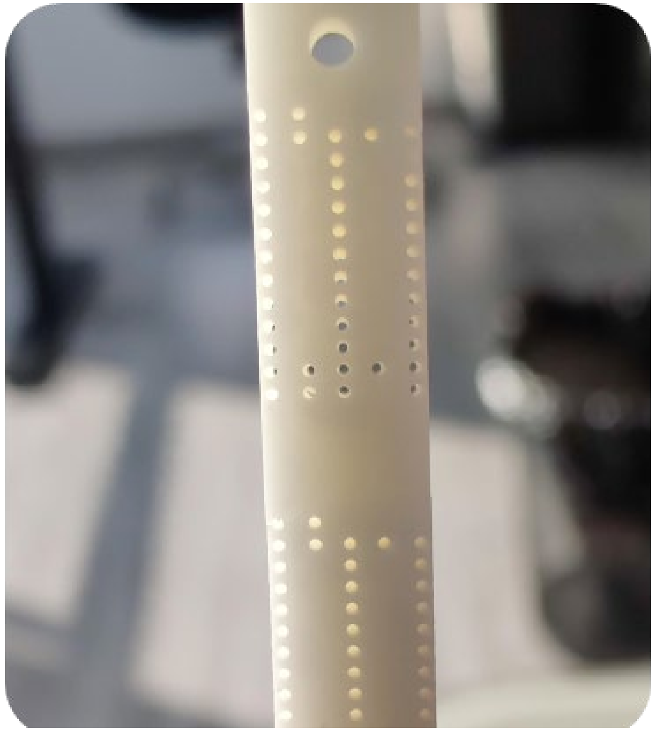
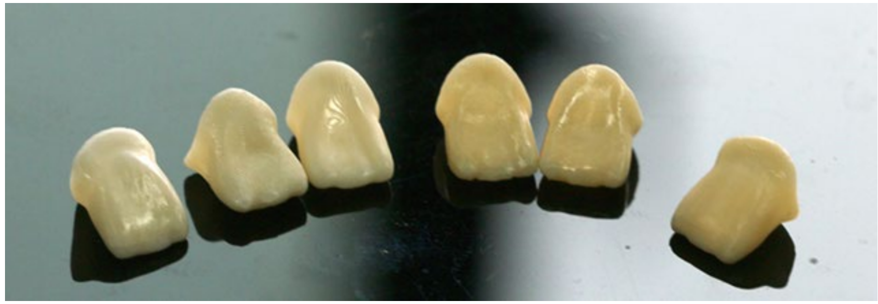
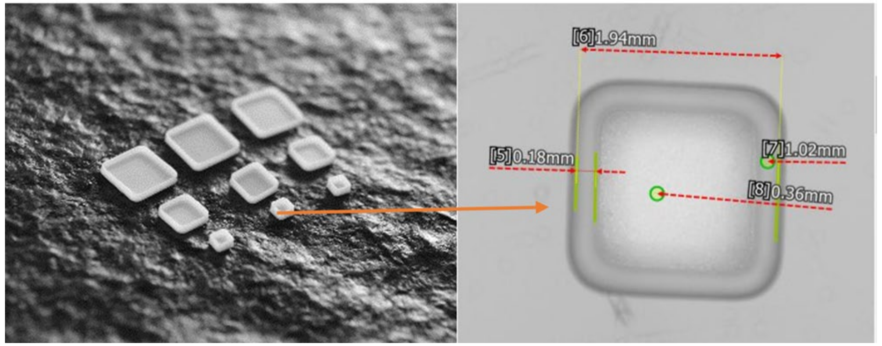
MSE 495 – Advanced Ceramics Technology

Michael Stuer (Empa) - Andrea Testino (PSI)

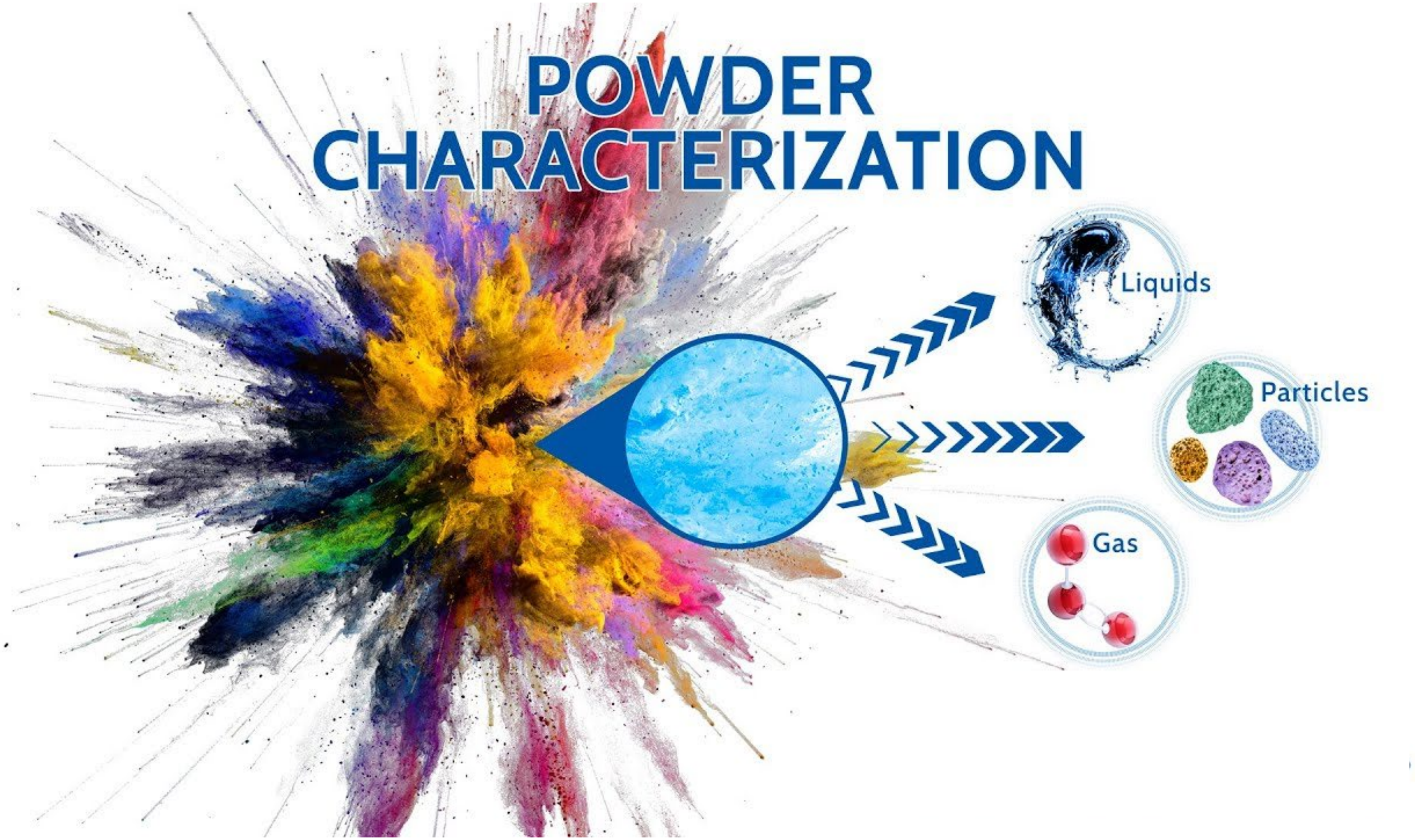
Week 2 – Powder characterization



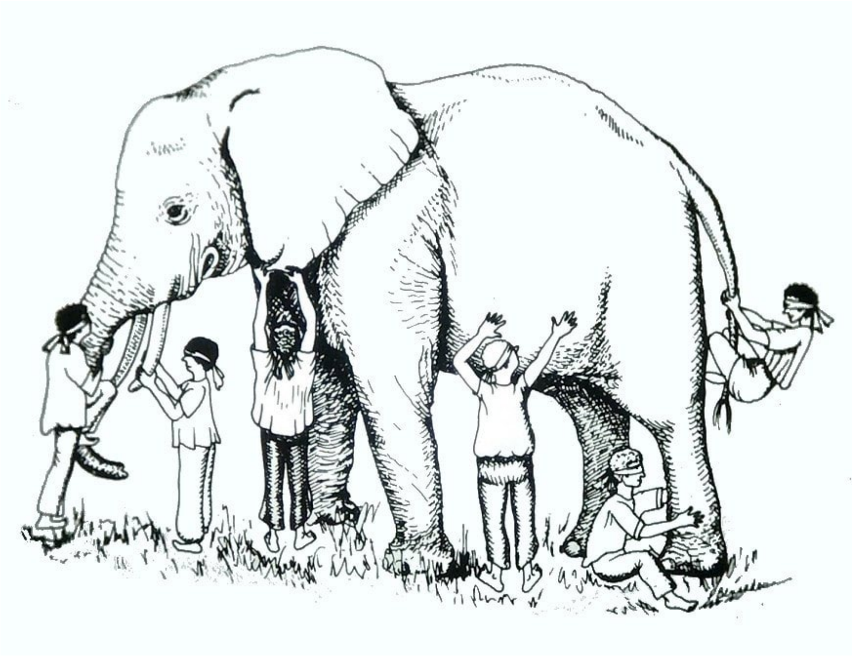




Introduction to powder characterization



Complementary techniques: it is just the minimum requirement

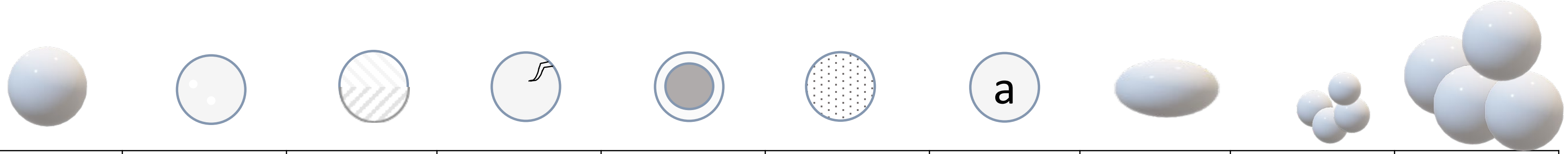


Do not be blind...

Minimum requirements for a generic materials

1. Diffraction (X, n) (LR, HR)
2. SSA and poreSD (e.g., N_2 sorption)
3. Density (e.g., He-pycnometry)
4. PSD (e.g., laser scattering methods)
5. Micrography (LR, HR)
6. Chemical composition (ICP, Local)
7. Spectroscopy (FTIR, Raman, XAS, NMR,…)

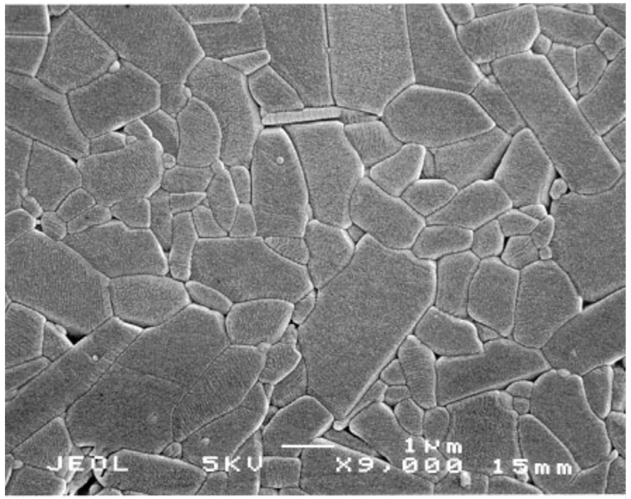
Example: multi-technique characterization



		Single crystal spherical particle	Internal close pores	Multi-domain	Open pores	Core-shell	Clusters segregation	(Partially) Amorphous	Different shape	Small aggregate	Aggregated particles
$/$$	Diffraction (X, n)	**REFERENCE**	🙁	🙂	🙁	🙂	😐	🙂	🙁	🙂	🙁
$$	SSA – PoreSD		🙁	🙁	🙂	🙁	🙁	🙂	🙁	🙂	🙁
$	Density		🙂	🙁	🙁	🙁	🙁	🙂	🙁	🙁	🙁
$	PSD		🙁	🙁	🙁	🙁	🙁	🙁	😐	🙁	🙂
$	Micrography (LR)		🙁	🙁	🙁	🙁	🙁	🙁	🙂	🙂	🙂
$$$	Micrography (HR)		🙂	🙂	🙂	🙂	🙂	🙂	😐	😐	😐
$/$$	Chem. Comp (ICP)		🙁	🙁	🙁	🙁	🙁	🙁	🙁	🙁	🙁
$$$	Chem. Comp (Local)		🙂	🙁	🙂	🙂	😐	🙁	🙁	🙁	🙁
$/$$	Spectroscopy		🙁	🙁	🙁	😐	🙂	😐	🙁	🙁	🙁

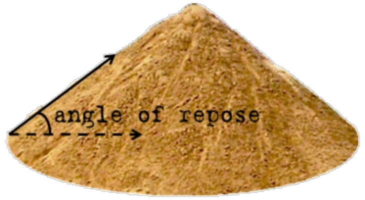
Why characterize powders?

- 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



Important Powder Characteristics

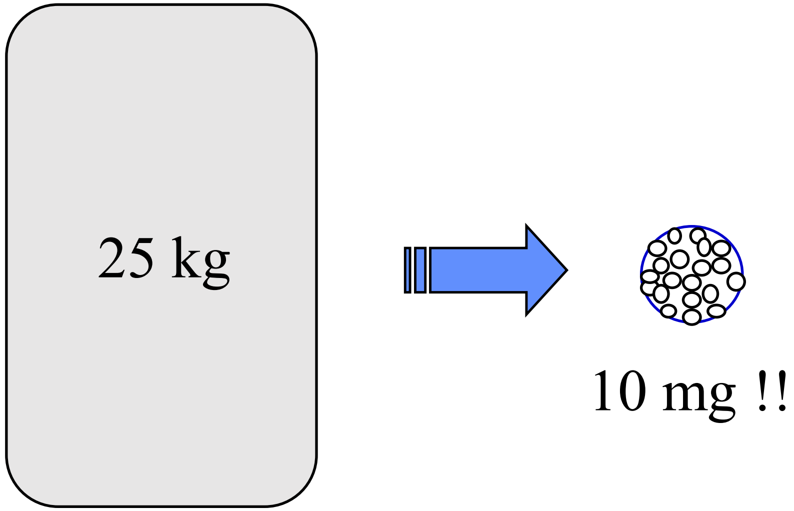
- Size and size distribution
- Morphology and shape factor - microscopy and image analysis
- Specific Surface Area - gas adsorption (N_2 , >0.1 m^2/g)
- Porosity (internal structure) - adsorption-desorption of gas, mercury porosimetry (MIP)
- Crystalline Phase - X-ray diffraction (crystallite size from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



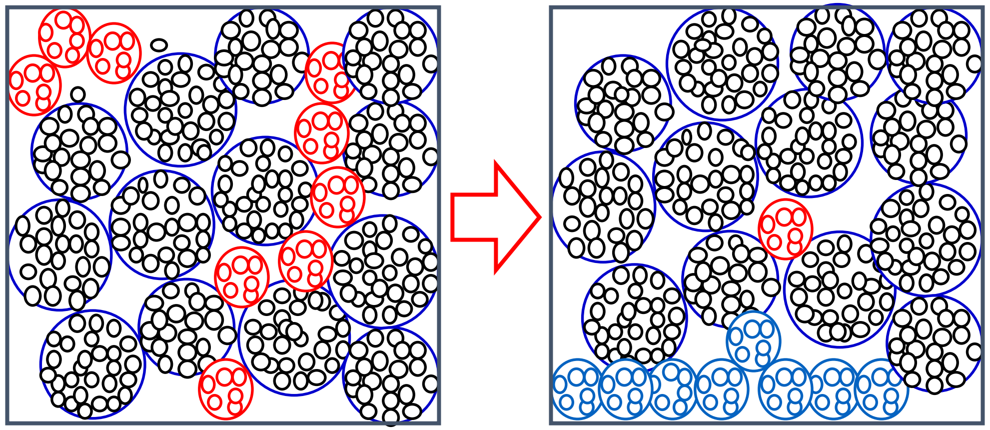
* L. Svarovsky, Powder Testing Guide, Elsevier Applied Science, London, 1987.

Sampling

- 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 - Golden Rules

Important that analytical sample representative of whole

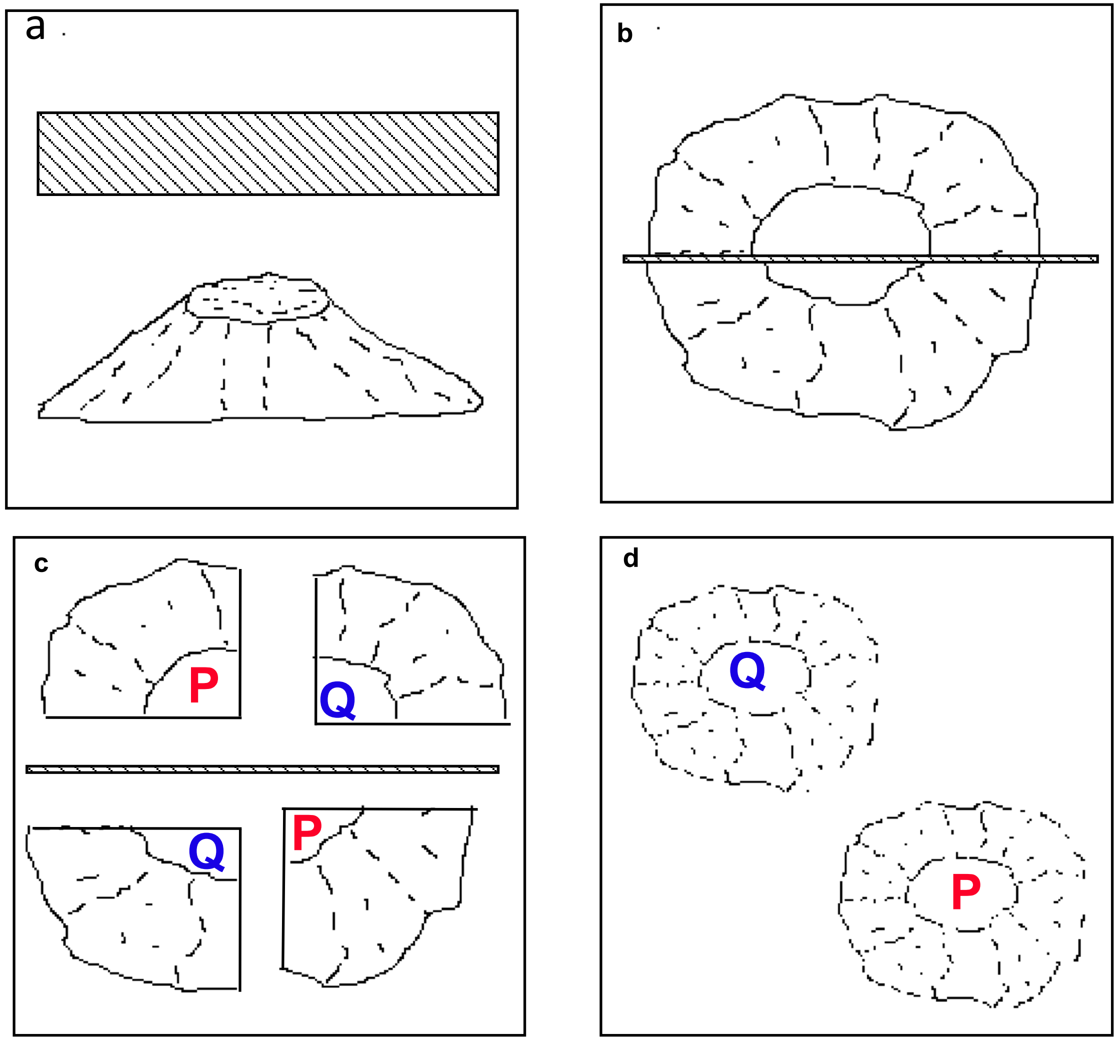
- "golden rules of sampling"* should be applied,
  - always sample a powder when it is in motion
  - take several small samples at different intervals rather than one larger sample

- Not always possible
  - other methods

Spinning Riffler or Rotary Sampler

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

Sampling - Cone and division into quarters



Very often -

- **Spatula in a pot**
- Mix pot first
- Take sample of medium

Sampling - Minimum number of samples

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

$$n = \left(\frac{t \cdot \sigma}{X}\right)^2$$

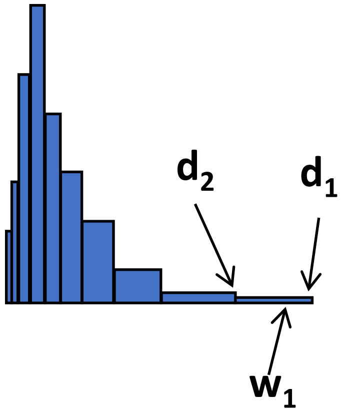
- t - t-distribution t ≈ 2 for a confidence level of 95%
- σ is the standard deviation of the distribution of our sample

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 form suspension: shaking/sonicate before sampling!

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), s_i^2 is the variance of the tolerated sample error
- r_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)

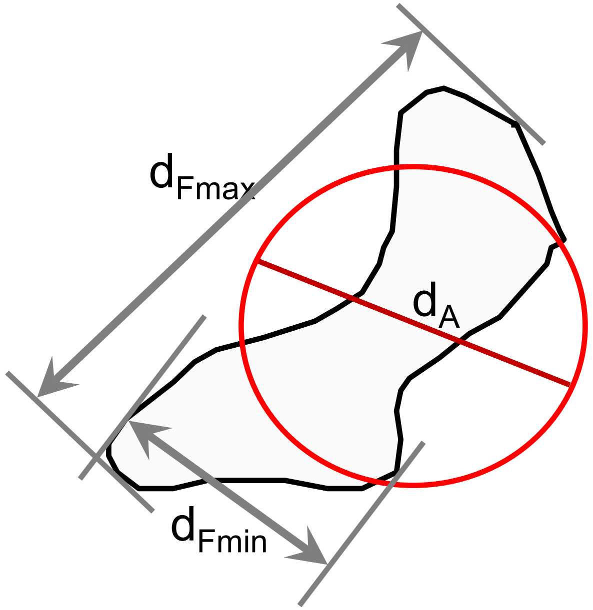
- e.g., for a sub-micron alumina (Alcoa A16SG) 0.3 mg is sufficient for s_i 0.05 **but**
- For a glass spheres with a broad distribution from 10 to 1000 microns need 200g !!!!

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

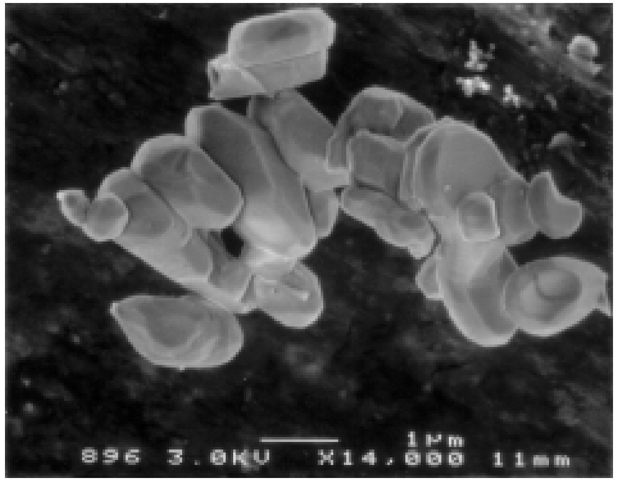
Different Particle Diameters

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 angles between 0 and 180°
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

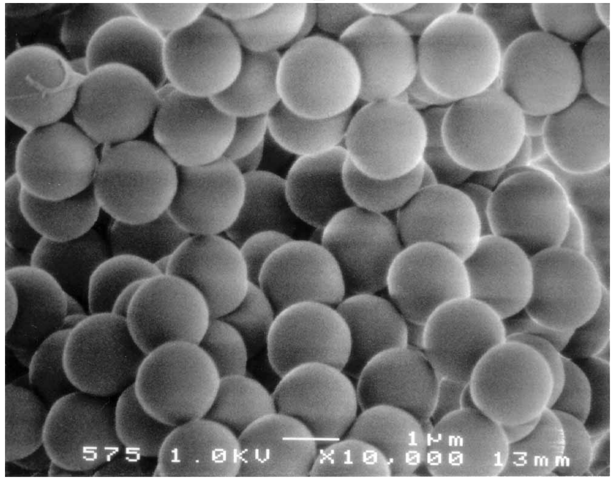
Diameters and distributions



Alumina – irregular shape



Silica - spherical



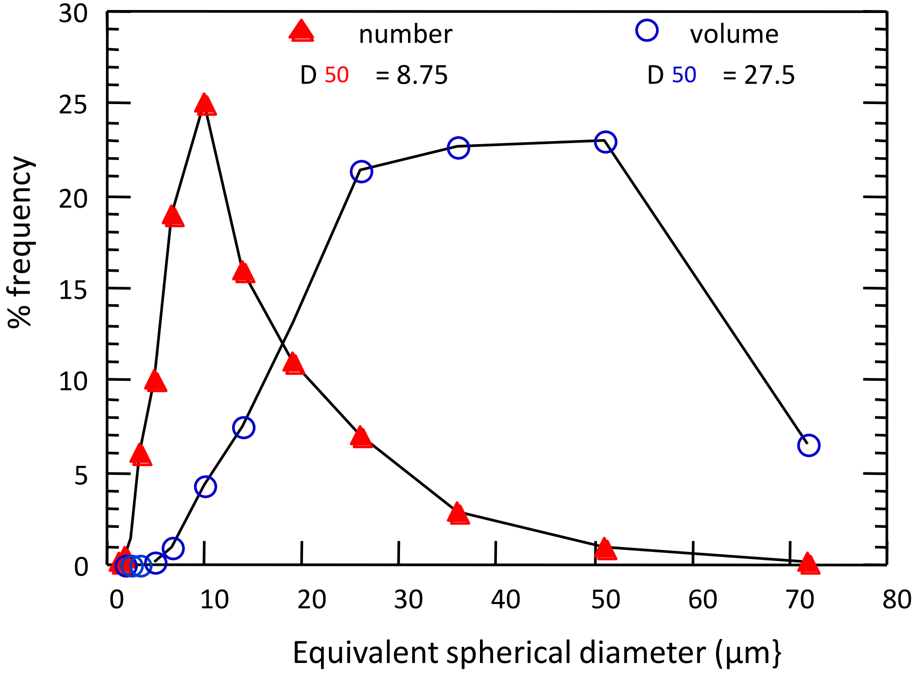
d_{Fmax} : Maximum Feret diameter
d_{Fmin} : Minimum Feret diameter
d_A : Equivalent circular diameter with same projected surface area as the particle

Sphericity (W_w):

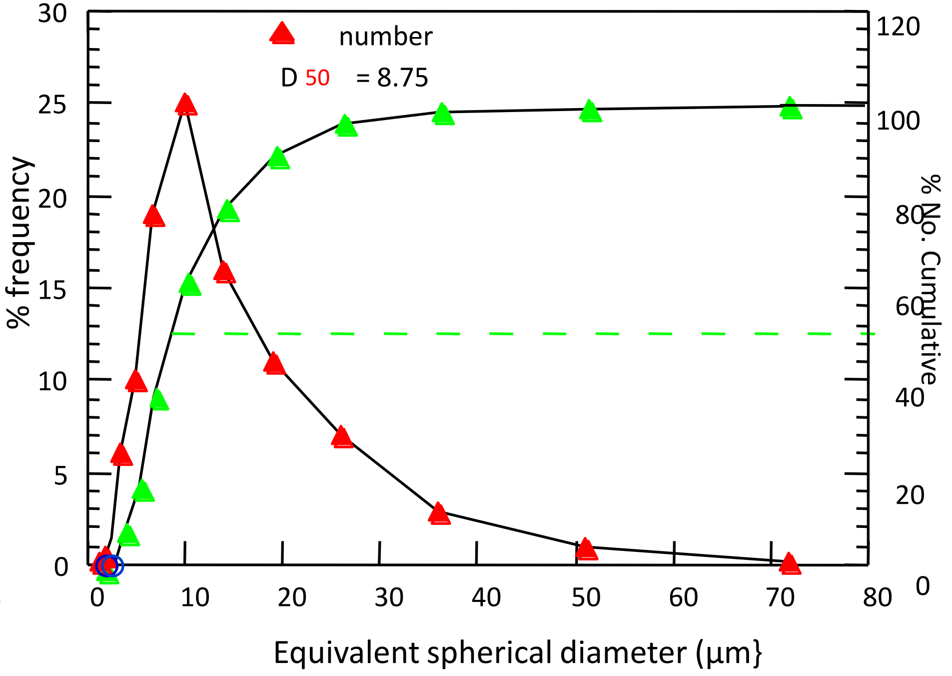
$$W_w = \frac{Specific\ surface\ area\ of\ a\ sphere\ with\ same\ volume\ as\ particle}{Specific\ surface\ area\ \text{of particle}}$$

Diameters and Distributions

- Number or volume - distribution base

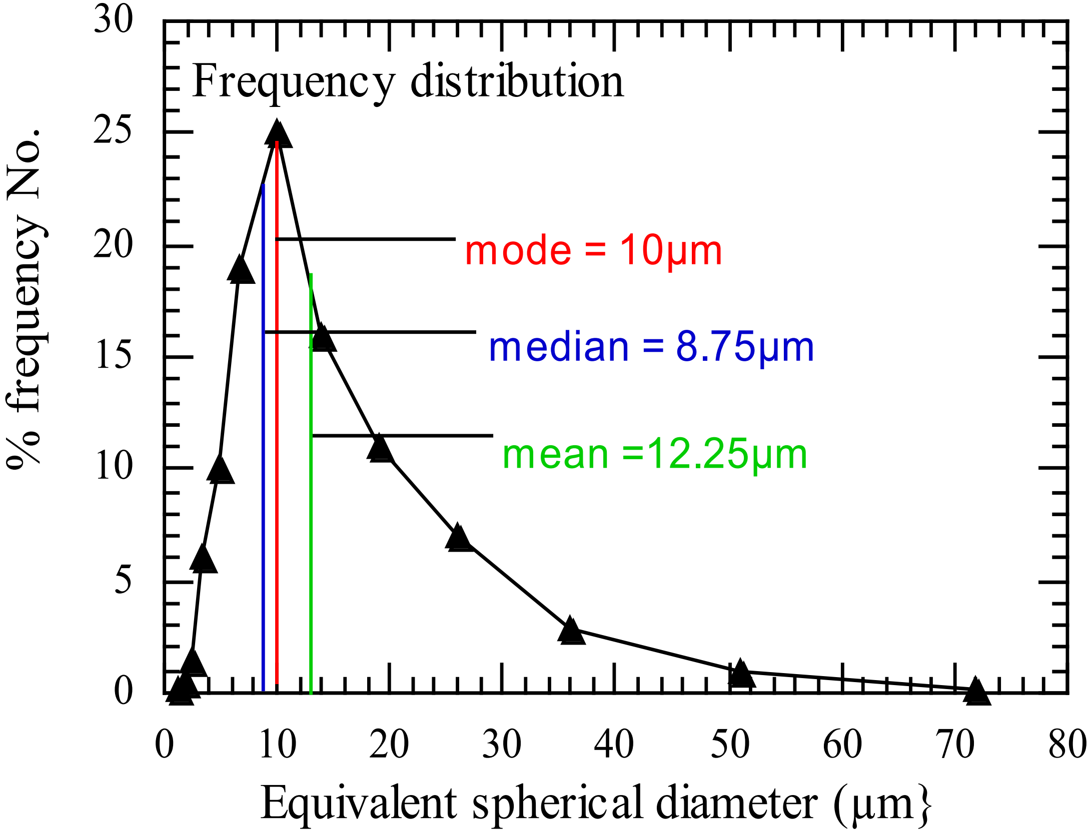


- Frequency or cumulative - Less than - Greater than



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

$$d_{BET} = \frac{6}{S_{BET} \cdot \rho}$$

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 - $D_{n50} = 1.12 \mu m$
Narrow size distribution $\sigma_{n50} = 0.55 \ \mu m$

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

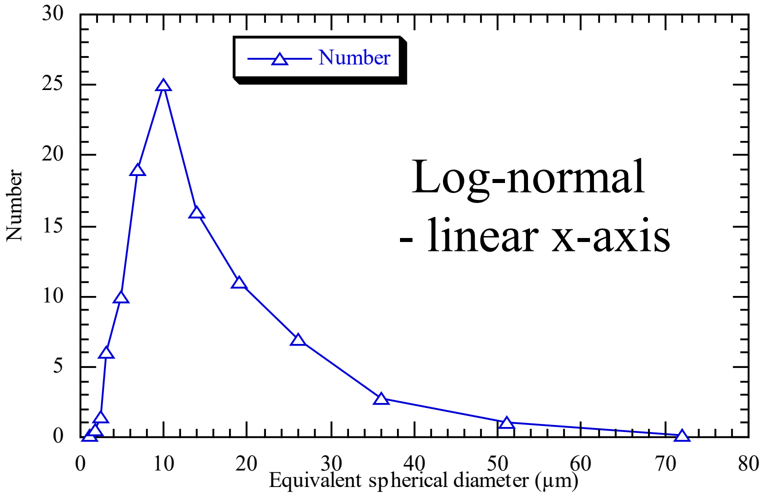
$$d_{vs} = \frac{\sum_{i=1}^{n} d_i^3 N_i}{\sum_{i=1}^{n} d_i^2 N_i} = 1.91 \mu m$$

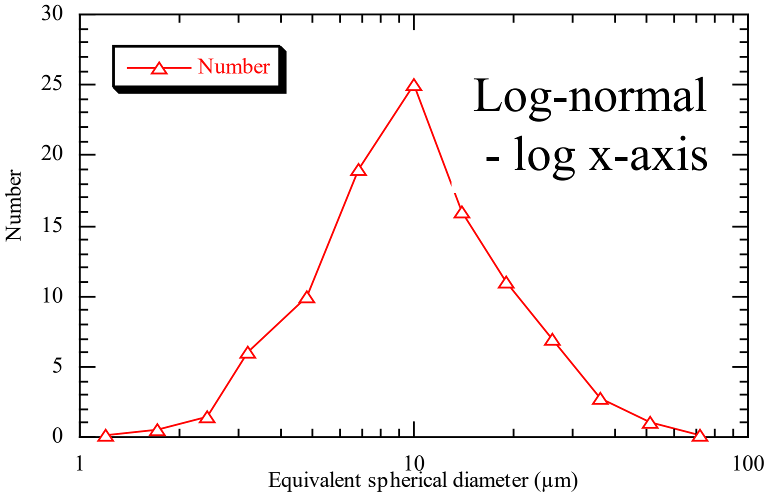
Volume - moment
(mass - moment)

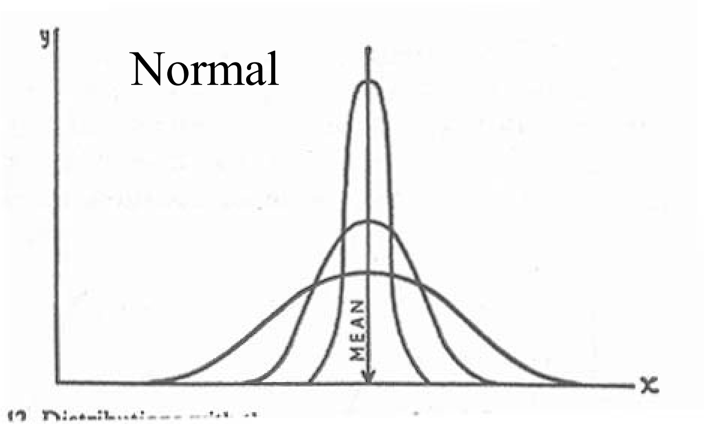
$$d_{4,3} = \frac{\sum_{i=1}^{n} d_i^4 N_i}{\sum_{i=1}^{n} d_i^3 N_i} = 2.21 \mu m$$

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

Types of distributions - graphical examples







At least, two quantities needed: mean (with indication of V, N) and span

Such as DV50 and DV10, DV90 or σ

Good review: Yu & Standish, Powder Technology **62** 101-118 (1990), https://doi.org/10.1016/0032-5910(90)80073-8

Types of Distributions & Widths

Types of distributions*

- **Normal**

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

- s 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

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

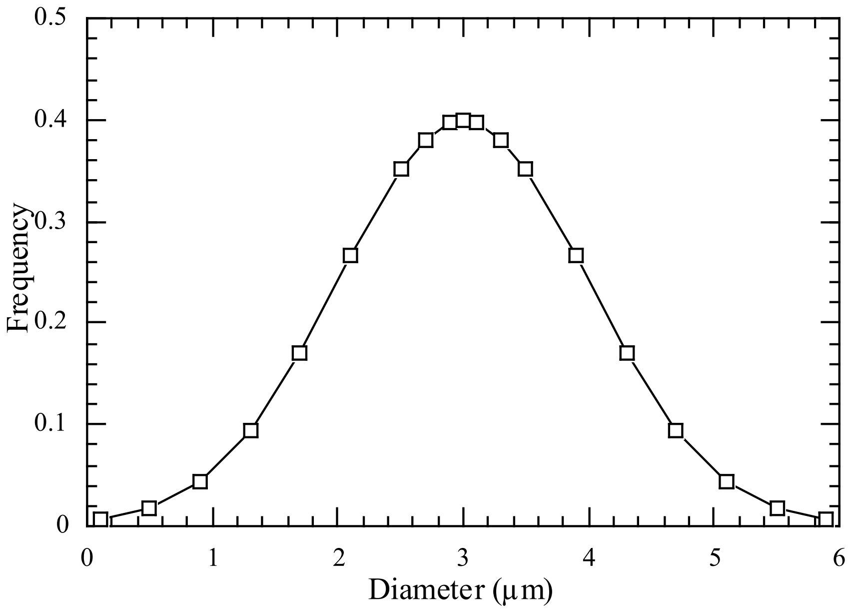
d_v: mean volume diameter
f_i: is the frequency of particles (as a volume) of that diameter
V: total volume for all of the diameter intervals

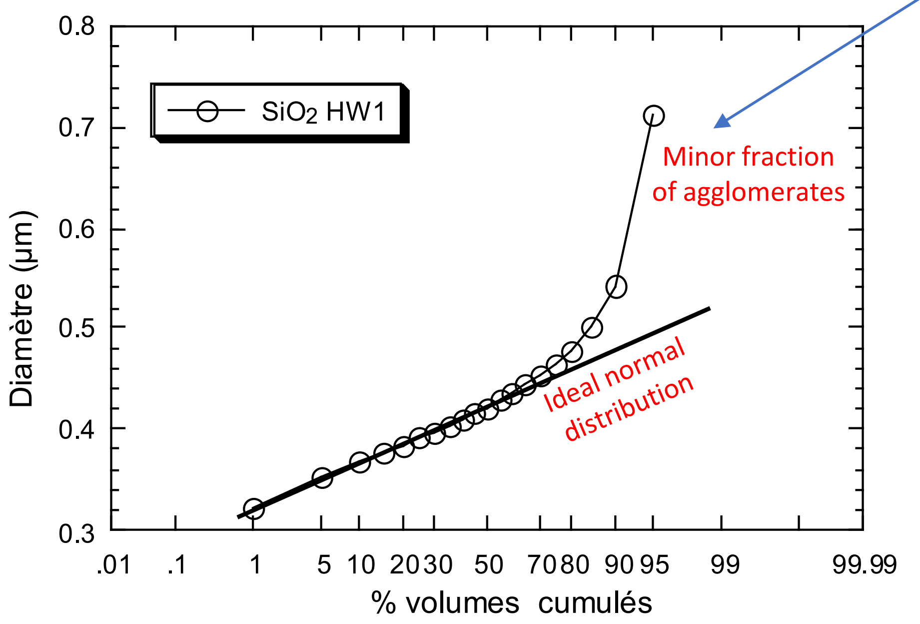
- Span = (d_{90} - d_{10}) / d_{50}

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

Normal Distribution

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





Minor fraction of agglomerates

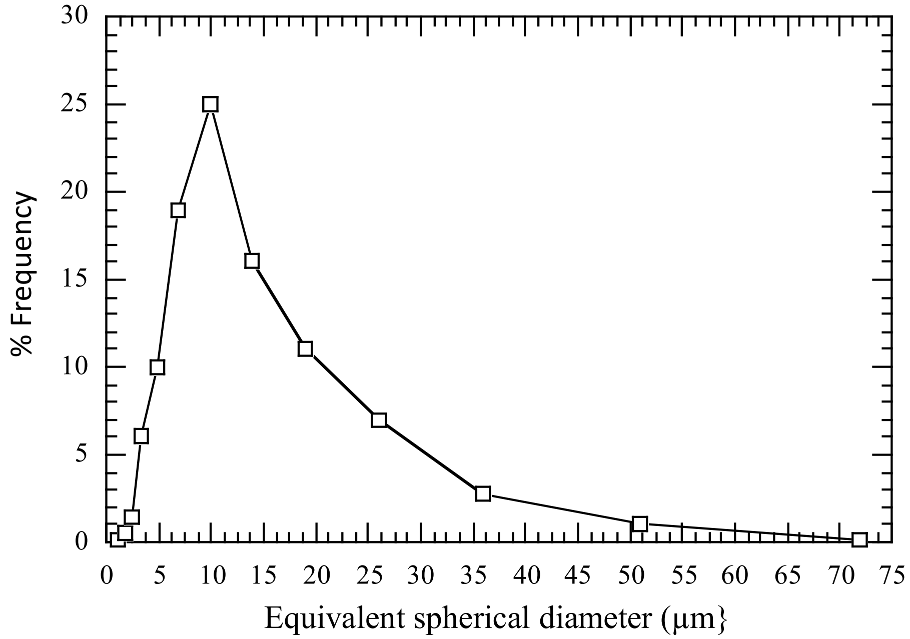
Ideal normal distribution

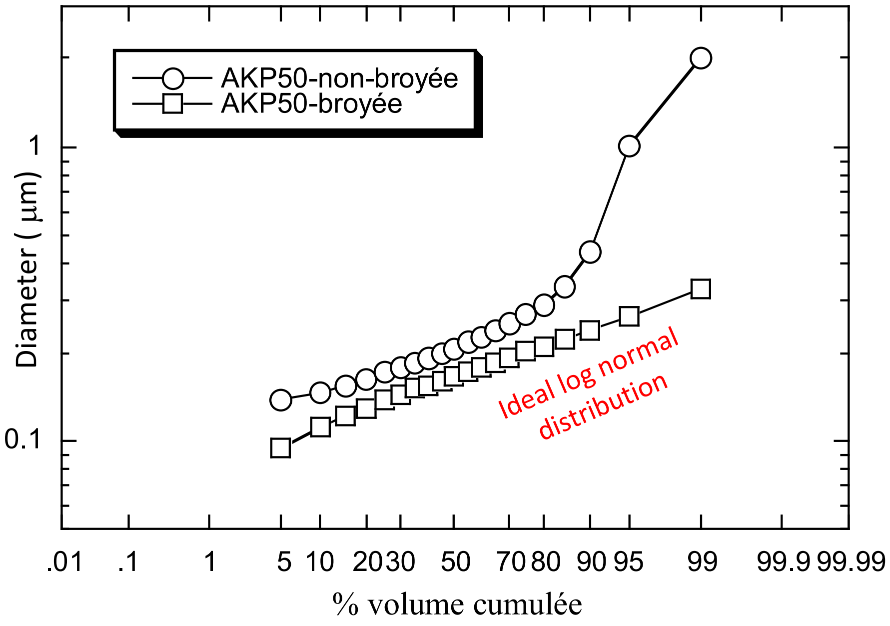
Small fraction of large particles: strong DLS signal!

- **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 (top-down processing, milled powders)

Break: question & discussion

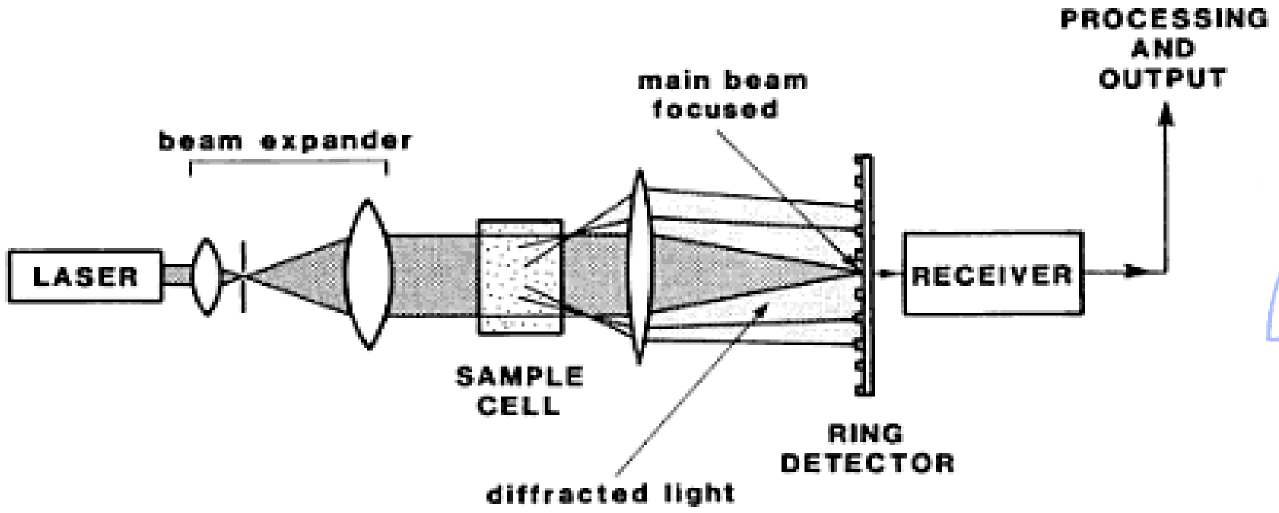
PSD: Current Methods - Brief review

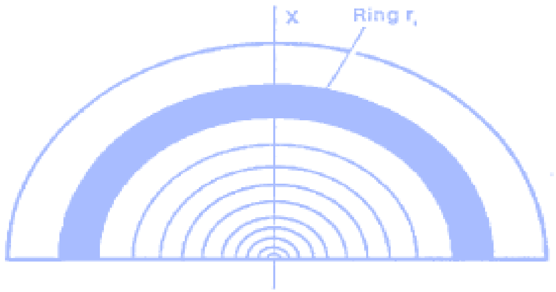
`Method	Medium	Size (µm)	Sample (g)	Time*	Measured Dia.
Microscopy					
Optical	Liquid/gas	400-0.5	<1	S-L	Projected area
Electron	Vacuum	400-0.001	<0.1	S-L	Férèt
Sieving	Air	8000-37	50	M	Sieve
	Liquid	5000-5	5-20	L	
Sedimentation					Stokes
Gravity	Liquid	100-0.5	<5	M-L	Mass
Centrifuge	Liquid	300-0.02	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)

Laser Diffraction





- Variation of the light intensity, I, with angle from the forward direction, q ,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, a =2pl/R, l 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 summarized 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 minimized 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 <u>spherical particle shape</u>.
- Each producer believes his algorithm for data reduction best
- Accuracy – reproducibility - better than 5% whole distribution*
- 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

Particle Shape - Regular Geometries

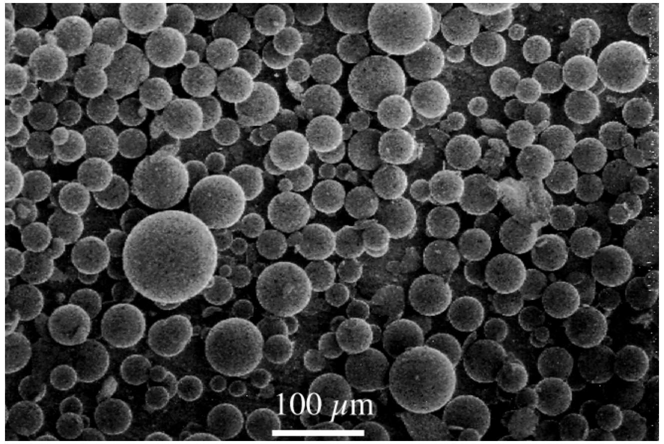
- Most instruments give as an output
  - Equivalent Spherical Diameter (ESD)
  - Often normalized on volume
- ONLY spheres will give comparable results
- Non-spherical particles ESD always smaller than real size and method dependent (Jennings & Parslow)[1]
- Comparison of ESD's from different methods

  - Shape factor - lot of work on clay minerals

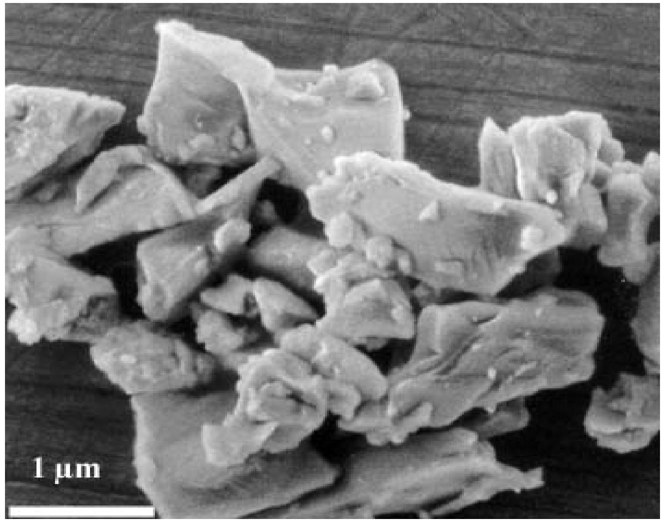
  - Morphology of particles studied not uniform

  - Difficult to compare Image Analysis and other methods

Theory



Reality



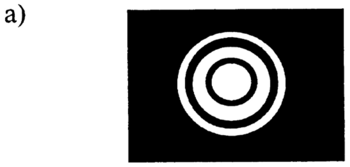
Never trust a PSD measurement without a micrograph!

[1] Proc. R. Soc. Lond. A 419, 137-149, 1988

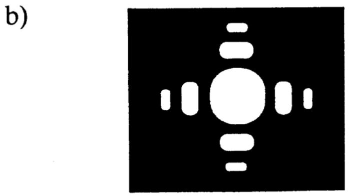
Laser Diffraction - Shape

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

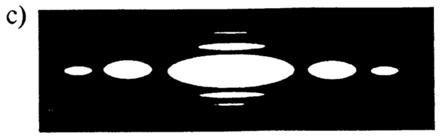
(a) Circular aperture



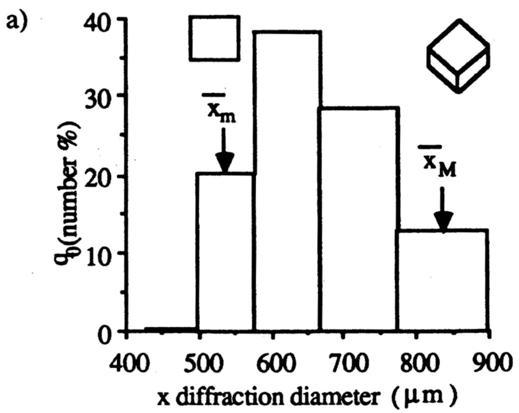
(b) Square aperture



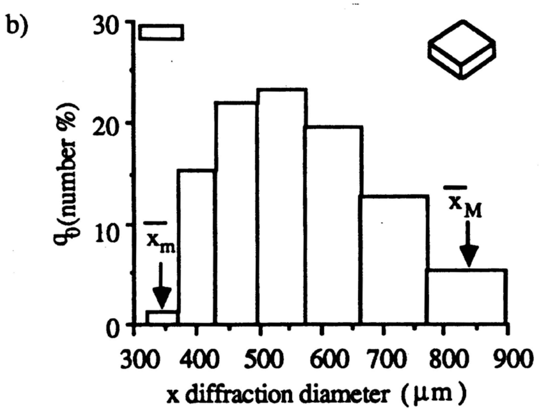
(c) Rectangular
aperture

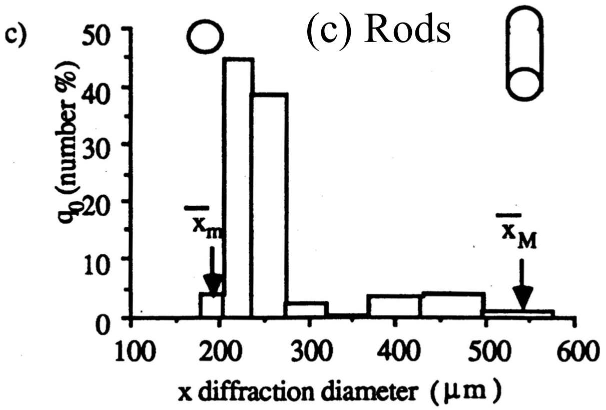


(a) Cubes



(b) Square plates

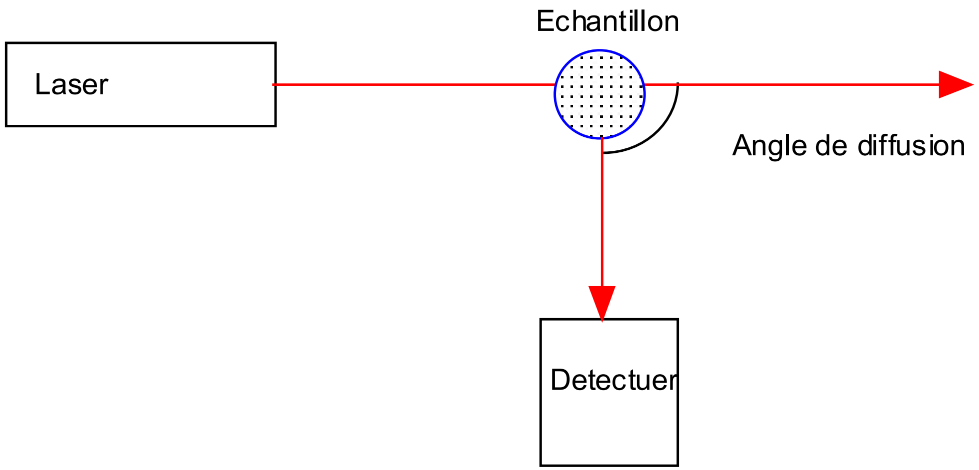



(c) Rods

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

Photon Correlation Spectroscopy - PCS

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



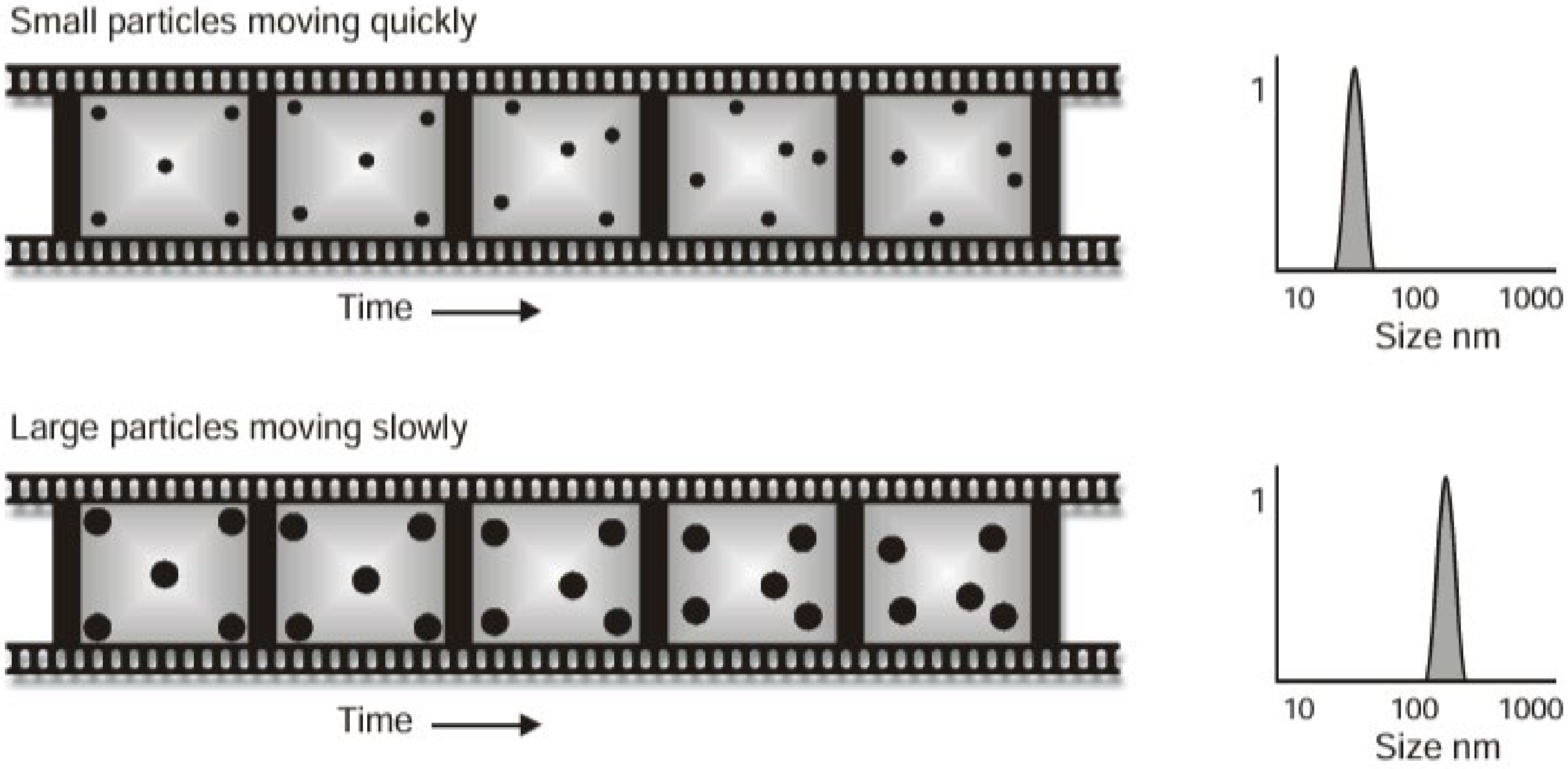
- Rayleigh limit R<< l

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

- 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,
- l 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!

Dynamic particle movement tracking



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+dt,
- Very good - narrow distributions (steep slope in ACF)
  - < 300nm (>1µm sedimentation)
- Very quick (< 1 min)

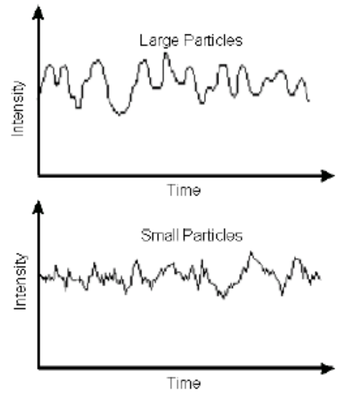
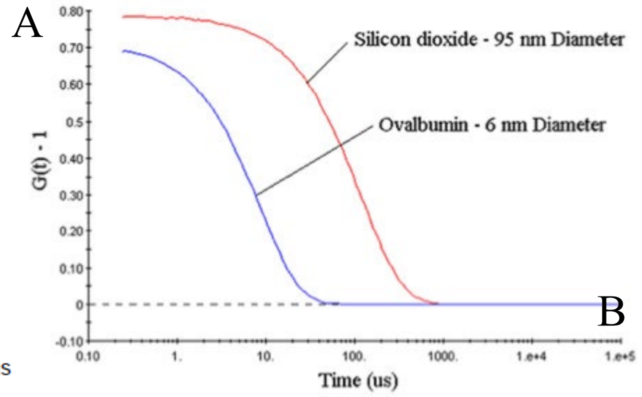


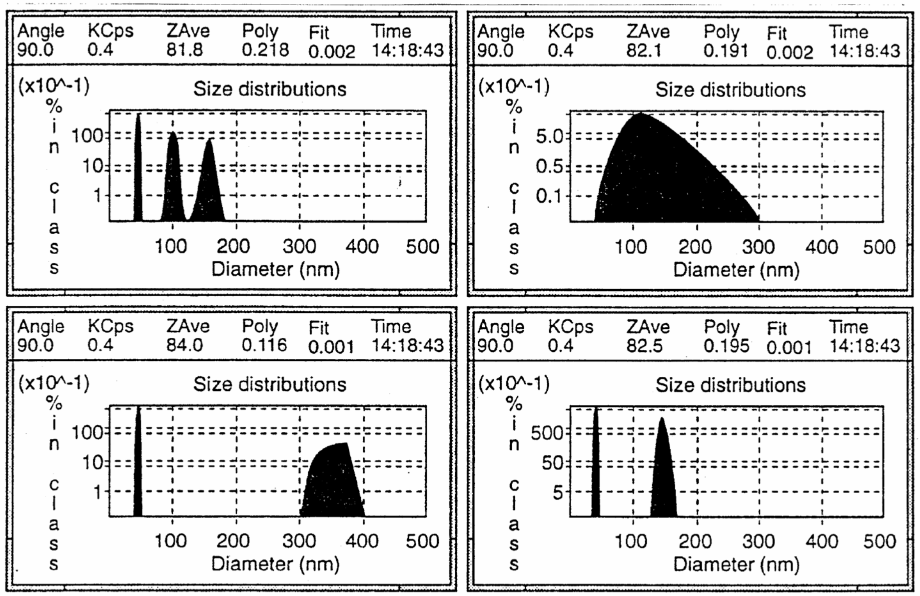
Figure 4: Typical intensity fluctuations for large and small particles

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



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



Angle	KCps	ZAve	Poly	Fit	Time
90.0	0.4	81.8	0.218	0.002	14:18:43
90.0	0.4	82.1	0.191	0.002	14:18:43
90.0	0.4	84.0	0.116	0.001	14:18:43
90.0	0.4	82.5	0.195	0.001	14:18:43

---

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

Brookhaven (X-ray or LED) disc centrifuge

X-ray

Without calibration or absorption correction

LED

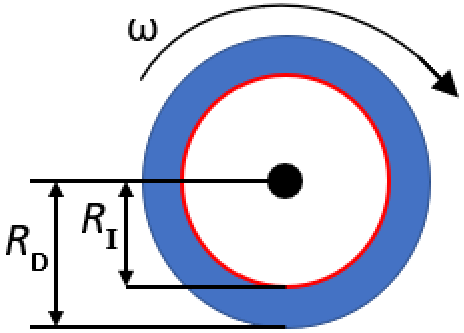
Some optical properties are needed (refractive index)

The final particle size distribution obtained from the BI-DCP depends on hydrodynamics to the extent that this dictates the time required for a band of particles to pass the detector. The optical correction becomes more difficult when materials with complex refractive indices are considered, such as metal and metal oxide particles. These sorts of samples are better suited to X-ray detection (XDC). Higher atomic mass nanomaterials tend to have higher densities, and thus sediment more rapidly. This is common with metal and metal oxide particles

Working principle

This analysis relies on a simplified form of light scattering, namely turbidity. Whereas static and dynamic light scattering rely on the quantification of scattered light to calculate particle size, turbidity only requires that you be able to measure the light *lost due to scattering and/or absorption*, essentially via a reduction in transmittance.

- $I_t = I_0 \exp(-Q_{ext} * C * L)$ where I_0 = incident intensity and I_t is transmitted intensity
- Q_{ext} = Extinction efficiency = $f(d_p, n_p/n_f, \lambda)$
- C = Mass concentration
- L = Path length (width of the fluid segment in the disc)
- Light is either absorbed or scattered, the sum of which is called extinction.
- Extinction is a strong function of particle size. ***Significant optical corrections are necessary for $d_p \leq 5$ µm***
- Sensitive, but less quantitative for high-density materials such as metal oxides where Q_{ext} is not easy to calculate accurately.



$$t = \frac{18 \cdot \eta_L \cdot \ln\left(\frac{R_D}{R_I}\right)}{\omega^2 \cdot \Delta\rho \cdot d_p^2}$$

$\Delta\rho = \rho_p - \rho_L$

Note that the relationship between time and particle size squared is inversely proportional.

Where:

t = time

η_L = viscosity of the liquid

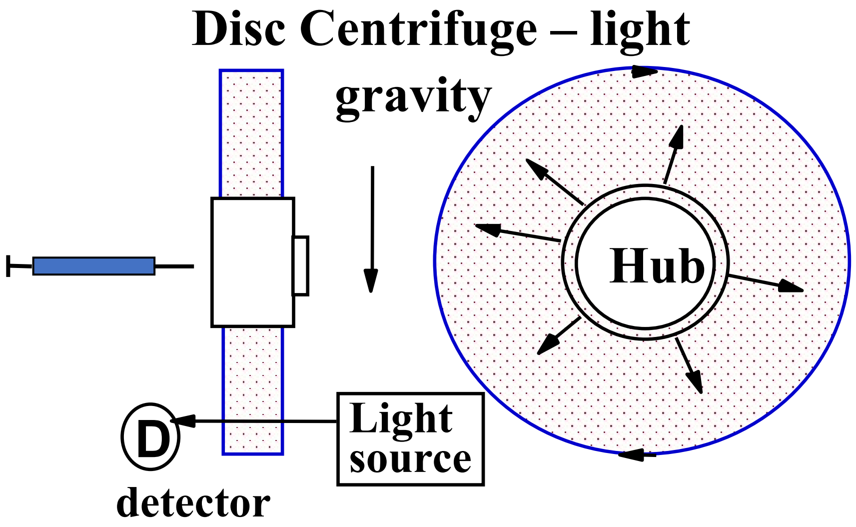
R_D = radius of the detector

R_I = radius to the meniscus

ρ_p = density of the particle

ρ_L = density of the liquid

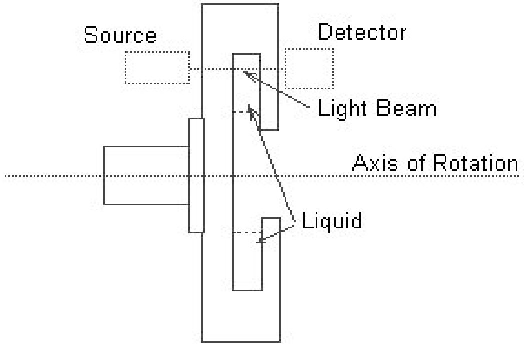
Differential Disc Centrifuge Particle Size Analyser (CPS-DC, CPS Instruments Europe)

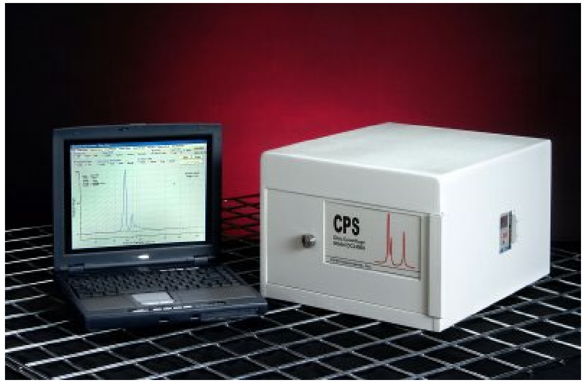


Analysis times

-10 – 60 minutes for 20nm particles

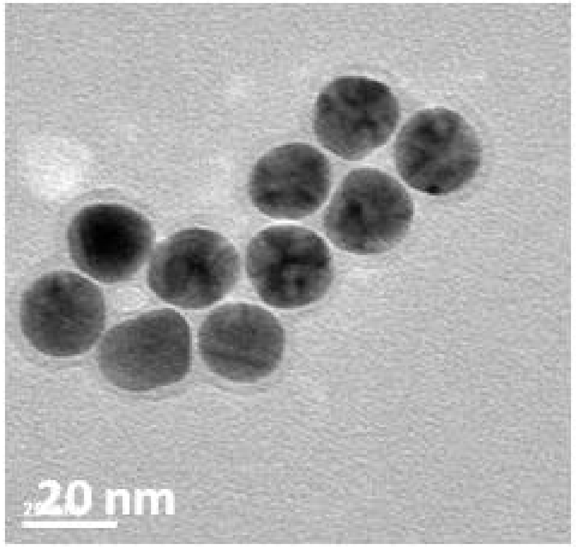
- Dynamic size range (5 nm 40 micron)
  - 40 mm to 20nm in 60 mins in a single run
  - From density gradient - sugar solution in disc
- Variable speed (special disc to maintain gradient)
- Few mg
- 24000 rpm – 900 km/h = 29000 g

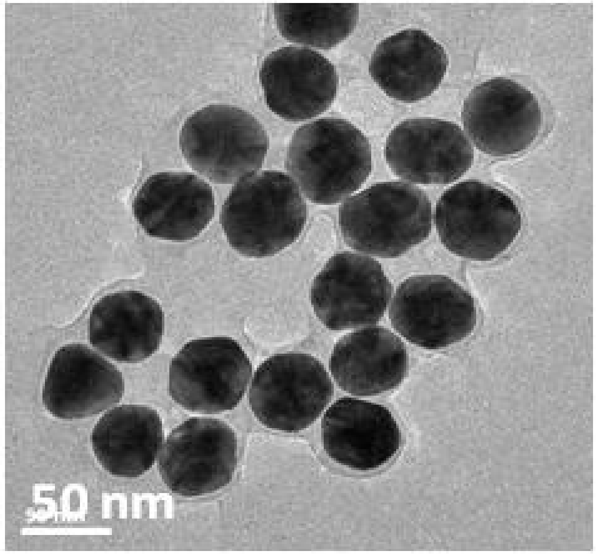




Gold – commercial – 20 & 50 nm – CPS – PCS - TEM

	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 (e.g., laser diffraction, DLS, …)
  - 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 PSD

- Get any information possible from supplier (size and size method, purity, SSA)

- Get a suitable image
  - optical microscopy >10 μm
  - electron microscopy <5 μm (SEM, TEM)

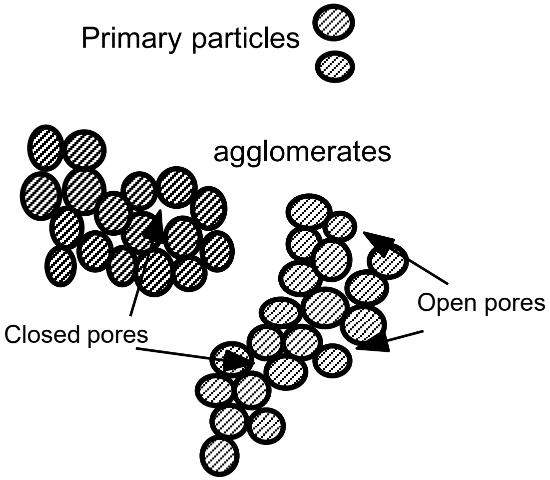
- Choose suitable method based on size range:
  - 0.1 to 1000 μm – laser diffraction good point to start if not elongated
  - 10nm to 1000nm Disc centrifuge (X-ray for inorganic)
  - 2-500nm DLS – care when broad distribution, colloidal stability
  - < 5 nm 2D Analytical Ultra Centrifugation

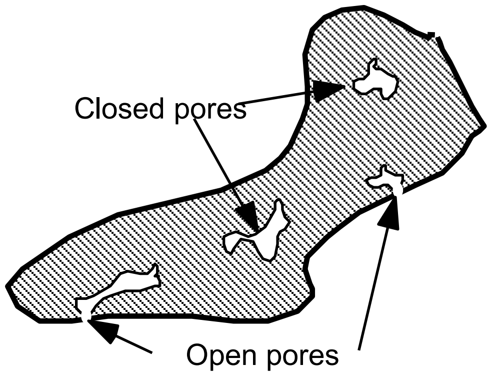
- Complex shape: Image Analysis

- Complementary methods: SSA, XRD, Zeta potential, imaging

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

Porosity and Specific Surface Area – Gas Adsorption

Nitrogen Adsorption – Desorption (NAD)

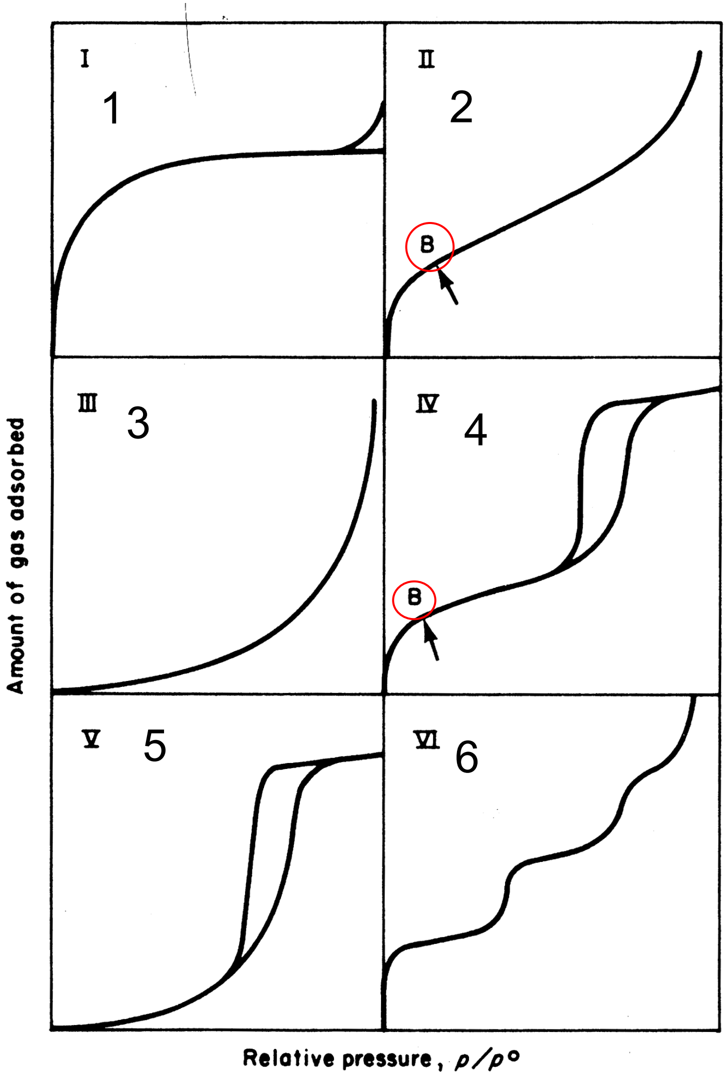
- Domain: 2 nm to 200 nm
  - micropores (<2 nm)
  - mesopores (2-50 nm)
  - macropores (>50 nm)
- Powder sample (dried) – evacuated – and cooled to liquid nitrogen temperature (-196°C).

- 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

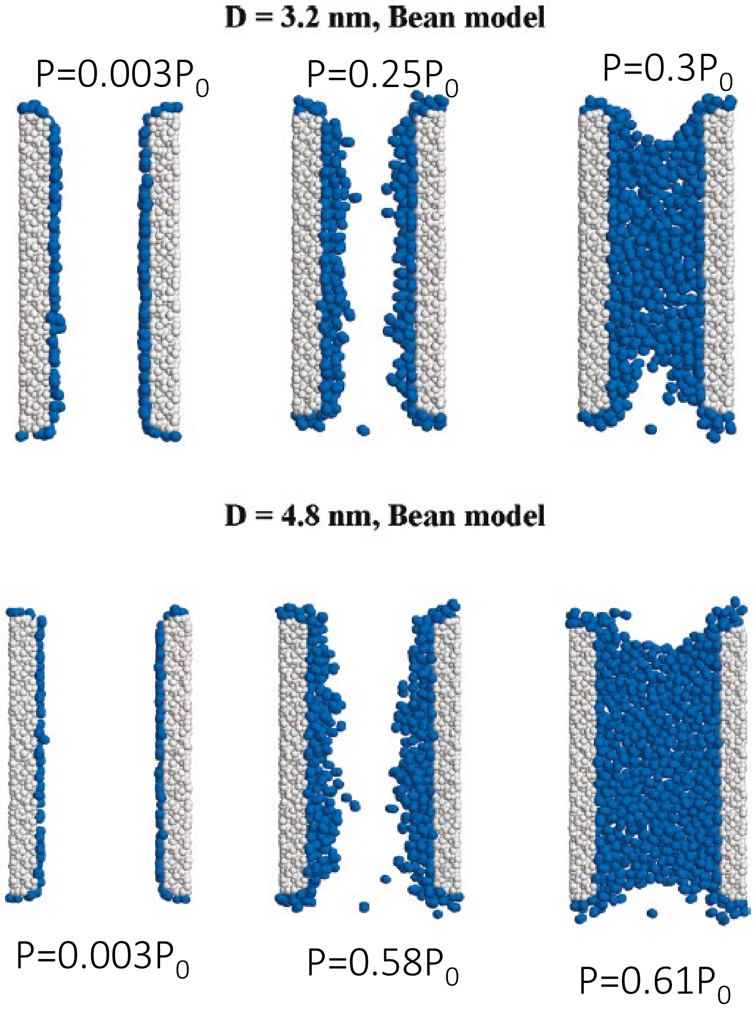
Micromeritics TriStar II Plus
Surface Area and Porosity Instrument

Adsorption isotherme

- 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



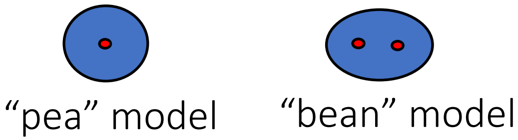
Atomistic modelling of N_2 adsorption on silica*



(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

Break: question & discussion

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)

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

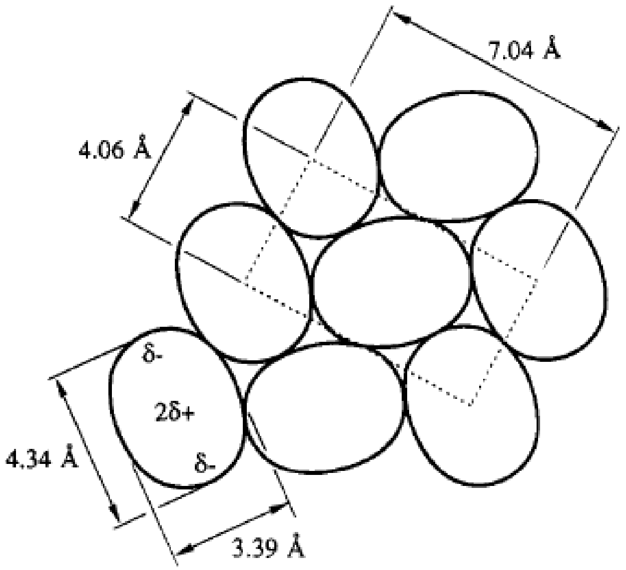
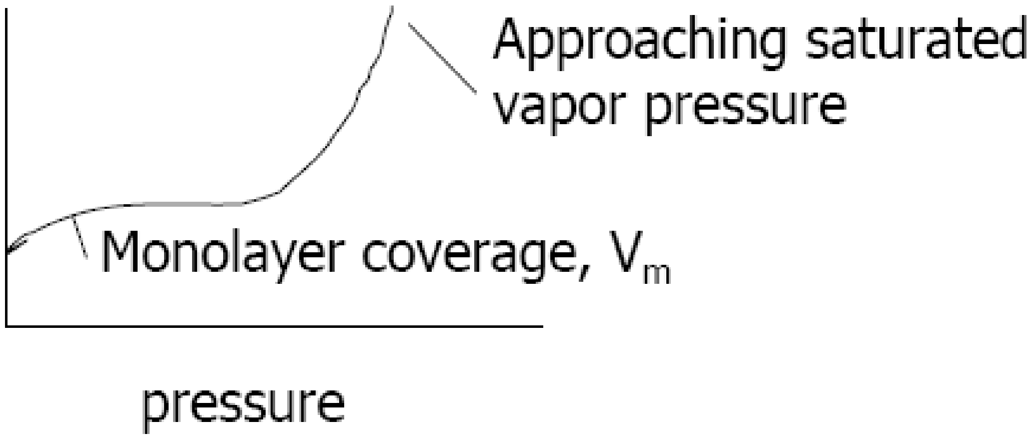


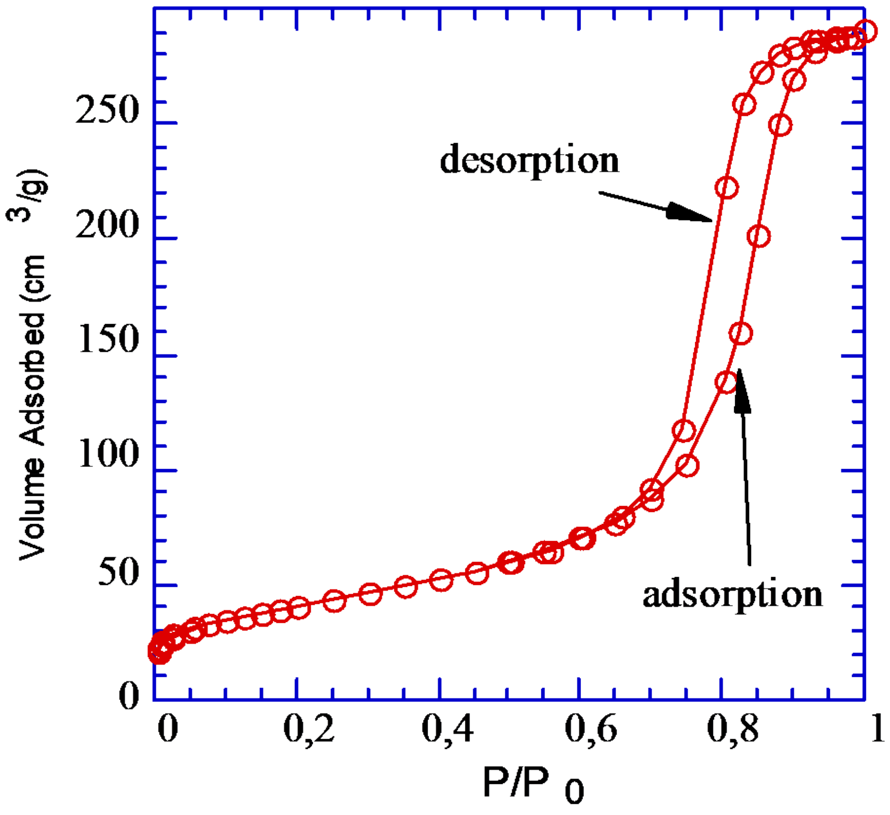
Figure 4. Compact "herringbone" structure of nitrogen molecules in a monolayer with $a(N_2) = 14.3$ Å^2. Molecules are parallel to the surface. In the dense layer adsorbed on silica molecules tilt away from parallel to give the similar but more compact arrangement with $a(N_2) = 13.5$ Å^2.

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 points BET method



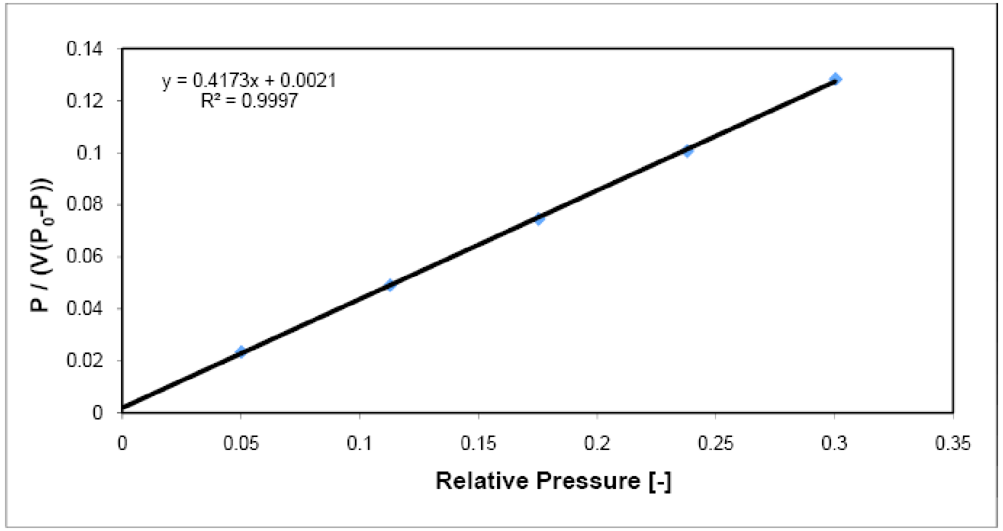
$$\overset{\mathbf{Y}}{\frac{P}{V_a(P_0-P)}} = \overset{\mathbf{C}}{\frac{1}{V_mC}} + \overset{\mathbf{m}}{\frac{C-1}{V_mC}} \cdot \overset{\mathbf{X}}{\left(\frac{P}{P_0}\right)}$$

- 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 linearized plot – example for gamma alumina CR125

$$\overset{Y}{\frac{P}{V_a(P_0-P)}} = \overset{c_i}{\frac{1}{V_m C}} + \overset{m}{\frac{C-1}{V_m C}} \cdot \overset{X}{\left(\frac{P}{P_0}\right)}$$

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 – 16.2×10^{-20} m^2 (Å^2)

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

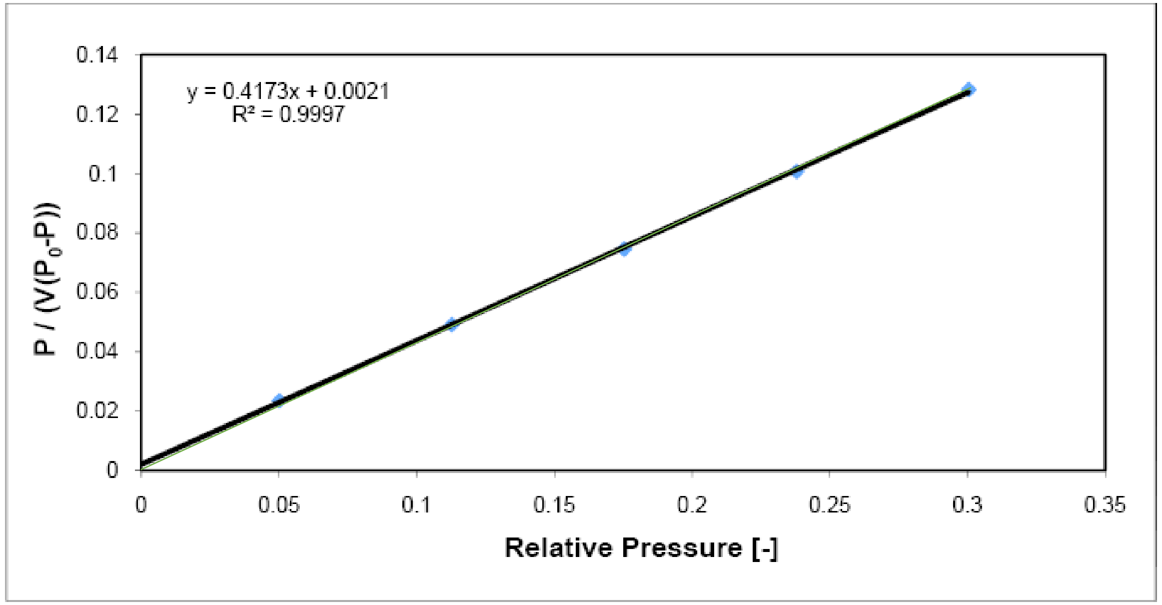
$$SSA = \frac{6}{\rho} \cdot \left(\frac{\sum n_i d_i^2}{\sum n_i d_i^3} \right)$$

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

BET linearised plot – Single point approximation

$$\overset{Y}{\frac{P}{V_a(P_0-P)}} \Rightarrow \overset{m}{\frac{1}{V_m}} \cdot \overset{X}{\left(\frac{P}{P_0}\right)}$$

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

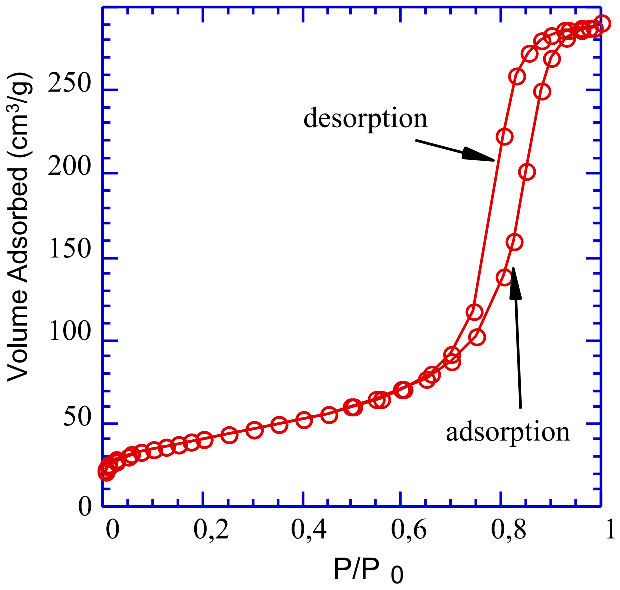
$$SSA = \frac{6}{\rho}\cdot\left(\frac{\sum n_i d_i^2}{\sum n_i d_i^3}\right)$$

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

*Monosorb Quantachrome, Flowsorb Micromeritics

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.



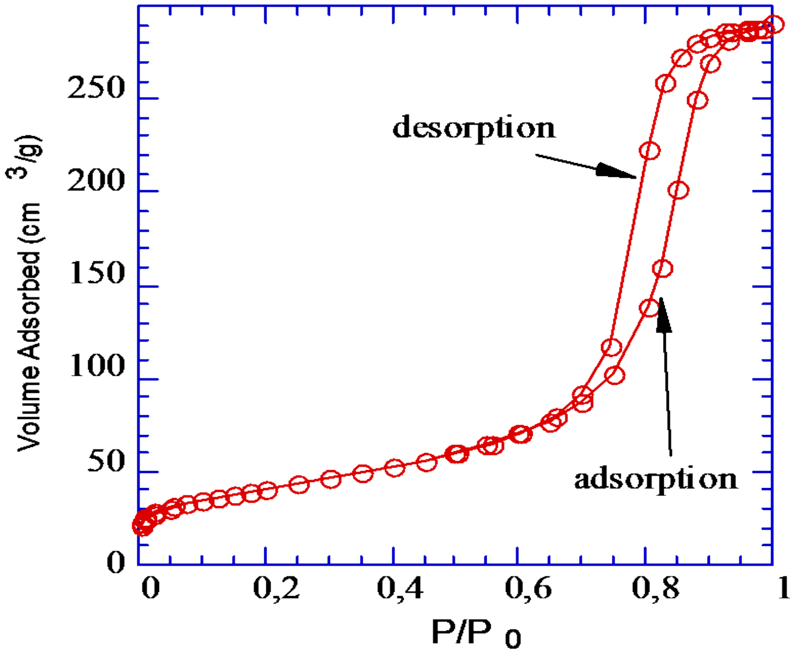
- Type 4 isotherm adsorption – condensation in pores
- Desorption shows hysteresis
- Pore diameter, 2r, evaluated from the Kelvin eq. Assume <u>cylindrical pores</u>

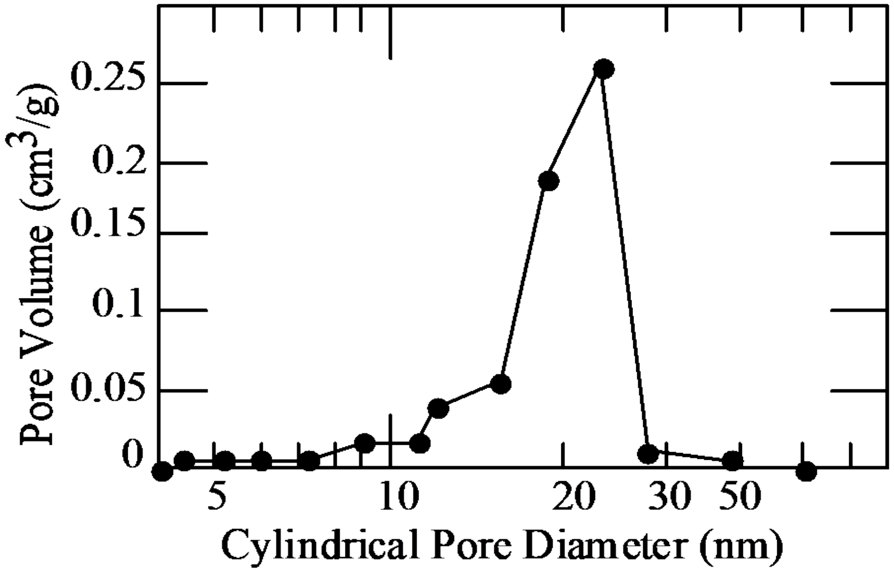
$$\ln\frac{P}{P_0}=\frac{-2\gamma_{lv}V_l\cos\theta}{(r-t)RT}$$

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





$D = \frac{4V}{A}$

- 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

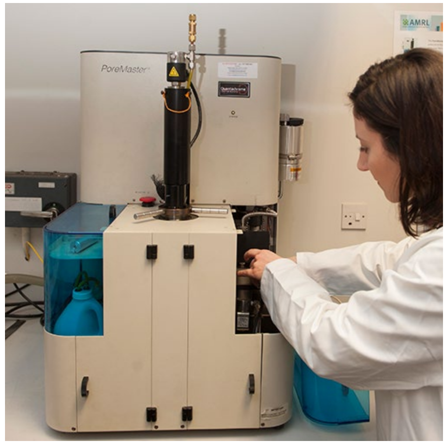
$$r = \frac{-2\gamma_{lv}\cos\theta}{P}$$

θ wetting angle Hg-solid,

γ_{lv} surface tension Hg

P applied pressure

Mercury Intrusion Porosimetry - MIP



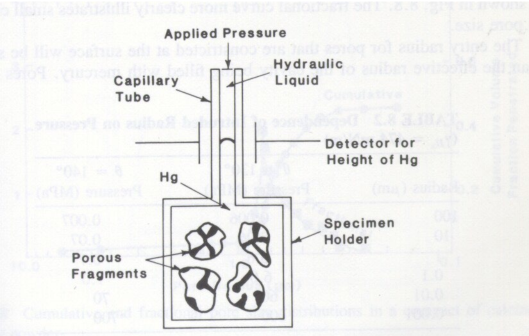


Fig. 8.6 Schematic of mercury penetration porosimetry technique.

Quantachrome poremaster

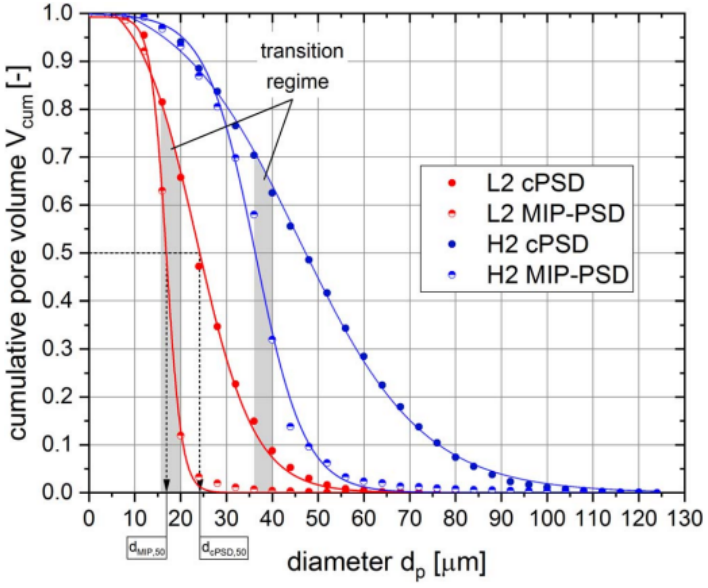


Figure 5. Cumulative pore volumes for cPSD and MIP-PSDs are shown for the materials L2 and H2. Curves are fitted with a sigmoidal function.

Example for metal gas distributor in water eletrolizers

Journal of The Electrochemical Society, **166** (4) F270-F281 (2019) F271

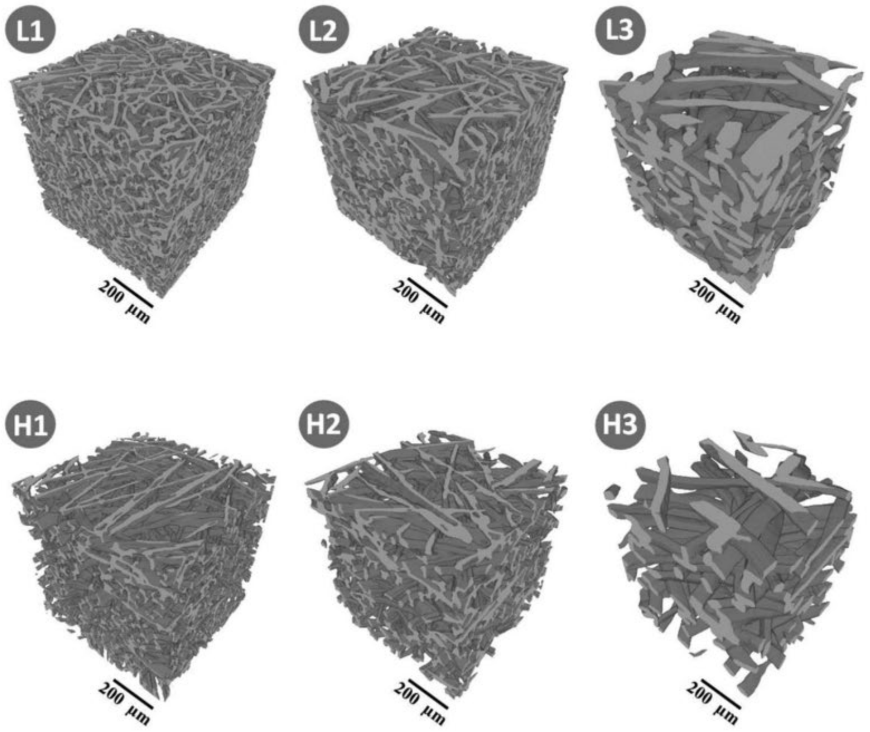


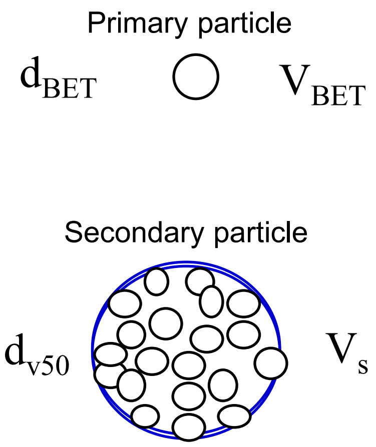
Figure 1. 3D surface renderings based on XTM data of the three fiber types 1, 2, 3 shown for the two nominal porosities of 56% (L) and 76% (H). The Ti solid phase is represented in gray and void phase in transparent, respectively.

In some case, large pores need to be characterized. Above tomography and on the left MIP measurements. These are complementary results. Nevertheless, MIP is much less time consuming and cheap measurement than tomography.

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} 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, excluding 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

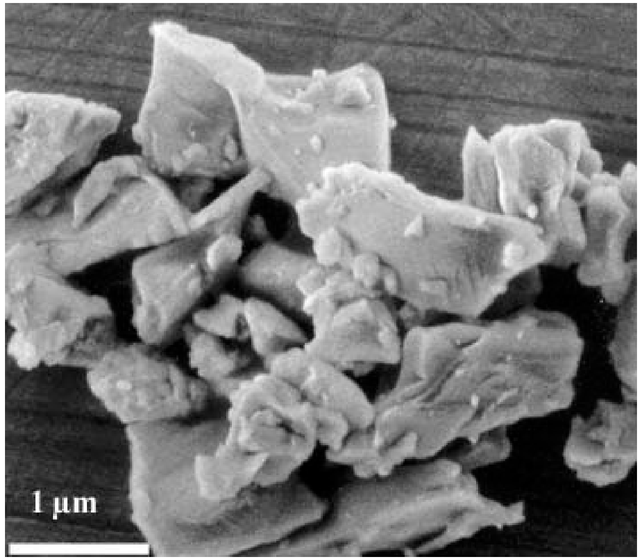
Aggregate: chemical bonds
Agglomerate: physical bonds

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

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

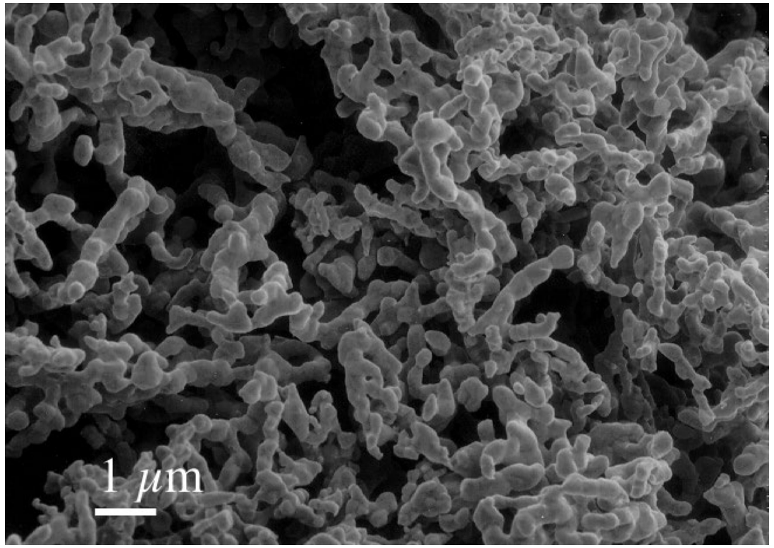
Agglomeration Factor, Fag

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

Break: question & discussion

Synchrotron based characterization techniques

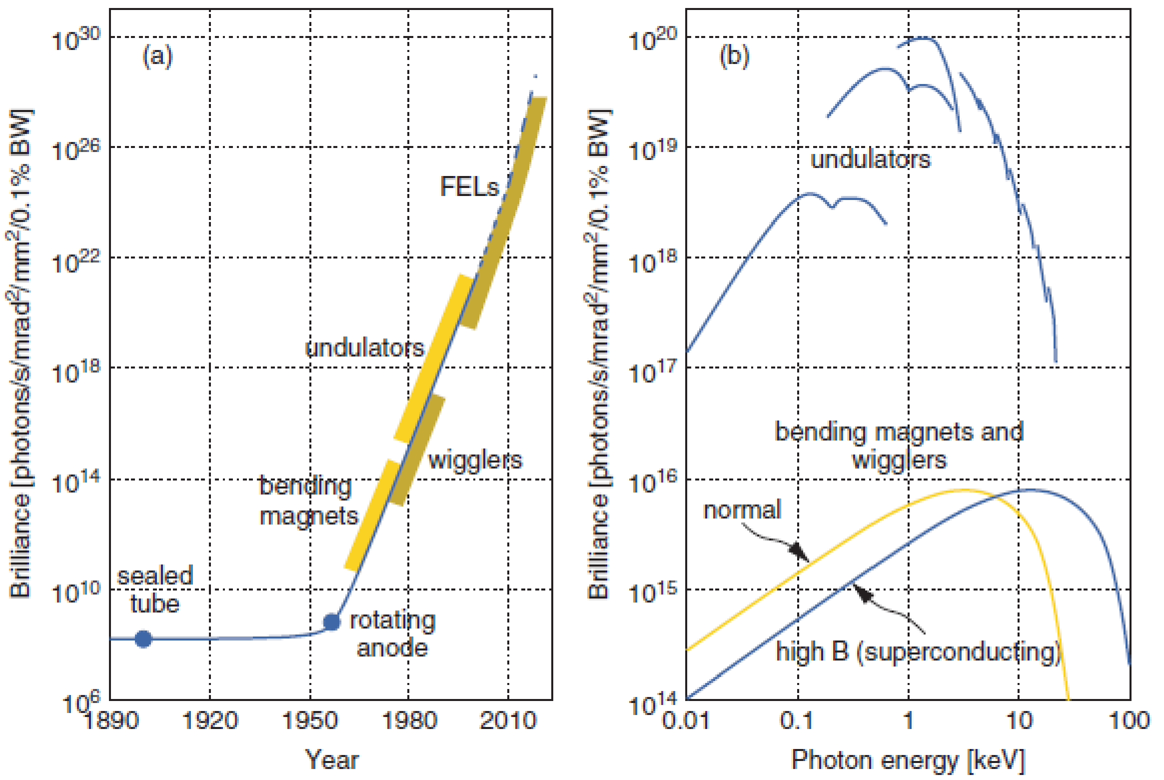
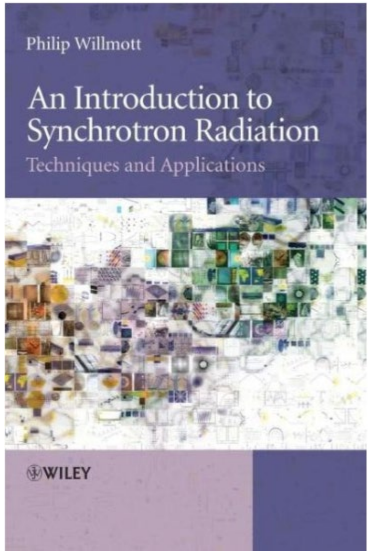


Figure 1.3 *The brilliance of x-ray sources. (a) A historical graph showing the enormous increase in brilliance starting in the second half of the twentieth century. (b) Typical spectral brilliance curves of devices commonly used in third-generation synchrotrons.*

Who is the expert in the filed?



Prof. Dr. Philip Willmott, PSI
https://www.psi.ch/de/lsc/people/philip-willmott

Synchrotron storage rings are very powerful sources of X-rays. Synchrotrons research facilities are nowadays designed and dedicated to generate tunable beams of electromagnetic radiation from the far infrared to the hard X-ray regime, with intensities (defined by their ‘flux’ or ‘brilliance’), many orders of magnitude greater than those produced by laboratory-based sources (see Figure 1.3).

What is a synchrotron?

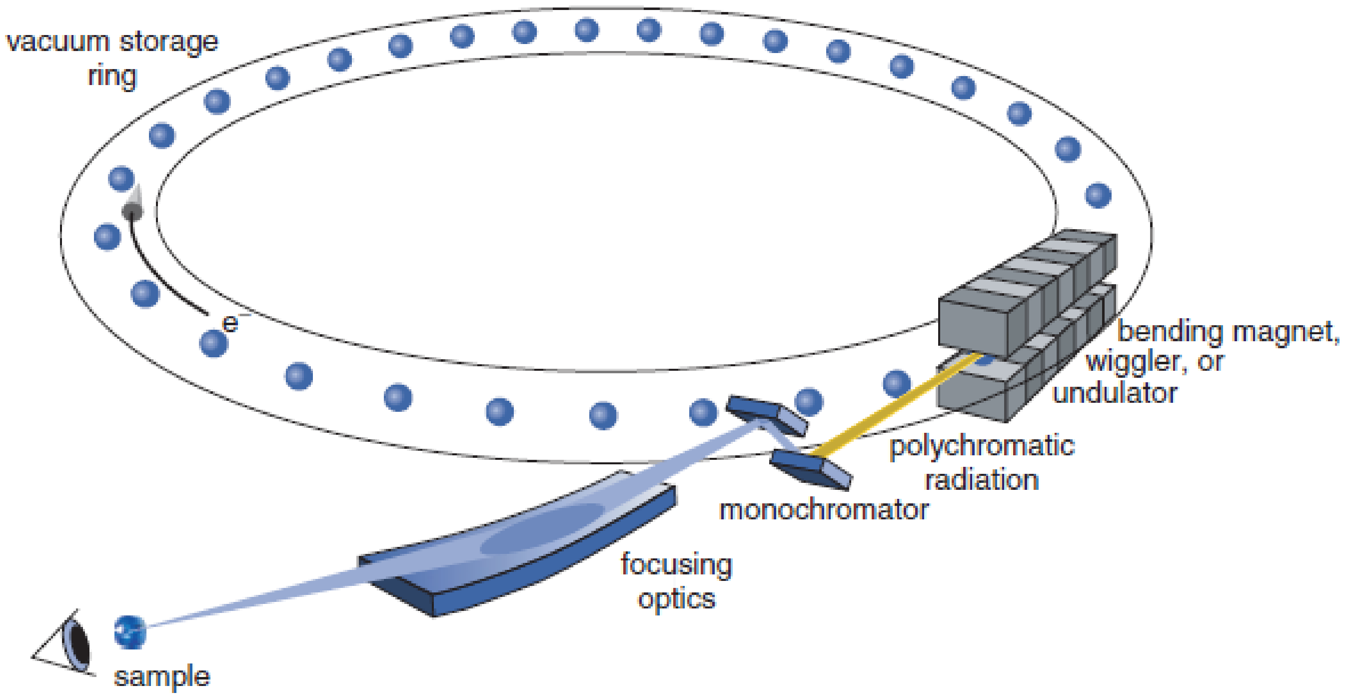


Figure 1.4 *Schematic of a third-generation synchrotron. Electrons moving at highly relativistic velocities in an evacuated storage ring emit electromagnetic (synchrotron) radiation as their direction is changed by bending magnets, used to steer them in a closed path, or by wigglers or undulators placed in straight sections of the storage ring, which 'shake' the electrons to and fro but keep an average straight trajectory. At the beamline, tangential to the storage ring, the radiation is normally (but not always) monochromated and focused using x-ray optics onto a sample.*

It generates a continuous flux of X-ray for each beamline.

What is a beamline?

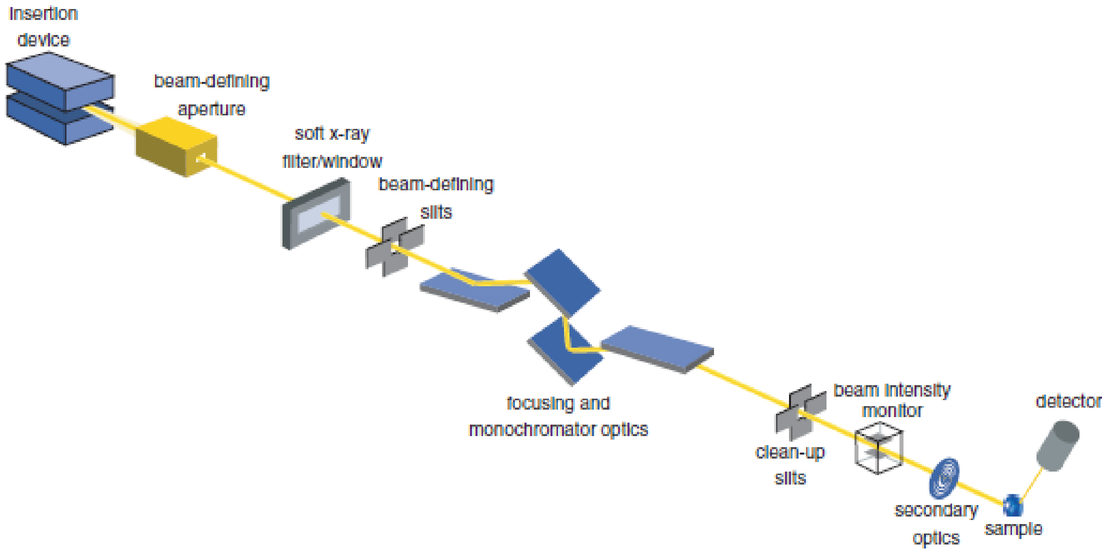
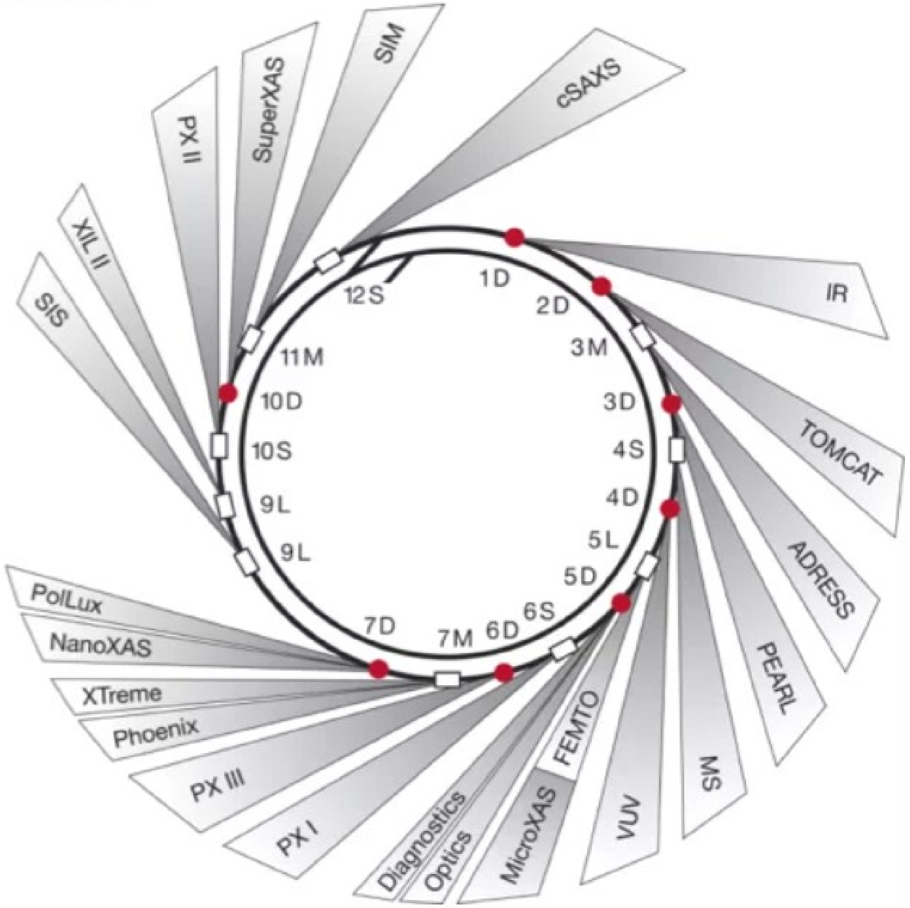


Figure 4.1 Typical components found at an x-ray synchrotron beamline.

Beamline Map: 16 beamlines are in user operation.



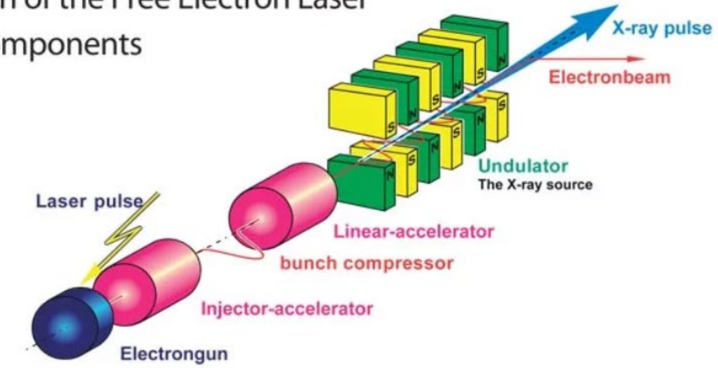
Overview SLS beamlines

What is a FEL?

The four major components of SwissFEL are

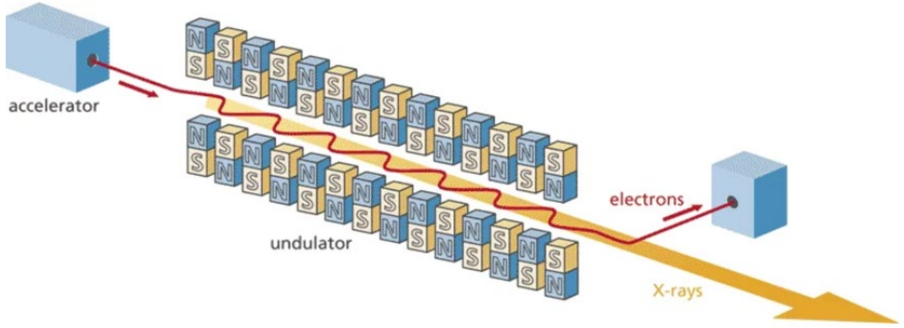
Schematic design of the Free Electron Laser
with different components

1) Electrongun
2) Injector
3) Accelerator
4) Undulator



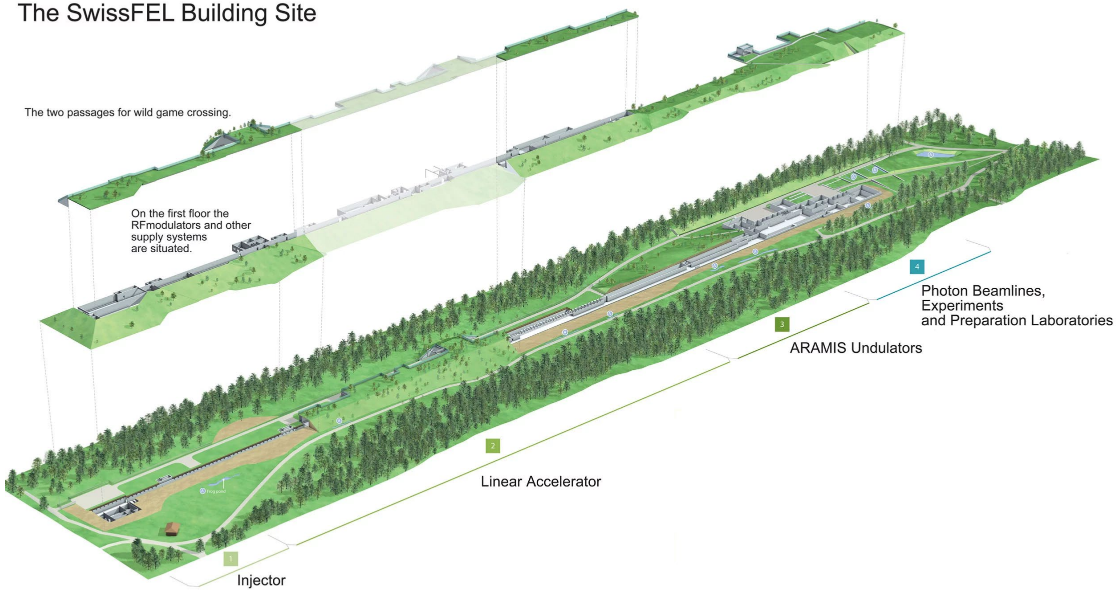
SwissFEL design

The undulator: where laser-like X-rays are born



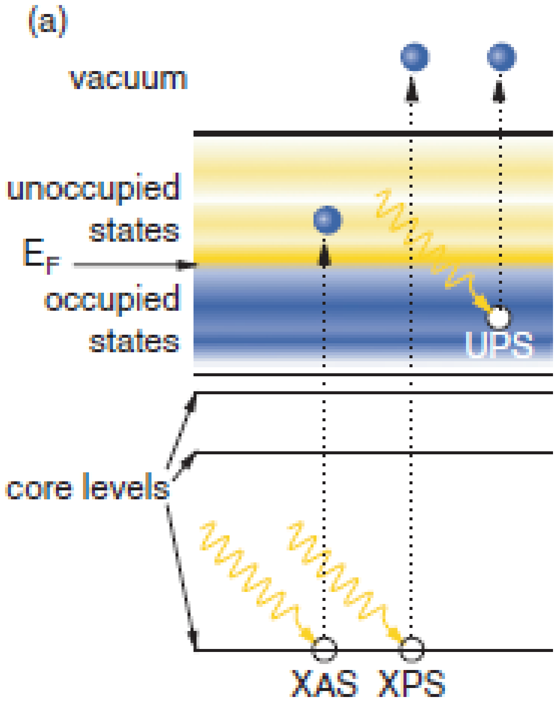
Schematic of SwissFEL undulator

The SwissFEL Building Site



It generates a pulses of X-ray, with extremely high brightness and focused beam (10^{12} of synchrotron) and very short (femtoseconds, 10^{-15} s).

X-ray adsorption spectroscopy (XAS): basic principles



The relationship between absorption and photoelectron spectroscopies. (a) XAS promotes core-level electrons to unoccupied valence-state levels and thereby probes these upper states by varying the incident photon energy. In contrast, in XPS and UPS, the electrons are directly promoted into the vacuum and their signal intensity as a function of emitted electron energy (or binding energy) is recorded for a fixed incident photon energy.

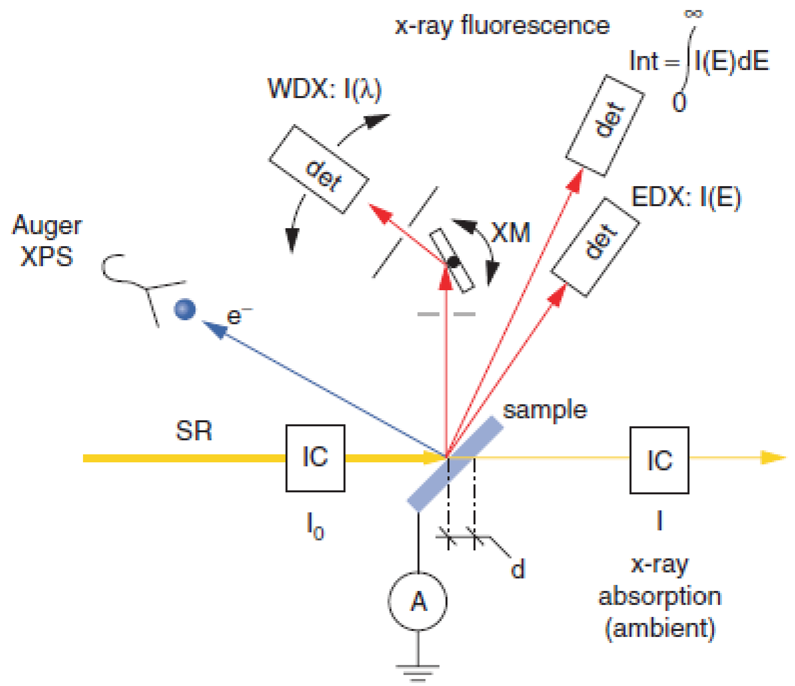


Figure 6.2 *X-ray absorption and x-ray fluorescence experiments. Monochromatic synchrotron radiation (SR) is allowed to impinge on a sample. X-ray absorption spectra can be performed by measuring the amount of light that passes through a thin sample. The x-ray intensities before entering the sample (I_0) and after (I) are measured using ionization chambers (IC) or other beam-intensity monitors, and is particularly suited for samples that cannot be placed in vacuum, such as in biological or catalytic experiments. The total electron current (A) can also be used to indirectly determine the absorption spectrum. In this case, the sample and detectors must be in vacuum. X-ray fluorescence spectra can be recorded, either using a crystal monochromator (XM) in wavelength-dispersive spectra (WDX), or by using a dispersive solid-state semiconductor device (EDX). The integrated fluorescence yield can also be used as a measure of absorption strength. Unwanted elastically scattered x-rays are best suppressed by placing the detector in the plane perpendicular to the polarization of the synchrotron radiation.*

UPS (ultraviolet photoelectron spectroscopy)
XPS (x-ray photoelectron spectroscopy)

X-ray adsorption spectroscopy (XAS): basic principles

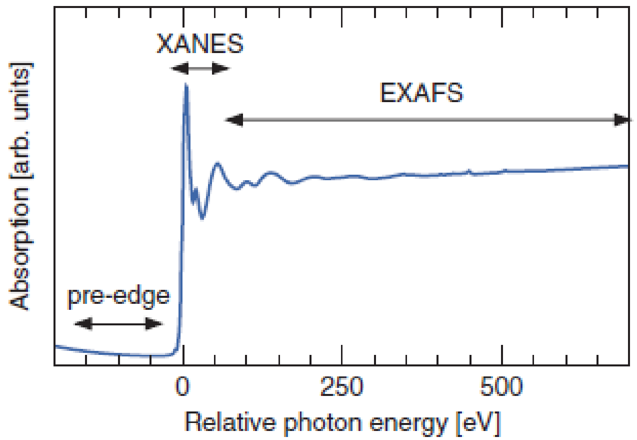


Figure 6.6 *The important regions of a typical x-ray absorption spectrum around a core-electron absorption edge. The energy scale is relative to the centre of the absorption edge. Some features may be found in the pre-edge region due to transitions of core-electrons to empty bound states. In the region around the absorption edge, one obtains x-ray absorption near-edge structure (XANES), dominated by transitions to unoccupied bound states. The absorption spectrum at energies from about 100 eV above the absorption edge often shows a series of oscillations up to as much as 1000 eV. This extended x-ray absorption fine structure (EXAFS) contains information about the local structure around the absorbing atom.*

Summary:

1. It is element specific;
2. It is very sensitive;
3. It allows identifying element oxidation state;
4. It allows the study of the chemical environment of a specific ion:
   - coordination
   - surrounding ions (shell)
5. It needs quite complex data reduction, using specific software and simulations;
6. It might be necessary to provide standard material as reference.

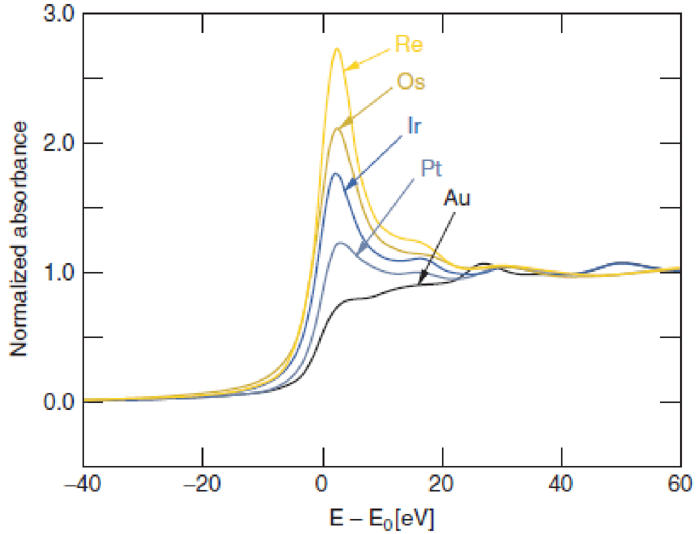


Figure 6.10 *XANES spectra comparing the L_3 absorption edges of five of the 5d-metals, rhenium to gold. Adapted from [3] with permission of the American Chemical Society.*

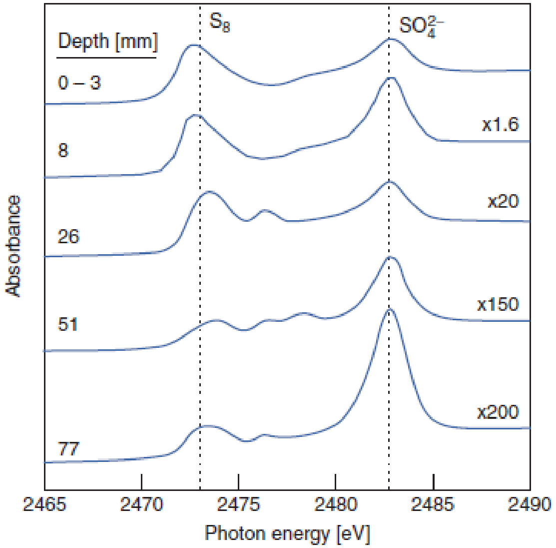


Figure 6.13 *Sulfur K-edge XANES spectra from samples taken at several depths from the woodwork of the Vasa. The two major peaks at 2473 and 2483 eV photon energy correspond, respectively, to elemental sulfur and SO_4^{2-} (i.e. sulfur in oxidation state +VI). These peaks bracket weaker signals from sulfur compounds in intermediate oxidation states. Adapted from [5] with permission of Macmillan Publishers Ltd.*

Break: question & discussion