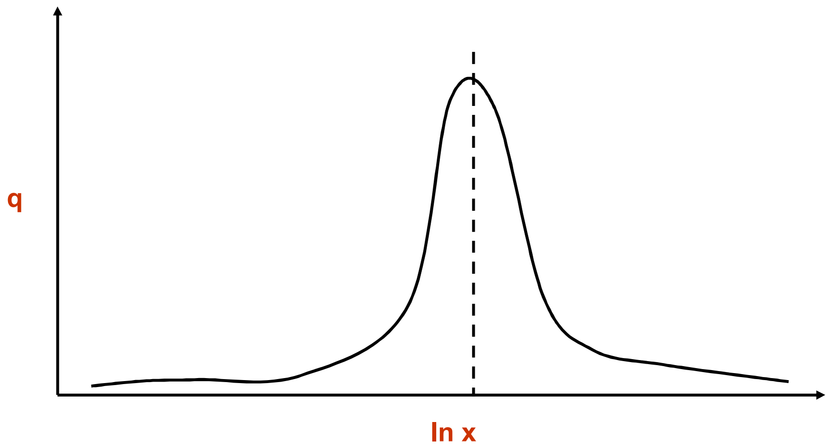
$$q_{LN}(x) = \frac{1}{s_z\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{\ln(x/x_{50})}{s_z}\right)^2\right]$$

45

JMBC course 2019
Pablo Garcia-Trinanes

45

Monodisperse distribution

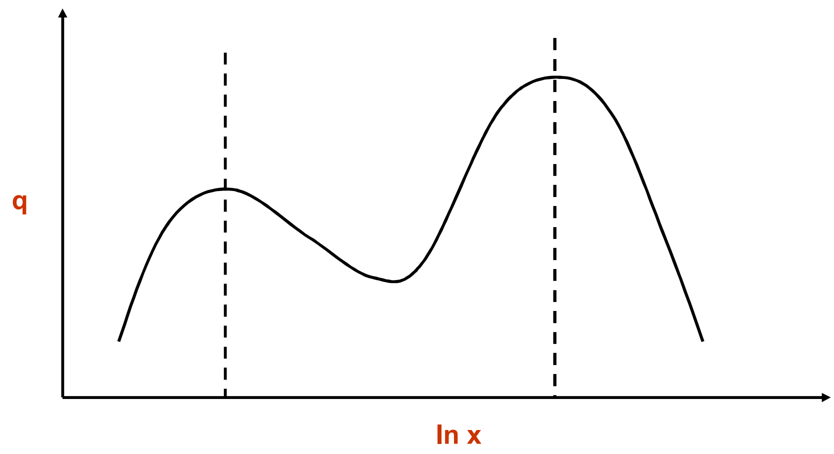


46

JMBC course 2019
Pablo Garcia-Trinanes

46

Bi-Modal distribution

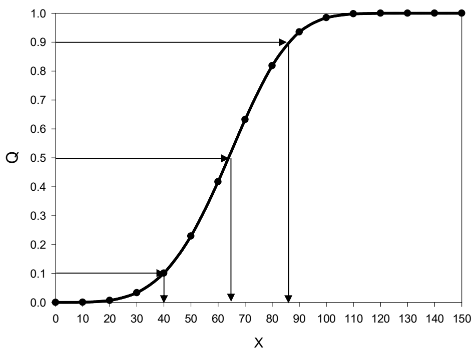


47

JMBC course 2019
Pablo Garcia-Trinanes

47

Special Sizes



x_{10} – smallest particles; less easily separated; *marker of attrition* propensity and (in wet) a marker of dispersion stability

d_{50} – median – *marker of central tendency*

x_{90} – largest particles – more easily separated if agglomerates – *marker of dispersion*

$$x_{10}, x_{50}, x_{90}$$

48

JMBC course 2019
Pablo Garcia-Trinanes

48

Transformations

Any normalized size-distribution

$$q_0(x) \qquad\qquad \int q_0(x)\,dx = 1$$

can be transformed to:

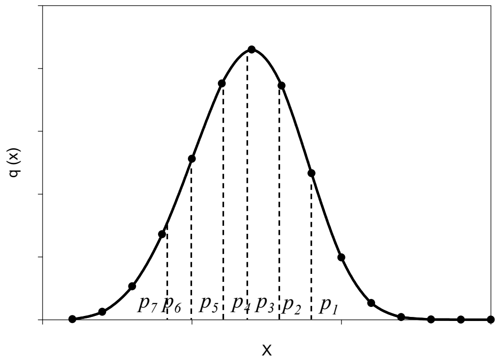
$$q_S(x) = \int_0^x q_0(x')\pi(x')^2\,dx' \qquad \text{Surface area distribution}$$

$$q_V(x) = \int_0^x q_0(x')\tfrac{\pi}{6}(x')^3\,dx' \qquad \text{Volume distribution}$$

(These transformations are valid for spheres only)

49

Matrix Representation



$$\mathbf{q} = \begin{bmatrix} q_1 \\ q_2 \\ q_3 \\ q_4 \\ q_5 \\ q_6 \\ q_7 \end{bmatrix}$$

50

Summary

- Statistics - mathematics
- Distribution functions contain:
  - Mean value
  - Width
  - & more
- Hard work ☹

51

JMBC course 2019
Pablo Garcia-Trinanes

51

Summary

- Particles are NOT equal !
- Particle property of interest …
  - Process dependent
  - Measurement dependent
- Many particles are non-spherical … believe me!
- Particles are NEVER alone !

… back to Overview

52

JMBC course 2019
Pablo Garcia-Trinanes

52

Coffee is particles too!

53

JMBC course 2019
Pablo Garcia-Trinanes

53

Have you forgotten sampling?

54

JMBC course 2019
Pablo Garcia-Trinanes

54

Sampling

"Sampling? That's easy!

You just put a container in the stream and wait for it to fill up or grab some from a bag"

55

JMBC course 2019
Pablo Garcia-Trinanes

55

Outline

1. Origins of problems in particle property analysis
    I. Why is sampling important?
    II. How many samples?
    III. How not to do it
2. Sampling from particulate systems
    I. Fundamental Principles of Representative Sampling
    II. Sample system design guidelines
    III. Real Life Industrial examples
    IV. Good samplers on the market
3. Sample preparation
    I. Example of Primary & Secondary Sampler "in line"
    II. Secondary Samplers
    III. Spinning Riffler
4. Sampling Summary

56

JMBC course 2019
Pablo Garcia-Trinanes

56

Why is sampling important?

- The main purpose of sampling is to drive a decision, generally the question we are seeking to answer is something like… *"is the process running as desired and making target quality ?"*

    The decision in this example being if OK – do nothing

    if not OK – employ some corrective actions
- Typical in process sampling – Powder physical or chemical composition – Key for troubleshooting work
- Decisions are made based on samples
    - **€** impact
    - Customer/consumer impact
- Saying from modelling applies equally to sampling

    Rubbish in = rubbish out, translated to sampling …..
    - Bad sample = potentially wrong decision

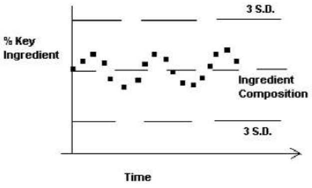
57

JMBC course 2019
Pablo Garcia-Trinanes

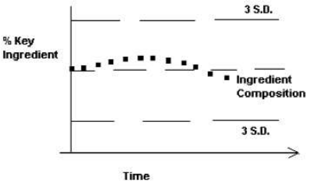
57

How many samples?

- Sample frequently:
    - Sampling error α 1 / number of samples. More samples = less error
- Sample randomly
    - Can pick up time dependent variations



Short cyclic variation



Long period variation

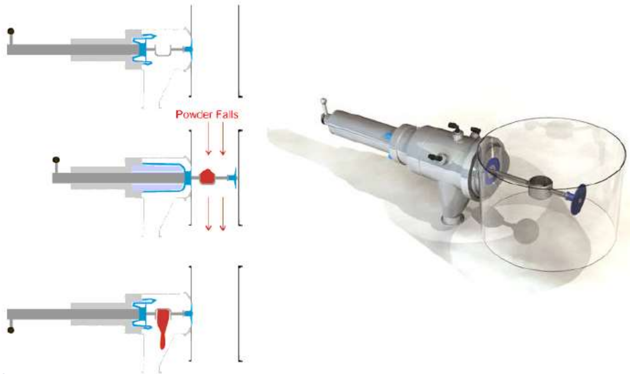
58

JMBC course 2019
Pablo Garcia-Trinanes

58

How not to do it

There are many vendors selling “nice” looking equipment which is not appropriate for non cohesive powders



59

JMBC course 2019
Pablo Garcia-Trinanes

59

The correct way to sample is known - we just need to do it !

- The principles of correct sampling are simple !
- Why then so much bad practice ?
- The practical challenges of turning theory in to practice.
- Correct sampling is some times more time consuming than “quick” ways –the quick fix should be OK ?

    [NO –as illustrated by many process commissioning examples]

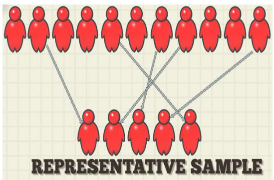
60

JMBC course 2019
Pablo Garcia-Trinanes

60

Fundamental Principles of Representative sampling

- It is true that it is easy to take a "sample" and indeed many companies are making money selling "sampling" equipment
- BUT –it requires a considered approach to take a REPRESENTATIVE sample



61

JMBC course 2019
Pablo Garcia-Trinanes

61

JMBC course 2019
Pablo Garcia-Trinanes

Fundamental Principles of Representative sampling

- 1. **Sample only from moving streams.** Can you take a representative sample from a pile, super sack etc.. NO !
- 2. Each particle must have an **equal probability** of being chosen. Whole **cross section of flow** must be sampled for same amount of time.
- 3. **The larger the sample the better!**
- 4. To track process fluctuations first establish the approximate **frequency of fluctuations**. Taking a "good" sample every 3 h on a process which is cycling every few min is still not much use (apply Statistical Process Control concepts).
- 5. Any secondary reduction of primary sample should not exceed **20:1 ratio**

62

62

Sample system design guidelines

1. Sample from the flowing powder stream with a trough with an opening at the top (min 30mm or 3x largest particle size)

2. **Provide constant velocity**, preferably use electric motors instead of pneumatic actuators.

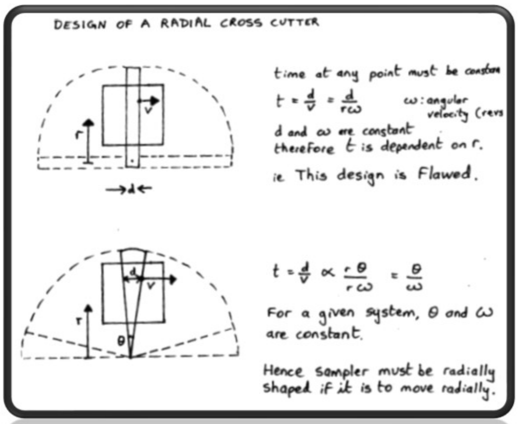
-If sampling in an arc, the opening should be segment shaped to compensate for faster movement away from centre of rotation.

3. The sampler trough must never become over filled.

63

63

Sample system design guidelines



64

64

Good samplers in the market

- Powder thiefs

65

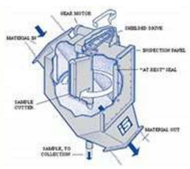
JMBC course 2019
Pablo Garcia-Trinanes

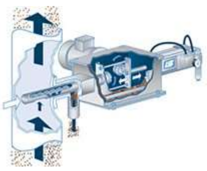
https://youtu.be/GBkjMwauEzE

65

Good samplers in the market

- Automatic samplers for flowing materials





Automatic Beak sampler, beak rotates in flow

https://youtu.be/pz9jGJ11tUQ

66

JMBC course 2019
Pablo Garcia-Trinanes

https://youtu.be/QBAmgRjAE9A

66

Sample preparation

Process stream	Gross sample	Laboratory sample	Test sample	Measurement sample
10^n kg	> kg	≈ kg	g	g or mg

Primary Sampler
✓ Takes the Gross sample

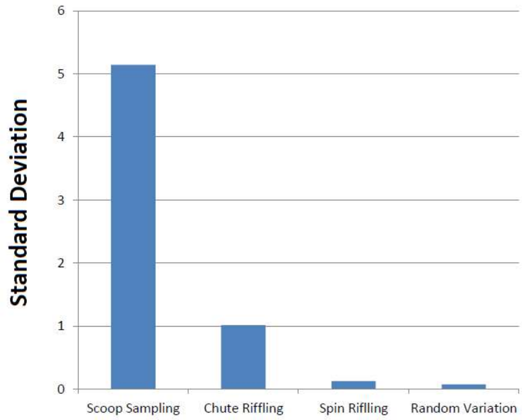
Secondary Sampler(s)
✓ Performs the necessary further splitting

Secondary samplers

Spinning Riffler

Chute Riffler

Spinning Riffler is Best



Best method to get representative samples

Sampling Method	Standard Deviation
Scoop Sampling	5.14
Chute Riffling	1.01
Spin Riffling	0.125
Random Variation	0.076

From Particle Size and Measurement, T. Allen, 3rd Edition,

69

JMBC course 2019
Pablo Garcia-Trinanes

69

Sampling summary

- Sample a moving stream of powder.
- Sample the entire stream of powder.
- Riffle the collected sample down to the appropriate size for analysis.
- Don't be tempted to take spot samples from static material.
- Sample frequently and randomly to capture time dependent variations.

–Time dependent variations often give clues to the source of variation.

70

JMBC course 2019
Pablo Garcia-Trinanes

70

(Some) References

- ISO 14488, Particulate materials - Sampling and sample splitting for the determination of particulate properties
- ISO 13320: 2009 Particle size analysis -- Laser diffraction methods (http://www.iso.org/iso/catalogue_detail.htm?csnumber=44929)
- Barrett, P. J. (1980). "The shape of rock particles, a critical review." Sedimentology, Vol. 27, pp. 291-303.
- T. Allen, Particle Size Measurement, 4^{th} ed. Chapman & Hall, London (1993)
- T. Allen, A.A. Khan. Critical evaluation of powder sampling procedures. Trans. Instn. Chem. Engrs. 238, CE 108/112 (1970)
- K. Sommer. Sampling of powders and bulk materials. Springer-Verlag. (1986)
- Henk G. Merkus, Particle Size Measurements; Fundamentals, Practice, Quality, Springer Particle Technology Series, Volume 17, (2009)
- The definitive guide for powder characterization. White paper. Micromeritics Instrument Corp. (2019)
- Henk G. Merkus, Gabriel M.H. Meesters. Particulate Products – Tailoring Properties for Optimal Performance; Springer (2014)
- Production, Handling and Characterization of Particulate Materials Editors: Henk G. Merkus, Gabriel M.H. Meesters, Springer (2016)

Acknowledgements

- A.F. Rawle – Malvern Instruments.
- David Smith – DJS Process Consulting Ltd.
- Henk G. Merkus – TU Delft.