Ceramic and Colloidal Processing MSE-326

Week 2

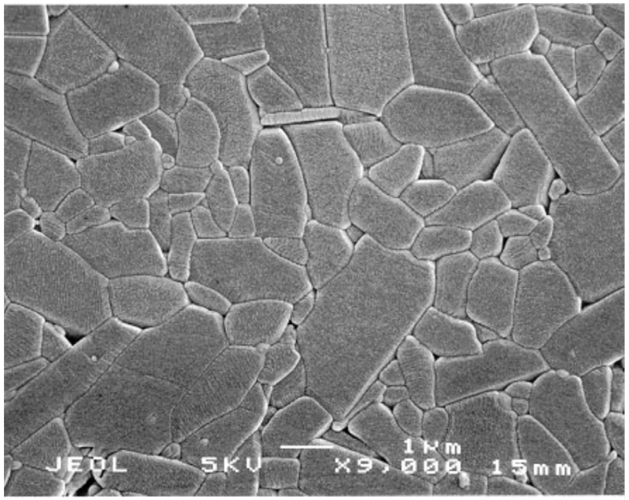
2. Powder Characterisation: physical, chemical and morphology

A. Testino

Prothèse de hanche

Why characterize powders?

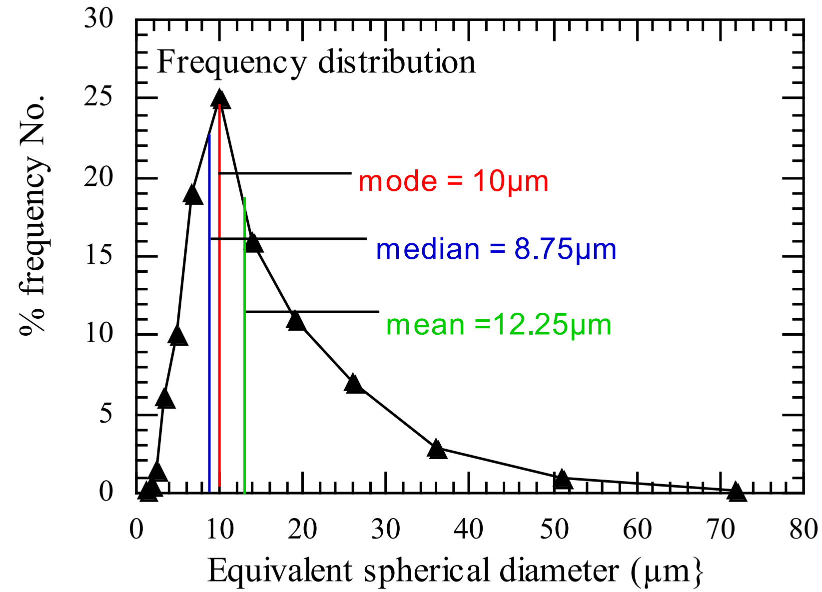
- Characteristics of the raw material – determines
  - manufacturing method
  - type of final microstructure
  - properties
- Lot to Lot - verification
  - essential to keep the same characteristics
- Sampling
  - verification that the sampling is done correctly
  - segregation
- Storage
  - evolution over time

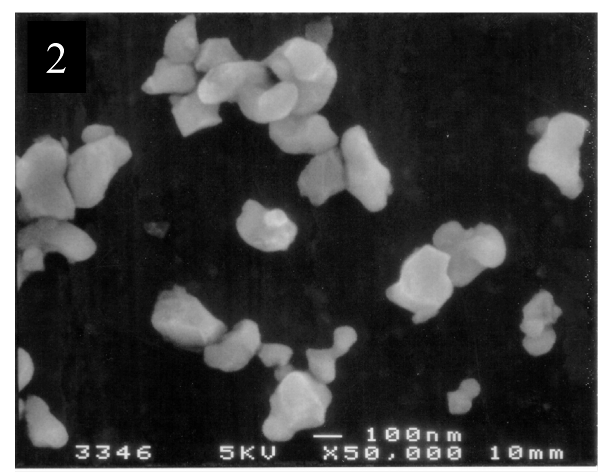


This week

Physical Characteristics
- Size & Distributions
- Sampling
- Shape

Methods
- Light scattering / diffraction
- Sedimentation – centrifugation
- Density, Porosity
- Adsorption generalities – very brief
- Specific surface area – nitrogen adsorption
- State of agglomeration
- Chemical characterization





Chapter 2.2

Powder size, d ⟶ Grain size, 5-10x d

Ch. 2.2 Powder Characterization

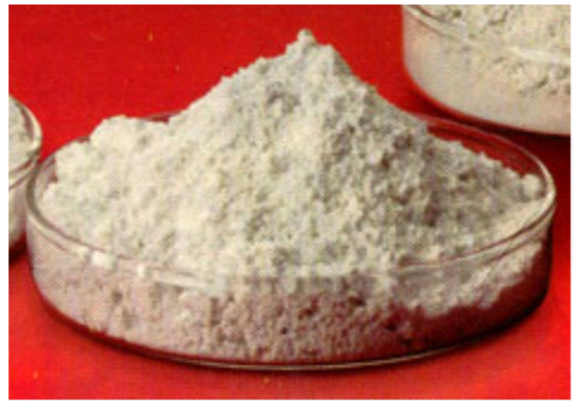
2.2.1 Introduction

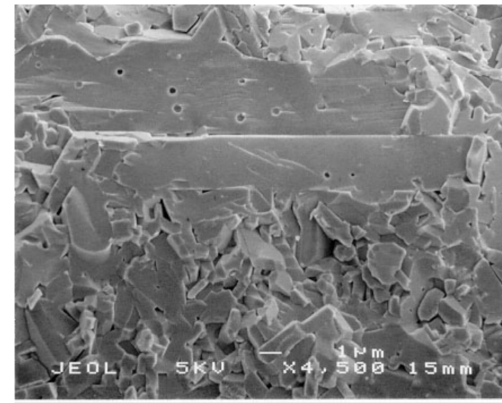
2.2.2 Sampling

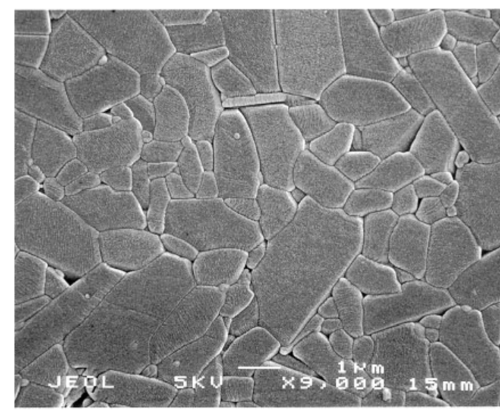
2.2.3 Physical characteristics

2.2.4 Chemical characterization

2.2.5. Phase composition



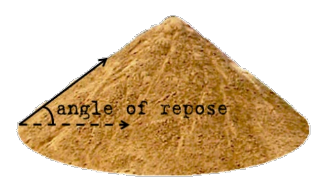




•**Les Céramiques,** J. Barton, P. Bowen, C. Carry & J.M. Haussonne, Les Traité des Matériaux, Volume 16, PPUR, 2005

Important Powder Characteristics

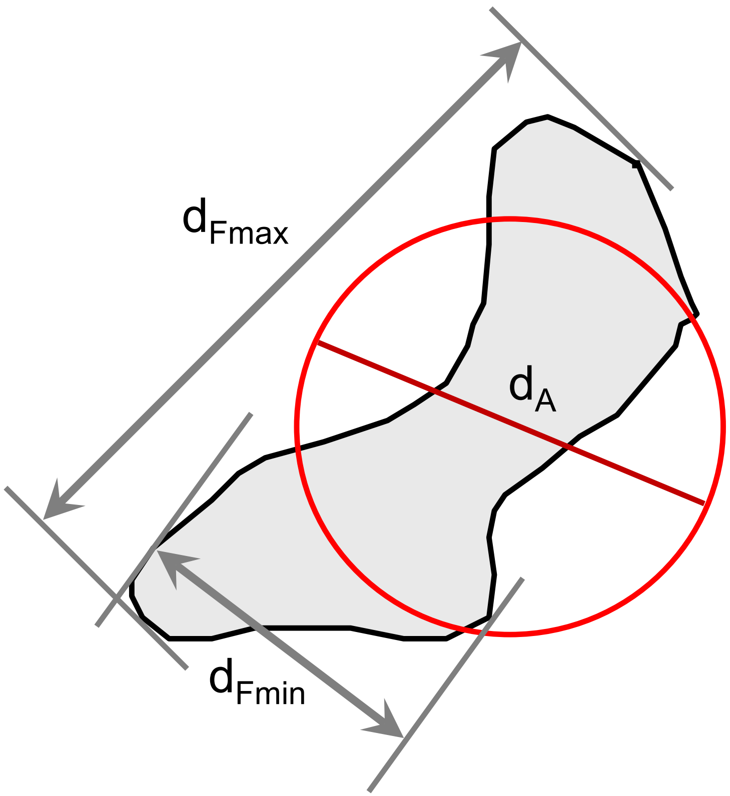
- Size and size distribution
- Morphology and shape factor - microscopy and image analysis
- Specific Surface Area - gas adsorption (N_2 , >0.1 m^2/g)
- Porosity (internal structure) - adsorption-desorption of gas, mercury porosimetry
- Crystalline Phase - X-ray diffraction (crystallite size from line broadening)
- Chemical Composition (purity, additives) - Ba/Ti or Ca/P ratios ceramics
- (% oxygen -metals)
- Homogeneity
- Density (absolute, apparent)* - poured, tapped, He pycnometry



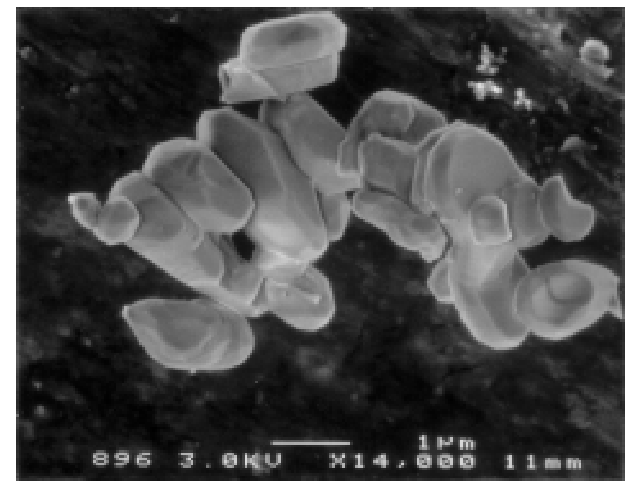
- Internal friction* - angle of repose, shear tester (Jenike cell: similar to viscosity meas.)
- Flowability and - Hall flow meter (Hausner ratio: tapped density/fluffy density)
- Compressibility* pressing (414 MPa)

* L. Svarovsky, Powder Testing Guide, Elsevier Applied Science, London, 1987.

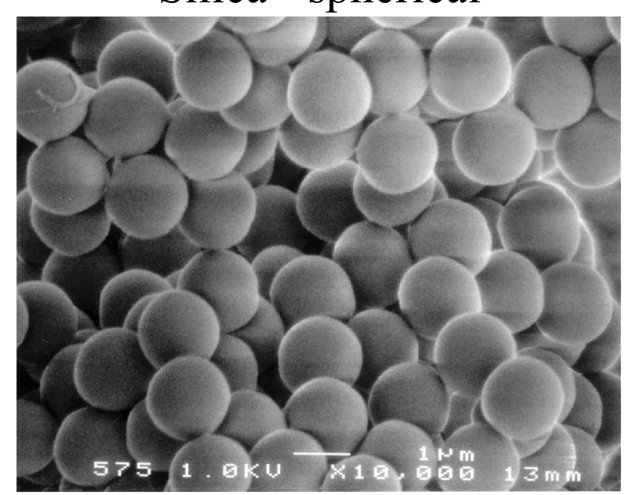
Diameters and distributions



Alumina – irregular shape



Silica - spherical



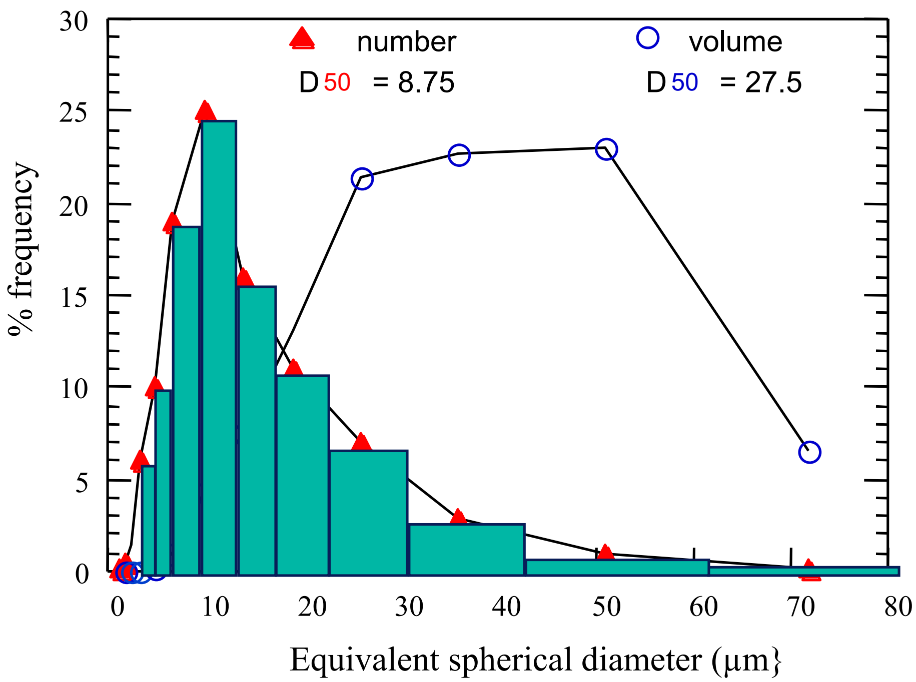
d_{Fmax} : Maximum Feret diameter
d_{Fmin} : Minimum Feret diameter
d_A : Equivalent circular diameter with same projected surface area as the particle

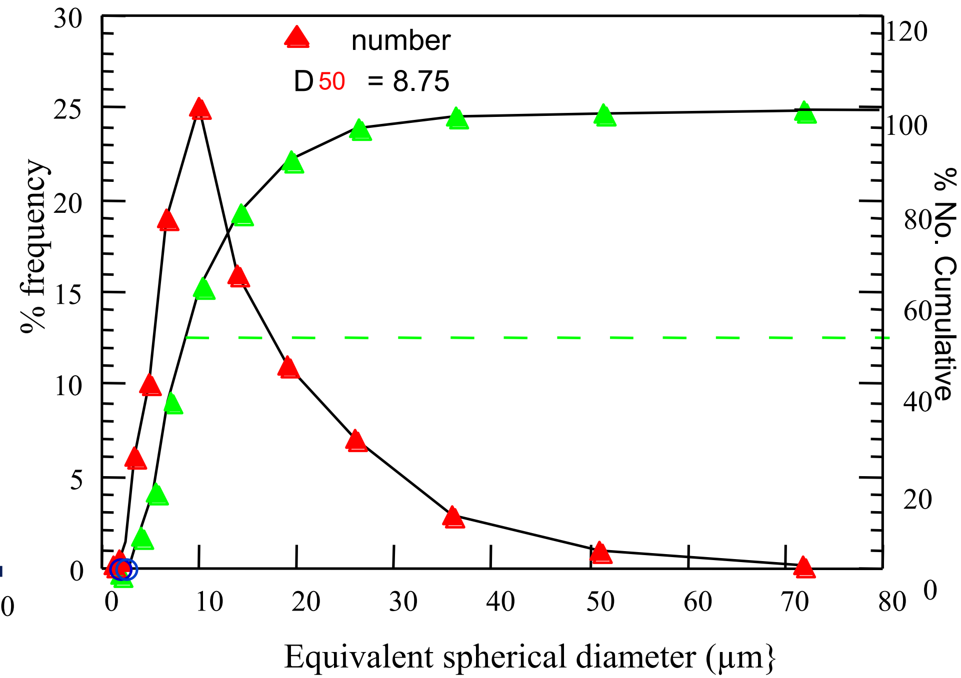
Different Particle Diameters

Diameter		Definition
Stokes diameter	d_{st}	Diameter of free falling sphere which would fall at the same rate as the particle in a given fluid
Seive diameter	d_T	Minimum square aperture through which the particle will pass
Volume diameter	d_v	Diameter of the sphere with the same volume as the particle
Surface diameter	d_s	Diameter of the sphere that has the same surface area as the particle
Projected area diameter	d_A	Diameter of the circle which has the same area as the projected area of the particle
Feret's diameter	d_F	Distance between two parallel tangents which touch the outline of the particle projection
Average Feret diameter	d_{Fav}	Average Feret diameter from diameters measured over all anlges between 0 and180°
Maximum Feret dia.	d_{Fmax}	Maximum distance between two parallel tangents which touch the outline of the particle projection
Minimum Feret dia.	d_{Fmin}	Minimum distance between two parallel tangents which touch the outline of the particle projection

Diameters and Distributions

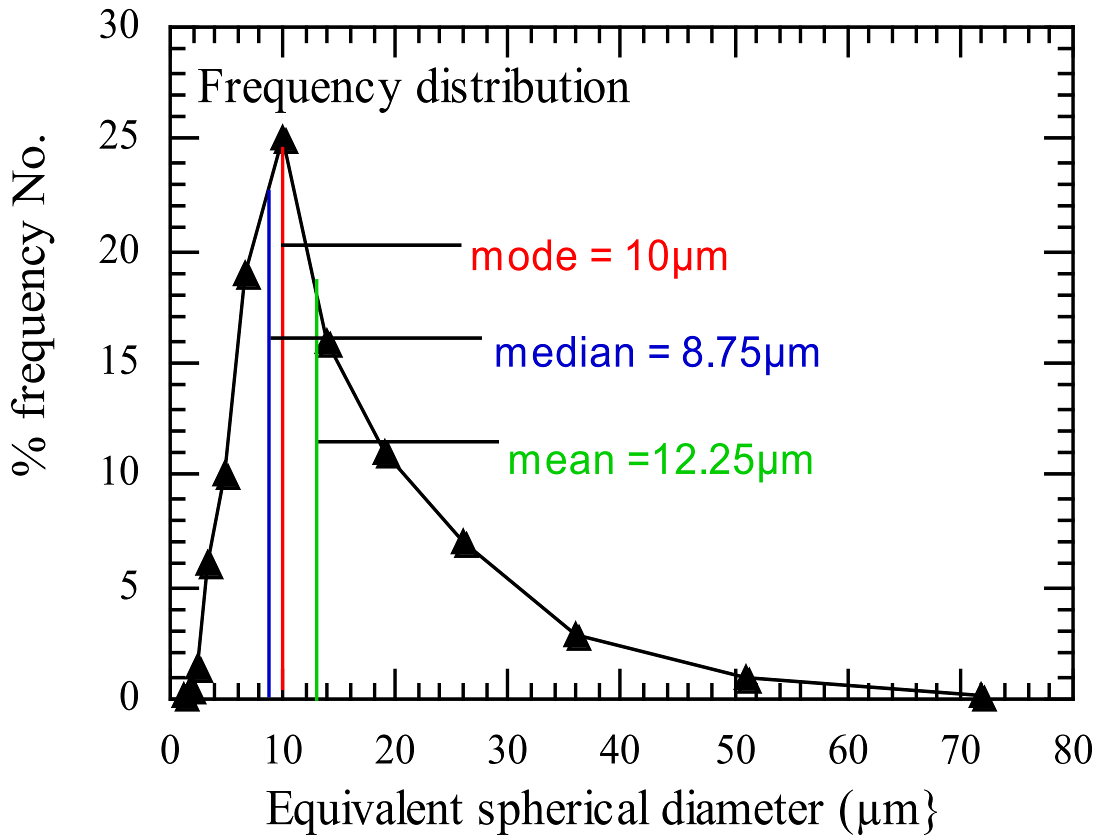
- Number or volume - distribution base
- Frequency or cumulative - Less than - Greater than





Distributions and Average Diameters

- Averages - central tendency -
- Mean - Mode - Median - for a normal distribution all are equivalent



Number - length

$$d_{nl} = \frac{\sum_{i=1}^{n} d_i N_i}{\sum_{i=1}^{n} N_i}$$

Number - volume

$$d_{nv} = \sqrt[3]{\frac{\sum_{i=1}^{n} d_i^3 N_i}{\sum_{i=1}^{n} N_i}}$$

Surface - volume

$$d_{sv} = \frac{\sum_{i=1}^{n} d_i^3 N_i}{\sum_{i=1}^{n} d_i^2 N_i}$$

Specific Surface Area

$$d_{BET} = \frac{6}{S_{BET} \cdot \rho} (\mu m)$$

Number - surface

$$d_{ns} = \sqrt[2]{\frac{\sum_{i=1}^{n} d_i^2 N_i}{\sum_{i=1}^{n} N_i}}$$

Length - surface

$$d_{ls} = \frac{\sum_{i=1}^{n} d_i^2 N_i}{\sum_{i=1}^{n} d_i N_i}$$

Volume - moment
(mass - moment)

$$d_{vm} = \frac{\sum_{i=1}^{n} d_i^4 N_i}{\sum_{i=1}^{n} d_i^3 N_i}$$

Distributions and Average Diameters – example - exercises

Silica powder – example - D_{n50} = 1.12µm
Narrow size distribution σ_{n50} = 0.55 µm

Diamètre cumulatif	Cumulatif	Diamètre fréquence	Fréquence
[µm]	[%]	[µm]	[%]
4.00	100.0	3.750	0.4
3.5	99.6	3.00	4.1
2.5	95.5	2.175	10.3
1.85	85.2	1.675	13.6
1.5	71.6	1.350	17.3
1.2	54.3	1.125	9.2
1.05	45.1	0.975	12.3
0.90	32.8	0.825	12.4
0.75	20.4	0.675	9.0
0.6	11.4	0.550	5.1
0.50	6.3	0.425	3.9
0.35	2.4	0.175	2.4

Number - surface

$$d_{ns} = \sqrt{\frac{\sum_{i=1}^{n} d_i^2 N_i}{\sum_{i=1}^{n} N_i}} = 1.41\mu m$$

Length - surface

$$d_{sl} = \frac{\sum_{i=1}^{n} d_i^2 N_i}{\sum_{i=1}^{n} d_i N_i} = 1.58\mu m$$

Number - volume

$$d_{nv} = \sqrt[3]{\frac{\sum_{i=1}^{n} d_i^3 N_i}{\sum_{i=1}^{n} N_i}} = 1.56\mu m$$

Surface - volume

$$d_{vs} = \frac{\sum_{i=1}^{n} d_i^3 N_i}{\sum_{i=1}^{n} d_i^2 N_i} = 1.91\mu m$$

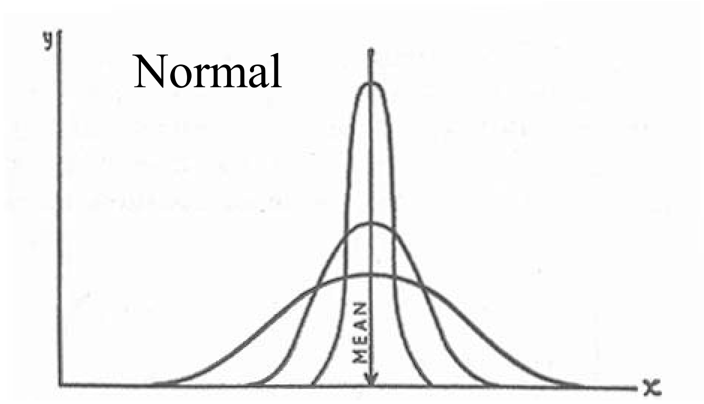
Volume - moment
(mass - moment)

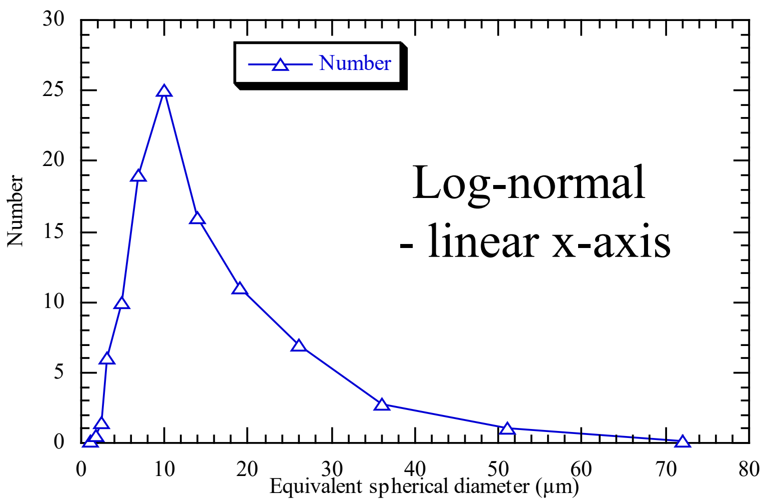
$$d_{4,3} = \frac{\sum_{i=1}^{n} d_i^4 N_i}{\sum_{i=1}^{n} d_i^3 N_i} = 2.21\mu m$$

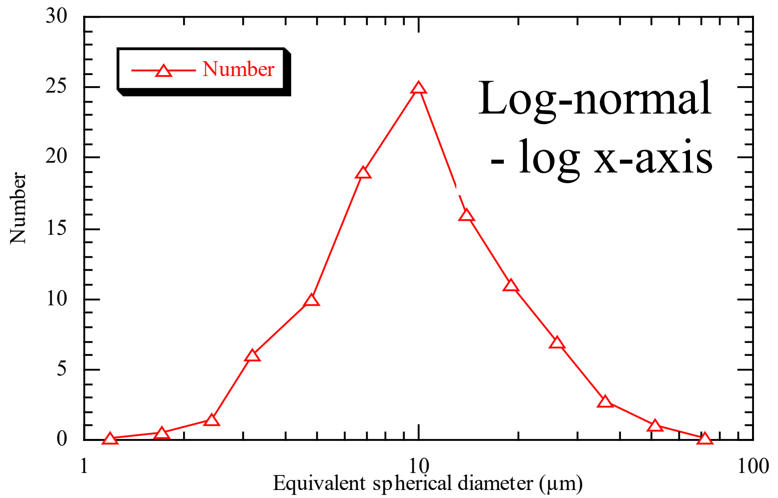
CONCLUSION
D_{43} = 2x D_{n50}……..
MUST DEFINE
DIAMETER

Types of distributions - graphical examples

- Types of distributions
  - Good review by Yu & Standish
  - Powder Technology **62** 101-118 (1990).







Types of Distributions & Widths

Types of distributions*

- **Normal**

$$y = f(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(x-\bar{x})^2}{2\sigma^2}\right]$$

- σ is the standard deviation

- **Log-normal** - x is simply replaced by ln x

- **Rossin Rammler** often used for milled or crushed materials

$$y = \frac{df(x)}{dx} = 100nbx^{n-1}\exp(-bx^n)$$

- n and b are material dependant constants

Widths of distributions

- Standard deviation- dispersion or width

$$\sigma_v = \sqrt{\left(\frac{\sum f_i (d_i - d_v)^2}{V}\right)}$$

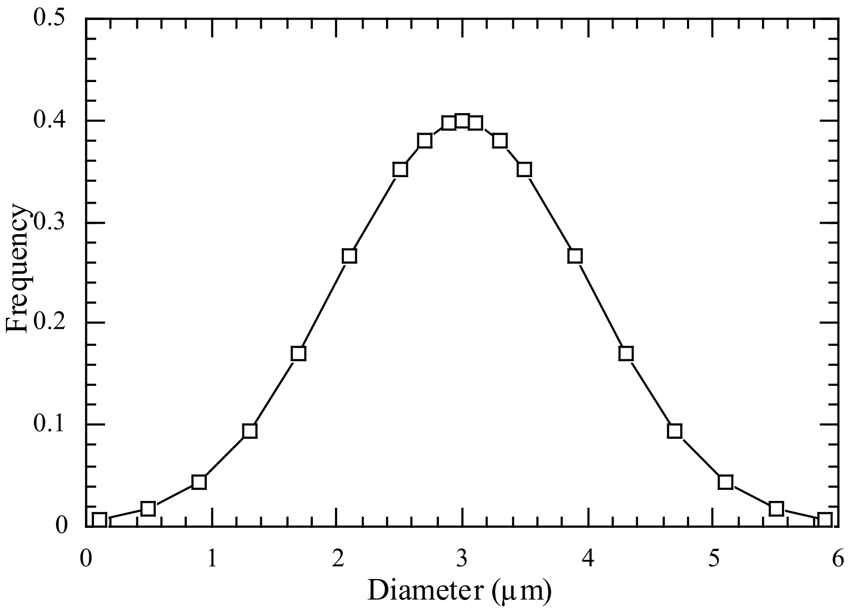
dv the mean volume diameter
fi is the frequency of particles (as a volume) of that diameter and V total volume for all of the diameter intervals

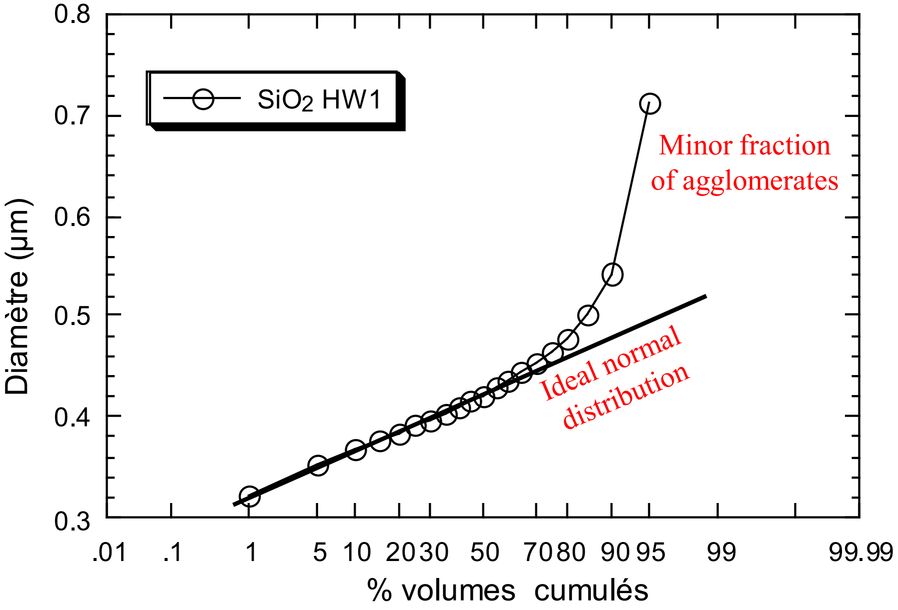
- Span = $(d_{90} - d_{10}) / d_{50}$

*T. Allen, "*Particle Size Measurement*", Fifth edition, Chapman and Hall, New York, 1997.

Normal Distribution

$$y = f(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(x-\bar{x})^2}{2\sigma^2} \right]$$

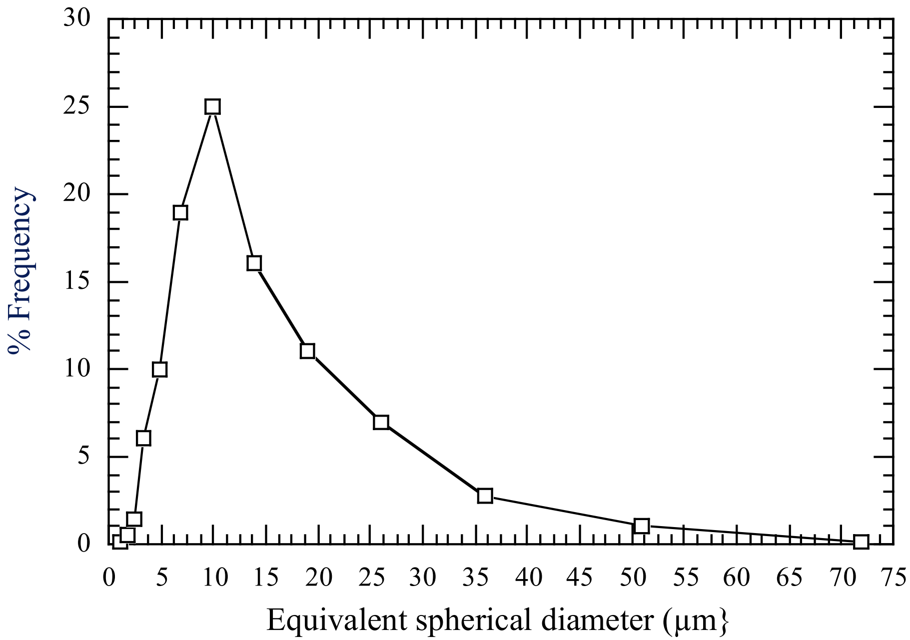


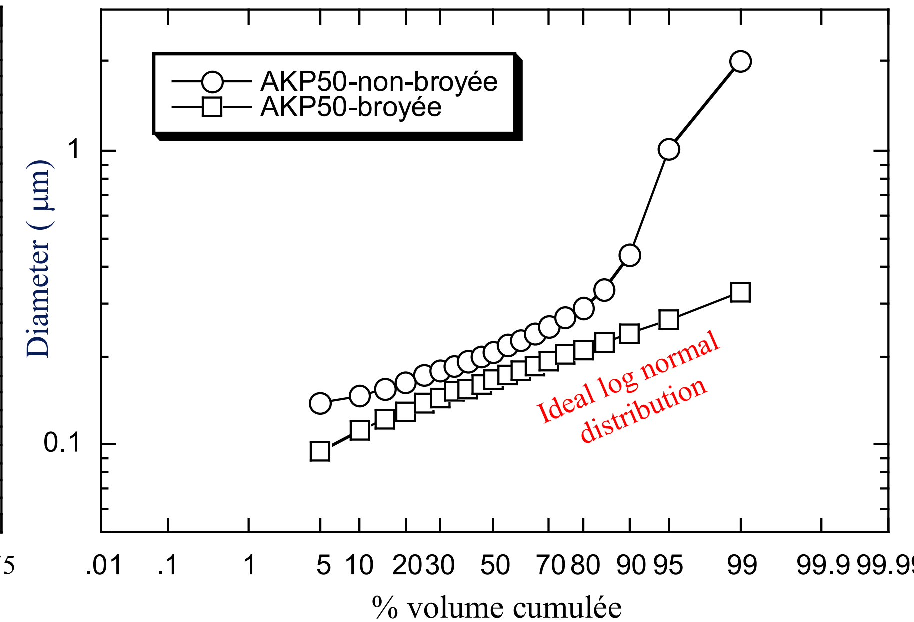


- Sieved Powders – narrow distributions – often follow a normal distribution

Log-Normal Distribution

$$y = f(x) = \frac{dF}{d(\ln x)} = \frac{1}{\ln \sigma_g \sqrt{2\pi}} \exp\left[-\frac{(\ln x - \ln \bar{x}_g)^2}{2\ln^2 \sigma_g} \right]$$





- Commercial ceramic powders –often follow a log-normal distribution
- Prof. Hofmann (Alusuisse) 22 of 30 commercial Al_2O_3 powders were close to log-normal

Typical ceramic powder: log normal distribution

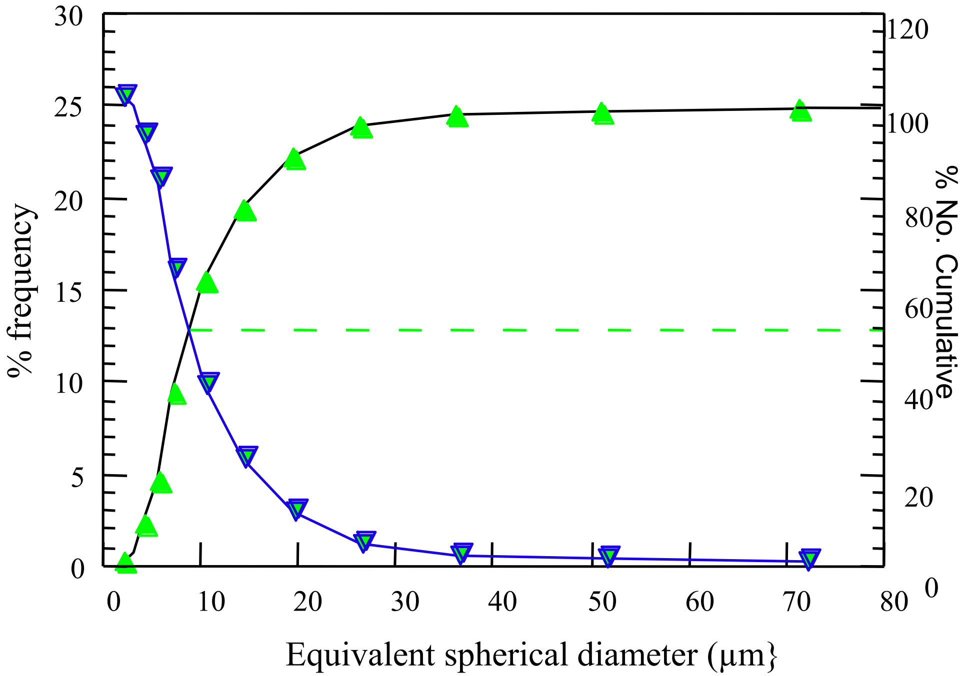
Distribution Rosin-Rammler (RR)

$$y = \frac{df(x)}{dx} = 100nbx^{n-1}\exp(-bx^{n})$$

n and b are constants
b – width
n - material

Integration gives
a cumulative distribution
(fraction greater than), R(%)

$$R = 100\exp\left(-bx^{n}\right)$$



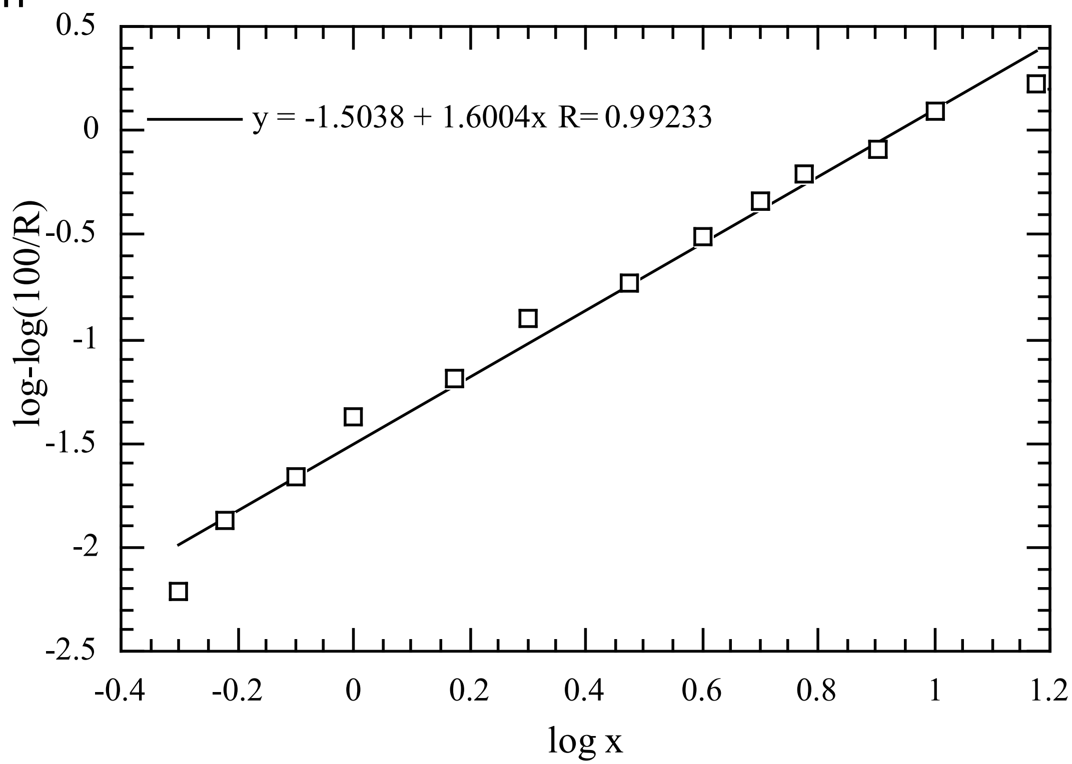
Distribution Rosin-Rammler (RR)*

$$R = 100\exp\left(-bx^{n}\right)$$

For n =1 ,
R = 100/e = 36.8%
= maximum of frequency distribution
= mode = x_m**

Often used for milled powders

Example - ground quartz



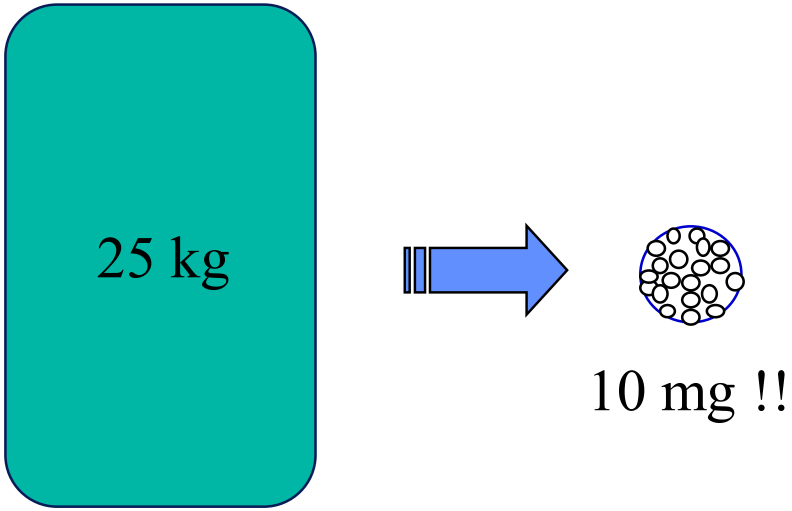
Linearized Form

$$\log\left[\log\frac{100}{R}\right] = C + n\log x$$

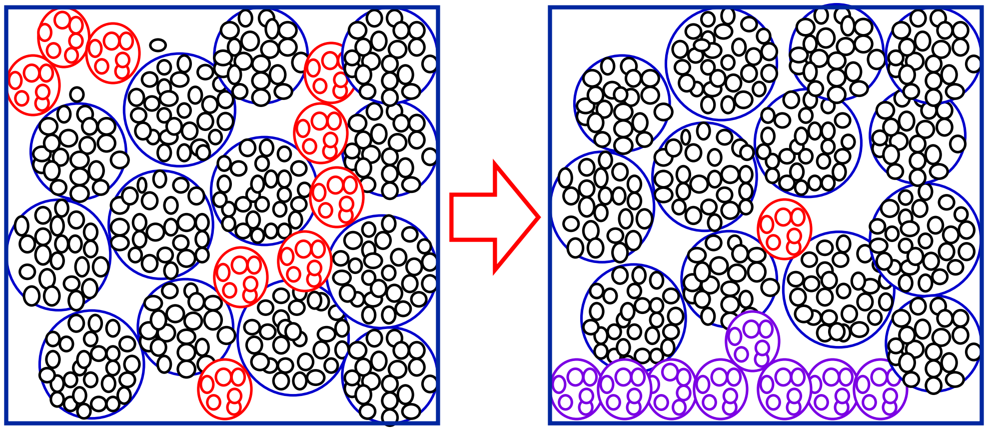
* RR (1933) applied to particle size distribution the Weibull probability density function (1927), see probability and statistic books.
** for more details see: T. Allen, Particle size measurement, vol 1., chapter 4.8.3 (third edition)

Sampling (1)

- Purchase 25 kg - 1000 kg
- Reproducible ceramic manufacturing process need
  - Constant powder quality
- Characterization use
- 50g – 10 mg
- Is our sample representative of the bulk lot?



- Possible segregation
- "Cornflakes/muesli" effect



Sampling (2) - Golden Rules

Important that analytical sample representative of whole

- "golden rules of sampling"* should be applied,
  - always sample a powder when it is in motion
  - take several small samples at different intervals rather than one larger sample

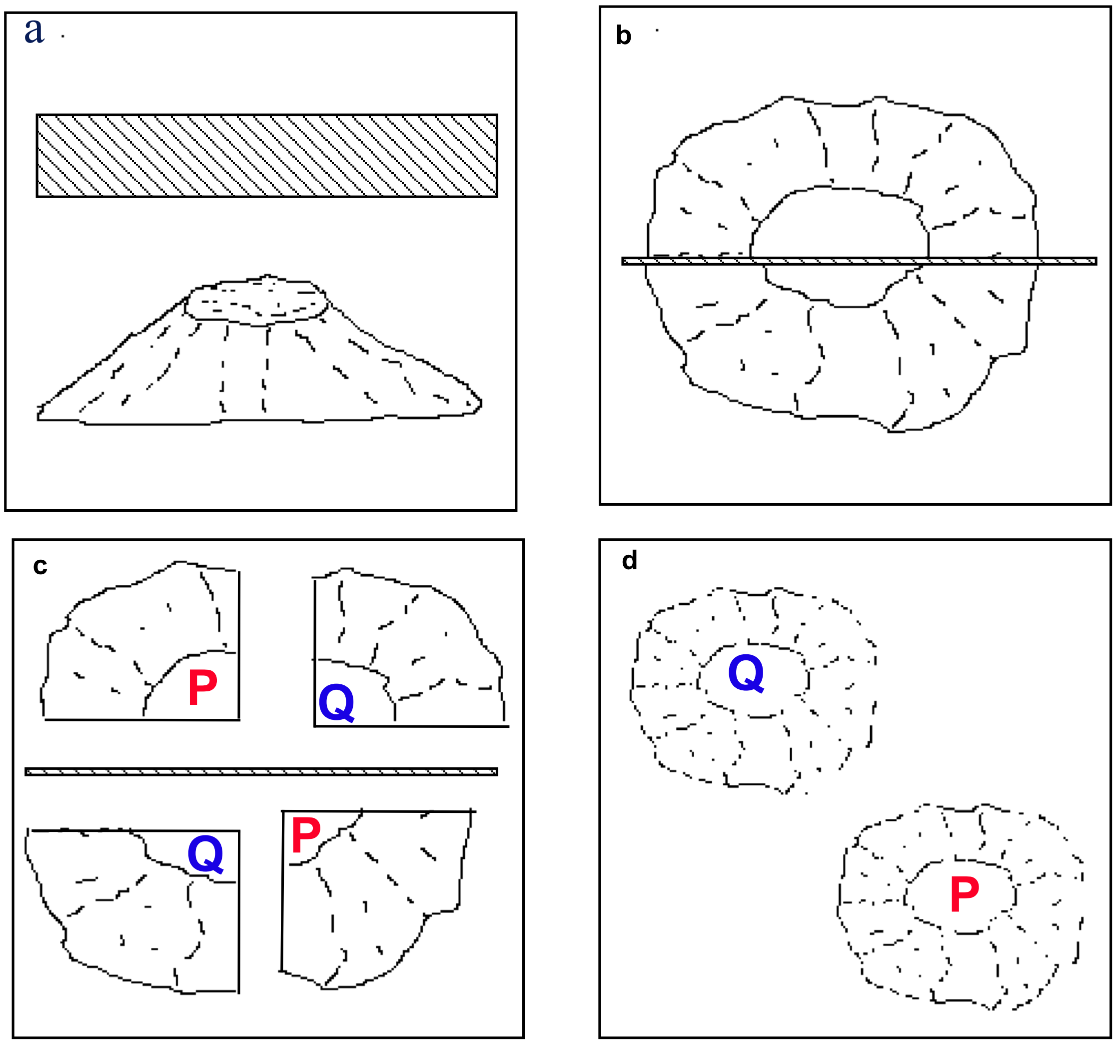
- Not always possible
  - other methods

Spinning Riffler or Rotary Sampler

*T. Allen, "*Particle Size Measurement*", Fifth edition, Chapman and Hall, New York, 1997.

Sampling (3) - Cone and division into quarters

1



♦Very often -

– **Spatula in a pot**

– Mix pot first

– Take sample of medium

Sampling (4) - Minimum number of samples

If we want to obtain a confidence level of 95% ($\pm X$; $X = D_{bulk} - D_{sample}$) of the median measured by our analytical technique, it is necessary to take n samples:

$$n = \left(\frac{t \cdot \sigma}{X} \right)^2 \qquad \text{Eq. 3.2.1}$$

- t - t-distribution $t \approx 2$ for a confidence level of 95%
- σ is the standard deviation of the distribution of our sample

PSD on 16 samples taken at random a batch of powder unmixed. → σ calculation.

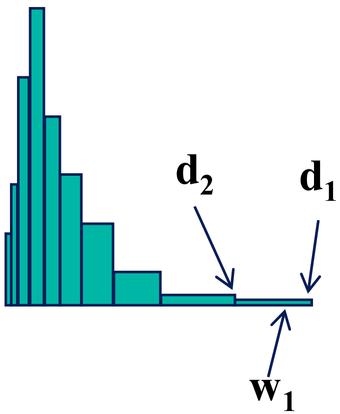
Then, 293 samples were needed for estimating a median of 3.1 μm of ± 0.1 (95% conf.)

With correct sampling using a rotary sampler: only 3 samples would have been needed.

Sampling - Minimum weight

- Minimum weight ,W_m, needed to have a representative sample
  - no matter what precautions are taken on sampling
- Related to the particle size distribution of the powder in question

$$W_m = 0.5\left(\frac{\rho_p}{\sigma_i^2}\right)\left(\frac{1}{w_1}-2\right)\left(\frac{d_1^3-d_2^3}{2}\right)\times 10^3$$

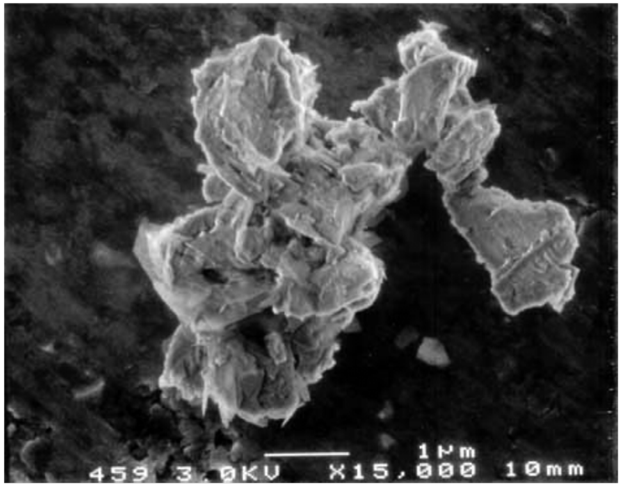


- W_m minimum weight (g), σ_i^2 is the variance of the tolerated sample error
- ρ_p powder density (g/cm3), w_1 mass fraction of largest size class sampled
- d_1^3 maximum diameter of largest size class sampled (cm)
- d_2^3minimum diameter of largest size class sampled (cm)

- e.g. for a sub-micron alumina (Alcoa A16SG) 0.3 mg is sufficient for σ_i 0.05 **but**
- For a glass spheres with a broad distribution from 10 to 1000 microns need 200g !!!!

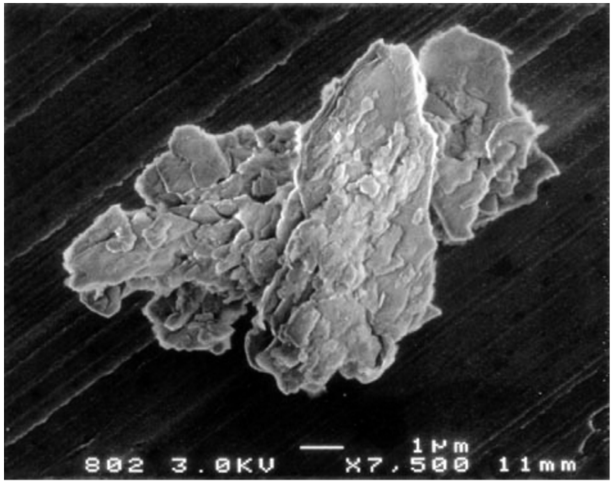
*T. Allen, "*Particle Size Measurement*", Fifth edition, Chapman and Hall, New York, 1997.

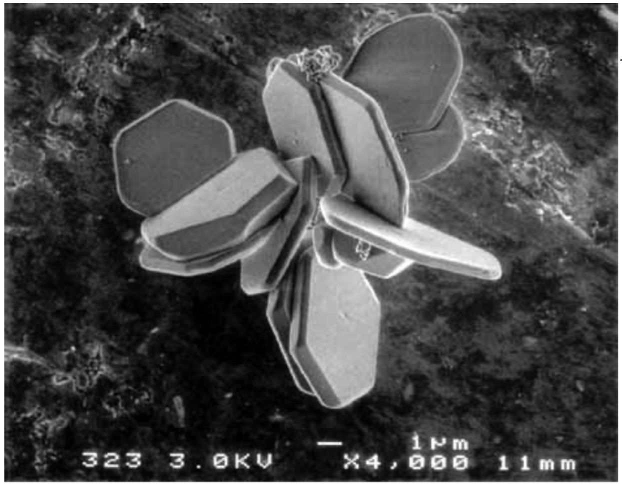
Morphology - Shape



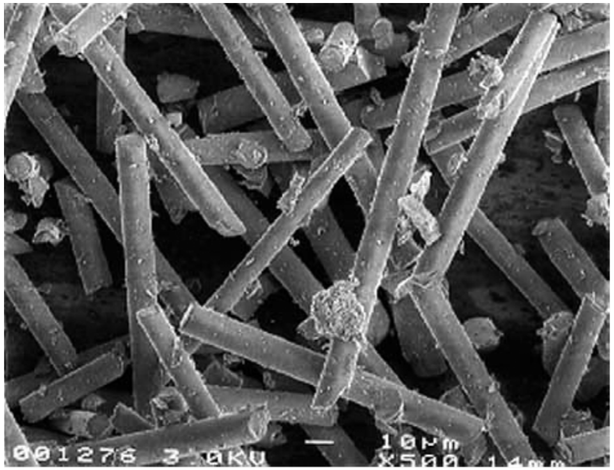
MgO milled

Kaolin





Alumina platelets



Glass fibres

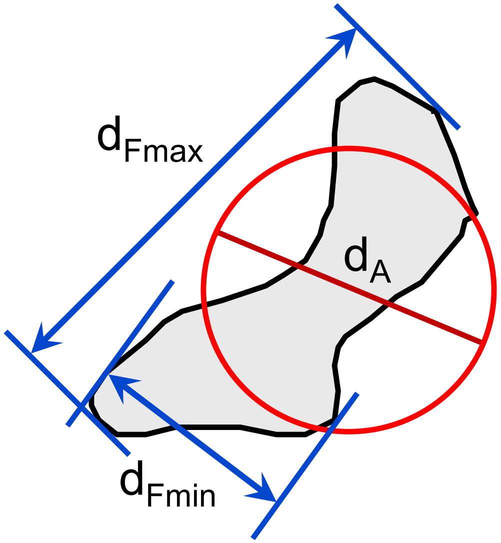
Morphology - Shape

- Form factor, F_f:

$$F_f = \text{Major axis / Minor axis}$$

- Ratio of Maximum Ferret Diameter to Minimum Ferret diameter

$$F_f = d_{Fmax} / d_{Fmin}$$



- Sphericity (W_w):

$$W_w = \frac{\textit{Specific surface area of a sphere with same volume as particle}}{\textit{Specific surface area} \text{ of particle}}$$

Current Methods - Brief review

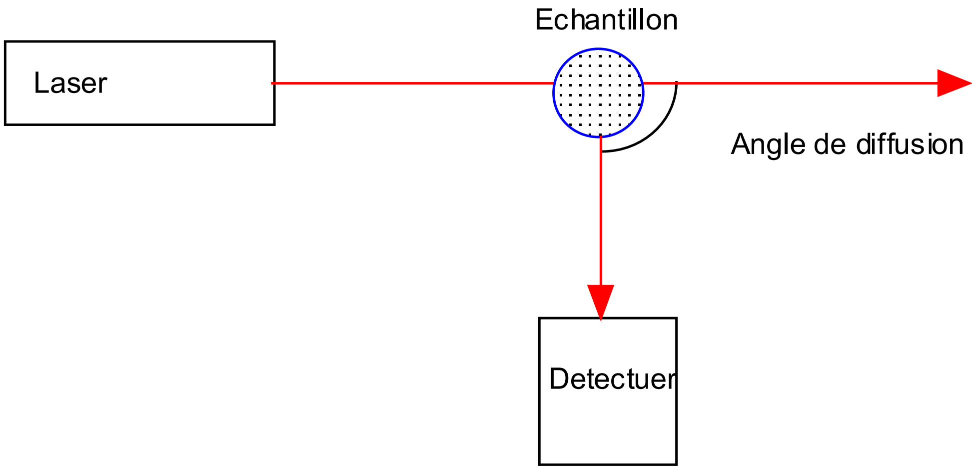
Method	Medium	Size (μm)	Sample (g)	Time*	Measured Dia.
Microscopy					
Optical	Liquid/gas	400-0.5	<1	S-L	Projected area
Electron	Vacuum	400-0.001	<0.1	S-L	Férèt
Sieving	Air	8000-37	50	M	Sieve
	Liquid	5000-5	5-20	L	
Sedimentation					Stokes
Gravity	Liquid	100-0.5	<5	M-L	Mass
Centrifuge	Liquid	300-0.02	0.01- 2	M	Projected area
Analytical Ultra Centrifuge		0.001…	<0.1	M-L	Hydrodynamic
Light Scattering					
Diffraction	Liquid/gas	3000- 0.05	<0.1-2	S	Volume
Dynamic	Liquid	0.5(1)-0.002	<0.1	S	Hydrodynamic
Tracking*	Liquid	>20nm	<0.001	M	Hydrodynamic
Electrical Sensing Zone (optical)	liquid	(1200) 250-0.4	<1	S-M	Volume
Gas Adsorption d_{BET}	Gas/Vacuum	5-0.005	<5	L	Surface-Volume

Analysis times S = short (< 20 min); M = moderate (20-60 min); L = long (>60 min)

*H. Graczyk, et al J.Aero.Med.&Pulm. Drug Deliv.(2014)

Photon Correlation Spectroscopy - PCS

- Dynamic light scattering (DLS) method or
- Photon correlation spectroscopy (PCS) or
- Quasielastic light scattering (QELS) (as it was first termed)



- Rayleigh limit R<< λ

$$I = \frac{I_0 16\pi^4 R^6 [(n^2 - 1)(n^2 + 2)]^2}{r^2 \lambda^4}$$

- Io is the incident intensity,
- $n = n_1/n_o$ relative refractive index for
- particle of refractive index n_1
- suspending medium n_o ,
- R is particle radius,
- λ the wavelength of light in the medium
- r the distance between the scattering particle and the detector.

- Dependence of the scattered intensity
- - Proportional R^6
- - Particle only twice the size
- will give 64 times the intensity.

Photon Correlation Spectroscopy - PCS

- Light scattered by particles*
  - Random thermal fluctuations - intensity of scattered light related - to diffusion coefficient D_t - d_h hydrodynamic diameter (=2R)
  - Auto Correlation Function (ACF) – relationship between scattered intensity at time t and t+δt,
- Very good - narrow distributions (steep slope in ACF)
  - < 300nm (>1µm sedimentation)
- Very quick (< 1 min)

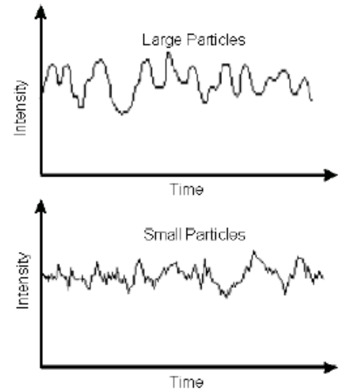
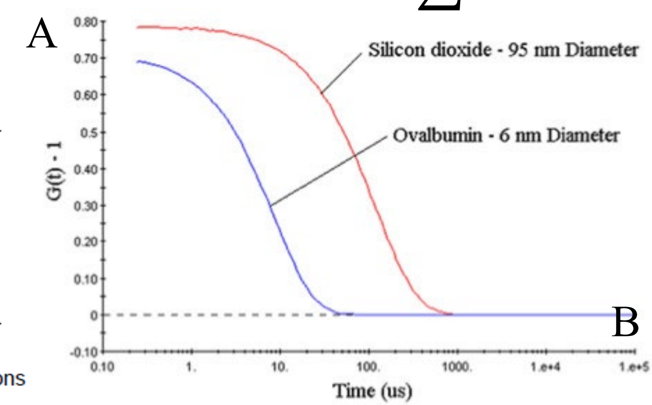


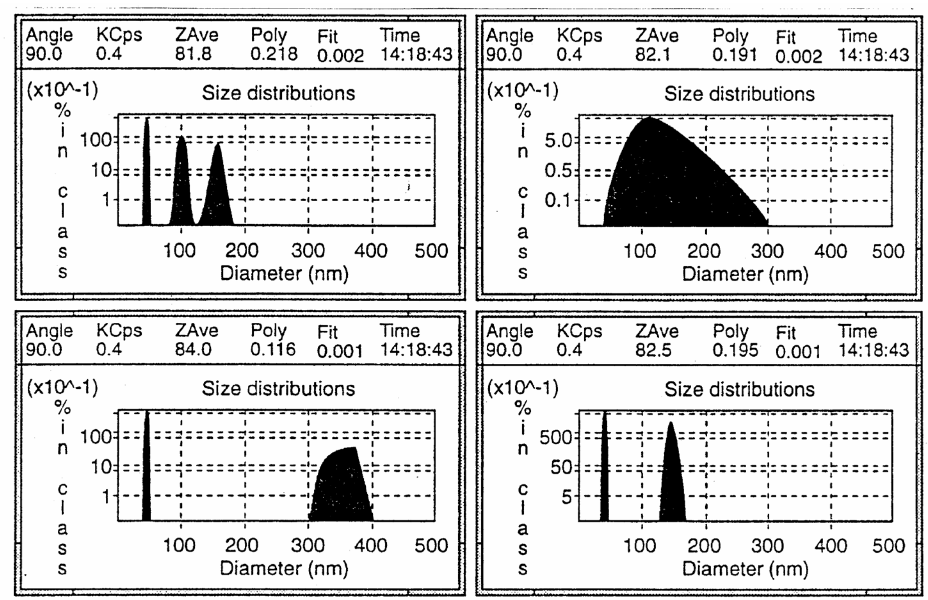
Figure 4: Typical intensity fluctuations for large and small particles

$$G(\tau) = A + B\sum e^{-2qD\tau}$$



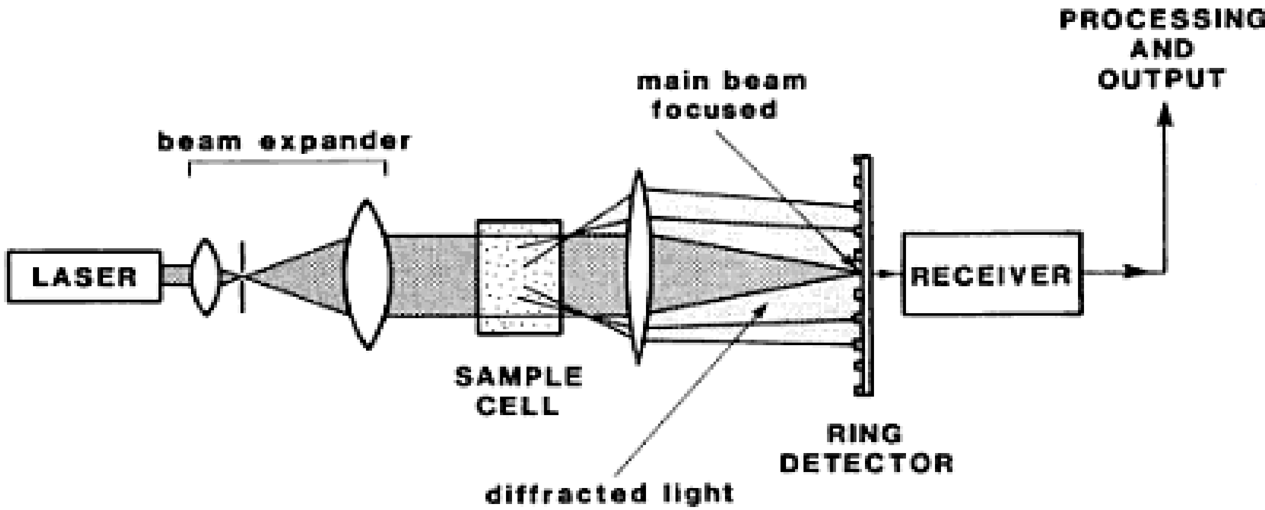
q (n, λ)– scattering vector, A intercept, B baseline

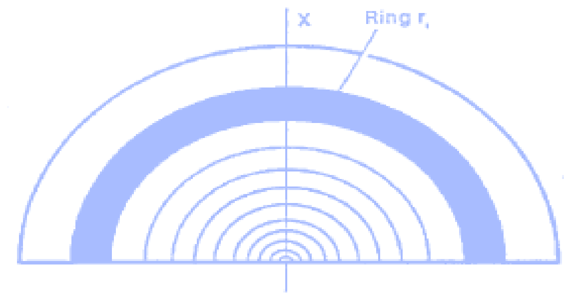
- Samples with wider distributions
  - the polydispersity index (PI) gives an idea of the spread of the PSD under investigation;
  - however the Laplace transform used in the analysis of the ACF is ill-defined
  - i.e. there is no unique solution



*B.Weiner in Particle Size Analysis, Eds. Stanley-Wood, N.G. and Lines, R.W., p.173, Royal Society of Chemistry, Cambridge, (1992)

Laser Diffraction





- Variation of the light intensity, I, with angle from the forward direction, θ ,for light scattered by diffraction for a powder is given by

$$I(\theta) = I_0 \int_0^\infty f(R)\left(\frac{RJ1\alpha\theta}{\theta}\right)^2 dR$$

- Io is the incident light intensity, α =2πλ/R, λ is the wavelength of the light, R particle radius
- J1 a Bessel function. A review of the various approaches used to derive particle size from this formulation is well summarised by Azzopardi

*B.J. Azzopardi «Particle Size Analysis », Ed. Stanley-Wood, N.G. & Lines, R.W., p.108, Royal Society of Chemistry, Cambridge, (1992)
"Principles, methods and Application of Particle Size Distribution analysis" J. P. M. Syvitski. Cambridge Univ. Press. 1991

Laser Diffraction

- Resulting diffraction** pattern can be described by diffraction theory (Azzopardi)
- Particles < 1µm full Mie theory*** has to be used
- Superposition of the diffraction patterns from each size represented in our powder
- Initial size distribution is "guessed"
  - theoretical diffraction pattern computed and compared with the real data.
  - differences minimised using a least squares method
  - residual gives a guide as to how well the optical model correctly represents the data
  - calculates the volume distribution as a fundamental result
  - All other information is derived from this result assuming a spherical particle shape.
- Each producer believes his algorithm for data reduction best
- Accuracy – reproducibility - better than 5% whole distribution -(Mohsen Khalili WCPT4, Sydney 2002*)
- Best for particles >4µm >x< 3000µm (down to 0.5 µm good, 0.1 µm possible)
- Fast <1 min! (Excluding sample preparation)

*M. Khalili et al “An Investigation to determine the precision for measuring particle size distribution by laser diffraction” World Congress on Particle Technology 4, Sydney 2002, Paper no 111

** diffraction theory or Fraunhofer *** combination of diffraction and scattering

Laser Diffraction – Silica spheres (Geltech)

- For spheres with a narrow size distribution at 1 µm - very good d_{v50}better than 1% cf image analysis

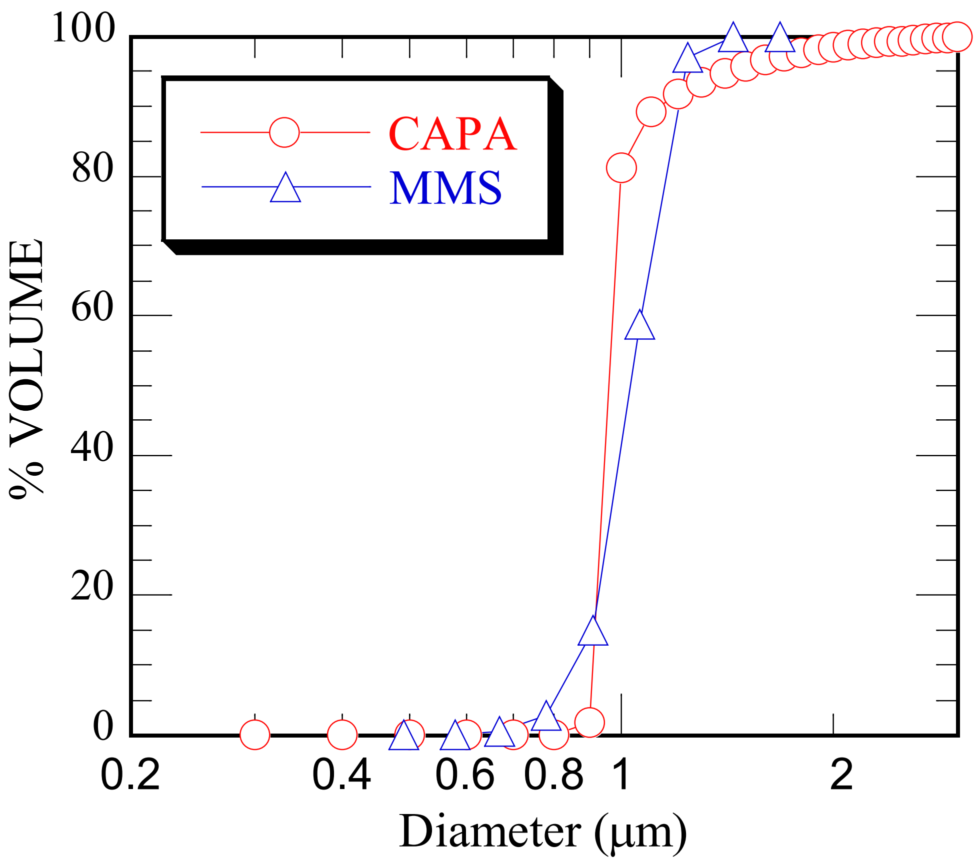


Image Analysis

d_{v50} -1.04 µm - *

Malvern Mastersizer S

(laser diffraction)

MMS d_{v50} -1.03 µm

CAPA- photocentrifuge

d_{v50} – 0.97 µm from 4 runs

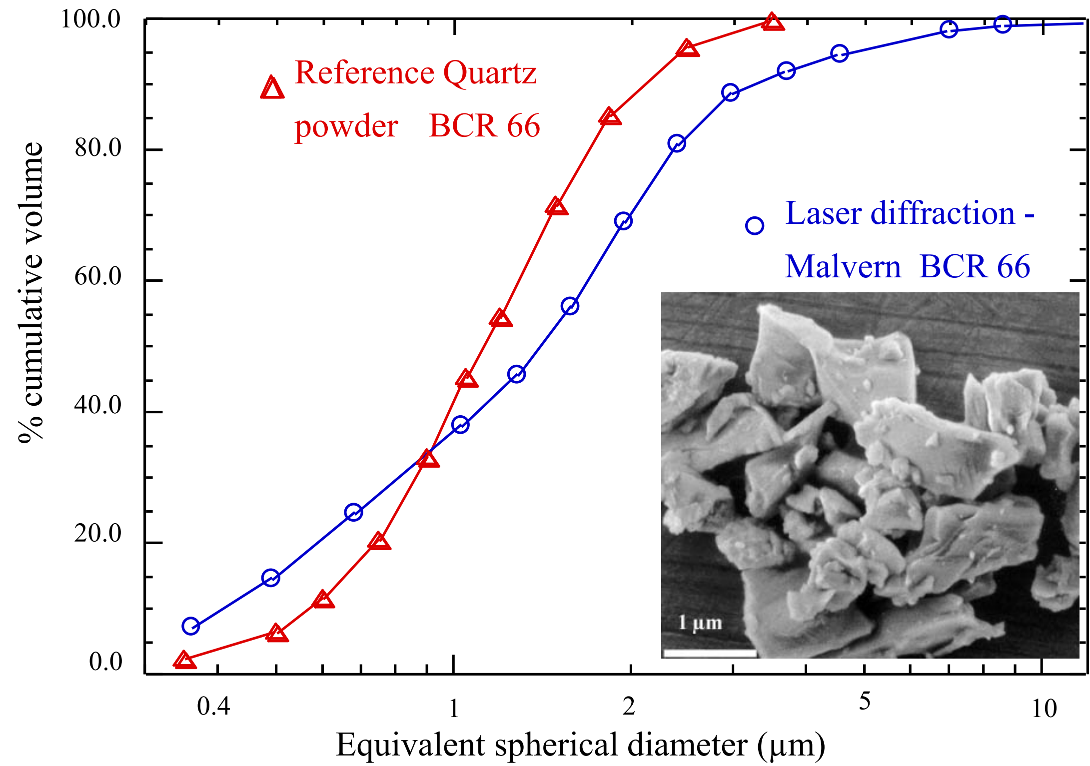
but lacking resolution need to repeat with higher resolution

*** Ajit Jilla - NIST**

Laser Diffraction – Ground Quartz BCR 66

- For spheres with a narrow size distribution at 1 µm - very good d_{v50}better than 1% cf image analysis

- Main limitations
- Distributions are broadened (fitting of diffraction pattern*)
- fine particles <1µm and the Mie theory has to be applied,
- when particles are non-spherical (particularly elongated particles)

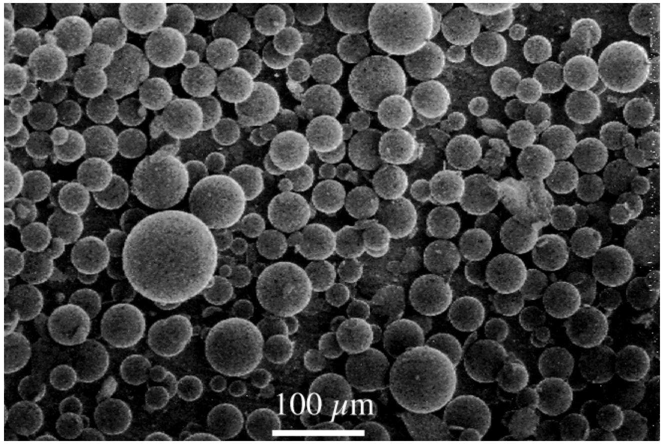


*R. Xu et al– Paper 41- « Particle size and shape analysis using light scattering, coulter principle, and image analysis»World Congress Particle Technology, Sydney, 2002

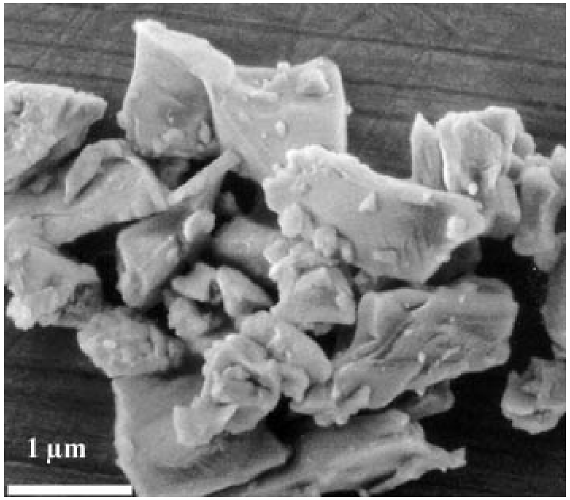
Particle Shape - Regular Geometries

- Most instruments give as an output
  - Equivalent Spherical Diameter - ESD
  - Often normalised on volume
- ONLY spheres will give comparable results
- Non-spherical particles ESD always smaller then real size and method dependent (Jennings & Parslow 1988*)
- Comparison of ESD's from different methods
  - Shape factor - lot of work on clay minerals
  - Morphology of particles studied not uniform
  - Difficult to compare Image Analysis and other methods

Theory



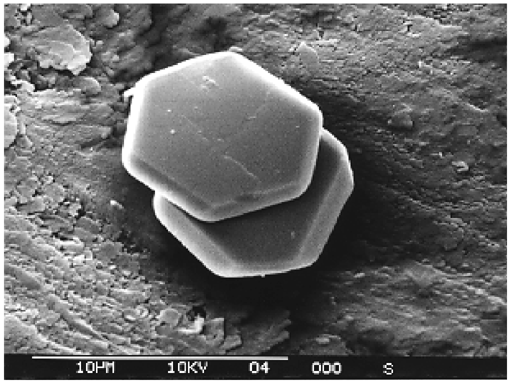
Reality



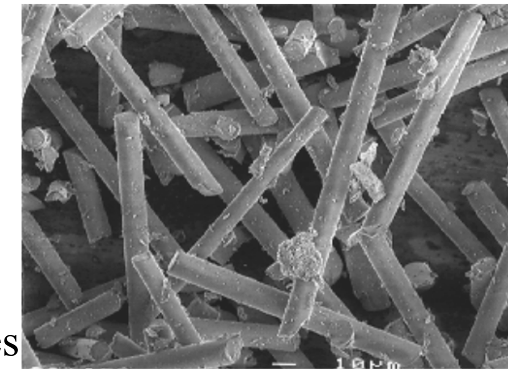
*Proc. R. Soc. Lond. A 419 137-149 1988

Particle Shape - Regular Geometries - Model & Real

Regular Morphology - Model Particles

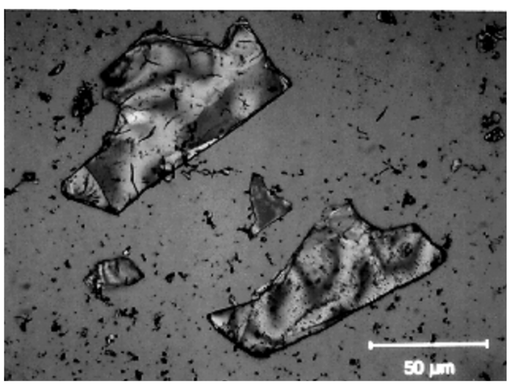


Alumina Platelets

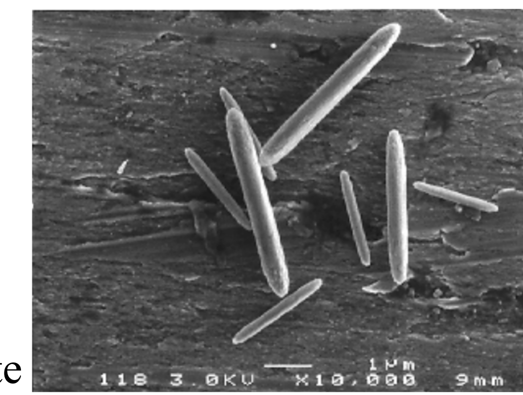


Glass Fibres

Real Particles



Mica Particles



Precipitated Copper Oxalate

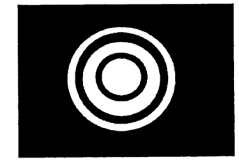
P. Bowen, J. Sheng, and N. Jongen, "Particle Size Distribution measurement of Anisotropic particles – cylinders and platelets - practical examples" Powder Technology,128, 256-261 (2002).

Laser Diffraction - Shape

- ♦ Shape limitation
  - ♦ non-spherical particularly elongated particles *
- ♦ Diffraction pattern need
  - ♦ X-Y resolution
- ♦ Gabas et al show can get min max dimensions

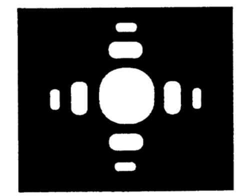
(a) Circular aperture

a)



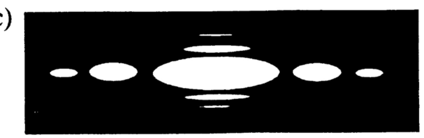
(b) Square aperture

b)

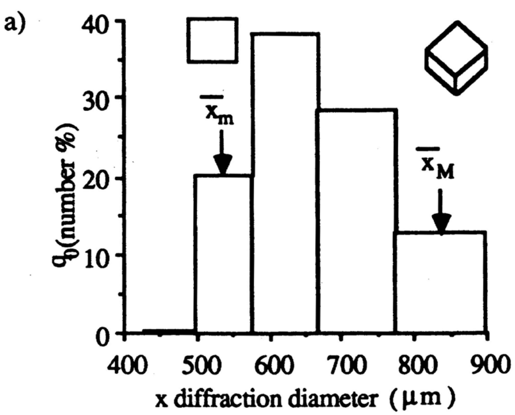


(c) Rectangular aperture

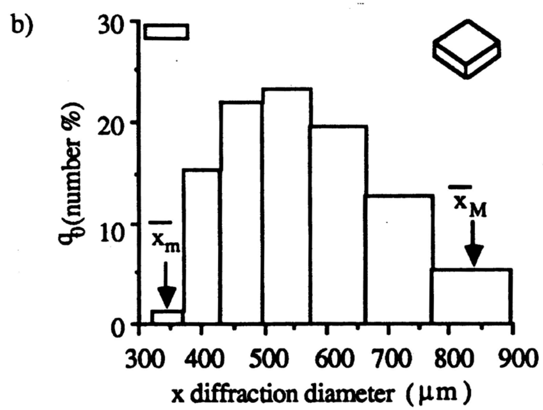
c)



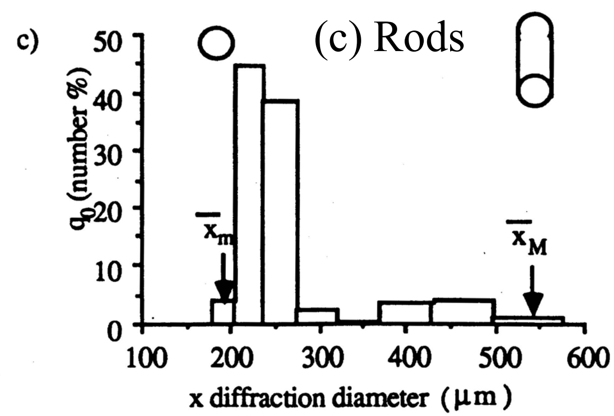
(a) Cubes



(b) Square plates



(c) Rods



*N.Gabas,N.Hiquily, C. Laguérie, Part.Part.Syst.Charact, II 121-126 (1994)

Specific Methods - Sedimentation

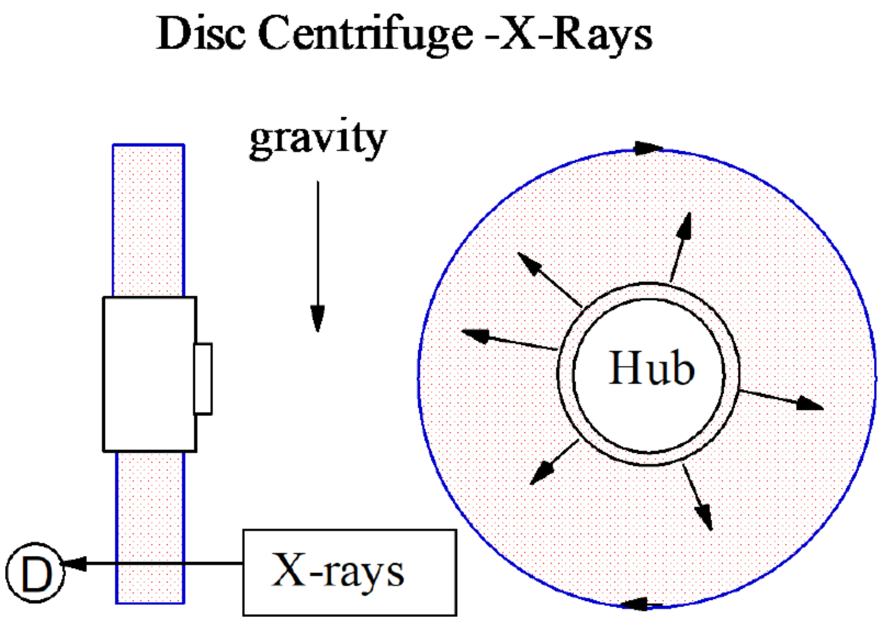
- Sedimentation velocity is calculated using Stokes law- FOR SPHERES
- Gravitational — Centrifugation

$$d = \sqrt{\frac{18\eta_0 H}{(\rho - \rho_0)gt}}$$

$$d = \sqrt{\frac{18\eta_0 \ln(x_1/x_2)}{(\rho - \rho_0)\omega^2(t)t}}$$

- d - particle diameter, — ηo - viscosity of the dispersion medium,
- H - sedimentation distance, — ρ - sample density,
- ρ_o - dispersing liquid density, — t - sedimentation time,
- g - acceleration due to gravity, — ω(t) - rotational angular velocity.
- x_1 - distance between the centre of rotation and the sedimentation plane,
- x_2 - distance between the centre of rotation and the measuring plane,

Brookhaven X-ray Disc Centrifuge



- Advantages
- X -ray absorption proportional to mass - volume
- Good correspondance with standard powders*
- Reasonably quick - 10mins (for 0.3 -3.0 µm)
- Large size range 0.01 -300µm
- Limitations
- Need 2-3 g of powder
- Suspension concentrated - particle-particle interactions
- Often difficult to match liquid viscosity-particle density for single run measurement
- X-ray absorption not strong for Al,Si

2

Differential Disc Centrifuge Particle Size Analyser (CPS-DC, CPS Instruments Europe)

Instrument	CPS-DC
Price (CHF)	117 000
Size range	5 nm - 40 microns
Disc Speed (rpm)	24 000
Variable speed	YES
Sample size	< 3 mg
Dynamic range	1000

Analysis times

-10-60minutes for 20nm particles

- Dynamic size range

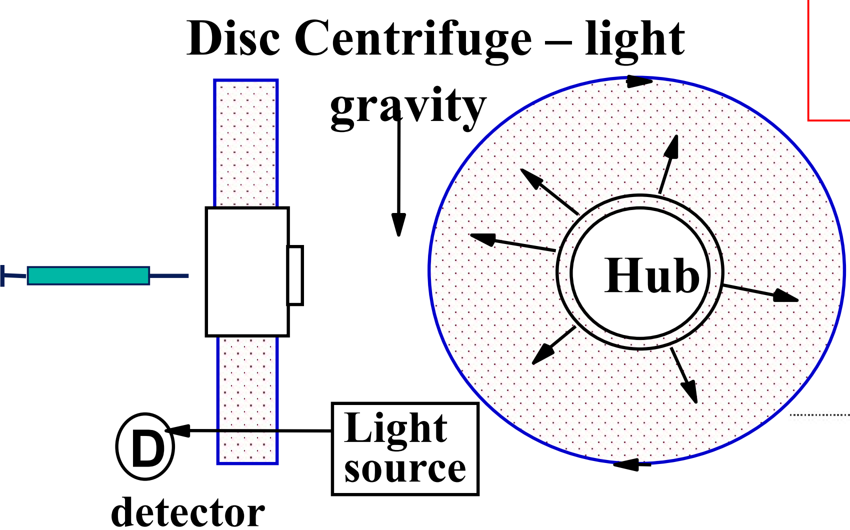
  -40 µm to 20nm in 60 mins in a single run

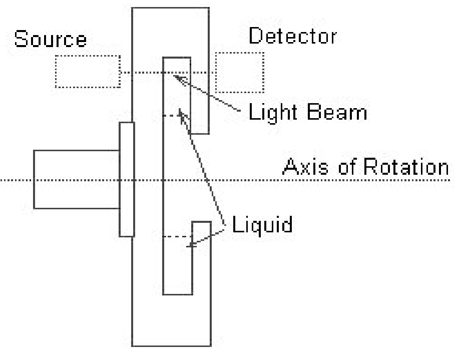
  -From density gradient - sugar solution in disc

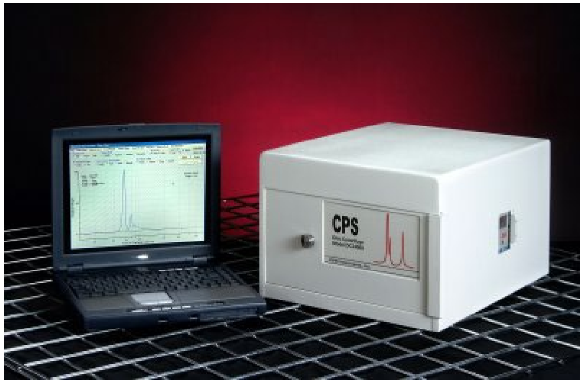
- variable speed (special disc to maintain gradient)
- 24000 rpm –

  900 km/hr = 29000 g

  High velocity!!!!!





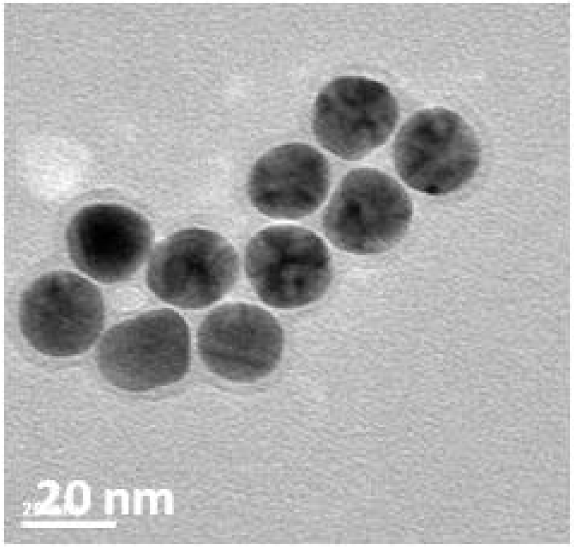


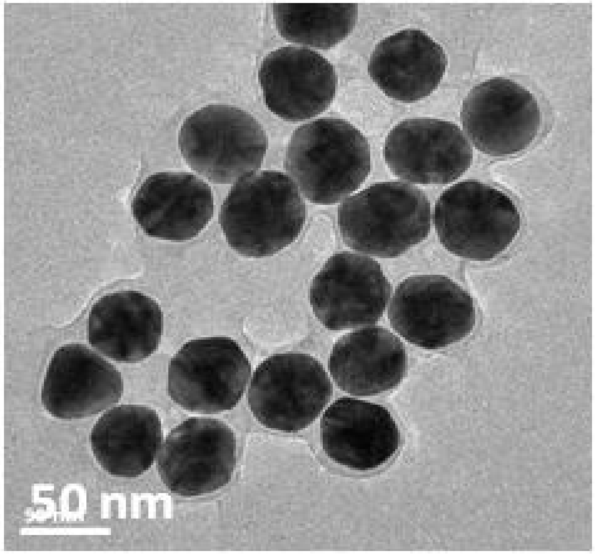
1

Gold – commercial – 20 & 50 nm – CPS – PCS - TEM

	Method	TEM	CPS	PCS
Gold Colloid 20 nm	D_{TEM} - D_{v50} (nm)	18.4	17.3	15.6
	Standard deviation (nm)	*1.9*	*0.1*	*0.3*
Gold Colloid 50 nm	D_{TEM} - D_{v50} (nm)	47.7	48.1	50.1
	Standard deviation (nm)	*2.3*	*0.3*	*1.2*

- CPS Very Good – comparison with
- TEM
  - Narrow SD – possible particle interactions
- PCS
  - 20 nm bit low
  - 50 nm bit high





A. Aimable, P. Bowen, J. Proc. & Appl. Ceramics, 4[3] 147-156 (2010).

Particle size description in documents

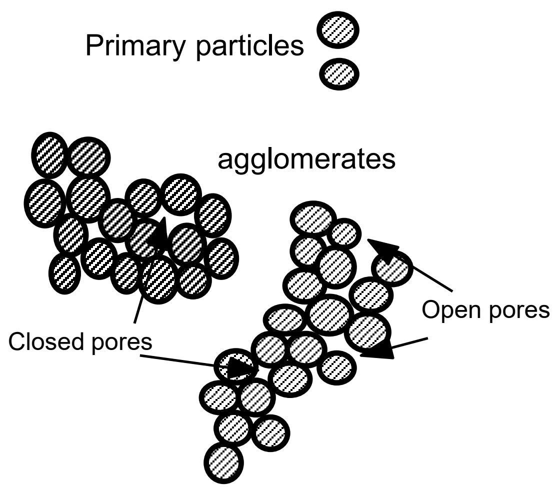
- When describing particle size data or measurements in a document the following details should be quoted
  - Type and supplier of instrument used (eg laser diffraction, Dynamic light scattering…)
  - The base to which the distribution is normalized (number, volume…)
  - How the sample was dispersed if using a suspension
- Further details can be added such as
  - Refractive index of particle and liquid used for light scattering model
  - Particle density for sedimentation methods
  - Strength of ultrasonic treatment
  - Volume of sample treated
  - Concentration of suspension (g/ml)
  - Pre-treatment for specific surface area measurements
  - Any other special detail you have noticed is important for reproducible PSD measurement

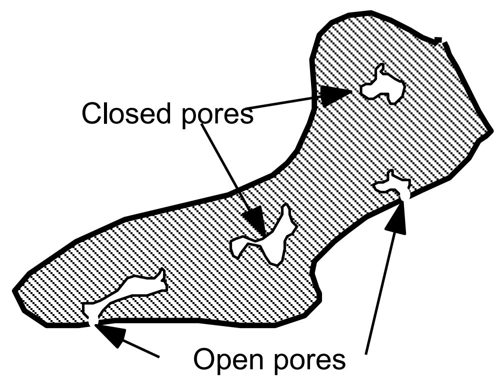
Steps in measuring a Particle Size Distribution

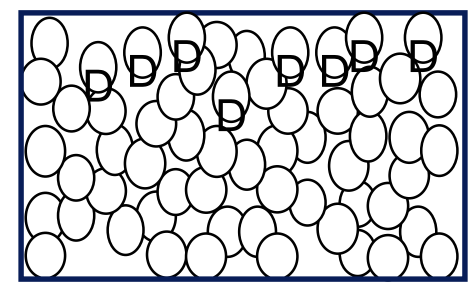
- Get any information possible from supplier (size and size method, purity, specific surface area)
- Get a suitable image
  - optical microscopy >10 mm
  - electron microscopy <5 mm (SEM, TEM)
- Why are you trying to measure the size – ceramics, drug delivery, catalysis
  - Choose suitable method **(NB protocols…see PTG website…..)**
- For 0.1 to 1000 µm – laser diffraction good point to start if not elongated
- For 10nm to 1000nm Disc centrifuge (X-ray for inorganic)
- For 2-500nm Photon correlation spectroscopy – care when broad distribution
- (< 10nm 2D Analytical Ultra Centrifugation…… (see Prof. Stellacci))
- For elongated or samples - Image Analysis best
- Complementary methods – (SSA, TGA, XRD, Zeta potential, (SEM,TEM, AFM)

Density, Porosity and Specific Surface Area

- Powders - nanosized – aggregation – open porosity
- Often thermal treatment during synthesis – possibility of closed pores
- Density lower than – theoretical – calculated from crystal structure
- High surface areas (HSA) and possibility of hydroxylated surface – e.g. hydrothermal $BaTiO_3$ – closed porosity formed while heating from 500 to 900°C





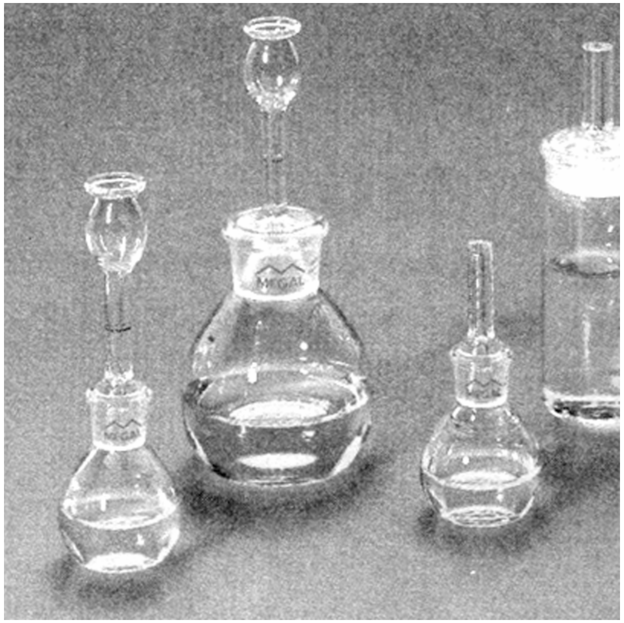


- Density (mass/volume) pure phase or powder from pycnometry, can use gas (helium) or a liquid (water, alcohol…)
- Apparent (bulk) density of a powder mass per unit volume - particles and interstitial porosity

Density - Pycnometry

- Calibrated chamber filled with fluid, measure mass (liquid) or pressure (gas) determines volume
- Dry sample of known mass placed in volume (for HSA powders not always trivial)
- Difference in mass or pressure allows calculation of sample volume and hence density.
- Compare pycnometry with that calculated from crystal structure
- LTP – Micromeritics – Accupyc 1330 (He gas pycnometer) – generally better than 1%
- Archimedes method, immersion in a liquid

$$\rho_{abs} = \frac{m_p}{v_p} = \frac{g}{cm^3}$$



- To measure open porosity – need to fill pores – water weigh dry and wet or
- from pore size distribution via nitrogen adsorption/desorption (NAD) or mercury intrusion porosimetry (MIP)
- Closed porosity from comparison between pycnometry (e.g. helium) and theoretical density – depending on sample purity.

Porosity and Specific Surface Area – Gas Adsorption

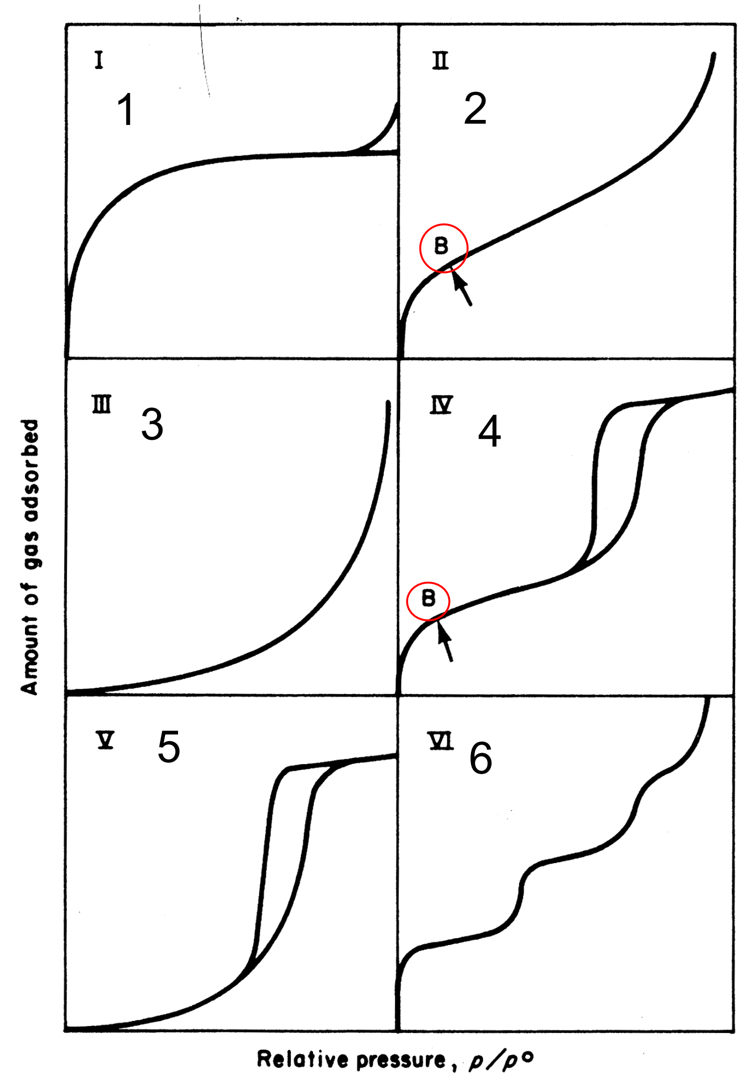
Nitrogen Adsorption – Desorption (NAD)

- Domain: 2 nm to 200 nm
  - micropores (<2 nm)
  - mesopores (2-50 nm)
  - macropores (>50 nm)
- Powder sample (dried) – evacuated – and cooled to liquid nitrogen temperature (-196°C).
- Drying is very important!!!!!!
- Normal conditions for ceramic powder
- Surface area - 200°C - 1 h under flowing nitrogen
- Porosity – 200°C 24 h – under vacuum

Micromeritics TriStar II Plus
Surface Area and Porosity Instrument

Adsorption isotherms

- Quantity adsorbed at constant temperature
  - as function of concentration of adsorbate in equilibrium with surface
  - Gasses – normally use partial pressure P/P_0
  - where P_0 is saturation pressure of adsorbing gas (at given T)
- Various molecules or gasses different sizes and affinities for surfaces
- e.g. N_2, Ar, Kr,– etc
- Many forms or types of isotherms - grouped into 5 classes by Brunaauer, Denning, Deming and Teller (1940) - a sixth exists – the stepped - rare but of theoretical interest
- Type 2 and Type 4 used for SSA and pore size measurement with nitrogen
- Type 1– microporous solids, Type 2 - non-porous solid
- Type 3 – 5 weak gas-solid interactions or strong interaction between adsorptive molecules
- Type 4 – mesoporous solid



Atomistic modelling of N_2 adsorption on silica*

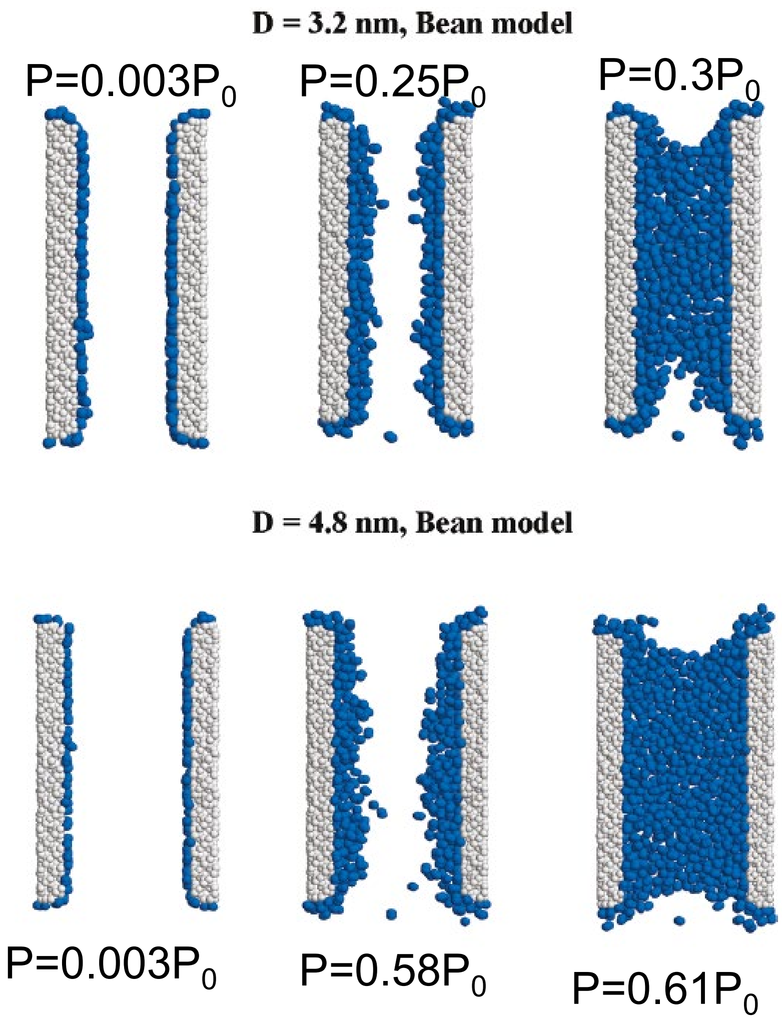


Figure 5. (Top) Typical molecular configurations for nitrogen in the silica **cylindrical nanopore** with D=3.2nm when the bean model is considered: (from left to right) $P=0.003P_0$,bean, $0.25P_0$,bean, and $0.30P_0$,bean. The white spheres are the oxygen atoms of the silica nanopore, and the blue spheres are the nitrogen atoms of the adsorbate molecule. (Bottom) Same as in the top image but for the nanopore with D = 4.8 nm: (from left to right) P = $0.003P_0$,bean, $0.58P_0$,bean, and $0.61P_0$,bean.

In the “pea” model, the nitrogen molecule is described as a single Lennard-Jones sphere. In the “bean” model (TraPPE force field), the nitrogen molecule is composed of two Lennard-Jones sites.

*Coasne et al Langmuir 2010, 26(13), 10872–10881

Langmuir Isotherm

- Langmuir – assumes dynamic equilibrium between molecules arriving at and leaving surface
  - only a monolayer adsorbed
  - no-lateral interaction
  - each site same adsorption energy
  - for dilute adsorptive concentrations

$$V_a = \frac{V_m bP}{1 + bP}$$

V_a quantity of gas adsorbed at pressure P
V_m quantity of gas to cover surface–monolayer
b empirical constant

- Estimation of surface from monolayer capacity V_m
- Surface area per g of material – S
  - Specific Surface Area - m^2/g
- more suited to chemical adsorption with limitation to monolayer
- Brunaeur, Emmett and Teller (BET)– extended to multilayer adsorption

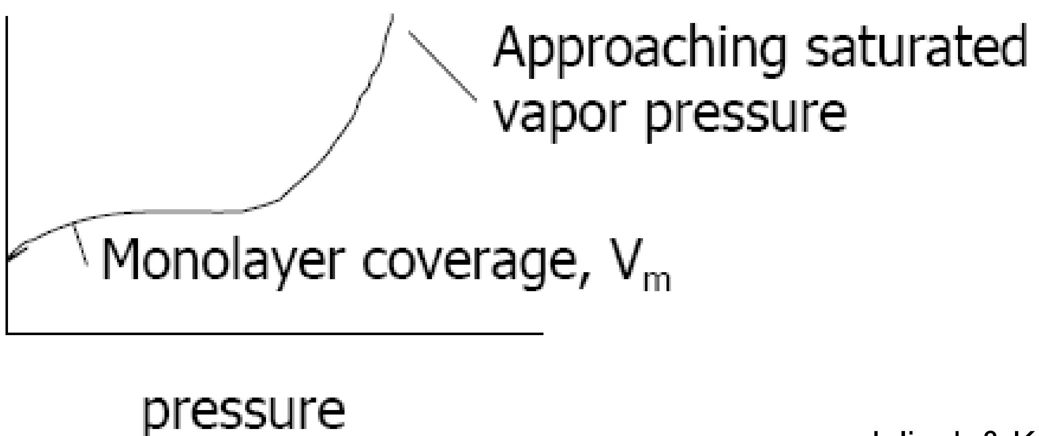
$$S = \frac{N_A V_m A_N}{V_0}$$

A_N area of surface occupied by a single adsorbed gas molecule
N_A Avogadro constant, V_0 = molar volume of gas [cm3/mol] (standard temperature and pressure, STP)

2

Multi-layer coverage - Brunauer, Emmett and Teller(BET)

- Surface does not have specific adsorption sites
- The first layer of molecules (monolayer) adsorb in a two-dimensional compact format
- The next molecules arrives and adsorb in a random fashion on the monolayer – layer by layer (condensation)
- The thickness of the film is only limited by the space above the surface –i.e. until next particle or surface is encountered.



« Packing » or arrangement of nitrogen molecules on surface

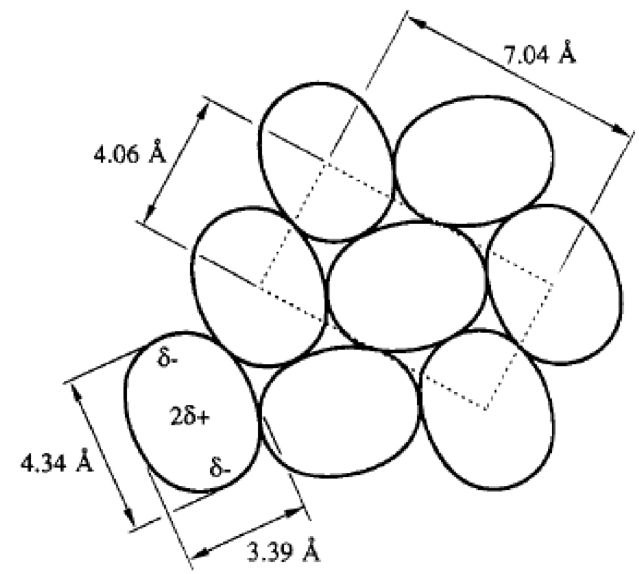
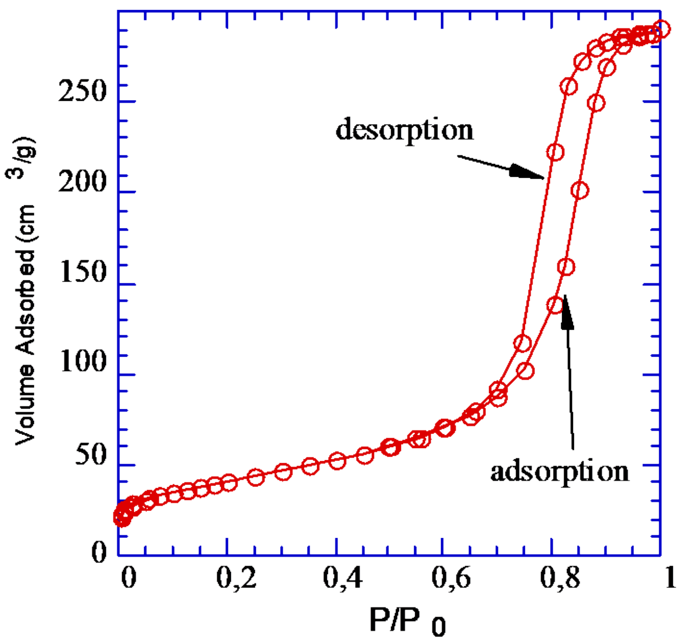


Figure 4. Compact "herringbone" structure of nitrogen molecules in a monolayer with $\alpha(N_2) = 14.3$ Å^2. Molecules are parallel to the surface. In the dense layer adsorbed on silica molecules tilt away from parallel to give the similar but more compact arrangement with $\alpha(N_2) = 13.5$ Å^2.

Jelinek & Kovats, Langmuir, Vol. 10, No. 11, 4225-5231, 1994

Specific Surface Area – Nitrogen Adsorption – BET Model

- Evaporation – condensation of layers are same after first layer
- Assumed infinite number of layers at $P=P_0$
- If applicable to the measured isotherm from the linear form of the BET equation
- V_m and C can be evaluated – normally limited to P/P_0 from 0.05 to 0.3
- collecting 5 data points – 5 point BET method



Y C m X

$$\frac{P}{V_a(P_0-P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C}\cdot\left(\frac{P}{P_0}\right)$$

- C is a constant related to the heat of adsorption of the first gas layer and heat of liquefaction of the adsorptive
- When BET representation is valid C is between 5 and 100 (but up to 300 can be accepted)
- If negative or very high indicative of microporosity – need to modify equation - if <5 adsorptive interaction strong

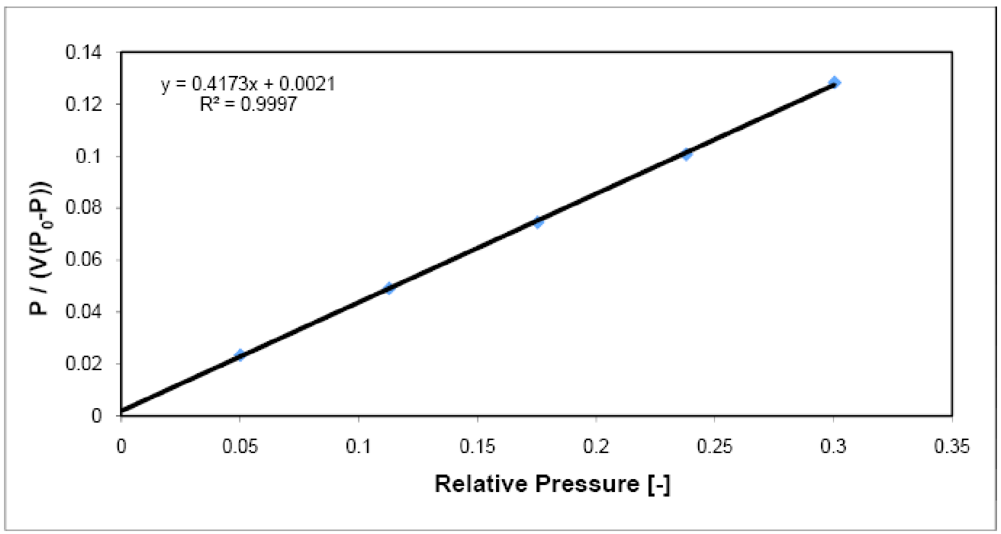
BET linearised plot – example for gamma alumina CR125

3

Y c_i m   X

$$\frac{P}{V_a(P_0-P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C}\cdot\left(\frac{P}{P_0}\right)$$

Sample Weight:	0.1033 g
Saturation Pressure:	742.97 mmHg
Surface Area:	**100.4830 m^2g^{-1}**



- When data follows the linear trend of the BET adsorption model - assume model describes the adsorption
- Use slope and the intercept to get the monolayer coverage – Vm –
- calculate the SSA – assuming the area occupied by a gas atom or molecule on the surface

$$S_{BET} = \frac{N_A V_m A_N}{V_0} = SSA$$

For A_N : use N_2 – 16.2 x 10^{-20} m^2 ($Å^2$)

- SSA from PSD CR125 = 13 m^2/g

$$SSA = \frac{6}{\rho}\cdot\left(\frac{\sum n_i d_i^2}{\sum n_i d_i^3}\right)$$

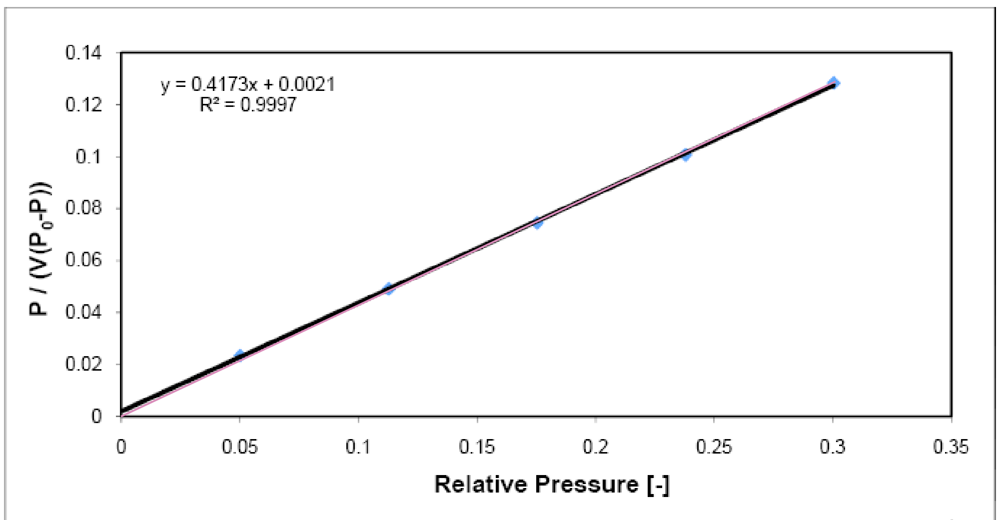
- d_{v50} = 200nm /d_{BET}= 17.6 nm
- Fag = 11.3

BET linearised plot – Single point approximation

Y → m X

$$\frac{P}{V_a(P_0 - P)} = \frac{1}{V_m} \cdot \left(\frac{P}{P_0} \right)$$

Sample Weight:	0.1033 g
Saturation Pressure:	742.97 mmHg
Surface Area:	**100.4830 m^2g^{-1}**



- c_i= 0.0021 $1/V_m\, c_i \sim 0$
- Equation simplified
- For CR125 gamma alumina
- 5 point = 100.7 m^2/g
- 1 point = 99.3 m^2/g
- Certain instruments* can use flow through gas system and collect single point measurement in 15 minutes – very useful if you have 20 samples to compare….

- SSA from PSD CR125 = 13 m^2/g

$$SSA = \frac{6}{\rho} \cdot \left(\frac{\sum n_i d_i^2}{\sum n_i d_i^3} \right)$$

- d_{v50} = 200nm /d_{BET}= 17.6 nm
- Fag = 11.3

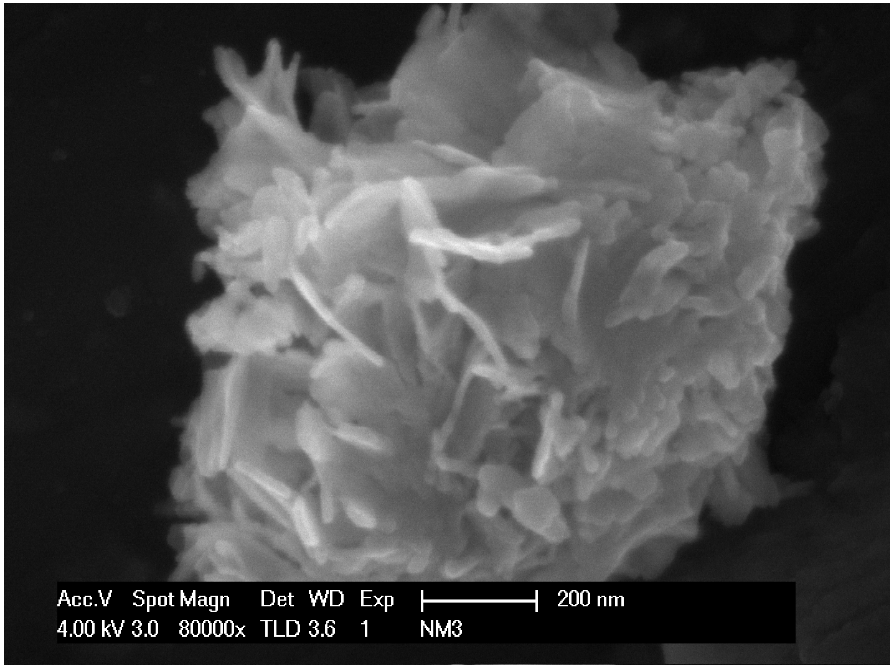
*Monosorb Quantachrome, Flowsorb Micromeritics

Nanometrology – 11 Protocols for Powder Characterisation

- Developed in COST Action 539 – ELENA – nanopowders for advanced ceramics - 22 countries – 48 labs needed standard protocols for partners or anyone using other instruments
- A basis for good laboratory and inter-laboratory practice and a bit of our experience...
- Available on LTP –Website - http://lmc.epfl.ch/PTG/research/powder characterisation/ nanometrology
- **Current status**:
  - Specific Surface Area (BET method) ✓
  - Particle size distribution with the X-Ray Disc Centrifuge (XDC) ✓
  - Particle size distribution by Photon Correlation Spectroscopy (PCS) ✓
  - Particle size distribution by Laser Diffraction (LD) ✓
  - Mean Crystallite Size by X-Ray Diffraction (XRD) ✓
  - Particle size distribution with Disc Centrifuge (light detection) (CPS) ✓
  - Density by helium pycnometry ✓
  - Themogravimetric analysis (TGA) ✓
  - Zeta Potential using Electrophoresis ✓
  - Nitrogen Adsorption Desorption (NAD) – porosity ✓
  - Zeta Potential using the Colloidal Dynamics - Acousto Sizer II ✓

2

Partner Powder -Hydroxy apatite ($Ca_{10}(PO_4)_6(OH)_2$



- Very Heavily agglomerated
- Fag = 230 (flake - 52)
- Shape plate-like
- Very difficult to characterize
- SSA – at EPFL 80 m^2/g
- SSA – from group 120 m^2/g
- Degassing temperature
- 200°C (LTP) vs 110°C!!!!
- Protocol….protocol…protocol…

NANOPOWDER METROLOGY

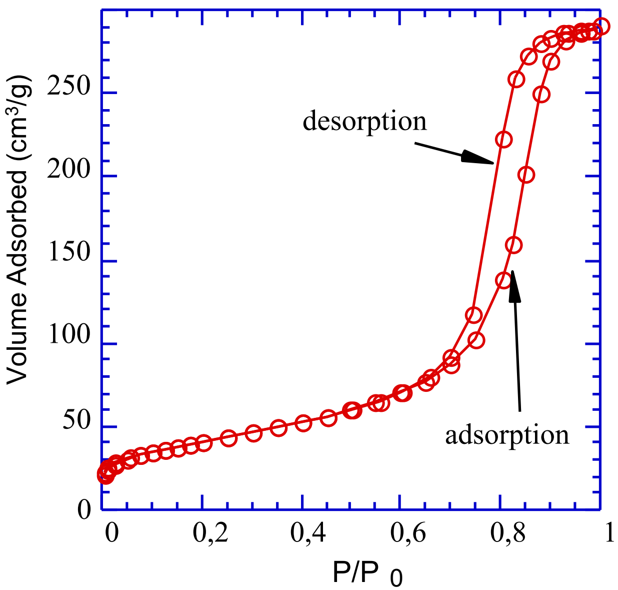
COMPARISON OF MEASUREMENTS BETWEEN GROUPS

Anne Aimable, Paul Bowen

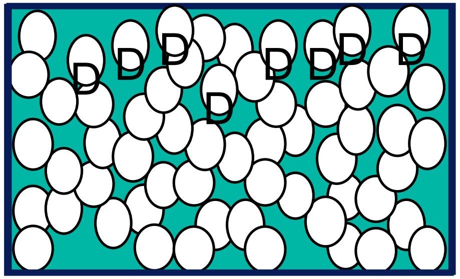
J. Proc. & Appl. Ceramics, 4[3] 147-156 (2010).

Porosity from Nitrogen Adsorption Desorption (NAD) Isotherms

The pore size distribution can be calculated based on the theory of capillary condensation, which is the process by which multilayer adsorption from the vapor into a porous medium proceeds to the point at which pore spaces become filled with condensed liquid from the vapor



- Type 4 isotherm adsorption – condensation in pores
- Desorption shows hysteresis
- Pore diameter, 2r, evaluated from the Kelvin eq. Assume cylindrical pores

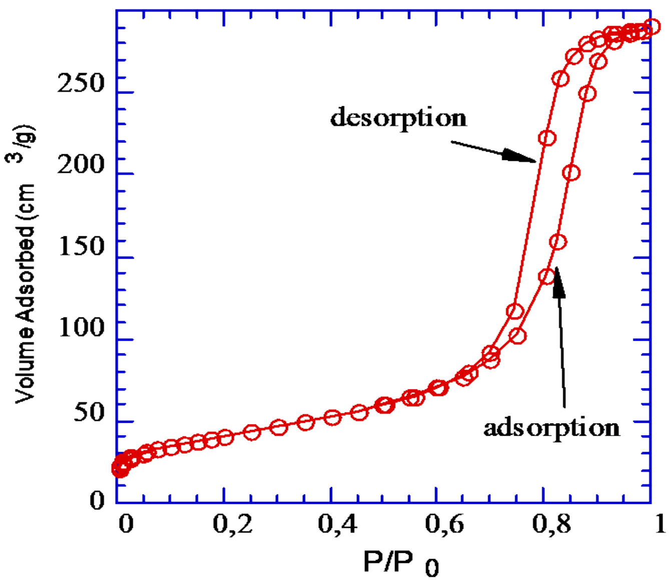


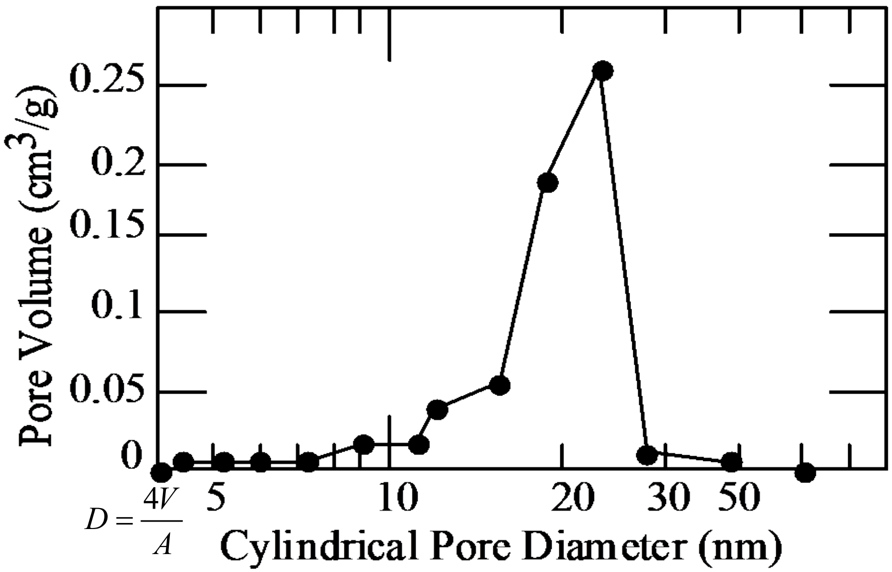
$$\ln \frac{P}{P_0} = \frac{-2\gamma_{lv} V_l \cos\theta}{(r-t)RT}$$

γ_{lv} surface tension at liquid-vapor interface,
t - thickness of adsorbed layer during adsorption,
T temperature in Kelvin
θ contact angle between liquid and pore wall (taken to be zero for N_2)

V_l molar volume of liquid,
R gas constant,

Porosity – Nitrogen Desorption





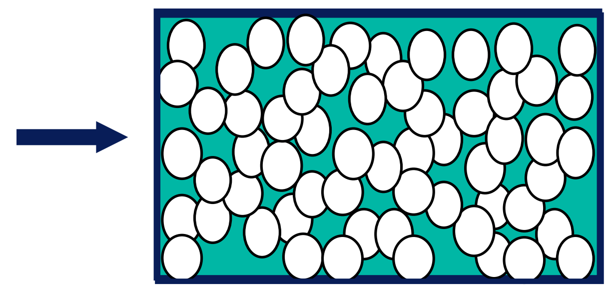
- Pore size distribution from Nitrogen desorption curve - Barret, Joyner and Halenda (BJH) mathematical approach to transform isotherm to distribution - discretisation

- Simple average diameter D for cylindrical pores calculated from geometry
  - total pore volume V and wall area A
  - Can use adsorption, desorption, even BET surface area
  - e.g. boehmite (AlOOH) Ads – 28.2, Des – 25.7, BET 25.7
  - median pore diameter from cumulative distribution – 30.5 nm

Mercury Intrusion Porosimetry - MIP

- Mercury Intrusion Porosimetry, MIP
- Nitrogen adsorption desorption, NAD limited to 2- 200nm (300 at push P_0 99.9…)
- Bigger pores from 250 microns to 2 nm with MIP

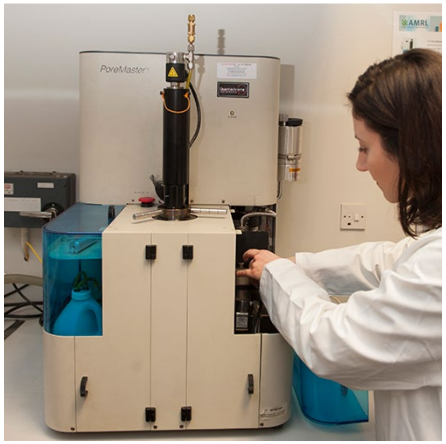
- Mercury does not wet most ceramic materials so in order to force mercury into the porous structure a pressure must be applied.
- Dry powder sample is placed in an ampoule which is then evacuated and then filled with mercury with different applied pressures.
- The capillary force necessary to penetrate a certain diameter pore can then be used to calculate the pore radius, r , assuming a cylindrical form for the pore , Washburn eq.
- 7.5 microns 1 bar, 3.5 nm 2000 bar, 1.5 nm – 5000 bar
- Compressibility of sample – destruction – sudden jump in pore frequency
- Hysteresis – ink-bottle pores – evaluated by multiple intrusion curves



$$r = \frac{-2\gamma_{lv}\cos\theta}{P}$$

θ wetting angle Hg-solid,
γ_{lv} surface tension Hg
P applied pressure

Mercury Intrusion Porosimetry - MIP



Quantachrome poremaster

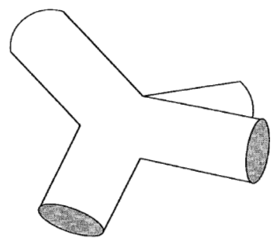


Figure 1. Cylindrical geometric model.

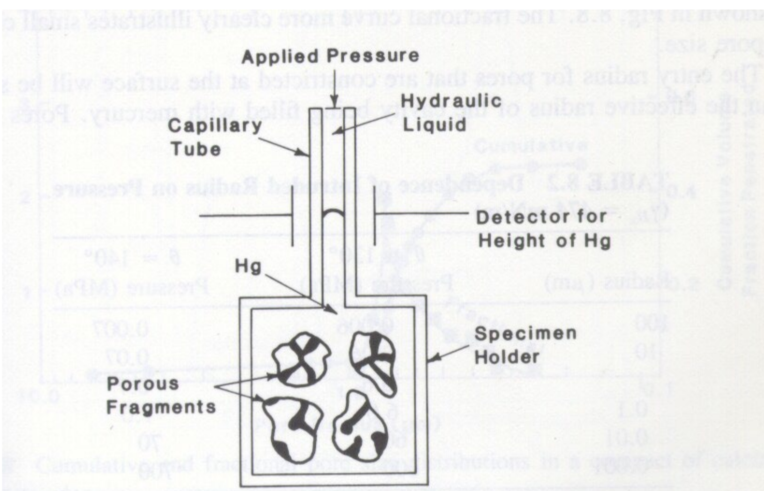
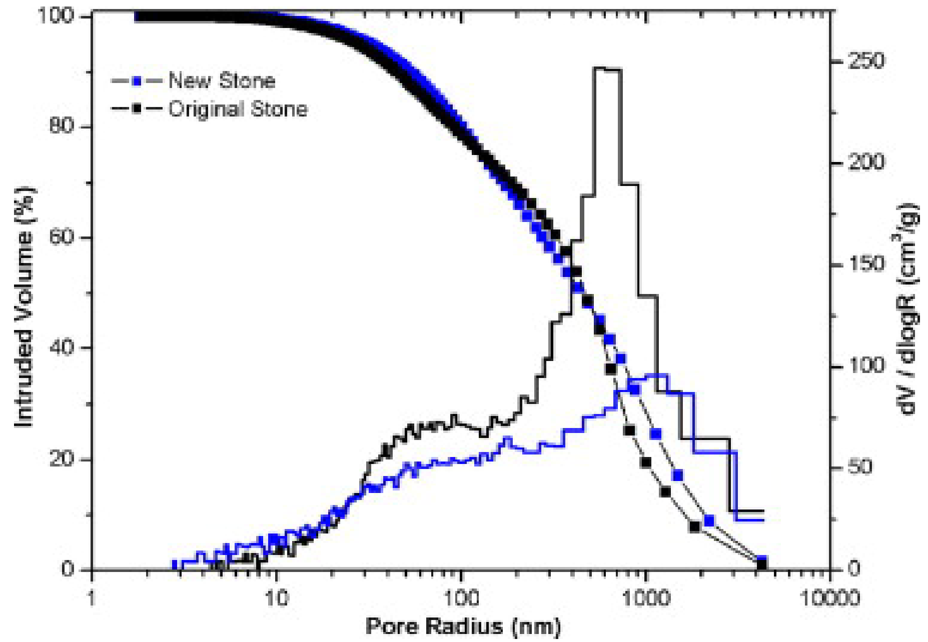


Fig. 8.6 Schematic of mercury penetration porosimetry technique.



MIP pore size distributions fro Archaeological (orginal stone) and laboratory samples (stone) .

Different consolidation treatments of the excavated foundation of the Poseidon Temple in Poros island, Greece, made by a friable, low strength type of local limestone.

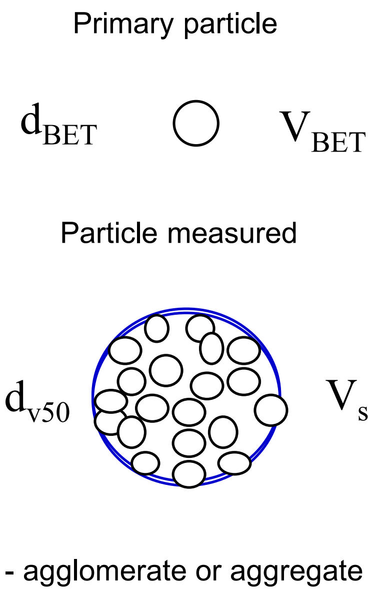
I. Karatasios et al, *Evaluation of consolidation treatments of marly limestones used in archaeological monuments* Construction and Building Materials, 23(8), 2009, 2803–2812

1

Porosity - Agglomeration Factor, Fag - Number, F_N

- Fine powders have the tendency to form agglomerates – no chemical bonds (during forming) or aggregates – chemical bonds (synthesis)[$]
- Define an agglomeration factor Fag or agglomeration number, F_N *,

$$F_{ag} = \frac{d_{v50}}{d_{BET}} \qquad d_{BET} = \frac{6}{SSA.\rho} \qquad F_N = \frac{V_s}{V_{BET}}$$



- Fag, very good indication of the degree of agglomeration allows comparison between powders and treatments

d_{v50} - median diameter (volume, µm),
d_{BET} is an average diameter (µm) calculated from specific surface area, SSA (m^2/g) measured by nitrogen adsorption (model BET),
ρ powder density (g/cm^3),
V_{BET} volume of sphere from d_{BET} ,

V_s volume of powder in agglomerate of given size, exluding pore volume (estimated from nitrogen desorption pore volume)

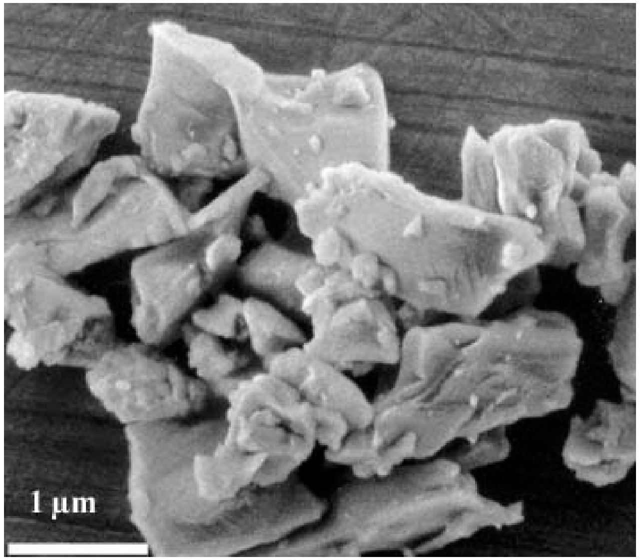
The 6 in the d_{BET} is a shape factor for a sphere, for cubes this is 7.44, parallelepipeds 9.38 and for flakes 24

*German International Journal of Powder Metallurgy Vol. 32 [4] 365-373 (1996)

$Alemán, J. V. *et al.* (IUPAC Recommendations 2007). *Pure Appl. Chem.* 79, (2007).

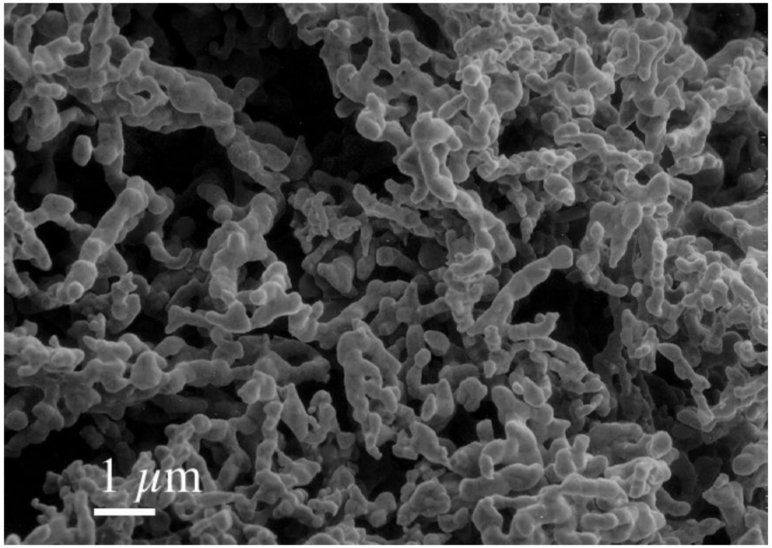
Agglomeration Factor, Fag

Ground Quartz Fag = 4 (sphere)
- NB Shape! Sharp particles = 3.4



parallelepipeds form factor 9.38 ,
Fag = 2.6

Cobalt powder - magnetic
Fag = 10



Primary particles approximately spherical

Chemical Characterisation

- The total composition of the whole defines the intrinsic properties of the material. Dopants of minor elements can be added (0.1 - 5%) (chemical analysis via ICP-OES or ICP-MS);
- Impurities Suppliers of raw powders often give an elemental analysis of the powder and the impurities contained. Subsequent chemical analysis should be performed when a process or property is particularly sensitive to impurities.
- The surface composition of a powder may differ from the overall composition. e.g. 0.6% SiO_2 in alumina - but at the surface 6% changes the charge from positive to negative. This can have an important influence on the suspension and on the sintering mechanisms.
- Techniques see - Surface analysis & Electron microscopy Courses
  - Electron microscopy – elemental spectroscopy
  - X-ray diffraction –XRD - (0.25-1% wt detection limit)
  - XRD also gives the crystal phase and
  - peak broadening can give crystallite size for grains <100-300 nm

Suppliers data…..

α-alumina

BAIKOWSKI

Les Marais Noirs Ouest, BP 501
F-74339 – LA BALME DE SILLINGY cedex
Tél. : 33 (0)4 50 22 69 02
Fax : 33 (0)4 50 22 28 92

Analysis Report

21/05/10

- Experimental -

BMA15

		18821
Specific surface area BET (m²/g)		14.9
PSD Horiba LA 920 (µm)	D10 D50 D90	0.11 0.15 0.22
Chemical analysis (ppm)	Na K Fe Si Ca	14 28 7.5 18 4

Yttrium aluminium garnet (YAG)

Les Marais Noirs Ouest, BP 501
F-74339 – LA BALME DE SILLINGY cedex
Tél. : 33 (0)4 50 22 69 02
Fax : 33 (0)4 50 22 28 92

Analysis Report

21/09/06

- Experimental -

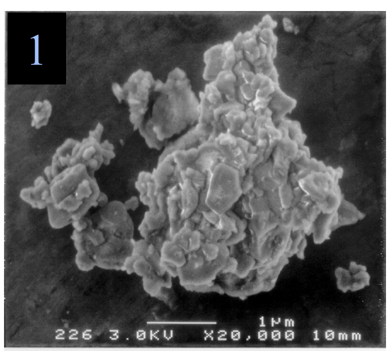
Milled YAG

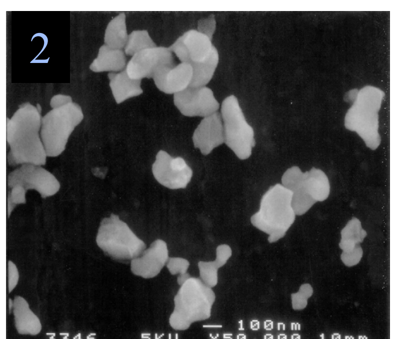
		13073-CR
Specific surface area BET (m²/g)		13.4
PSD Horiba LA 920 (µm)	D10 D50 D90	0.19 0.27 0.80
Chemical analysis (ppm/YAG)	Na K Fe Si Ca Cr Mg Ce	6.7 35 14 94 4 1.7 2.2 37.2

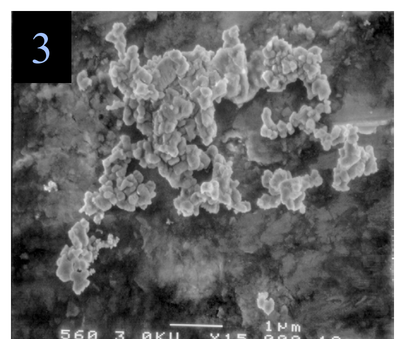
3

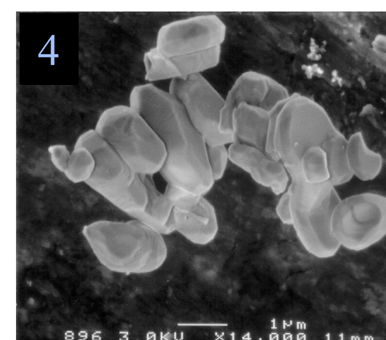
Example: 1 raw synthetic powder (Al_2O_3), 4 different powders

		1	2	3	4
Median diameter (volume)*	D_{v50} (μm)	0.27	0.26	0.21	2.5
Distribution - width	D_{v10}	0.15	0.17	0.15	0.9
	D_{v90}	1.27	0.69	0.44	3.8
Specific Surface Area	m^2/g	8.9	9.8	10.7	1.37
	D_{BET}	0.168	0.154	0.141	1.1
Agglomeration Factor	F_{AG}	1.61	1.68	1.48	2.27
Chemical composition – impurity levels	% Al_2O_3	99.5	99.99	99.99	99.7
	Fe (ppm)	100	4	8	300
X-ray Diffraction - phase purity	% alpha	>98	>98	>98	>98
Thermogravimetric analysis (%organic additive, %humidity)	% wt	0, 0.83	0, 1.0	3.0, 0.2	0, 0.2
Apparent density (granules)	g/cm^3	1.06	1.1	1.2	-
Isoelectric point (for wet processing)	pH	8.8	9.0	9.0	6.7
Price	€/kg	5-20	80-100	80-100	5-20









Learning Outcomes and questions

Acquired knowledge

- Typical characteristics of powders
- Size distributions: common methods
- Sampling: Methods and minimum weight
- Agglomeration factor
- Density: absolute (theoretical) and apparent
- Open porosity, closed
- Specific surface area: nitrogen adsorption, BET method

Questions (more in depth questions in exercises)

- What are the 2 essential parameters to describe a size distribution?
- What is the most common assumption about the shape of a particle?
- How to measure size distributions from 25-1000 µm?
- How to measure sizes < 300nm?
- How to measure the specific surface of a powder?
- How to measure the porosity of a powder or a powder compact (green body)?