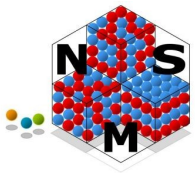
# Particle characterization

## WHY – WHAT – HOW – WHERE ?

Henk G. Merkus

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# **Why?** (cf. Stonehenge)

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# Why PSD characterization?

- H. Heywood, PSA conference 1947

  **"PSD analysis is not an objective in itself, but it is a means to an end being:**

  **the correlation of powder properties with**

  - **product properties in some application**
  - **their manufacturing process quality"**

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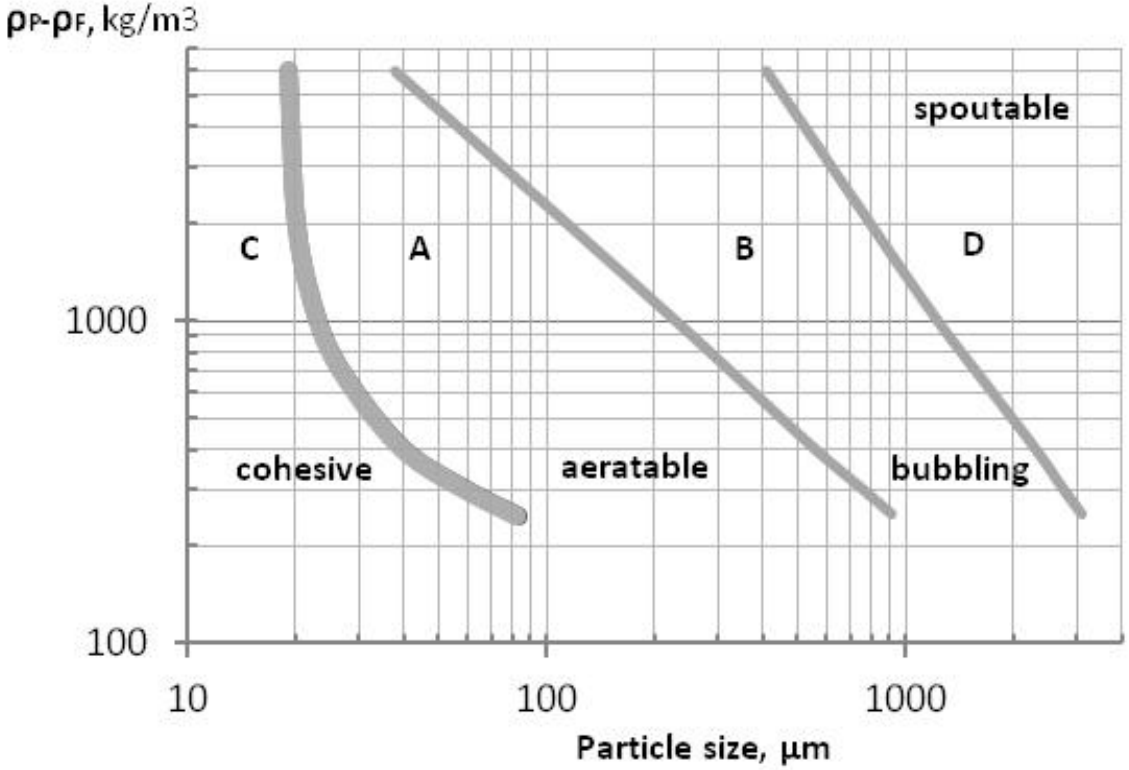
# RELATION WITH PROCESS PROPERTIES

## Geldart fluidization diagram

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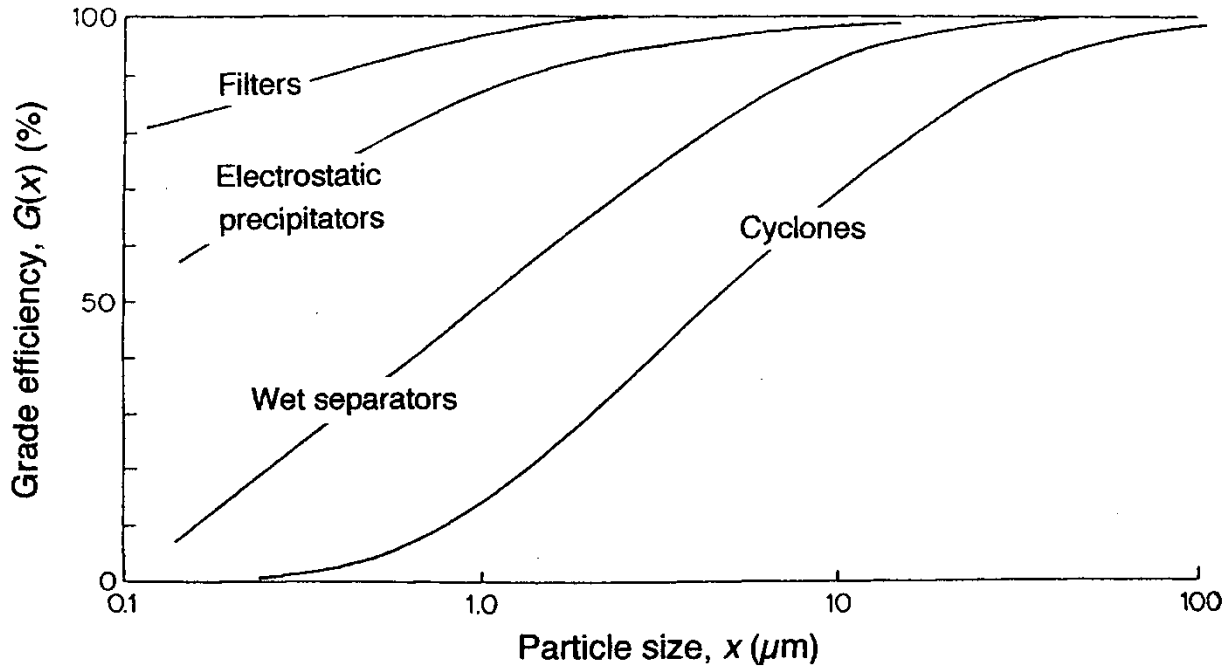
# RELATION WITH PROCESS PROPERTIES




Typical grade efficiency curves

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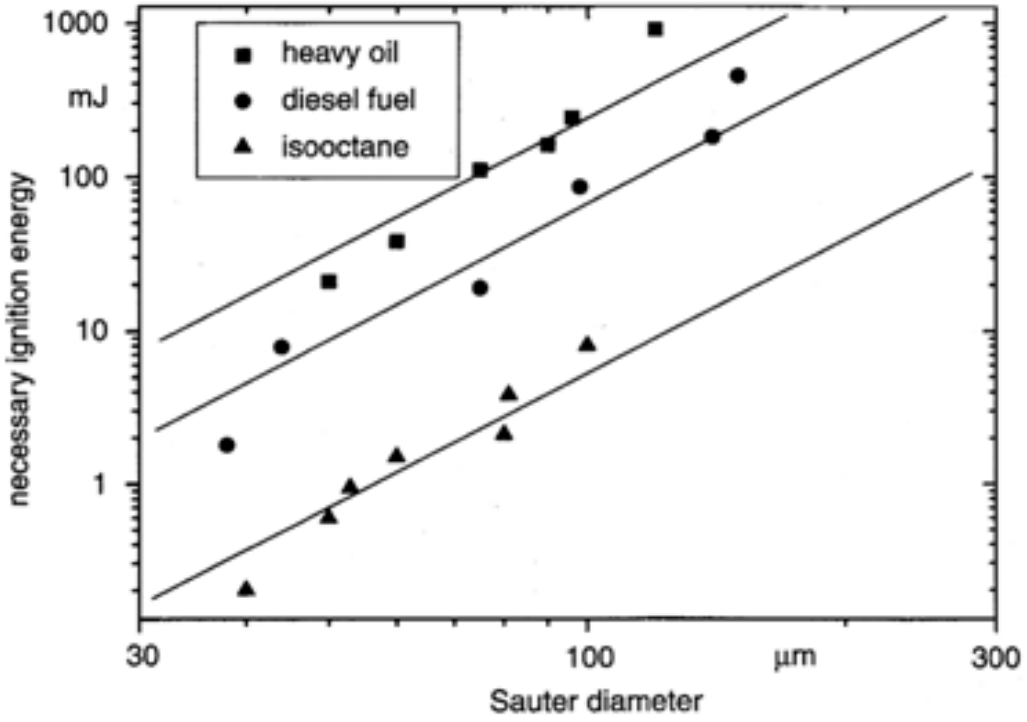
# RELATION WITH PRODUCT PROPERTIES

## Effect of particle size on Minimum Ignition Energy for 3 mists

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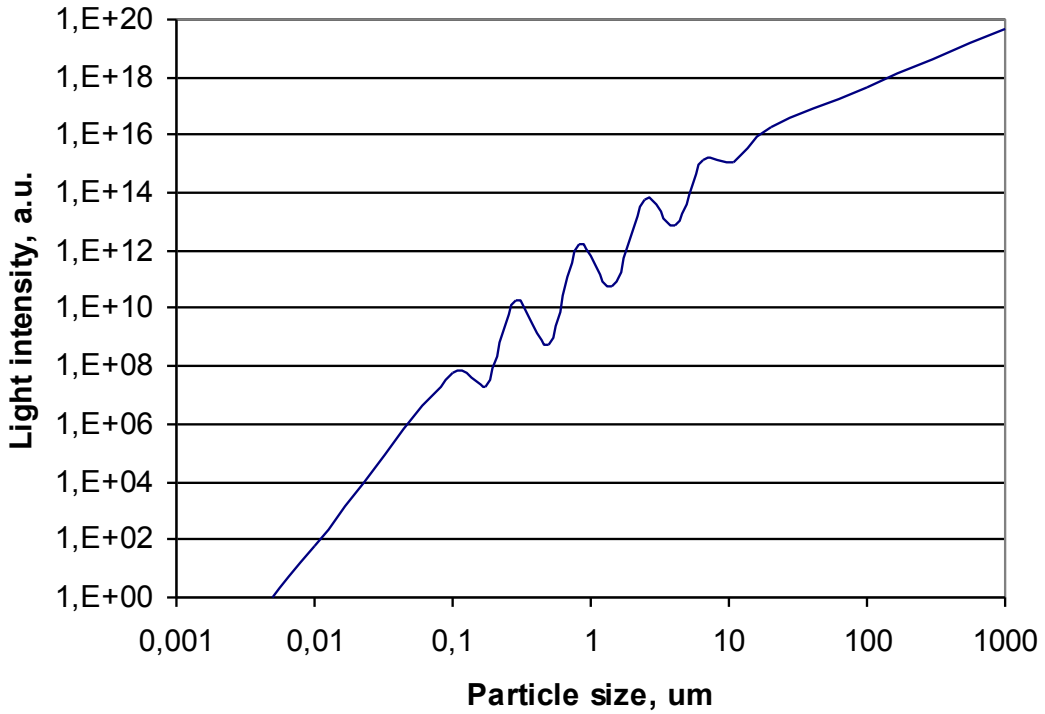
# RELATION WITH PRODUCT PROPERTIES




Scattered light intensity single particles

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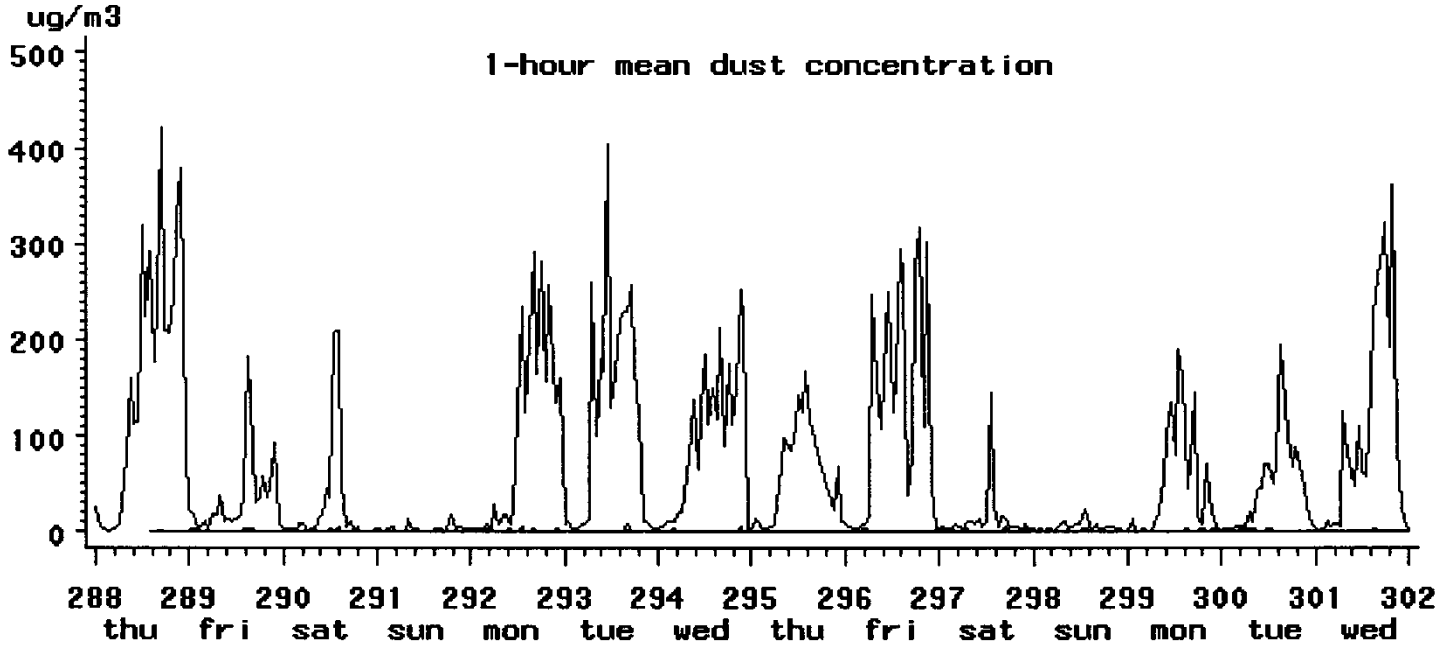
# RELATION WITH PROCESSES




Coal and ore dust emission Rotterdam Harbor 1997

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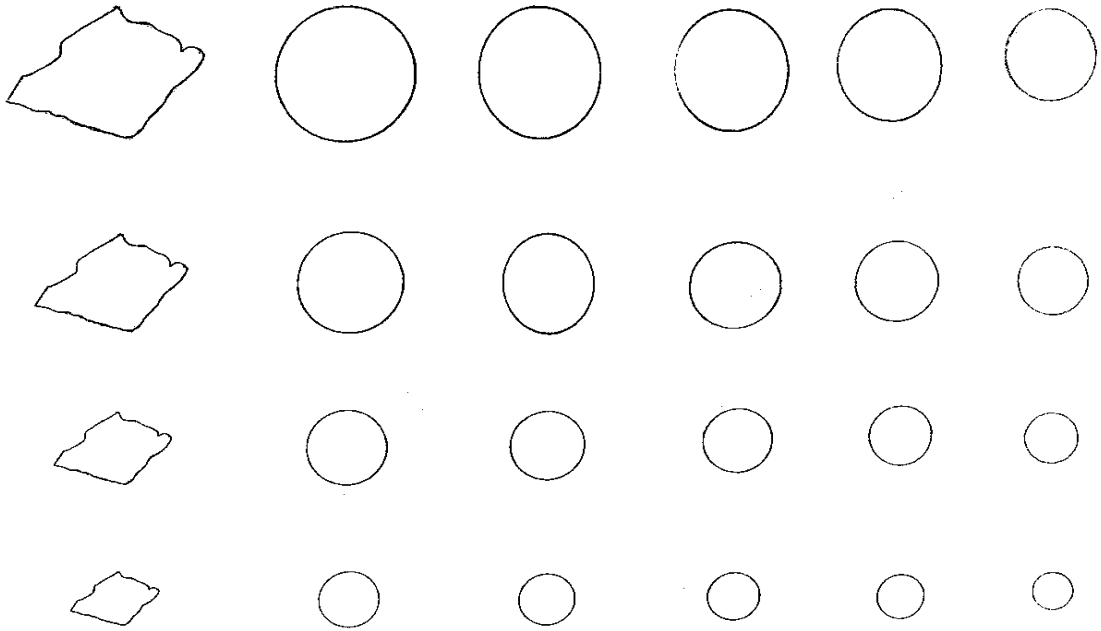
# What?

- Particle size (distribution)
  - some length; equivalent sphere diameter
  - characteristic PSD parameter(s)
- Particle shape (distribution)
  - macroshape; mesoshape; microshape
- Porosity (distribution)
  - pore volume; pore size distribution
- Specific surface area

# Equivalent particle size



**projection** **area** **sieve** **volume** **sedimentation**
**low Re** **high Re**

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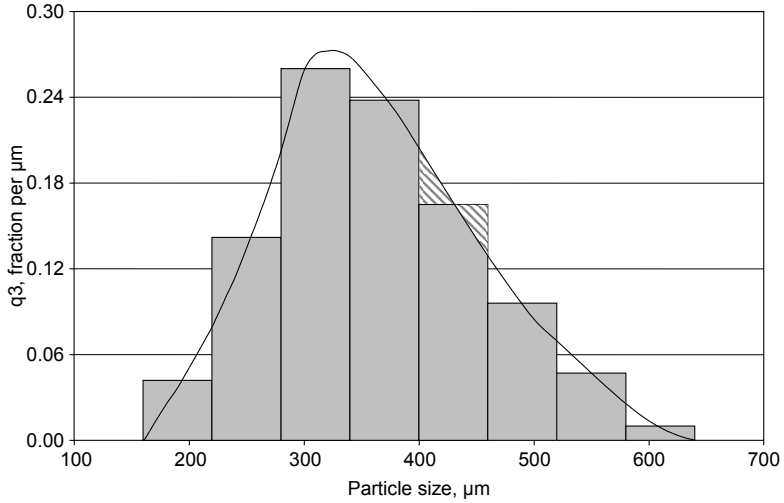
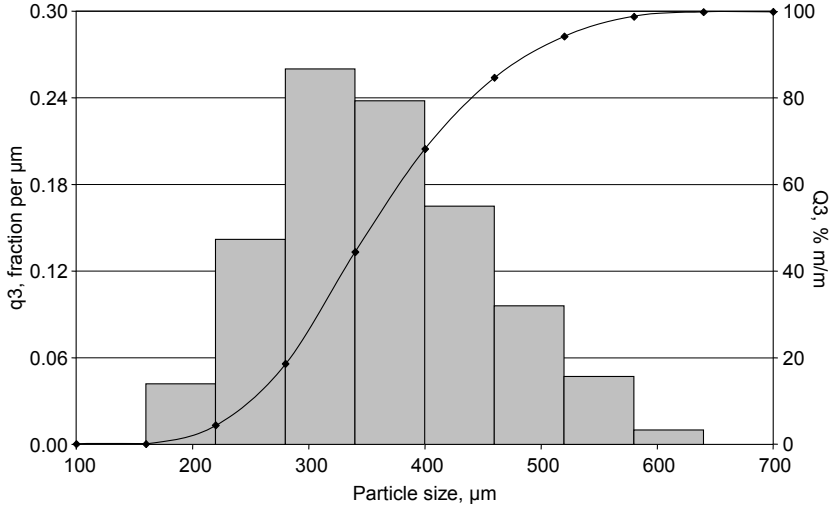
# Particle size distributions




Frequency/Density

Cumulative undersize

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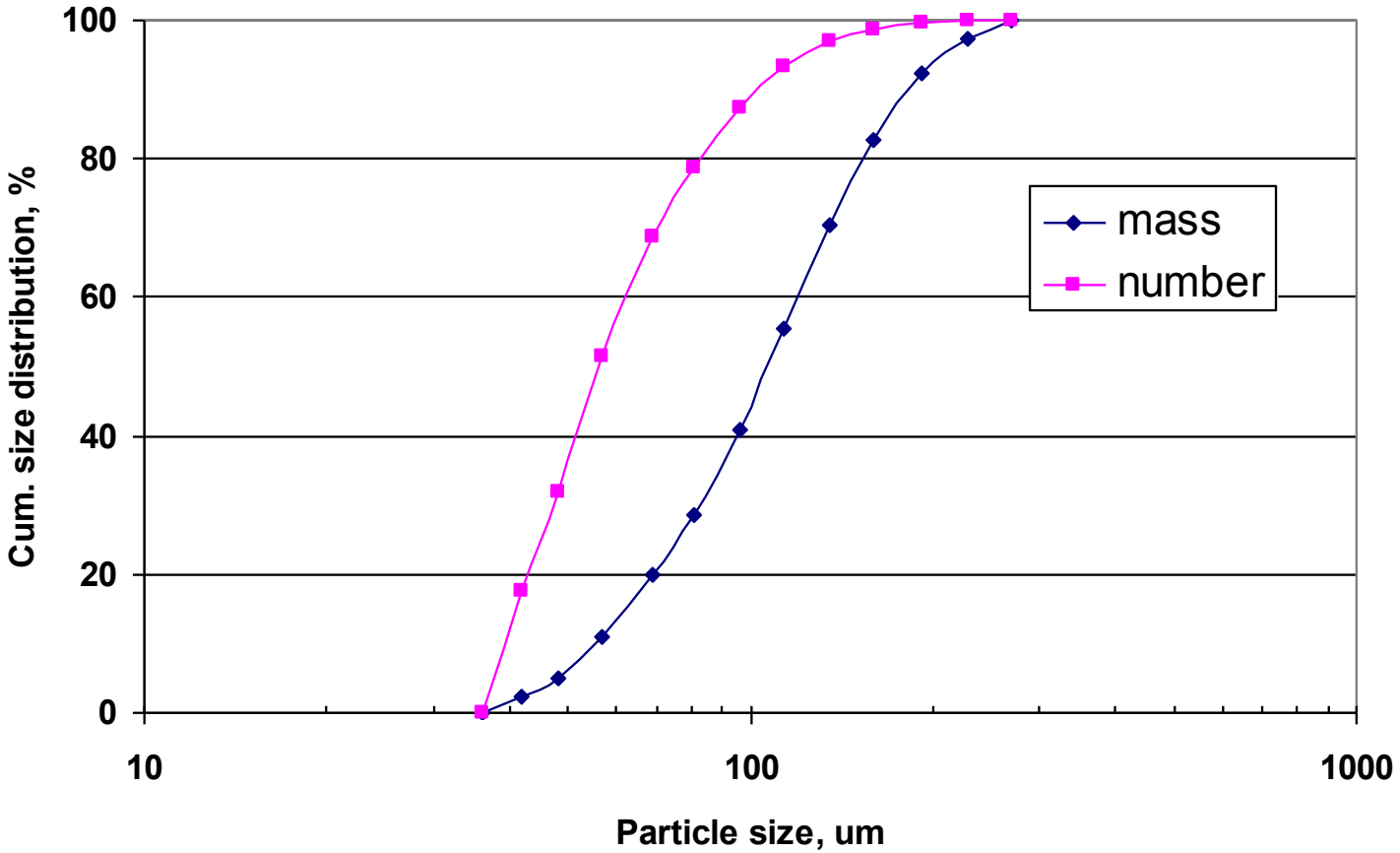
# Particle Size Distributions

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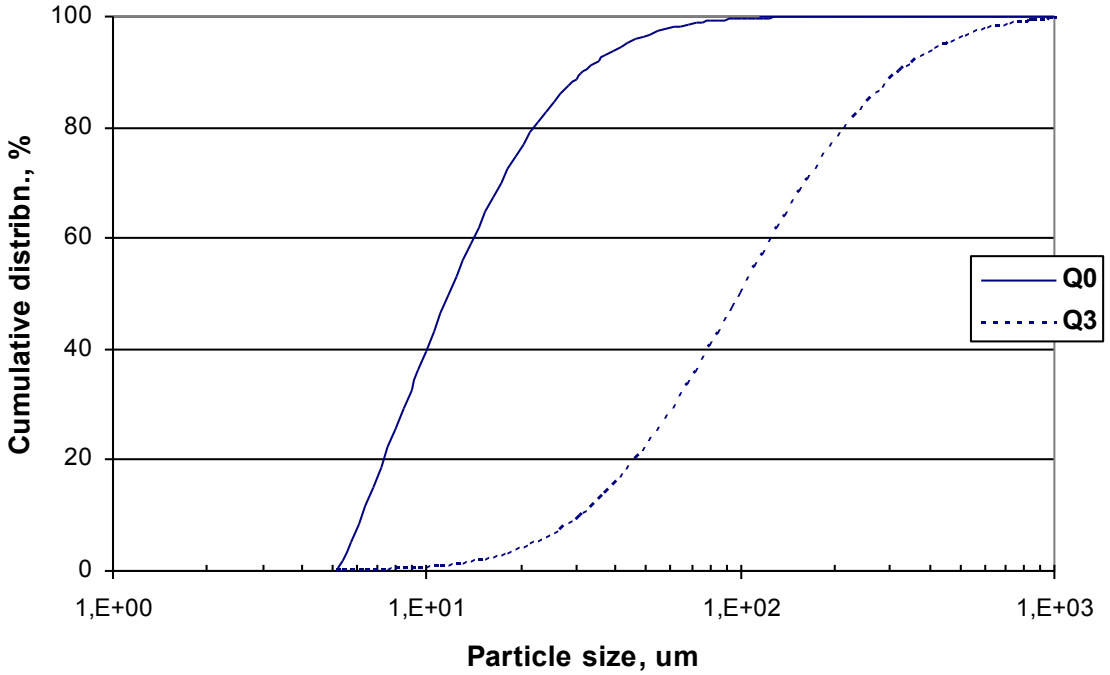
# Particle Size Distributions

Log-normal PSD; sg = 2.5; $D_{90;3}/D_{10;3}$ ~10




Here: ~ 85% n/n < $D_{10;3}$; ~1% n/n > $D_{50;3}$ and ~ 0.004% n/n > $D_{90;3}$

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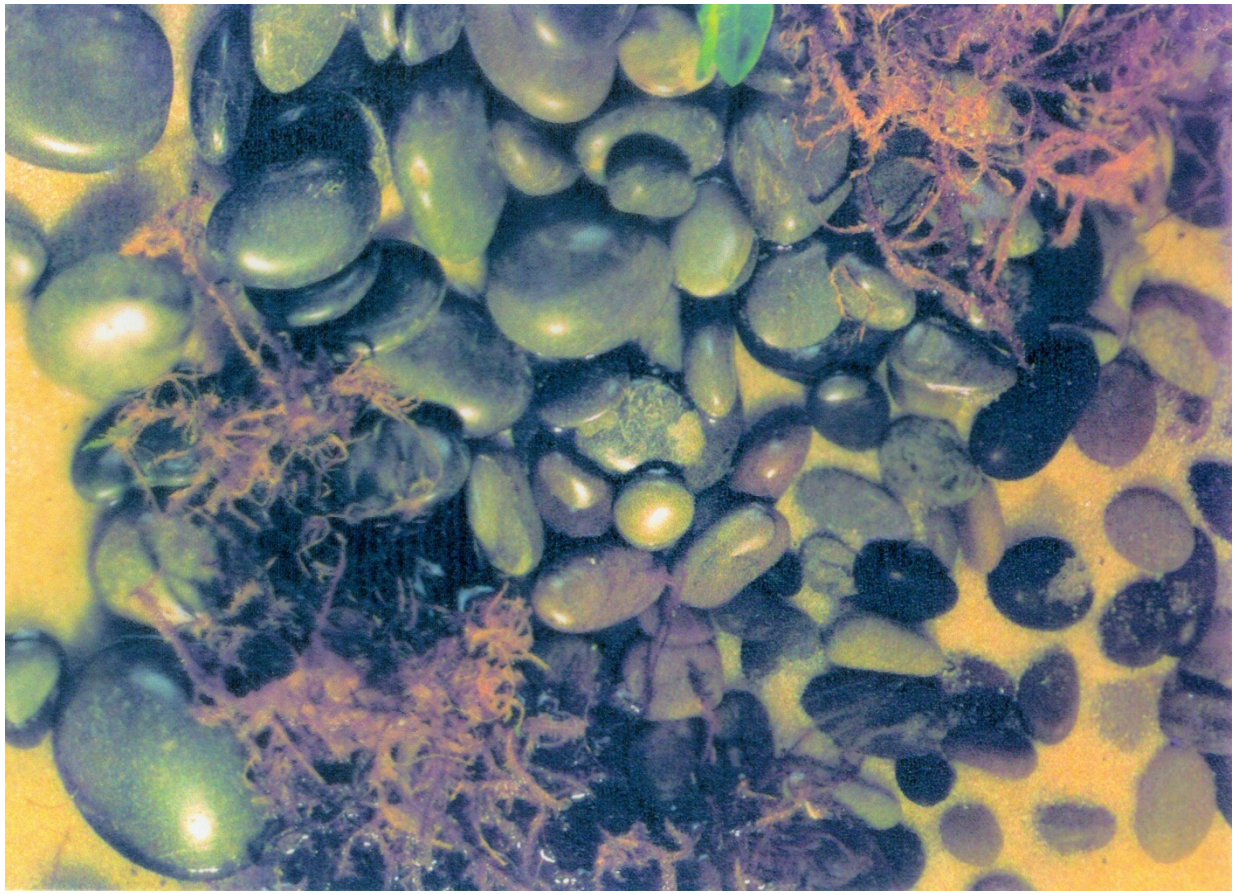
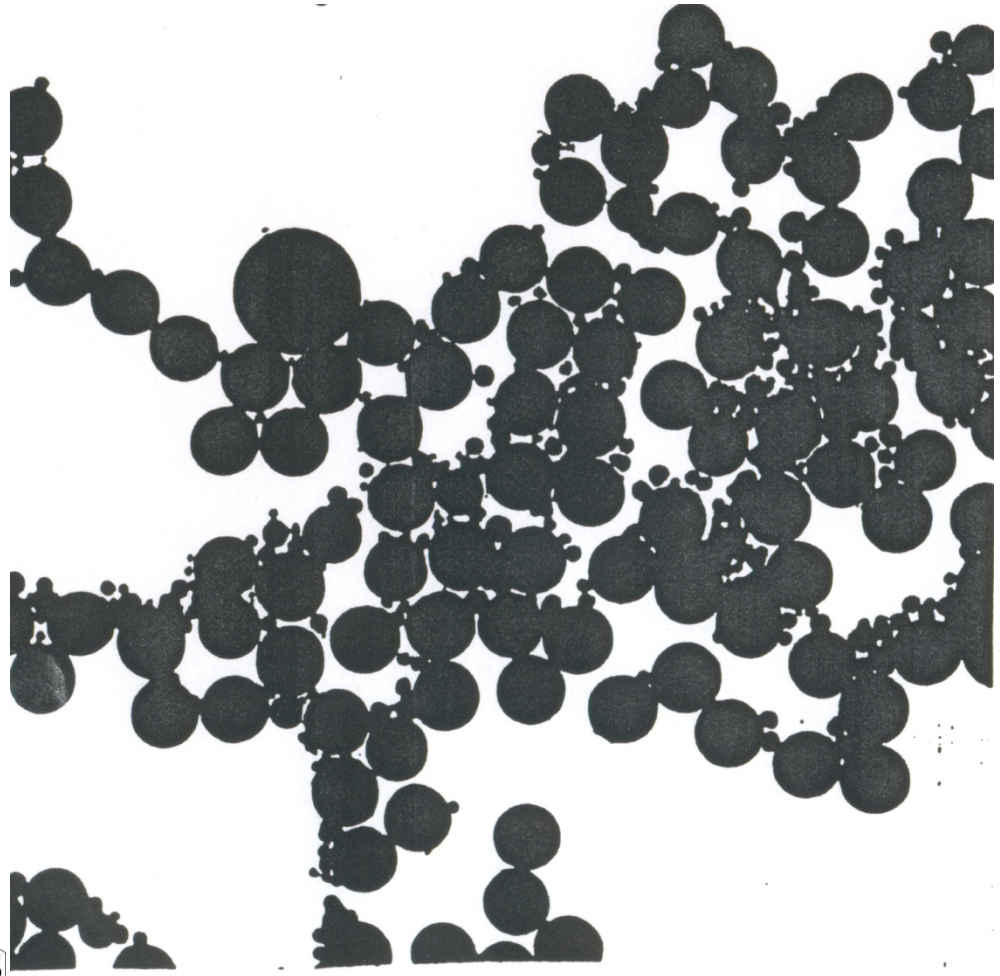
# Understand your challenge for quality



# Understand your challenge for quality



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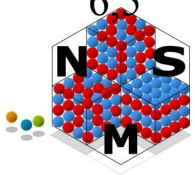
# Weighted mean size values (ISO 9276-2 and 7)

- Number-weighted mean: $\langle D_{1,0} \rangle = \langle x_{1,0} \rangle = \Sigma n_i D_i / \Sigma n_i$
- Area-weighted mean: $\langle D_{3,2} \rangle = \langle x_{1,2} \rangle = \Sigma n_i D_i^3 / \Sigma n_i D_i^2$
- Volume-weighted mean: $\langle D_{4,3} \rangle = \langle x_{1,3} \rangle = \Sigma n_i D_i^4 / \Sigma n_i D_i^3$
- Mean volume diameter: $\langle D_{3,0} \rangle = \langle x_{3,0} \rangle = (\Sigma n_i D_i^3 / \Sigma n_i)^{1/3}$
- ***Example***: **1 particle 1 µm + 1 particle 10 µm**
- Ratio length 1:10; area 1:100 and volume 1:1000
  - $\langle D_{1,0} \rangle = 5.50$ µm (= (1*1+1*10)/2 = 11/2)
  - $\langle D_{3,2} \rangle = 9.18$ µm (= (1*1+1000*1)/(1+100) = 1001/101)
  - $\langle D_{4,3} \rangle = 9.99$ µm (= (1*1+10000*1)/(1+1000) = 10001/1001)
  - $\langle D_{6,5} \rangle = 10$ µm (= (1*1+$10^6$*1)/(1+$10^5$) = 1.000.001/100.001)

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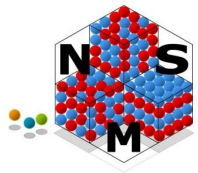
# Weighted mean size values, uses

- Number-weighted mean = arithmetic mean: e.g. in health effects, contamination of surfaces
- Surface area-weighted mean = Sauter mean: e.g. in fuel combustion, droplet evaporation rate, explosion behavior
- Volume-weighted mean = De Brouckere mean: e.g. in combustion equilibrium
- Don't use (statistic) median size for product quality!

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# Questions

- Relevant characteristic(s) and precision defined?
- Can we discriminate good and poor products?
- **In view of required precision:**
  - How many particles must be analyzed
  - Size and/or shape
  - Random or segregated mixture (sampling)
  - Choice of measurement method
  - Choice of measurement technique/instrument

# Method

- Method is more than technique
- Method includes:
  - Sampling
  - Dispersion
  - Measurement
  - Reporting
  - Validation (instrument, operator, method)

# Sampling, a major challenge

# Sampling, sample splitting

- Representative sample
- Sampling errors
- Quantification of sampling precision
- Sample splitting equipment
- Golden rules

# Representative sample

- Same composition as bulk product that it represents within stated interval at stated level of significance
- All constituent elements have equal probability of being sampled, given their proportions

# Types of sampling

- **Product** — Tons
  - Stream, heap, wagon
- **Primary sampling** — Kilograms
  - Industrial environment
- **Secondary sampling** — Grams
  - Laboratory
- **Tertiary sampling** — Milligrams
  - Instrument

# Sampling errors

- **Fundamental error**
  - Due to discrete nature of particles with differences in size, shape, density, etc.
  - Can be calculated through statistics.
  - Lower limit sampling error.
- **Segregation error**
  - Due to distribution heterogeneity in a mixture.
  - Can only be estimated from measurements.

# Fundamental error number statistics

- **Quasi-2 component mixture**
- **Number fractions: p and (1-p)**

- Binomial statistics: $$Var(p) = s_p^2 = \frac{p \cdot (1-p)}{n}$$

- Poisson statistics: $$Var(n) = s_n^2 = \bar{n}$$

- **n particles (total or in fraction)**

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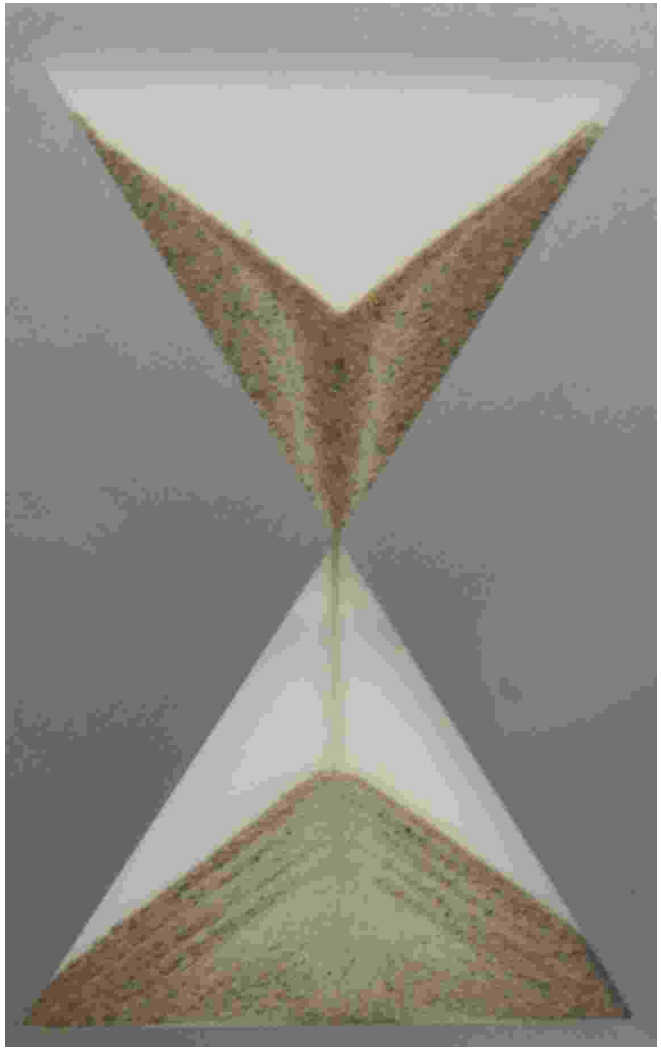
# Segregation in heap



**Segregation error cannot be calculated; can only be measured**

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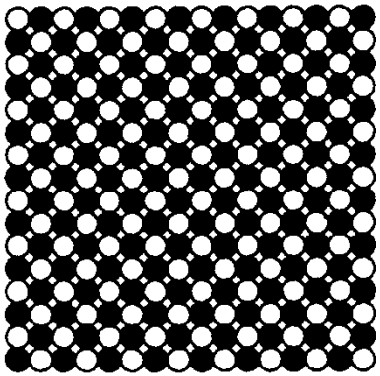
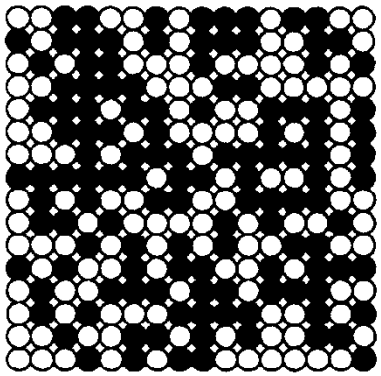
# Particulate mixtures

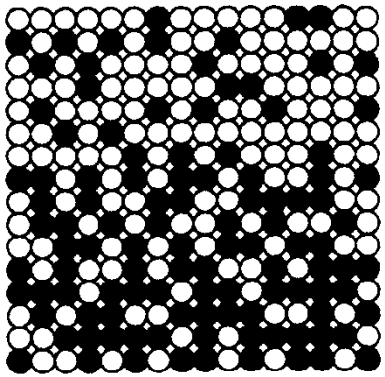
perfect



random



segregated



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# Repeatability sampling methods, 50 g

T. Allen and A.A. Khan, The Chem Engineer 1970, 108-112

| Mixture | sand – sugar | coarse – fine sand |
|---|---|---|
| Mass fraction | 0.60 – 0.40 | 0.60 – 0.40 |
| Particle size, μm | 420/500 – 420/500 | 420/500 – 150/250 |
| Density, kg/m$^3$ | 2650 – 1635 | 2650 – 2650 |
| Method | St. Dev. mass fraction | St. Dev. mass fraction |
| Scoop sampling | 0.058 | 0.068 |
| Cone/quartering | 0.063 | 0.051 |
| Table sampling | 0.021 | 0.021 |
| Chute riffling | 0.011 | 0.010 |
| Rotary riffling | 0.0027 | 0.0013 |
| Fundam. error | 0.0009 | 0.0008 |

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# Sample preparation errors

- Contamination — dust, remainders, corrosion
- Losses — dusting, remainders
- Chemical changes — oxidation, ad-/de-sorption
- Physical changes — moisture, attrition, breakage
- Human errors 1 — **unconditioned grab sample**
- Human errors 2 — mislabeling, losses
- Human errors 3 — fraud, sabotage

# Golden rules sampling

- Quantify and optimize sampling errors
- Sample where material is well mixed
- Sample when material is in motion
- Use sample containers without constraints
- Do not overfill sample containers
- Use rotary sample splitters
- Make for each product a SOP and Protocol

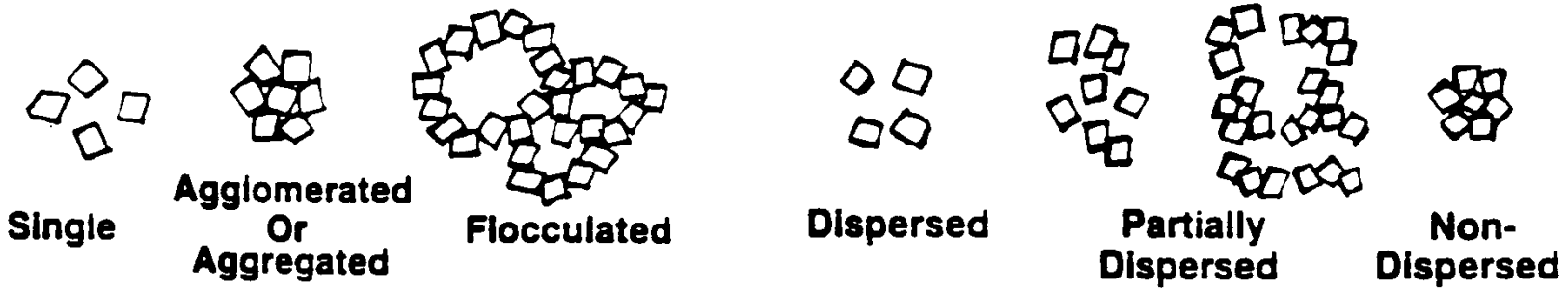
# Dispersion of powders in liquids and air

# Dispersion goals

- Primary particles, free of agglomerates, etc.
- No breakage, dissolution or swelling of particles
- Stable dispersion during measurement

# Particle configurations

**before dispersion** **after dispersion**

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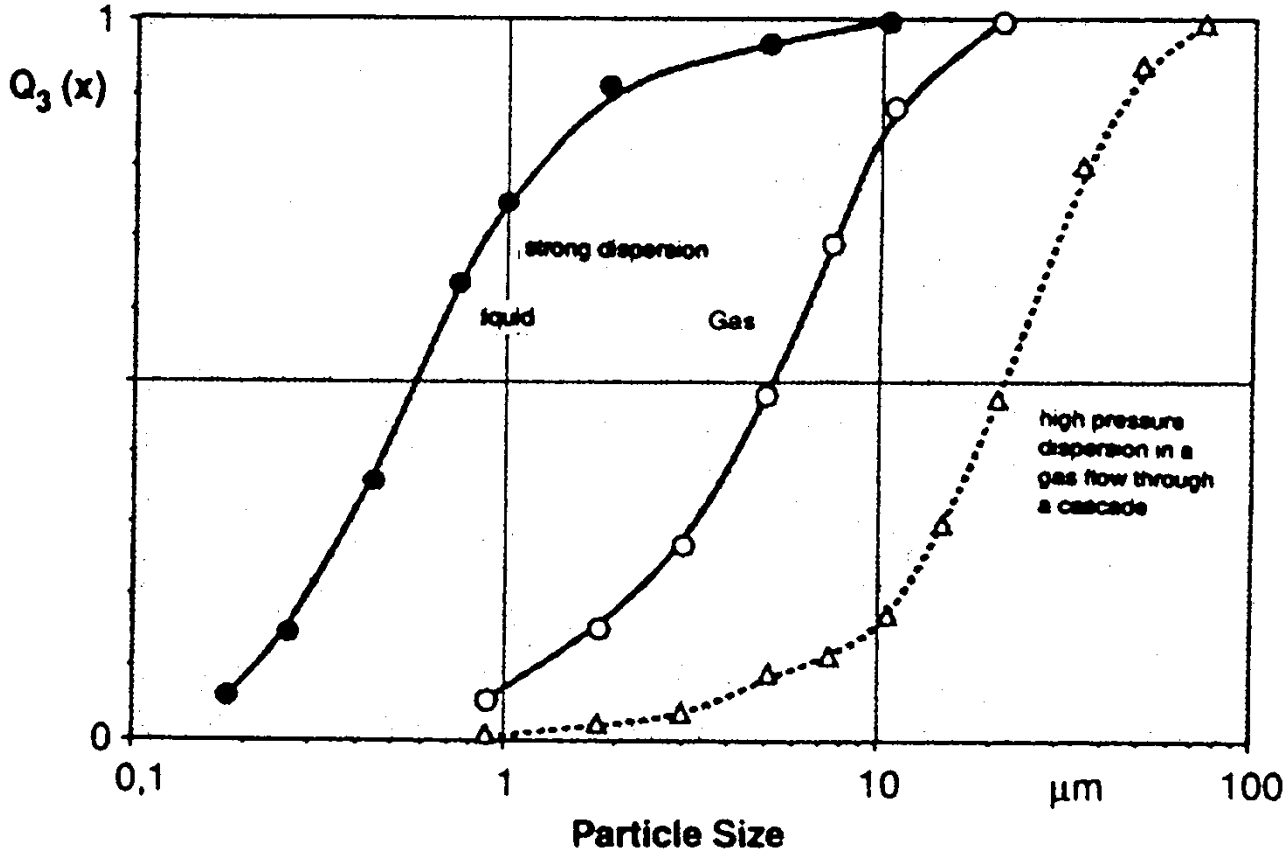
# Fundamental liquid dispersion steps

- Wetting of solid, plus displacement of air
- De-agglomeration of clusters
- Stabilization of dispersed primary particles in suspension

# Influence dispersion conditions

(gas and liquid; R. Polke et al, Part.Part.Syst Charact.8 (1991) 1-7)

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# How for particle size ?
# Measurement techniques

- Counting: number-based
- Area/cross-section-based
- Volume/mass-based
- Light/sound intensity-based

➢ Depends on technique

# How for particle size ?

- Fingerprint techniques
- Separation techniques
- Particle ensemble techniques
- Various techniques

# Fingerprint techniques

- Microscopy (optical, SEM, TEM)
- Image analysis
- Chord length
- Electrical sensing zone
- Flow cytometry
- Optical particle counters
- Phase Doppler anemometry
- Time of flight

# Separation techniques

- Air classification
- Electrical mobility analysis
- Hydrodynamic chromatography
- Impaction
- Sedimentation (gravity; centrifugal; FFF)
- Sieving
- Size exclusion

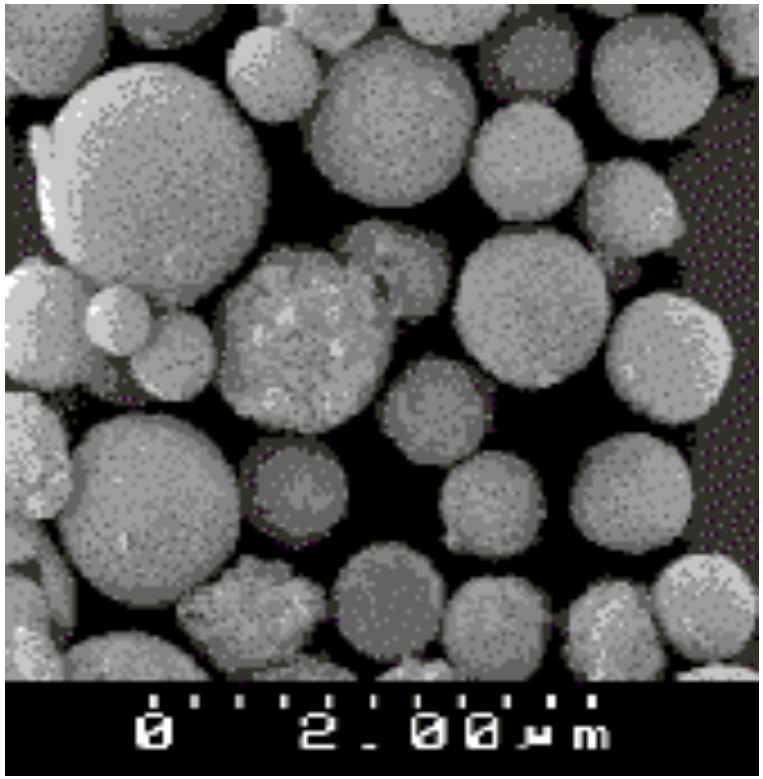
# Particle ensemble techniques

- Dynamic light scattering
- Electro-acoustic
- Laser diffraction
- Ultrasound extinction
- Nuclear magnetic resonance
- Small-angle X-ray scattering

# Various techniques

- Hegman gauge
- Permeability of packed column

# Microscopy/Image analysis
## Interpretation of magnified images

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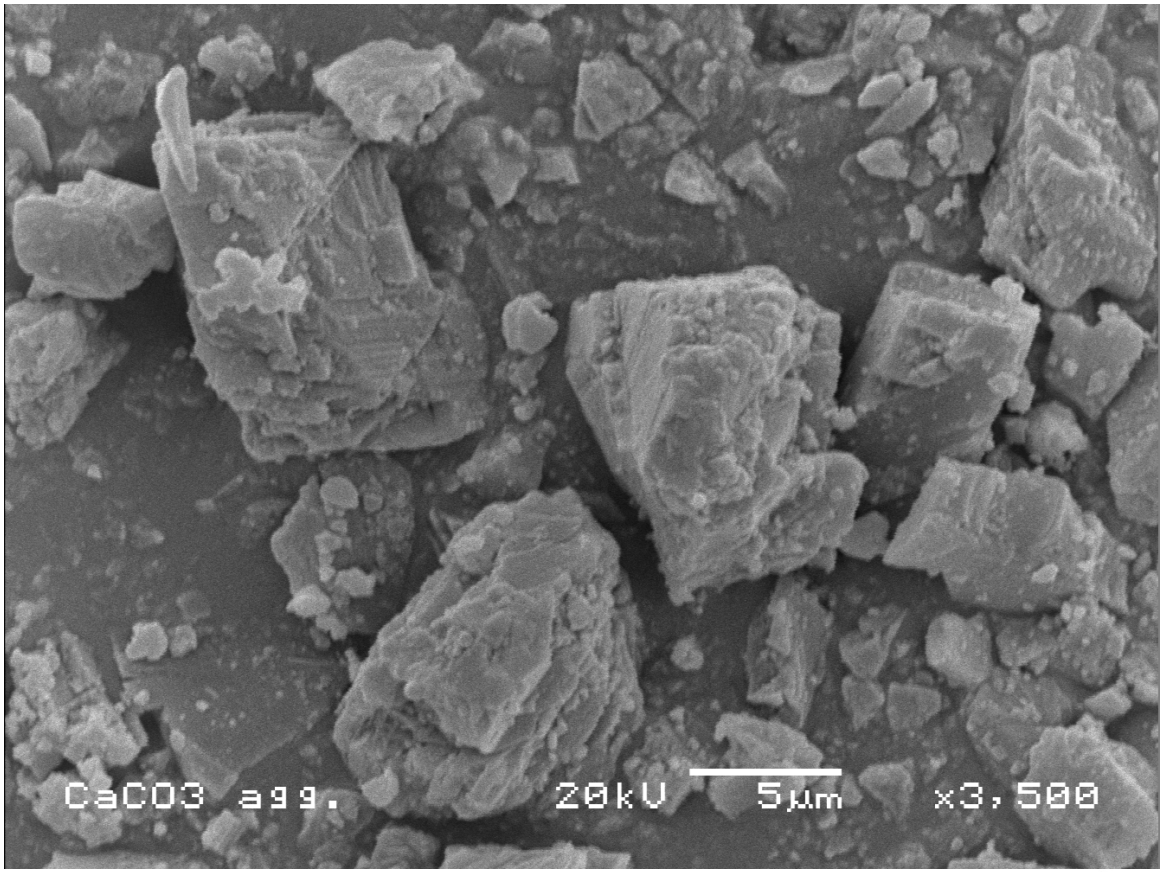
# Microscopy/Image analysis

- What do you want to measure?
- Select sufficient magnification (size, shape)
- Problems with overlapping particles
- Visualisation: good qualitative check on particle shape and dispersion quality

# Microscopy: visualisation

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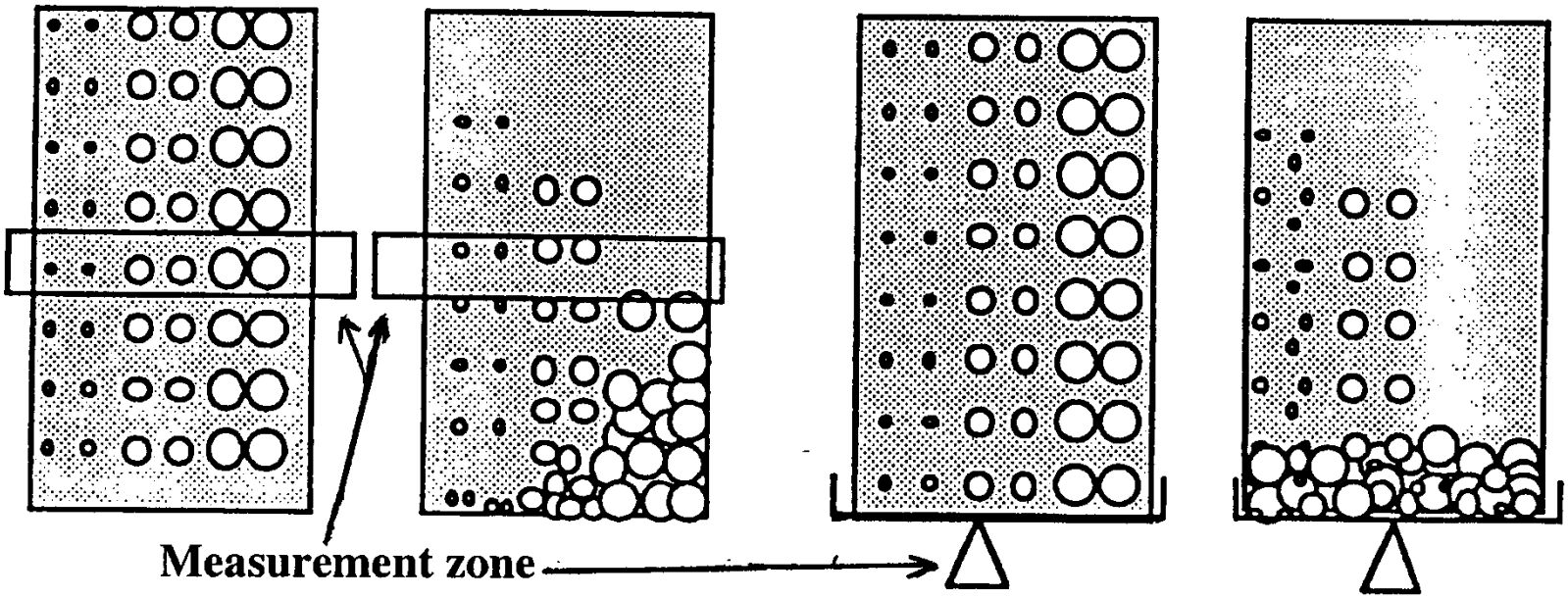
# Sedimentation

- Homogeneous or line start
- Laminar settling: Re < 0.25
- Particle interaction/ concentration
- Concentration measurement:

  mass; X-ray; optical

# Gravity sedimentation

## Settling + X-ray absorption/weighing against time




**Stokes' law:** $D_{St}^2 \tilde{=} 18\eta H/(\rho_s - \rho_l)gt$

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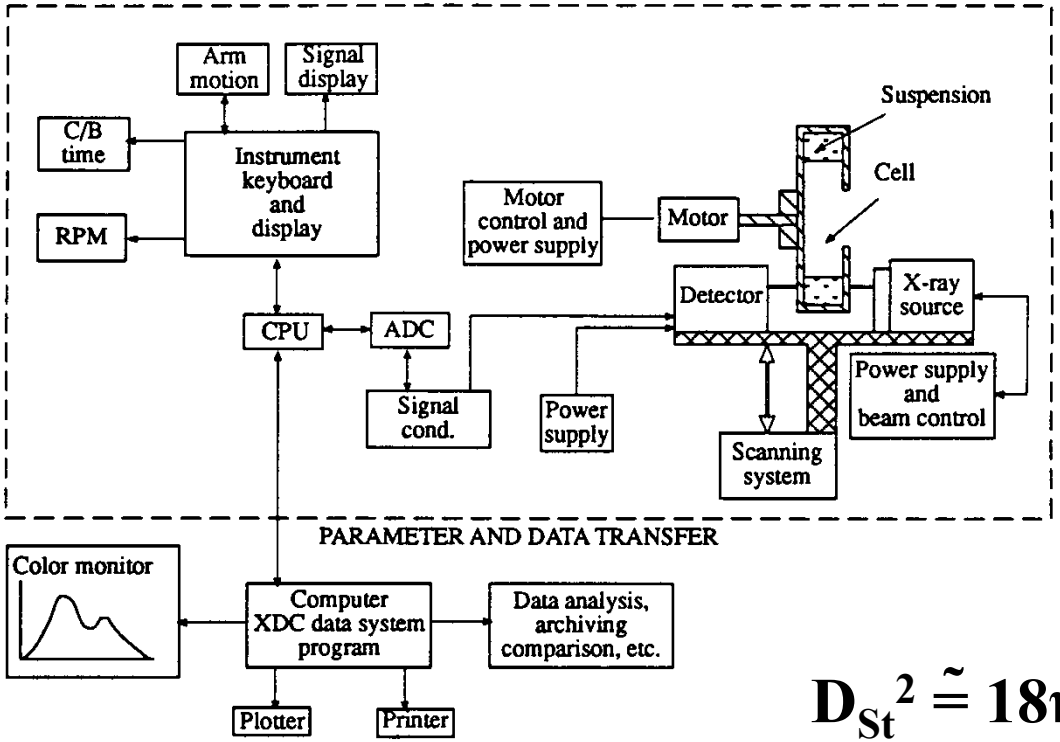
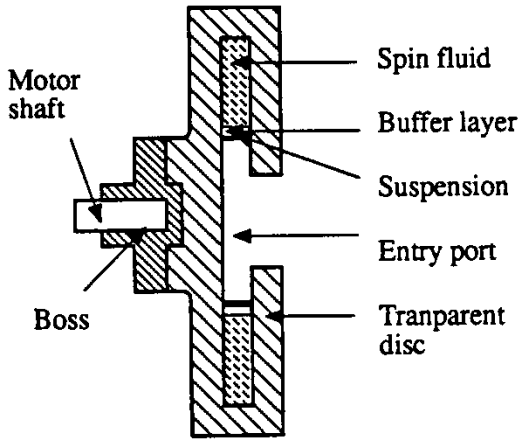
# Centrifugal sedimentation

## Settling + radiation absorption against time




$$D_{St}^2 \cong 18\eta.\ln(R_d/R_o)/(\rho_s - \rho_l)\omega^2 t$$

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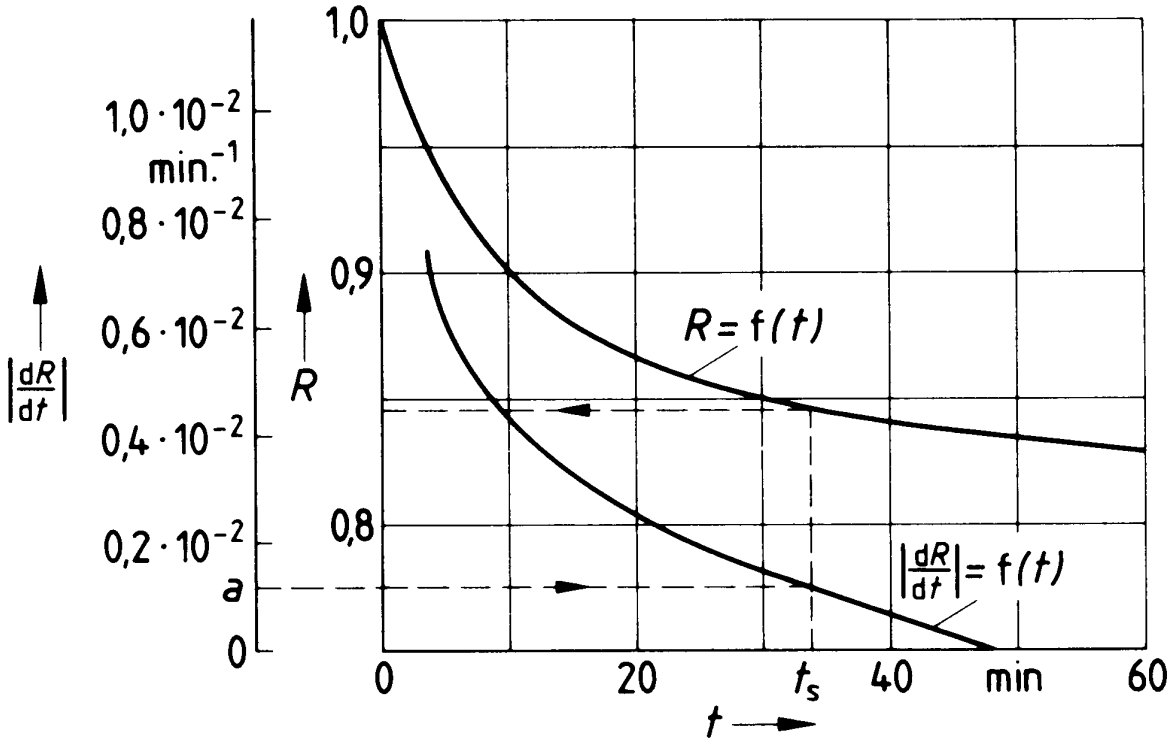
# Sieving

- (Non-) passage through sieve apertures
- Weighing of sieve residues
- Dry or wet
- Different sieve types:
  - Woven wire sieves
  - Plate sieves
  - Electroformed sieves

# Sieving process




**R = residue**

**dR/dt = sieving rate**

**a = end point**

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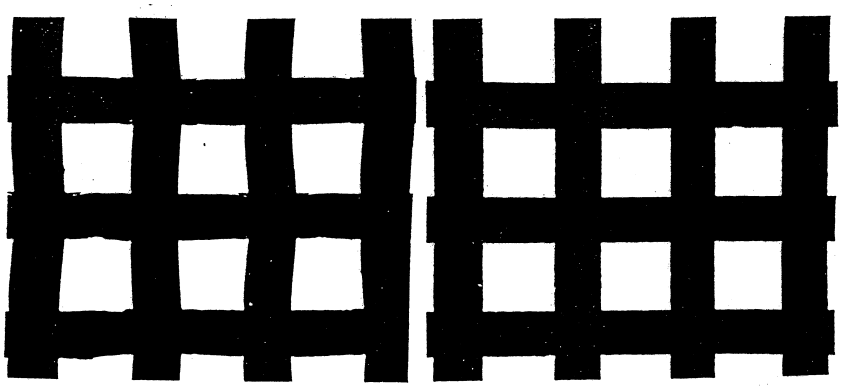
# Sieving critical points

- Load on sieves
- Damage
- Sieve specifications: calibration needed



Woven-wire
125 µm

Electroformed
125 µm

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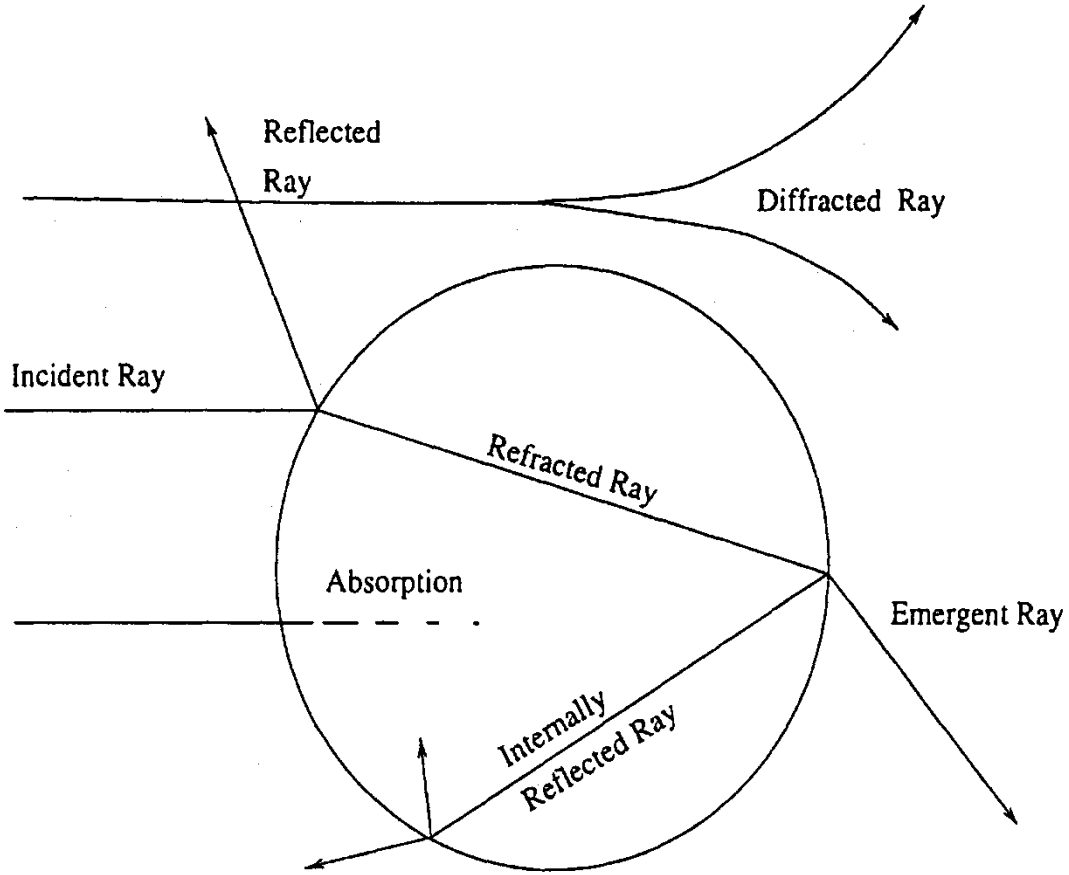
# Light scattering




**interference**

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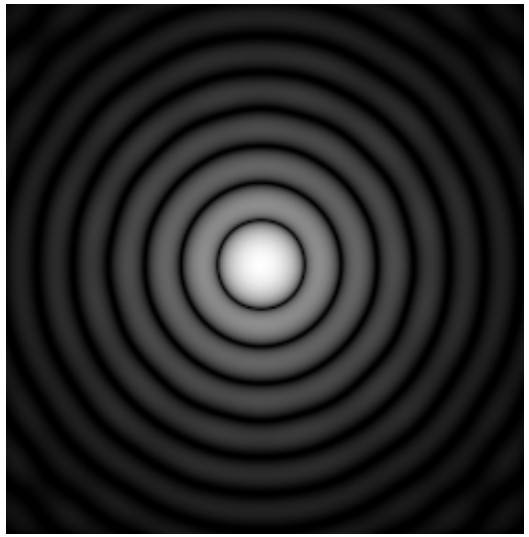
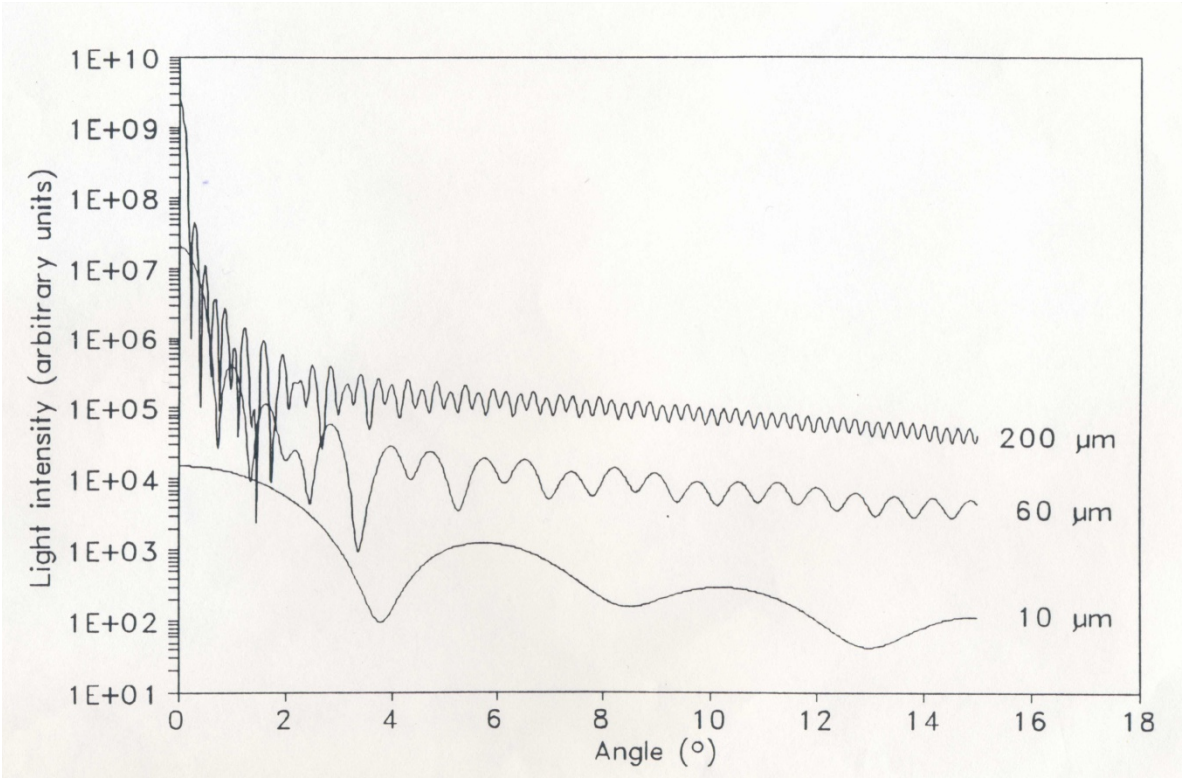
# Laser Diffraction

## Deconvolution of angular scattering pattern



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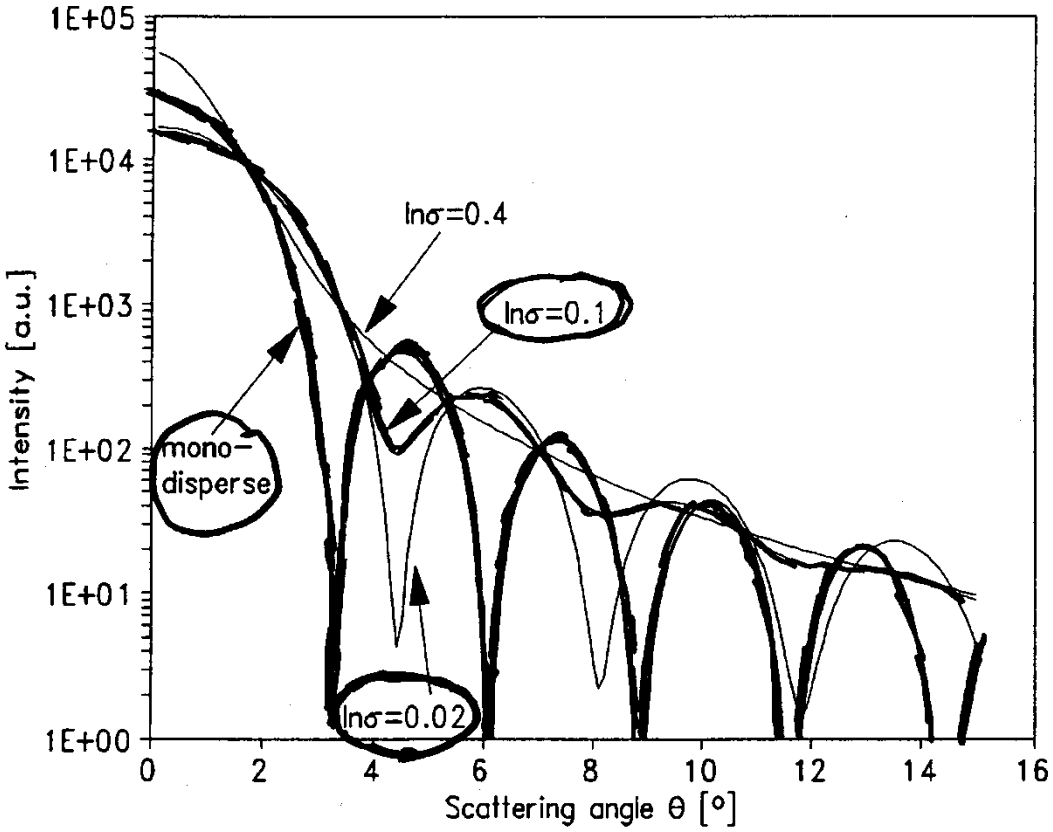
# Scattering patterns

lognormal PSD around 10 um; m = 1.22

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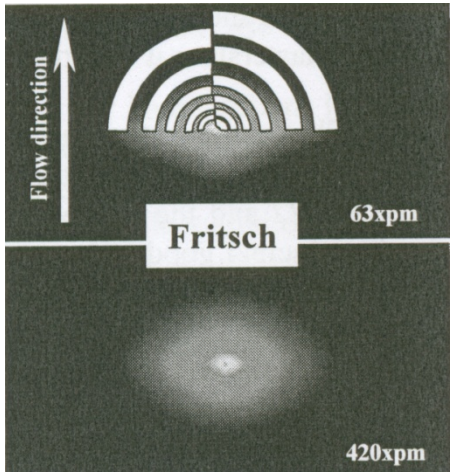
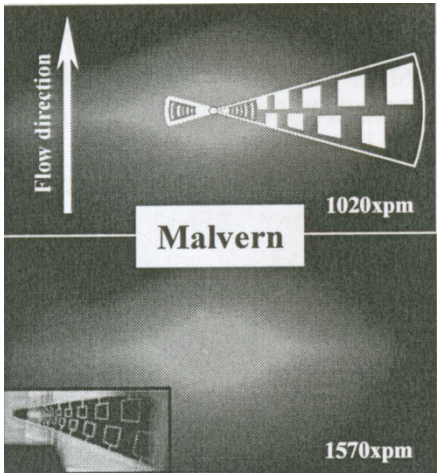
# Laser Diffraction

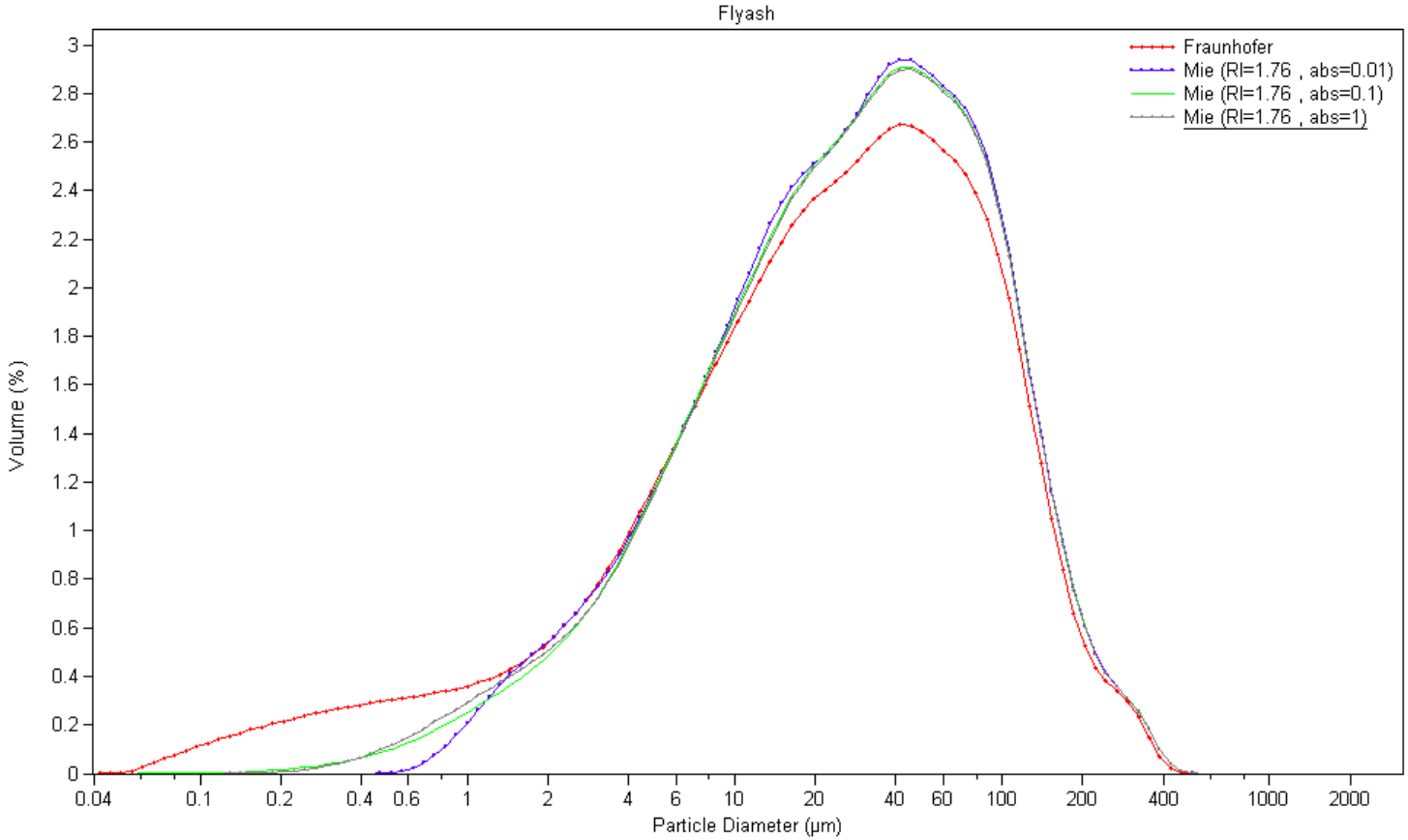
- Model: Mie or Fraunhofer
- Concentration: single/multiple scattering
- Detector type




**CCD; CMOS**

# Laser Diffraction: model

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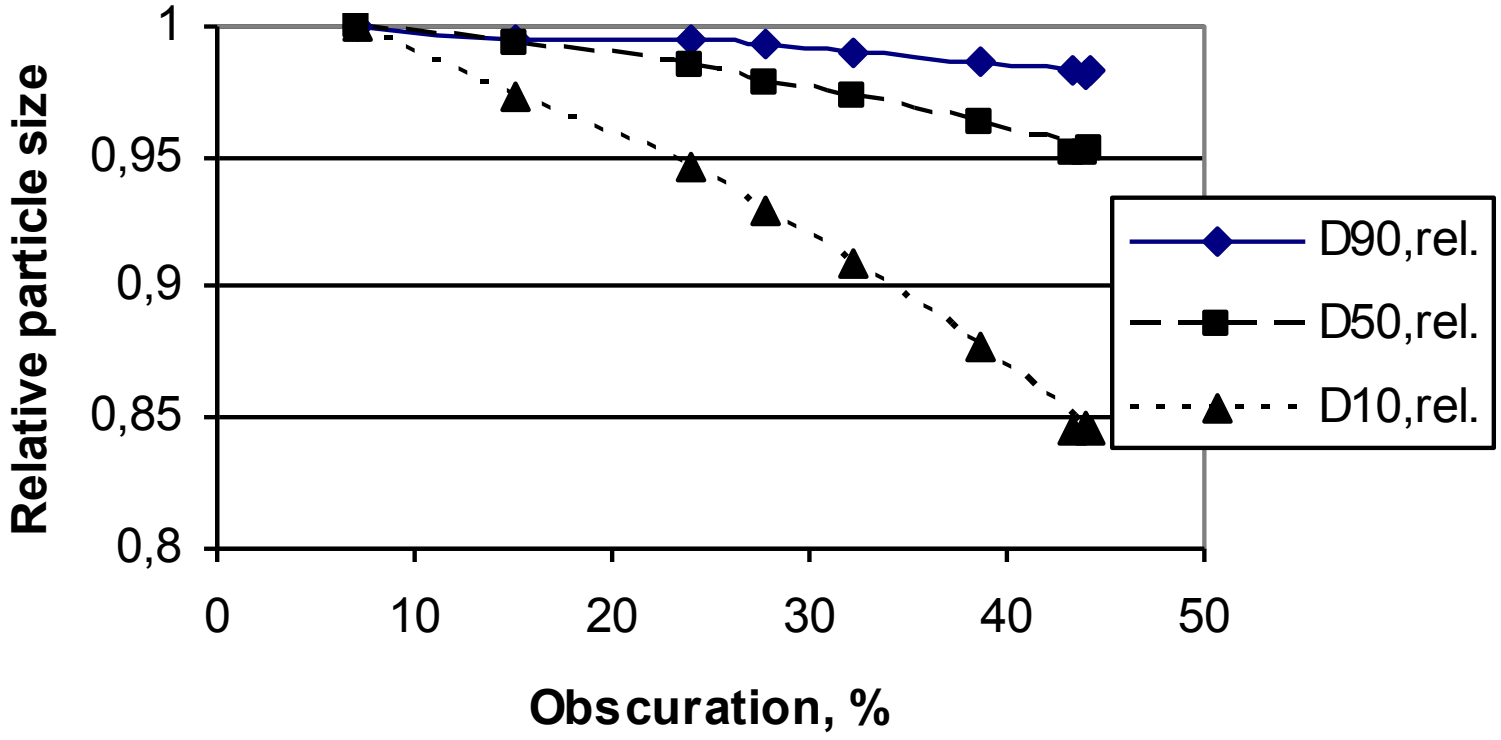
# Laser Diffraction: concentration

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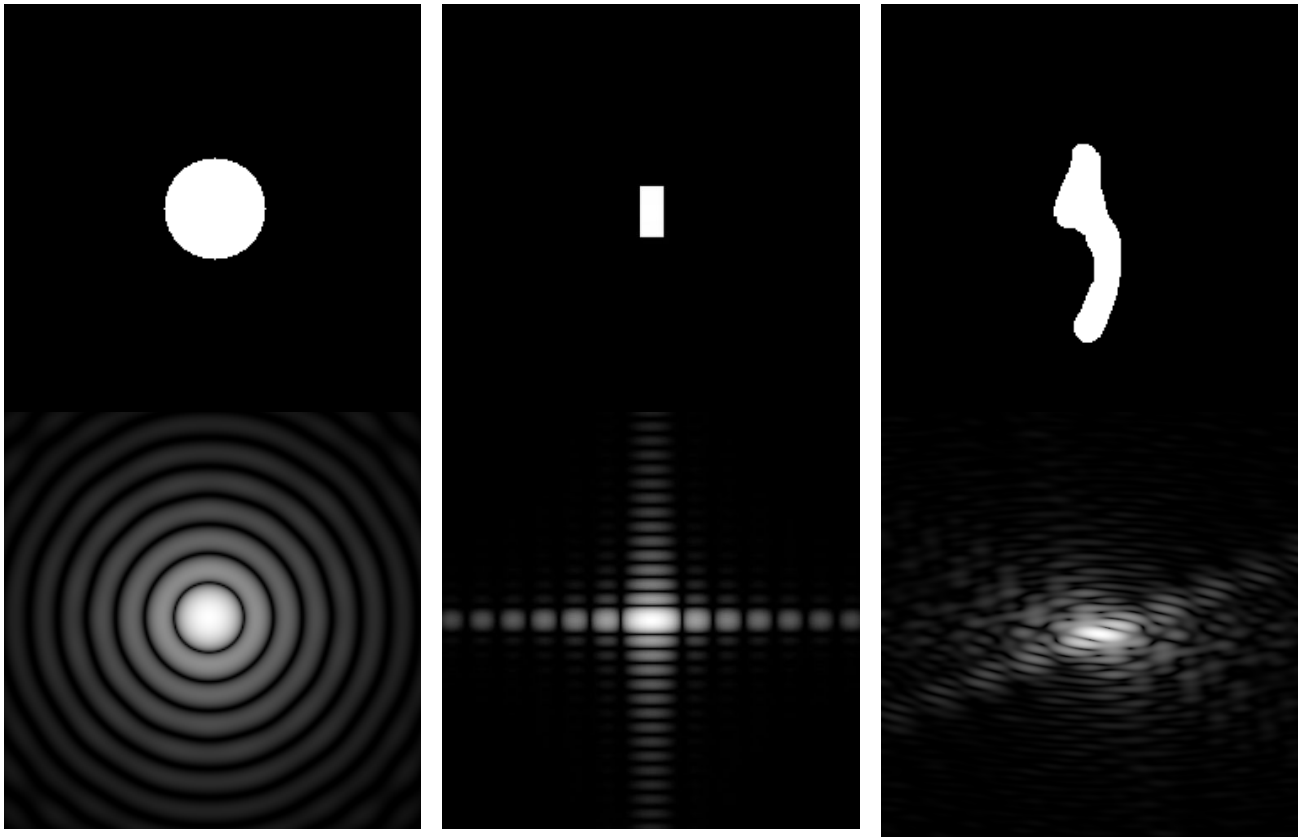
# Laser Diffraction: particle shape



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# Dynamic Light Scattering
## (DLS, PCS, QELS, DWS)

- Brownian motion of particles---Diffusion
- Fluctuation of light scattering intensity at stated angle
- Faster fluctuation at smaller particle size
- Interpretation: correlation or particle tracking
- Stokes-Einstein equation: $Đ = k_B T/3\pi\eta D$

# How: size quality aspects techniques

- Choice of relevant PSD parameter(s)
- PSD range allowed (in instrument)
- Concentration range allowed (in instrument)
- Total analysis time (incl. sample preparation)
- Stability of measurement (noise; drift)
- Costs (investment; operation; personnel)

# Size quality aspects instruments

- Precision: repeatability; reproducibility
- Bias
- Accuracy
- Resolution
- Sensitivity (detection/determination limit)
- Traceability
- Quality of reporting and maintenance

# Techniques 1 (selection)

| | Range µm | Repeat. % rel. | Resol. % rel. | Sensit. % v/v | Meas.tim. min. |
|---|---|---|---|---|---|
| Micr./Im.an. | 0.3-500 | ≥ 1* | ≥ 1* | ≥ 1* | ≥ 5 |
| SEM | 0.01-500 | ≥ 1* | ≥ 1* | ≥ 1* | ≥ 10 |
| Grav.sedim. | 0.3-200 | 1-3 | 5-10 | 2 | ≥ 15 |
| Centr.sedim. | 0.02-10 | 1-3 | 5-7 | 2 | ≥ 15 |
| Sieving | 5-$10^5$ | 0.5 | 10-40 | 0.5 | 20 |
| Laser Diffr. | 0.1-$10^4$ | 0.5 | 10-40 | ~ 5 | 1 |
| DLS | 0.005-1 | 2-5 | ~ 30 | ~ 10 | 1 |

* depends strongly on magnification/sample prep.

# Techniques 2 (selection)

| | Size type | Quantity | Comments* |
|---|---|---|---|
| Micr./Im.an. | Area/length | Number | D + W; *S* |
| SEM | Area/length | Number | D; *S* |
| Grav.sedim. | Stokes | Mass | W; *S/M*; *ρ* |
| Centr.sedim. | Stokes | Mass/Opt. | W; *S/M*; *ρ/RI* |
| Sieving | Sieve | Mass | D + W; *M/L* |
| Laser Diffr. | Scatter | volume | D + W; *S/M*; *RI* |
| DLS | Hydrodyn. | Scatter int. | W; *S*; *RI* |

* D, W: Dry, Wet measurement
* *S, M, L*: Small, Medium, Large sample size
* *ρ* = Density; *RI* = Refractive Index

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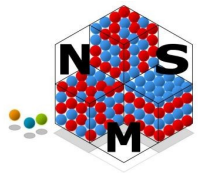
# Common error sources

- Choice of incorrect PSD parameter
- Lack of operator capability (education)
- Incorrect sample
  - **too small; too few increments; non-representative; contamination**
- Incorrect dispersion
  - **concentration; agglomerates; dissolution; air bubbles; conditions**
- No visual examination under microscope
- Using wrong technique, conditions or parameters (***RI*, $\rho$**)
- Inadequate instrument calibration/validation/maintenance
- Not using written standards and instructions
- Poor reporting

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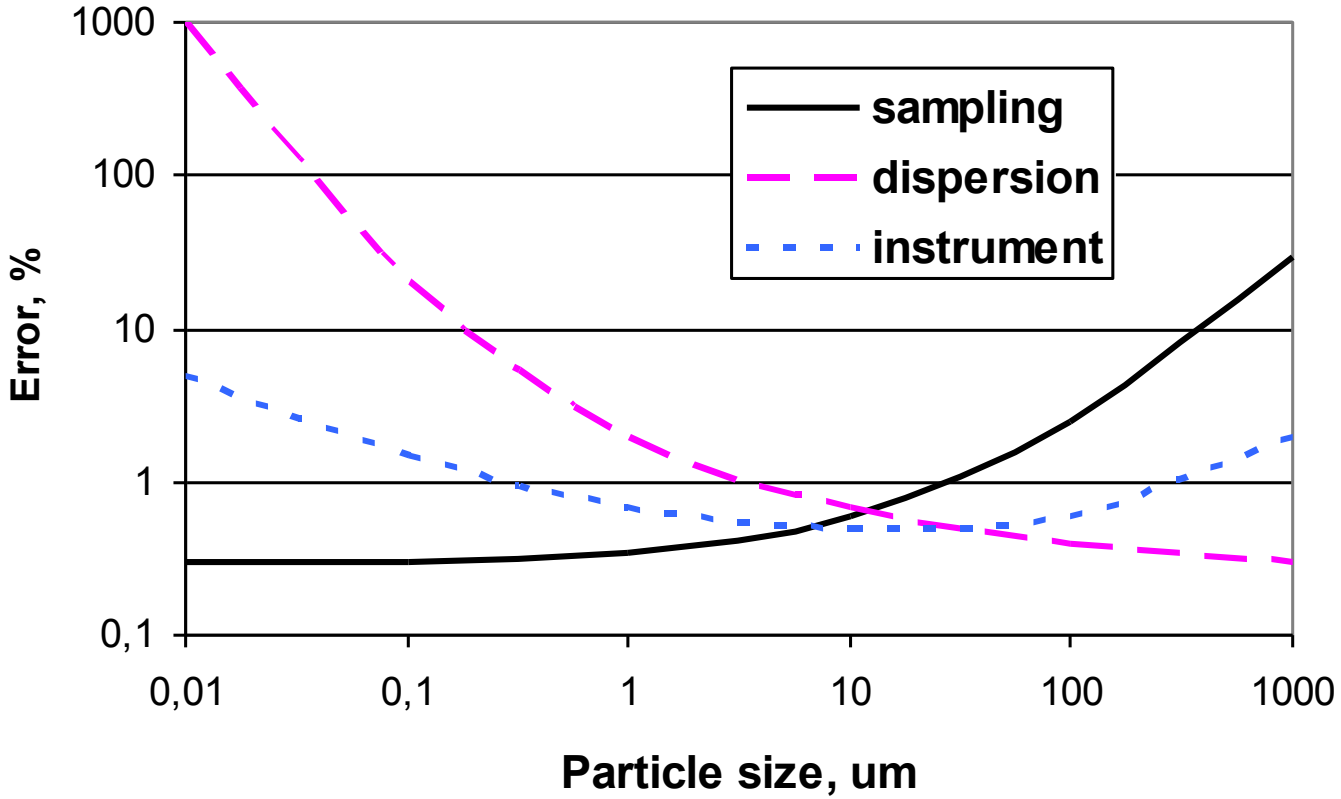
# Error sources PSD measurement

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# Where?

- Off-line in laboratory

  (adaptation for optimum measurement conditions;

  easy tests for quality aspects; other instruments)
- At-line in laboratory near process

  (as off-line measurement; often automated)
- On-line in parallel line to process

  (adaptation for temperature/pressure possible)
- In-line in process line
- In-situ at specific point in reactor

# Improve quality

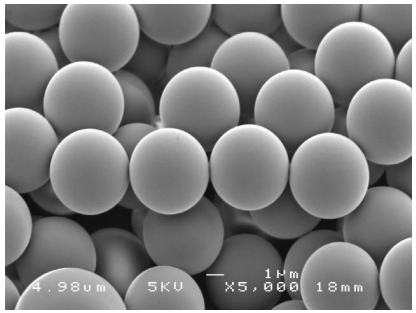
- Written standards (ISO, ASTM, etc.)
- (Standard) Reference materials
- Quality control charts (instrument/operator)
- Use of statistics
- Knowledge (books, courses, journals)
- Experience (and self-criticism)
- Understand your challenge

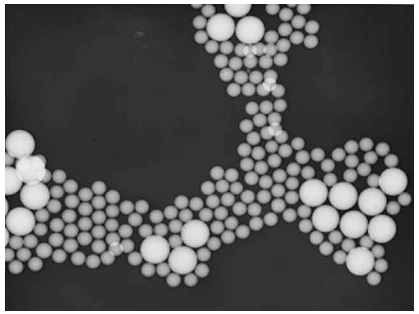
# Written standards

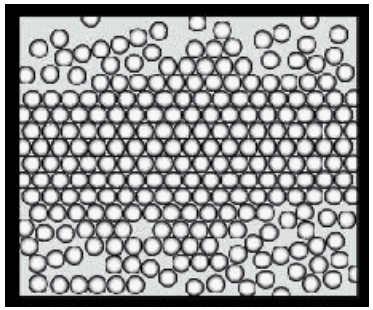
- Standard nomenclature and symbols
- Standard PSD representation
- General background and requirements:
  - sampling, dispersion
- Specific techniques: advice and requirements
- Specific products: test methods
- ***They tell how to measure***

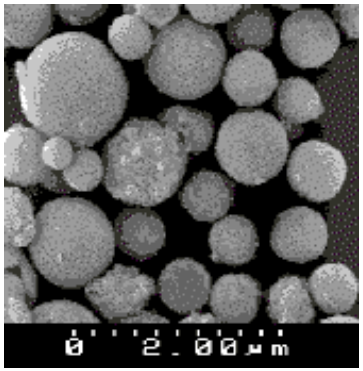
- ISO, Pharmacopoeia, SOP's

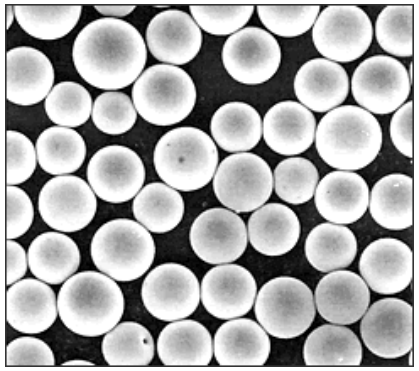
# Reference materials

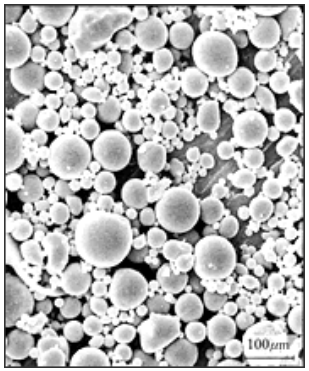






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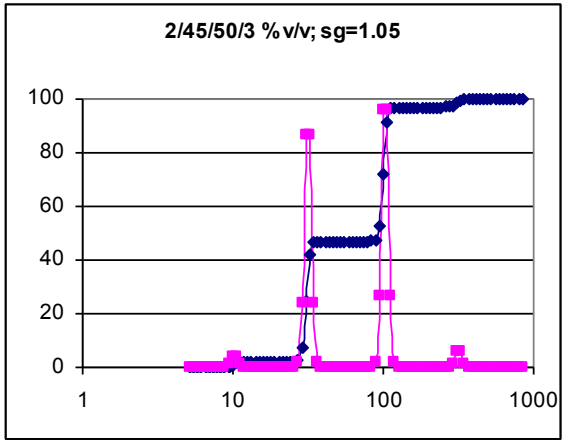
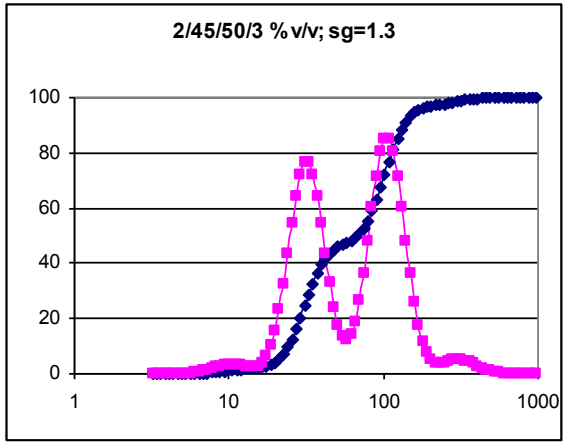
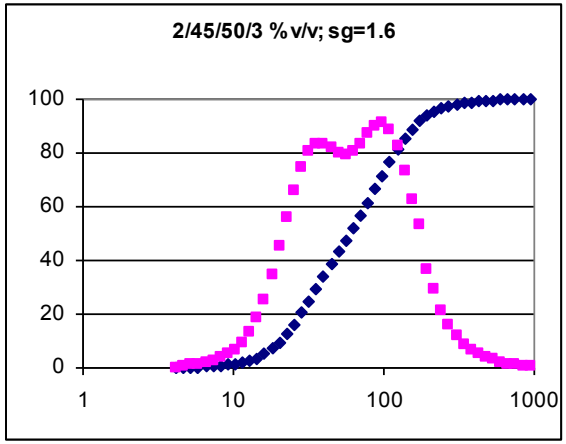
# Reference materials (picket-fence mixture)




High resolution

Medium resolution

Low resolution

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# Understand your challenge !!

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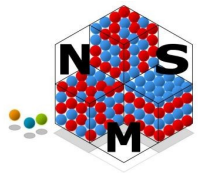
# CONCLUSIONS

- Consider your choices on

  **WHY – WHAT – HOW – WHERE**

  carefully in relation to product requirements and after adequate, critical investigation of quality and costs!
- Characterization is **more** than just size!
- Check performance regularly.

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# Literature

- In addition to Martin Rhodes' book:
- Henk G. Merkus, Particle Size Measurements - Fundamentals, Practice, Quality; Springer 2009.
- Henk G. Merkus, Gabriel M.H. Meesters (eds.), Particulate Products – Tailoring Properties for Optimal Performance; Springer 2014.
- Plus coming book on Production and Handling of Particulate Materials, Springer 2015.