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HORIBA Scientific

HORIBA Instruments Incorporated

Irvine, California

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Modern Particle Characterization Techniques

Introduction

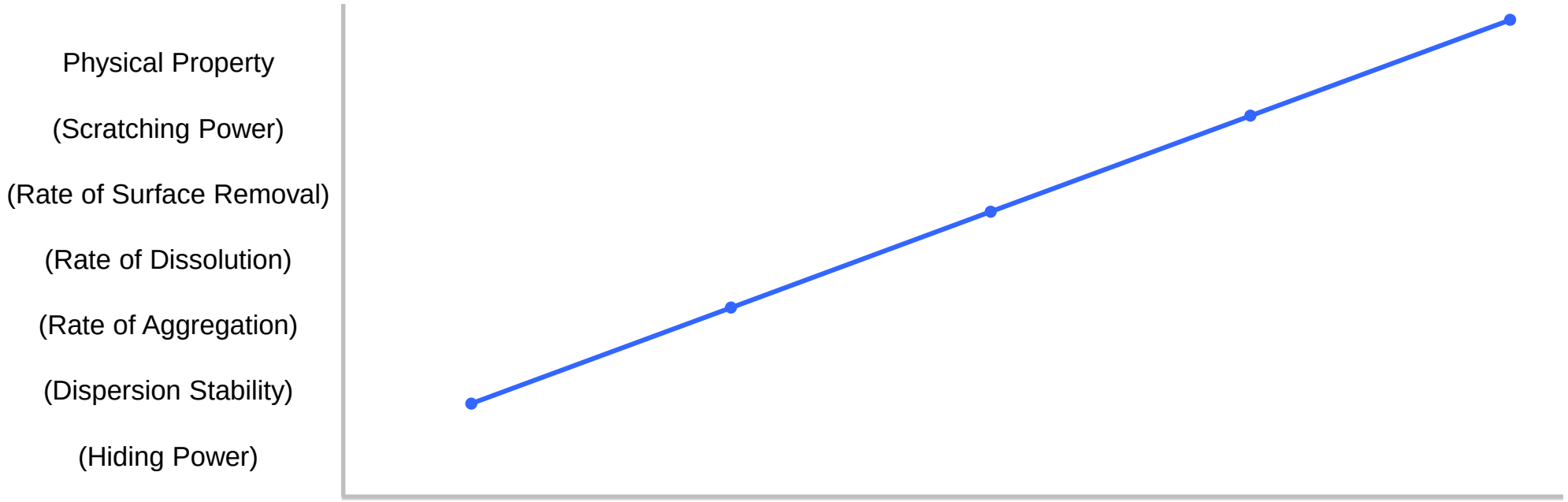
April 22, 2020

Why Characterize Particles?

Particle physical properties material behavior and processing across a number of industries

Industry		Industry	
Ceramic	 	Construction	
Oil/rubber	 	Chemical	
Battery		Pharmaceutical	
Electricity		Food/Drink	 
Automobile		Paper/Pulp	 
Mining		Ink/Toner	 

How will the data be used?



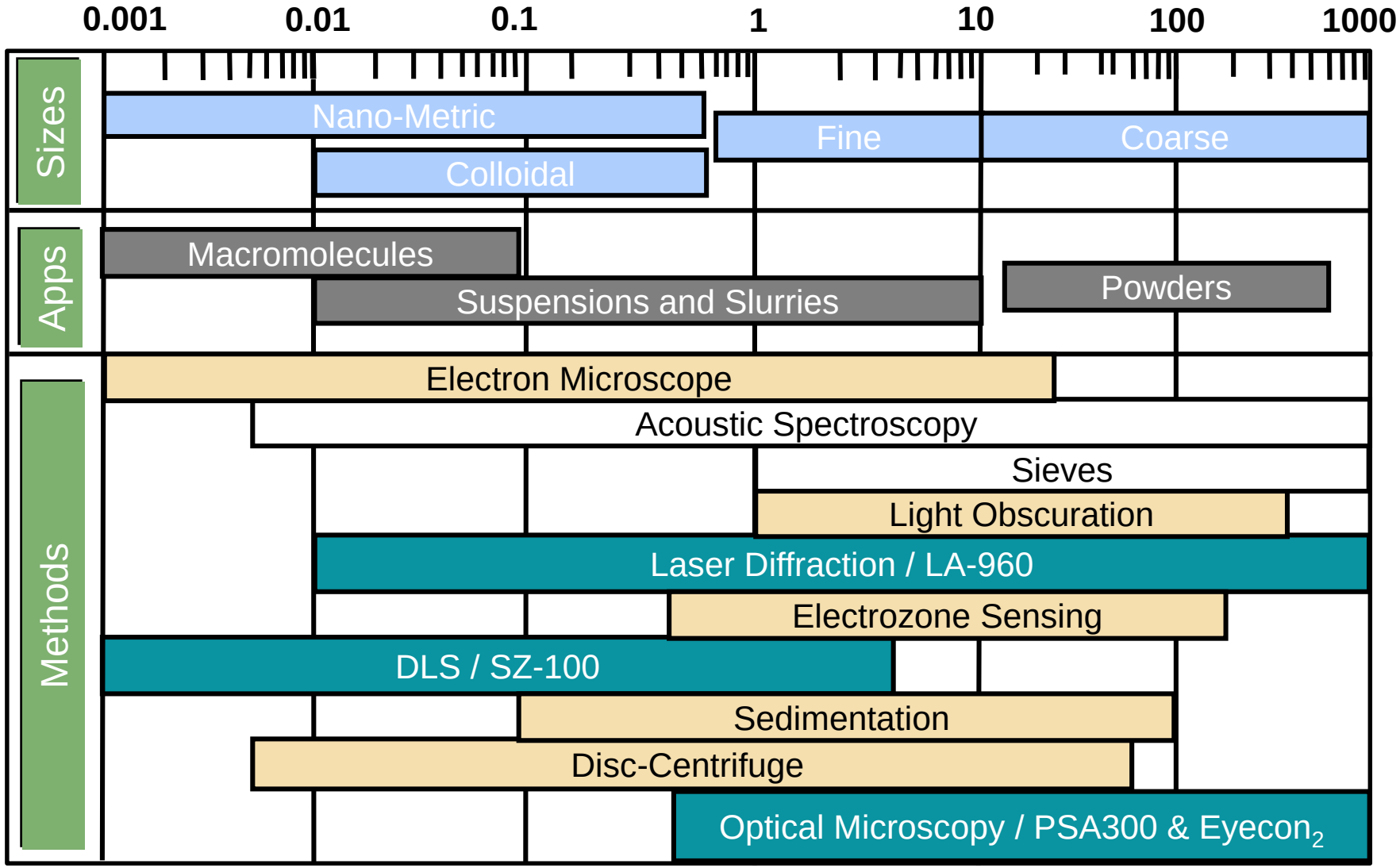
Particle Characterization Methods

- Particle Sizing
- Particle Counting
- Surface Area
- Porosimetry
- Zeta Potential
- Particle Shape
- Many More

Particle Sizing Techniques

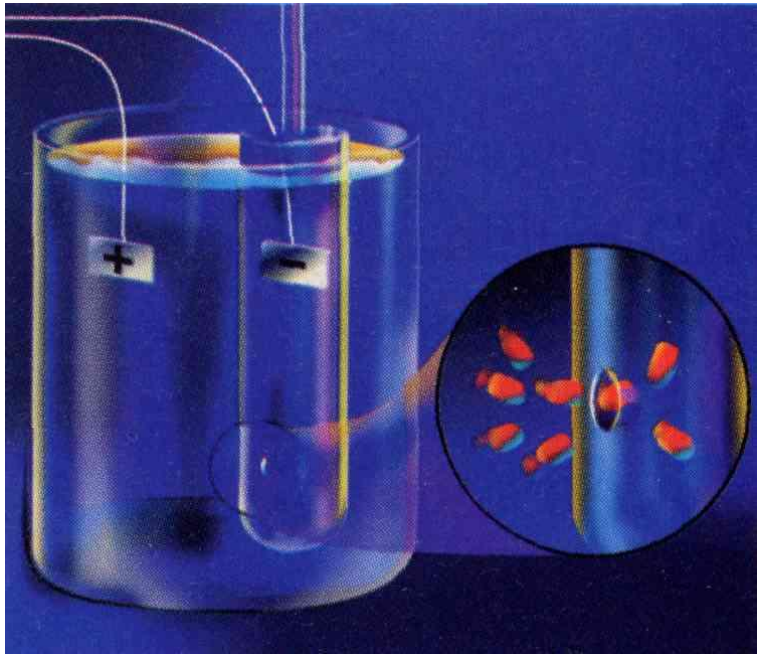
- Sedimentation
- Coulter Counter
- Laser Light Scattering
- Dynamic Light Scattering
- Image Analysis
- Nano Particle Tracking
- Many More

Size Range by Technique (µm)



Electrical Zone Sensing

- Coulter Principle
  - Based on change in conductivity of aperture as particle traverses.
  - Requires conducting liquid.
  - Directly measures particle volume and counts.
  - High resolution
  - Used for blood cell counting more than industrial applications



Sedimentation

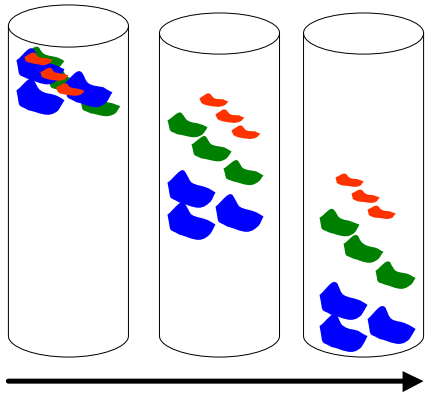
- Stokes Law

$$D = \sqrt{\frac{18\mu V_p}{(\rho_p - \rho_l)g}}$$

V_p	=	Settling velocity of discrete particle
g	=	Gravity constant
ρ_p	=	Density of Particle
ρ_l	=	Density of Carrier Fluid
μ	=	Viscosity of Carrier Fluid

Note: assumes settling of spherical particle
Under-sizes compared to other techniques if non-spherical

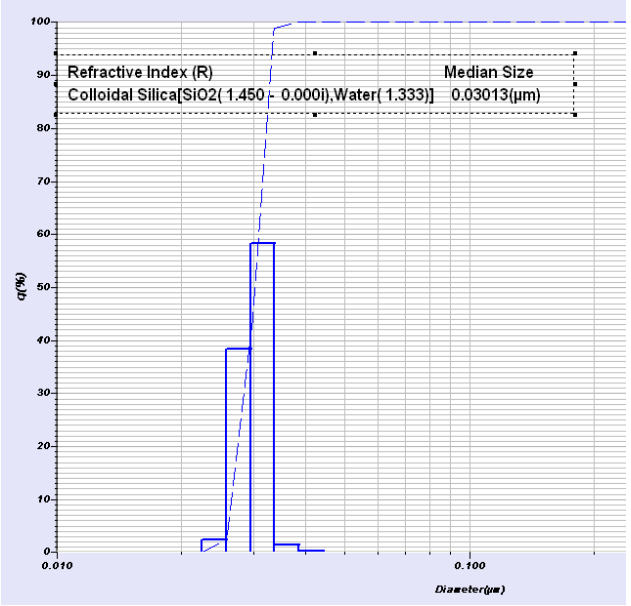
Sedimentation of same density material in a viscous medium

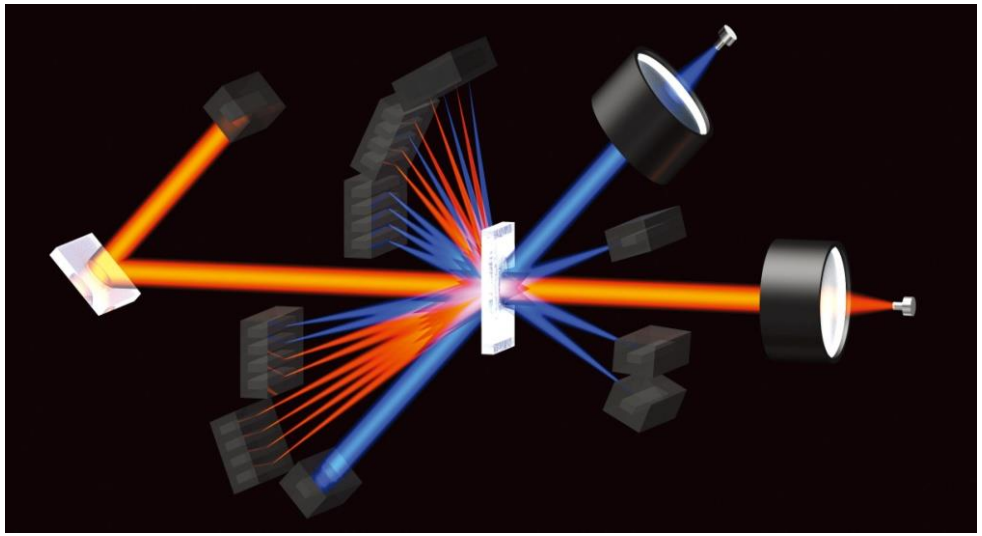


Time

Laser diffraction

Silica ~ 30 nm



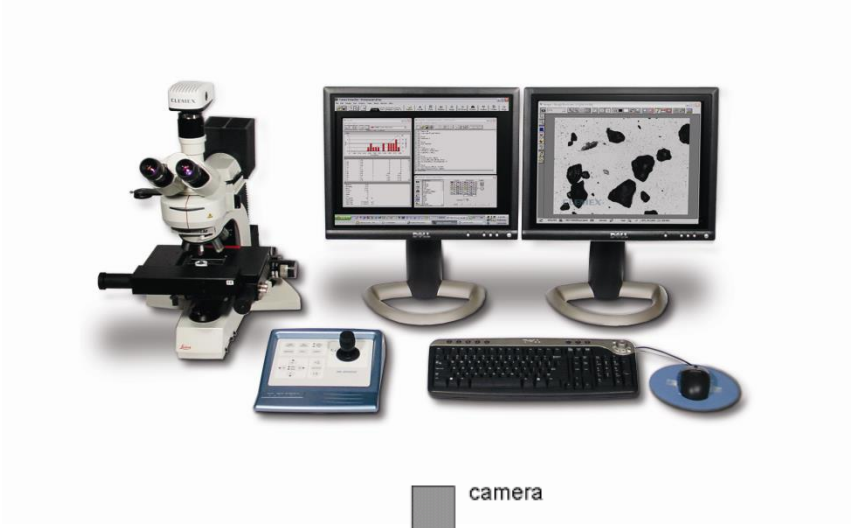


Laser Diffraction

- Particle size 0.01 – 3000 µm
- Converts angular variations in scattered light to particle size distribution
- Quick, repeatable
- Most common technique
- Suspensions & powders

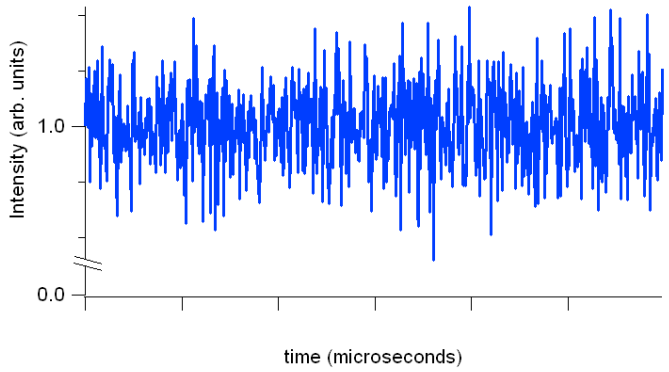
Automated Microscopy

Static:
Particles fixed on slide,
stage moves slide

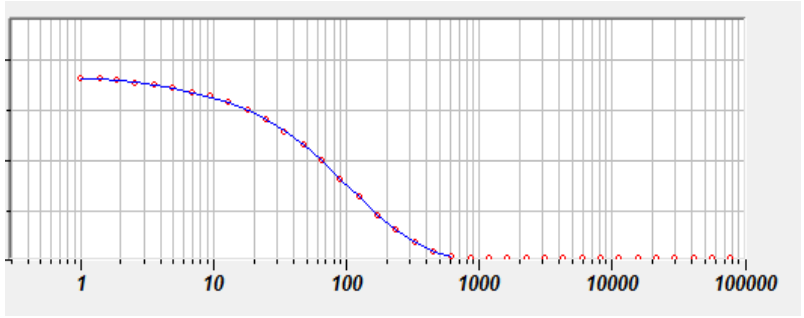


Dynamic:
Particles flow past camera(s)

DLS – Dynamic Light Scattering



Nanogold ~ 50 nm



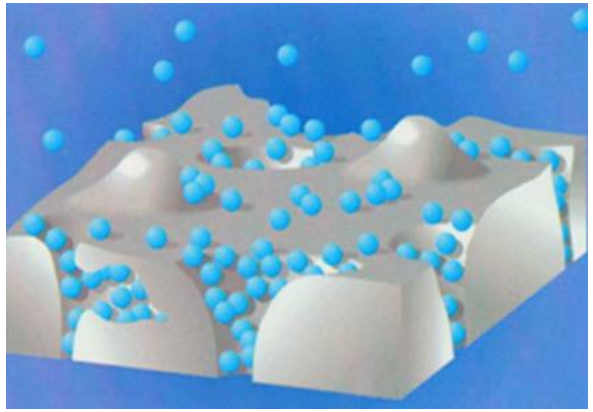
- Particle size < 1 nm – 8 µm
- Converts intensity variations in scattered light to particle size distribution
- Quick, repeatable
- Suspensions

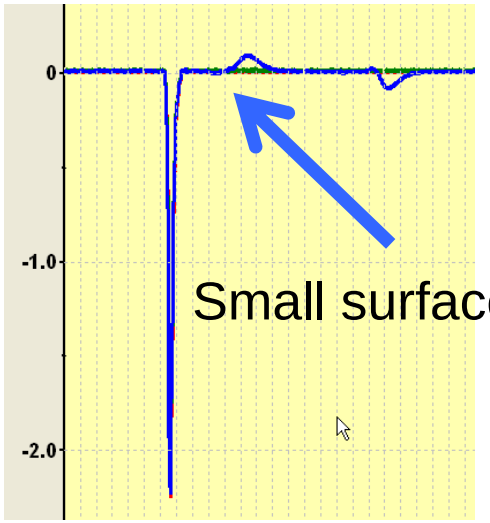
	Z-average Diameter, nm
Run 1	50.5
Run 2	51.1
Run 3	49.2
Run 4	51.5
Run 5	49.7
Run 6	50.9
Avg.	50.5
Std. Dev.	0.9
COV	1.7 %

Sedimentation Particle Sizing Approaches

- Homogeneous
- Line Start
- X-ray Irradiation
- Light Irradiation
- Cell Moves
- Source Moves
- Gravity Sedimentation
- Centrifugal Sedimentation
- Many More

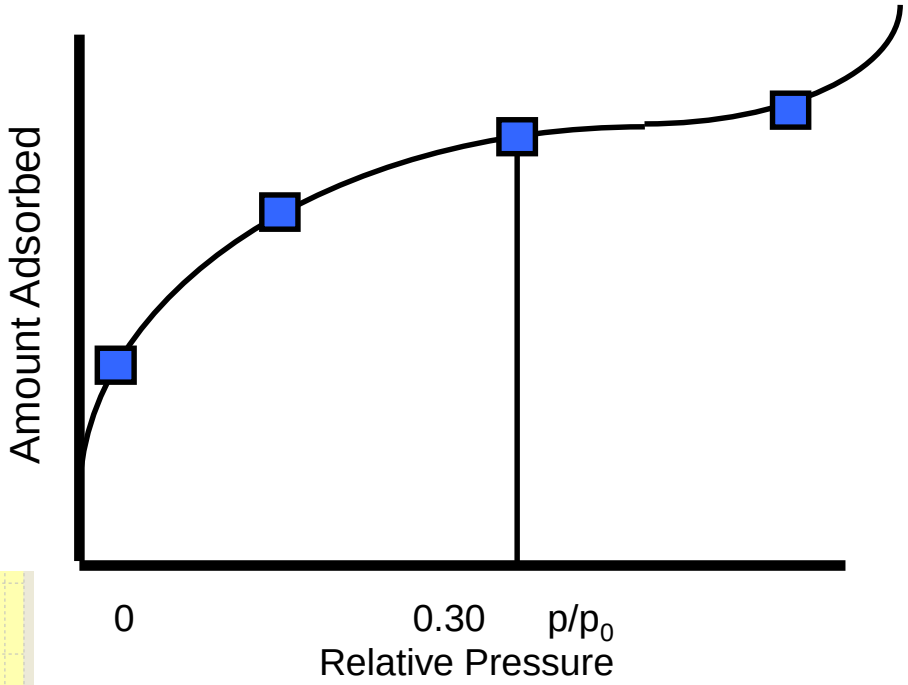
BET Surface Area



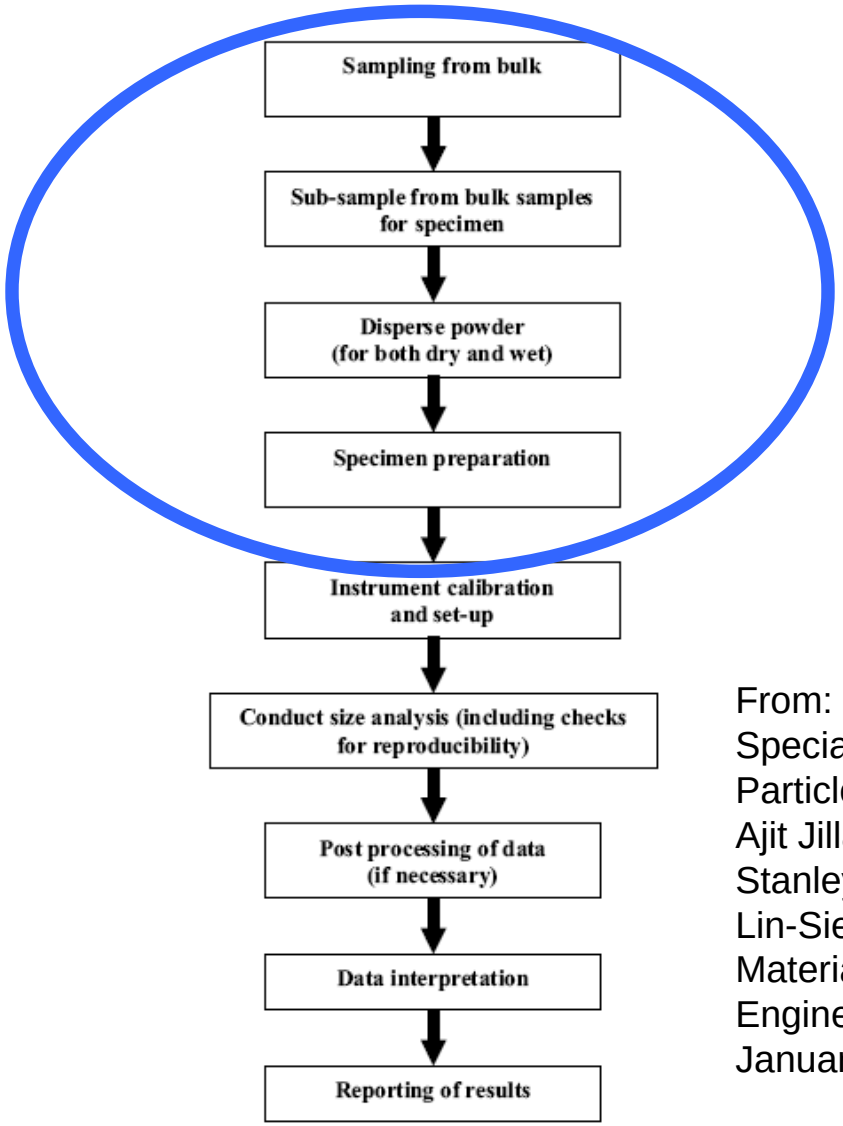


Small surface area

Large surface area



Particle Analysis Workflow



From: NIST Recommended Practice Guide
Special Publication 960-1
Particle Size Characterization
Ajit Jillavenkatesa
Stanley J. Dapkunas
Lin-Sien H. Lum
Materials Science and
Engineering Laboratory
January 2001

All analytical determinations start with sampling (PCA is no exception)

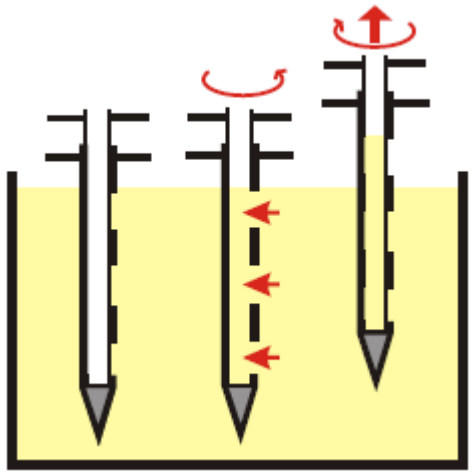
- A representative sample is the key to drawing any scientific conclusion
- This process is seemingly easy, but really complicated
- It is a science of its own so needs some discussion
- It is especially important for broad size distributions
- It is often overlooked by users

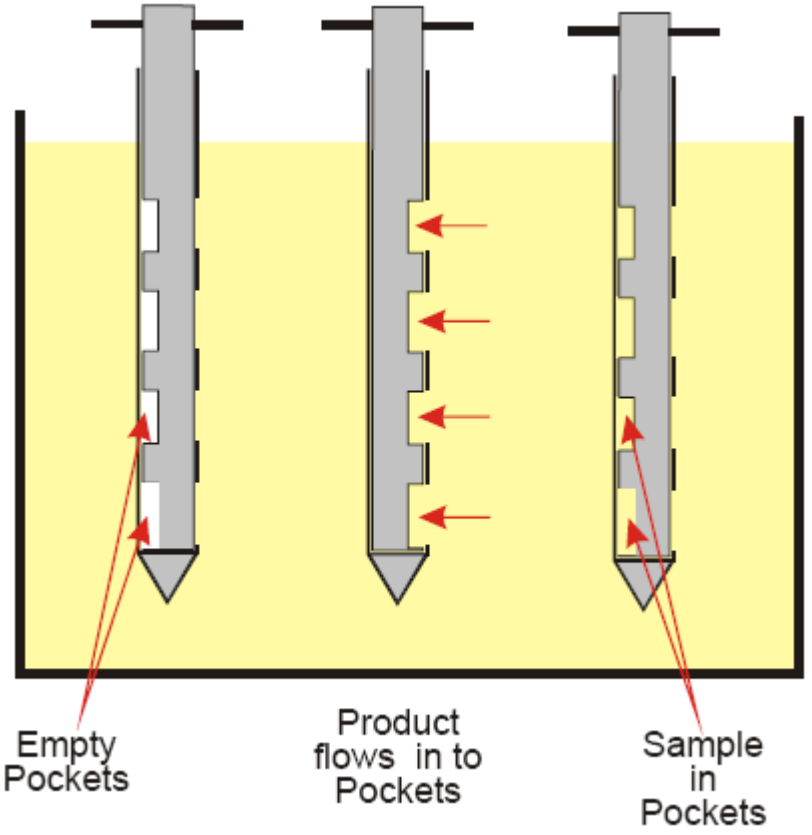
Reliability of selected sampling methods using a 60:40 sand mixture

Sampling Technique	Standard Deviation
Cone and Quartering	6.81
Scoop Sampling	5.14
Table Sampling	2.09
Chute Slitting	1.01
Spinning Riffling	0.146
Random Variation	0.075

Allen, T. (1997). Particle Size Measurement Volume 1: Powder Sampling and Particle Size measurement fifth edition., Page 21. Chapman & Hall.

Sampling from Drums

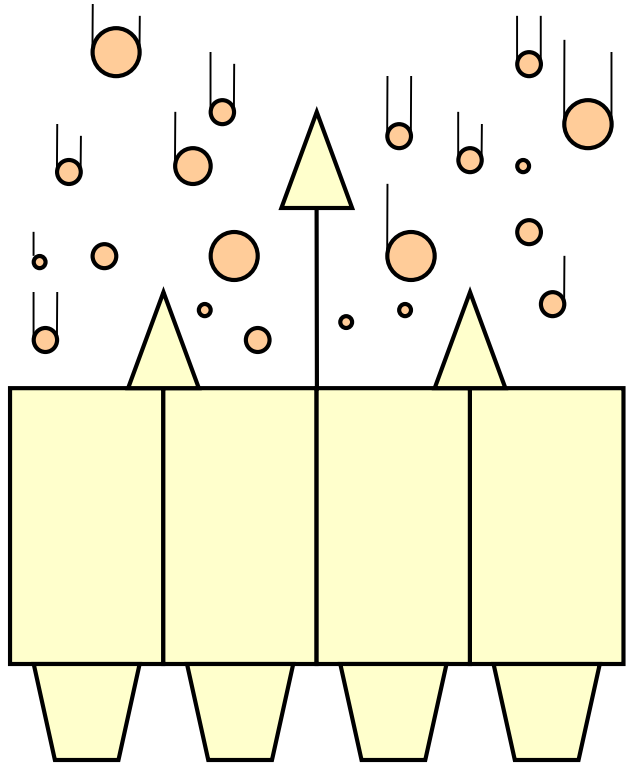




www.samplingsystems.com

Technique: Chute Riffling

Chute splitting allows sample to vibrate down a chute to vanes which separate the mass into two portions. Each portion moves further where they each are divided into two parts, now giving four parts. This is often continued until 8 or 16 portions are obtained.



Sample Dividers

Laboratory sample divider PT 100

- *for pourable powders and granules*
- *feed size up to 10 mm*
- *division into 6, 8 or 10 representative samples*

Laboratory rotary tube sample divider PKZ 1000

- *for pourable powders and granules*
- *feed size up to 10 mm*
- *various division ratios*

Sample splitter RT

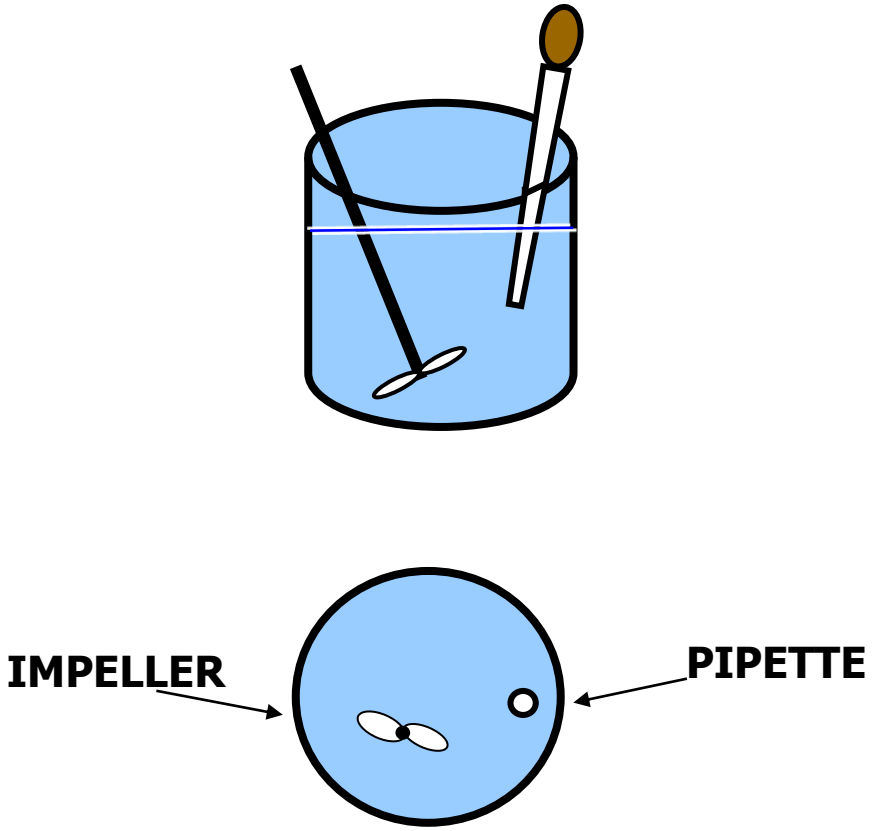
- *for bulk materials*
- *feed size up to max. 50 mm*
- *division into 2 samples*

Technique: Sampling from Beaker

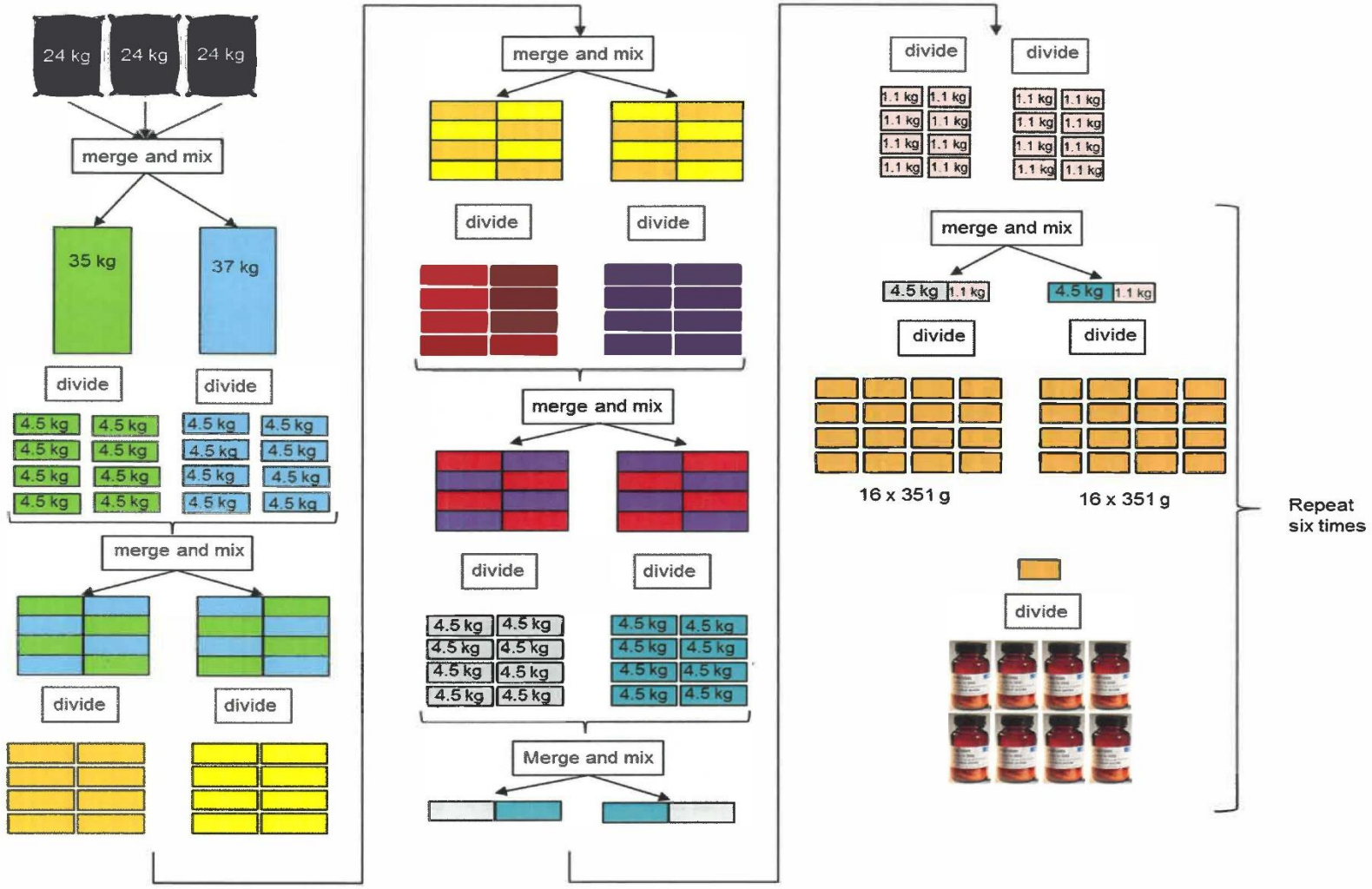
Liquid should be in motion vertically and horizontally to ensure good mixing.

Pipette should be about one-third of the way from the bottom when extracting sample.

Alternative: When mixing powders into a slurry: make paste, pipette from paste



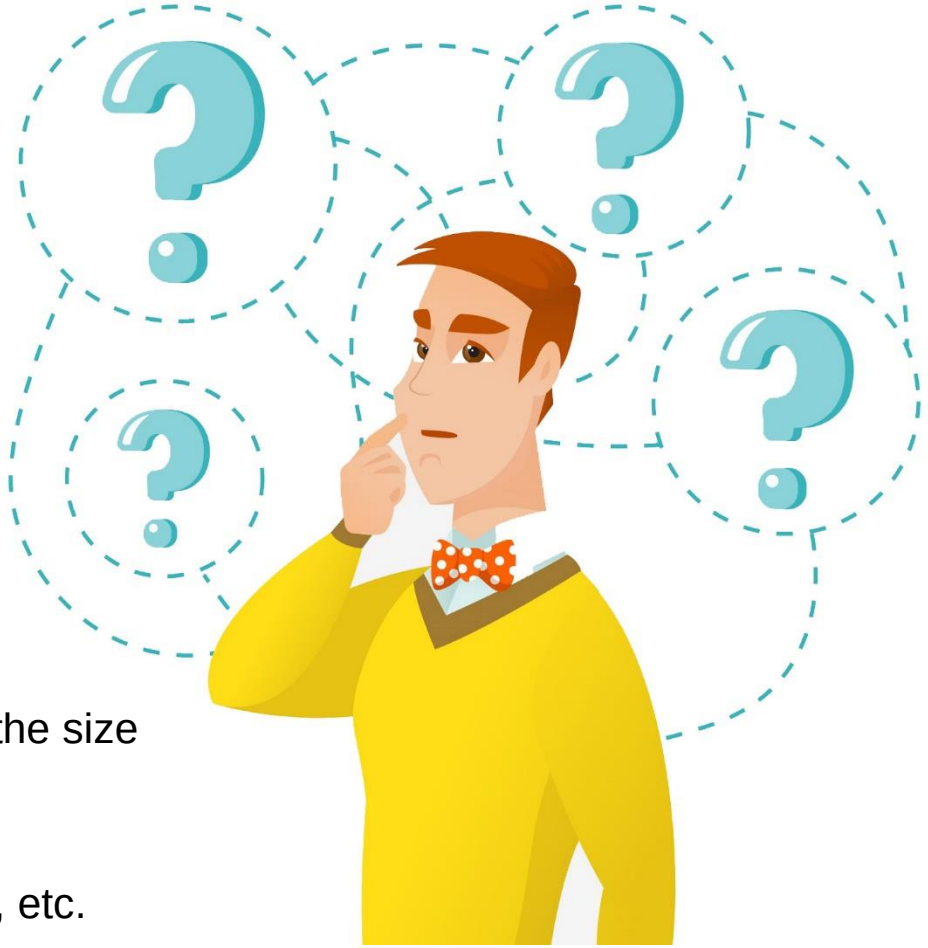
Preparation of a Corundum Particle Size Reference Material



Reference: Joint Research Centre (2018) Certification Report – The Certification of Particle Size distribution of Corundum: ERM-FD069, Luxembourg: Publications office of the European Union

Now you have a sample what comes next? (Sample Preparation)

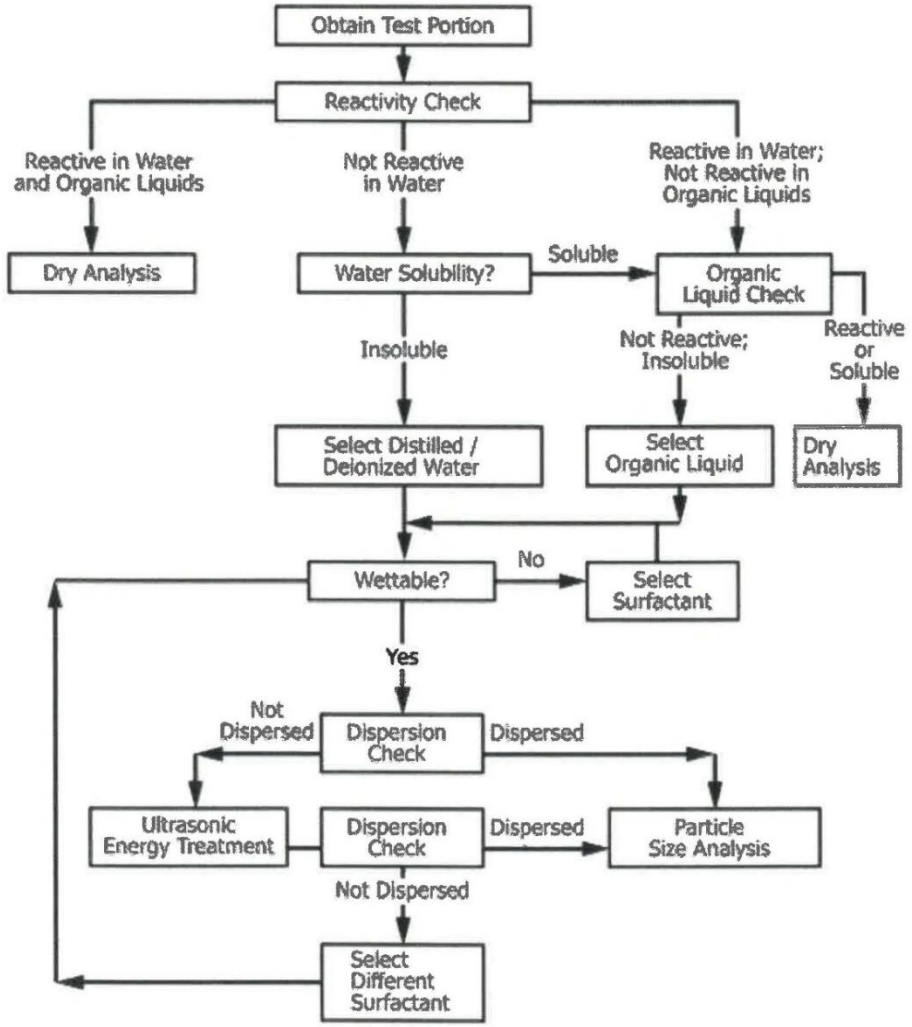
- Most typical method is to match the process which produced the sample
  - High Energy or low energy
- How are others in your industry doing the analysis?
  - This can be a huge time saver
- Who will possibly be viewing my data?
  - Standard preparation may already be specified
- How do you wish to see your sample?
  - Primary particles or how they truly exist
- Possible challenges in preparation
  - What tools are at my disposal and how do they effect the size
- What will I be trying to do with the data?
  - Data Matching, performance prediction, new research, etc.



Sample Preparation tools at your disposal

- All sorts of dispersing media
  - Organics and Inorganics
- All sorts of dispersants and surfactants
  - McCutcheon's Directory has loads of them
- All sorts of mixing devices
  - Magnetic Mixers all the way to Waring Blenders
- All sorts of ultrasonic devices
  - Baths to high energy probes
- Dispersion available during measurement
  - Assure sample stability throughout an analysis

General Dispersion Procedures



Reference: ASTM International (2016) Standard Guide for Liquid dispersion of Metal Powders and Related Compounds for Particle Size Analysis, Designation: B821 – 10, Page 2.

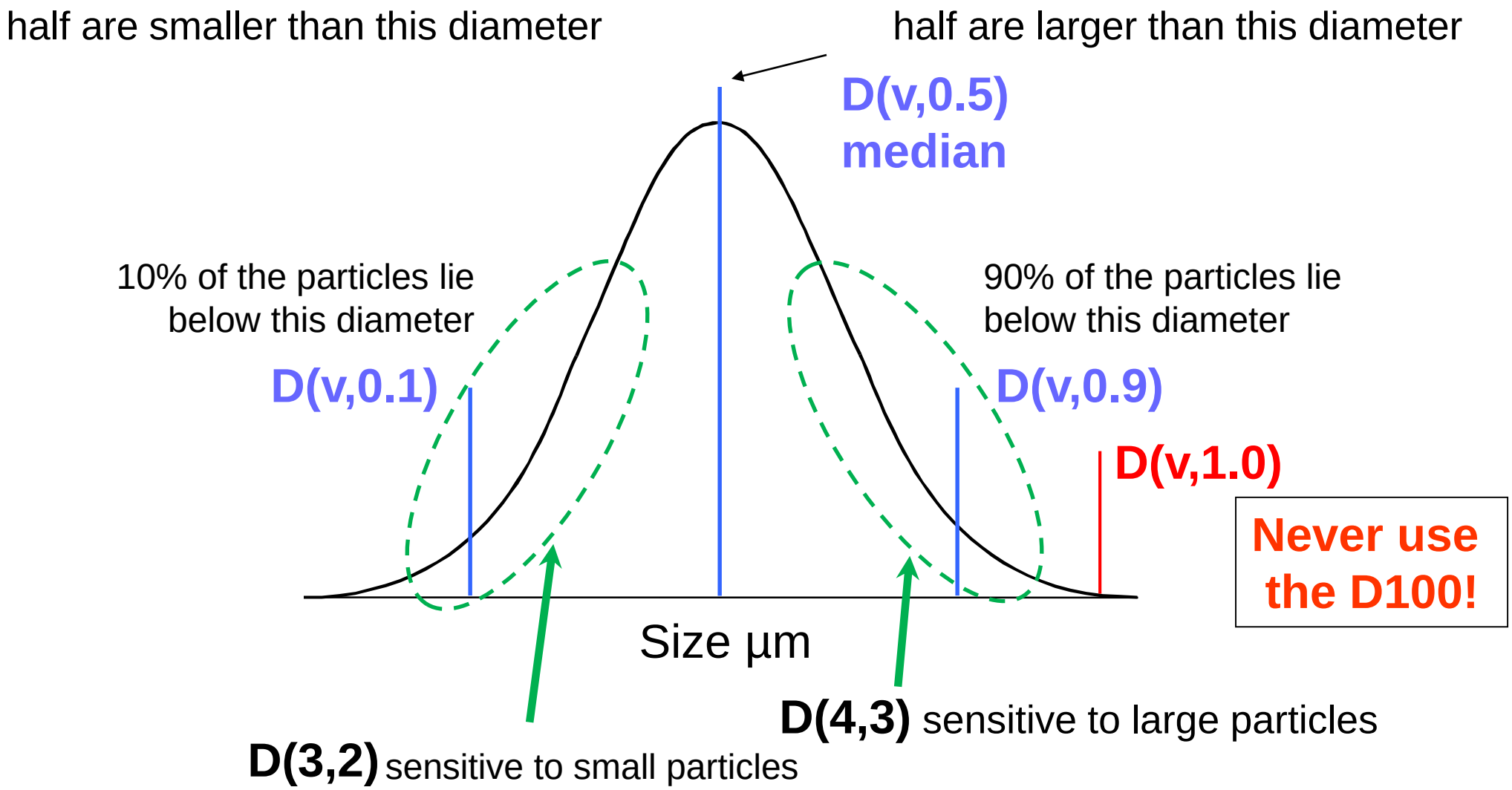
Recommended Dispersion Procedures

Material	Carrier Liquid	Surfactant	Surfactant Concentration	Ultrasonic Treatment		
				Type	Power Level, W	Time, min
Chromium carbide	water	none	...	none	...	...
				or[A]		
				bath	25	5
Copper	water	Tween 21[B]	3–5 drops[C]	bath	80	1
Ferroalloys	isopropyl alcohol	Tween 21[B]	10 %	bath	80	1
Iron/steel	water	Tween 21[B]	3–5 drops[C]	bath	80	1
Manganese sulfide	water	Tween 21[B]	3–5 drops[C]	bath	80	1
Molybdenum	water	sodium hexametaphosphate	0.01 %	probe	160	3
				or		
				bath	80	10
				or[A]		
				bath	25	5
Nickel	water	Tween 21[B]	3–5 drops[C]	bath	80	1
Tantalum	water	sodium hexametaphosphate	0.01 %	probe	160	3
				or		
				bath	80	10
Tantalum carbide	water	sodium hexametaphosphate	0.01 %	probe	160	3
				or		
				bath	80	10
				or[A]		
				bath	25	5
Tungsten	water	sodium hexametaphosphate	0.01 %	probe	160	3
				or		
				bath	80	10
				or[A]		
				bath	25	5
Tungsten carbide	water	sodium hexametaphosphate	0.01 %	probe	160	3
				or		
				bath	80	10
				or[A]		
				bath	25	5

[A] As described in Test Method B430.
[B] Tween 21, chemically known as polyoxyethylene[6] sorbitan monolaurate, is manufactured by Croda International PLC, and is available from various chemical suppliers.
[C] Three to five drops Tween 21 in 30 to 50 mL water.

Reference: Joint Research Centre (2018) Certification Report – The Certification of Particle Size distribution of Corundum: ERM-FD069, Luxembourg: Publications office of the European Union

Most Common Statistics

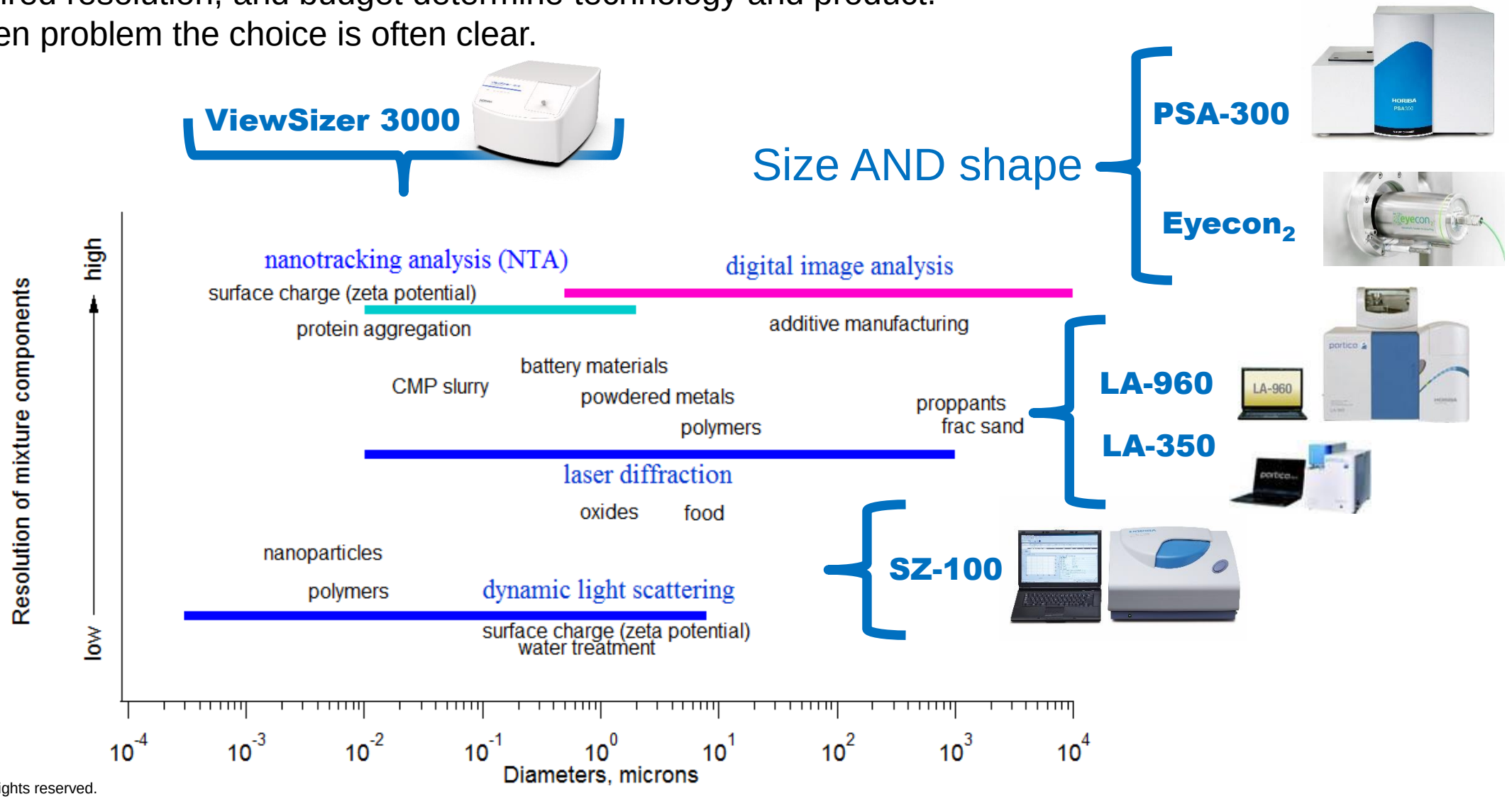


What conclusion can be reached from the data

- The distribution became larger or smaller
- Some aspect of the distribution has changed
- The particle distribution got broader or narrower
- The two modes can be analyzed separately
- There are too many coarse particles in the sample
- The two sets are data are similar or different
- The two techniques produce similar or different data

Which Analyzer?

Size, desired resolution, and budget determine technology and product.
For a given problem the choice is often clear.



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Modern Particle Characterization Technique Series II:
Laser Diffraction

Thursday, May 28, 2020

Thank you

Omoshiro-okashiku

Joy and Fun

Terima kasih

Gracias 谢谢

Σας ευχαριστώ πάρα πολύ

Danke Tack ska du ha Grazie

THANK YOU

ขอบคุณครับ Obrigado Большое спасибо

ありがとうございました Cảm ơn Merci 감사합니다

Dziękuję