PARTICLE ANALYSIS FOR INDUSTRIAL PRODUCT SUCCESS

Sophia Yan, PhD

May 14, 2020 11am PDT

COVALENT ACADEMY

EPISODE 07

RSVP at:
https://bit.ly/covalent07

Covalent metrology

- **Founded 2016**
- **Testing, measurement & characterization Platform**
- **30 team members (13 PhDs)**
- **9,500 ft² lab in Sunnyvale**
- **1-Stop-Shop Source for Answers**
  - 30 instruments in-house
  - 6 partnerships with instrument makers
  - 11 partner labs
  - 6 corporate “tool shares”
- **>275 customers** (80% repeat)

Covalent technical groups and organization

hello@covalentmetrology.com

Electron & Scanning Probe Microscopy

(SEM/TEM, AFM, EDS, EELS, Nanoindent, acoustic microscopy)

Surface Analysis

(XPS, Auger, ToF-SIMS, dSIMS)

Optical Microscopy & Spectroscopy

(Laser Confocal, White Light, Chromatic Aberration, Spectral Ellipsometry, UV-Vis-NIR Spectroscopy)

Materials/ PC Board FA

(Cross Sections, Inspections, Dye & Pry)

X-Ray Characterization

(XRD/XRR, XRF, µCT)

Chemical Analysis

(ICPMS, GCMS, FTIR, Raman, Solid & Solution NMR, 2D NMR)

Nanoparticle Analysis

(DLS, PSA, Particle Zeta Potential)

Bulk Properties Characterization

(DSC, TGA, DMA, Rheometry, Tensile Test, Pencil Test, Surface Zeta Potential)

Dr. Sophia Yan

- **PhD Materials Science and Engineering, University of Delaware**

- **8 years of industry work experience supporting**
  - Product development and renovation
  - Process optimization and manufacturing implementation
  - Raw ingredient screening
  - Quality issue trouble-shooting

- **Expertise in material characterization tools**
  - Particle analysis: laser diffraction, DLS, zeta-potential, microscopy
  - Bulk property: rheometry, DSC, TGA

Episode 7 outline

- **Particle size analysis techniques**
  - Basics and technique selection
  - In-house capabilities at Covalent

- **Particle size analysis for industrial product success**
  - Quantum dots for use in capacitor
  - Battery electrode material
  - Therapeutic delivery carrier
  - Drug tablet
  - Ceramic for vehicle mechanical parts
  - Slurry for 3D printing and chemical mechanical polishing
  - Abrasive for dry polishing
  - Paint pigment

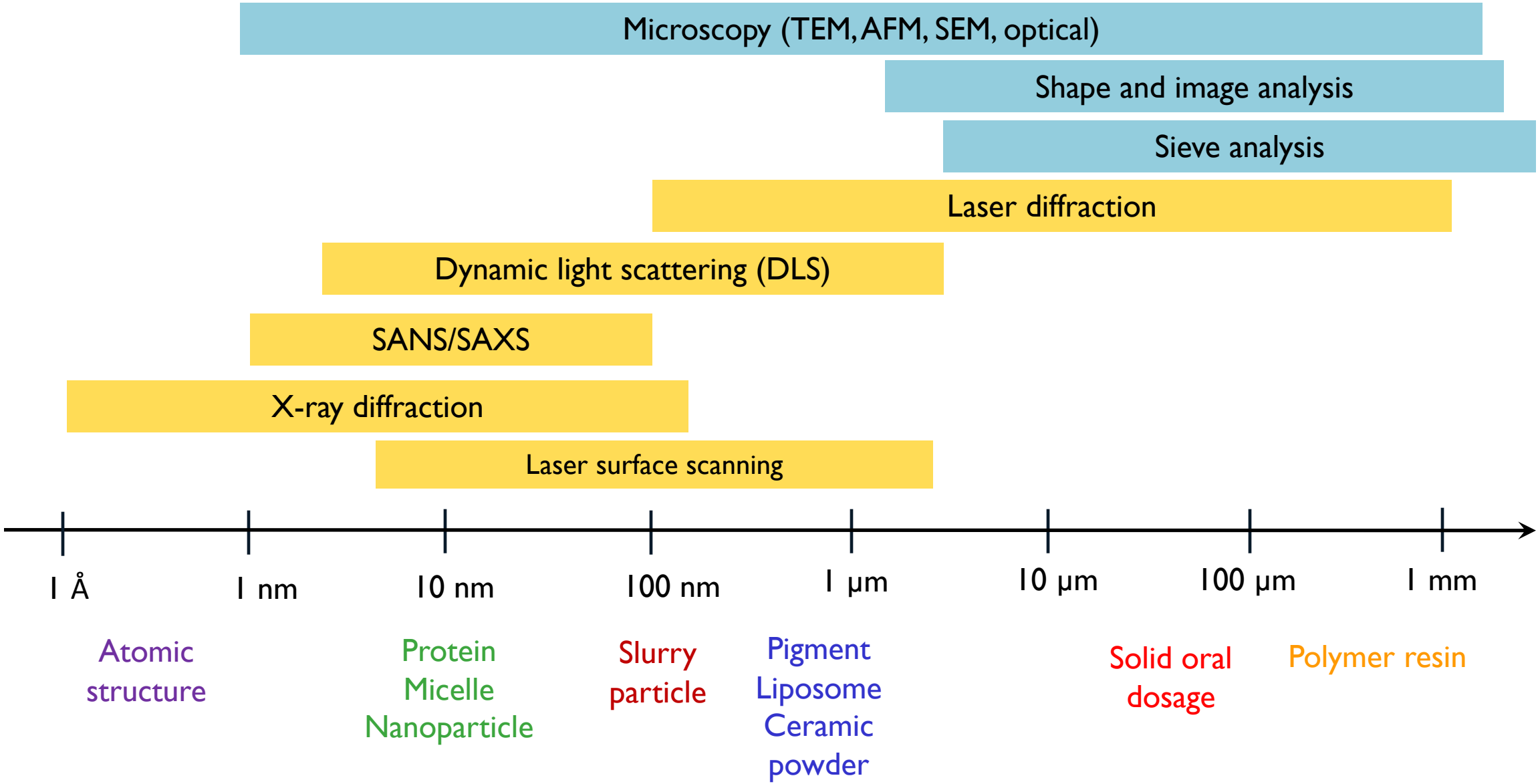
- **Next Episode**

- **Question and Answer**

COVALENT METROLOGY

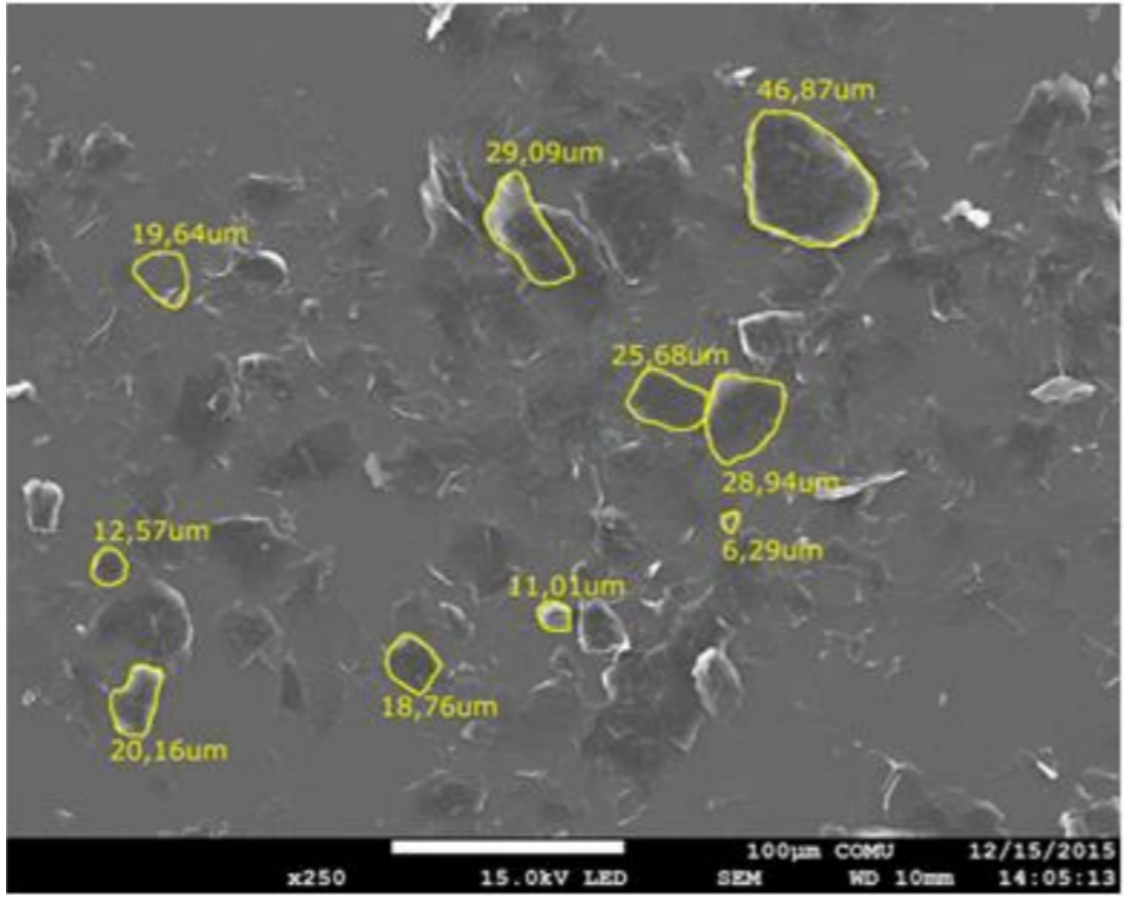
What are the existing techniques for particle size analysis?

Overview: direct and indirect characterization for particle size



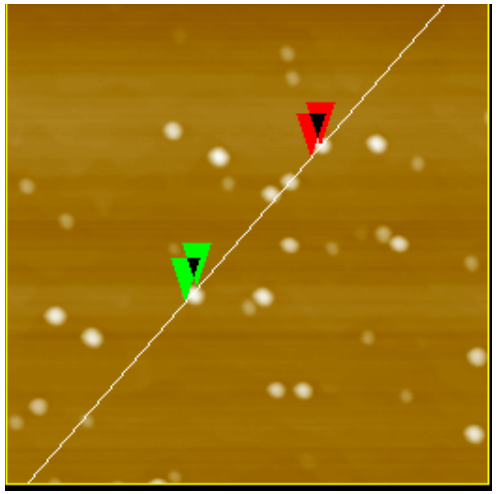
Microscopy for direct particle size analysis

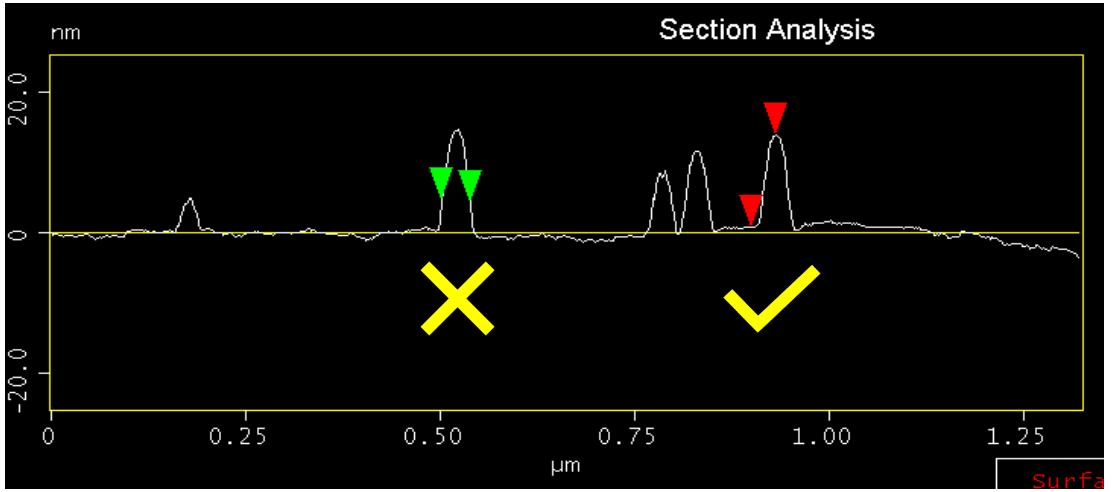
SEM: graphene oxide flakes



Özçakır et al., Proceedings of the World Congress on Recent Advances in Nanotechnology 2016

AFM: gold nanoparticles





Microscopy for direct particle size analysis: pros & cons

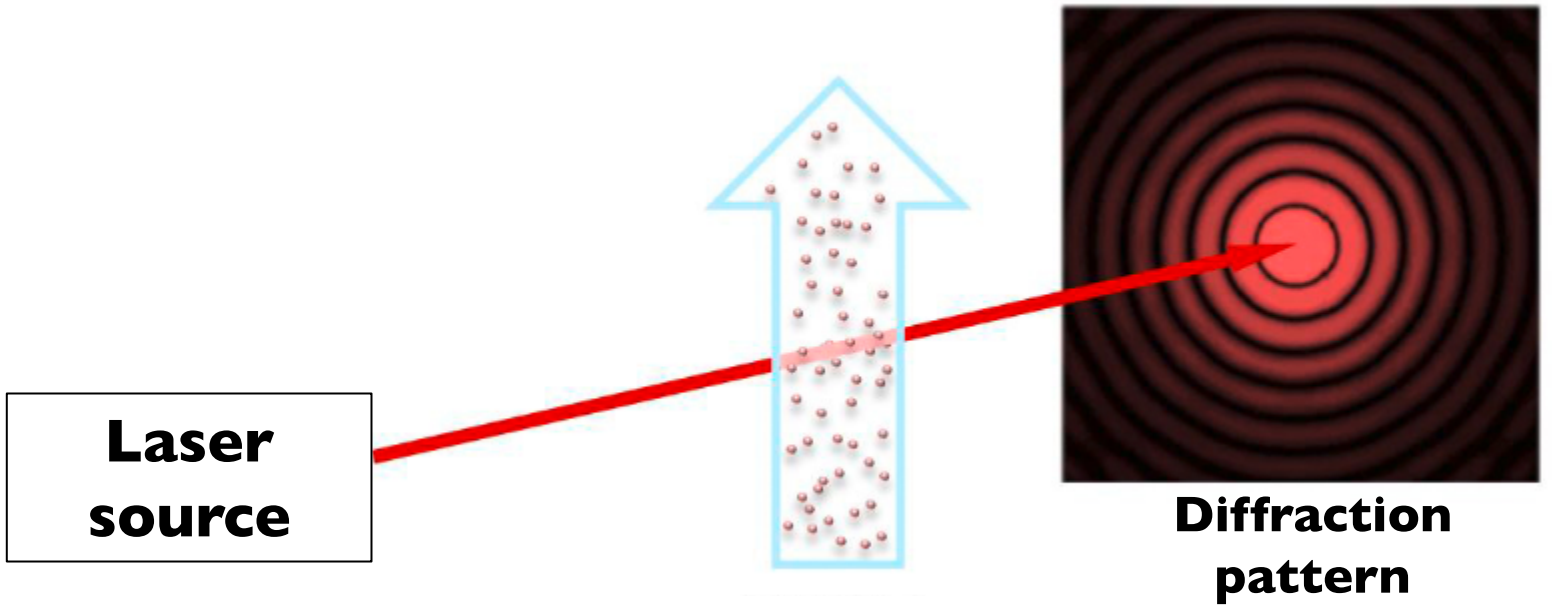
Pros

- Direct measurement on target particles
- Small sample volume
- Obtain particle morphology (bonus)
- Identify presence of particle aggregates

Cons

- Not measuring overall particle size distribution
- Solvent evaporation during sample prep may impact observed particle size

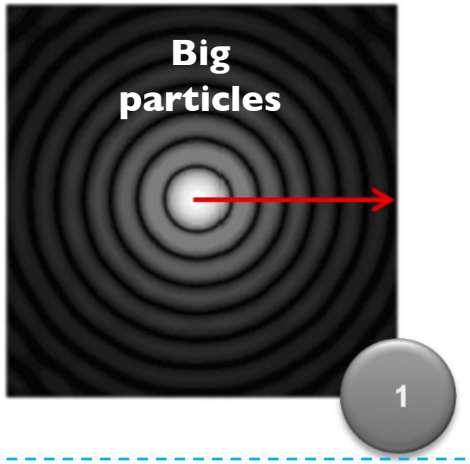
Laser diffraction – instrument setup



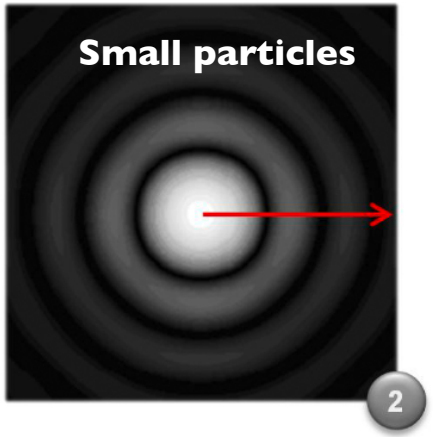
https://wiki.anton-paar.com/us-en/laser-diffraction-for-particle-sizing/

Laser diffraction for indirect particle size analysis

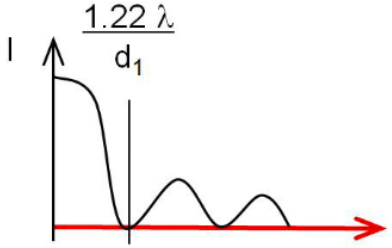
2D diffraction pattern

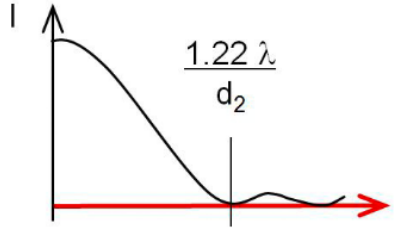


$d_1 > d_2$

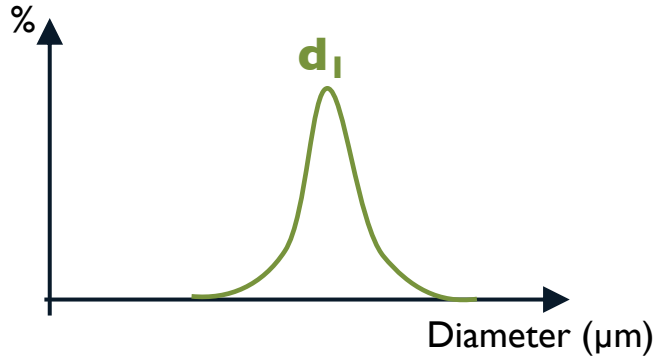


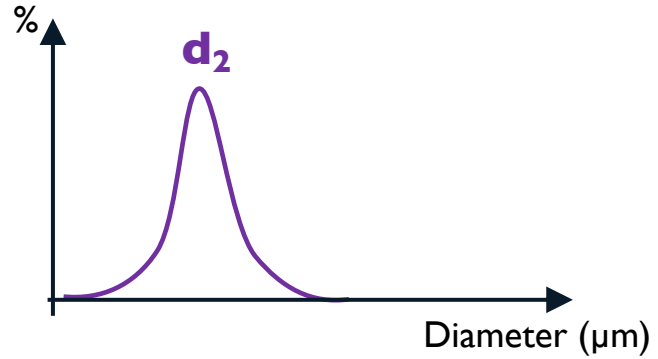
1D radial intensity curve





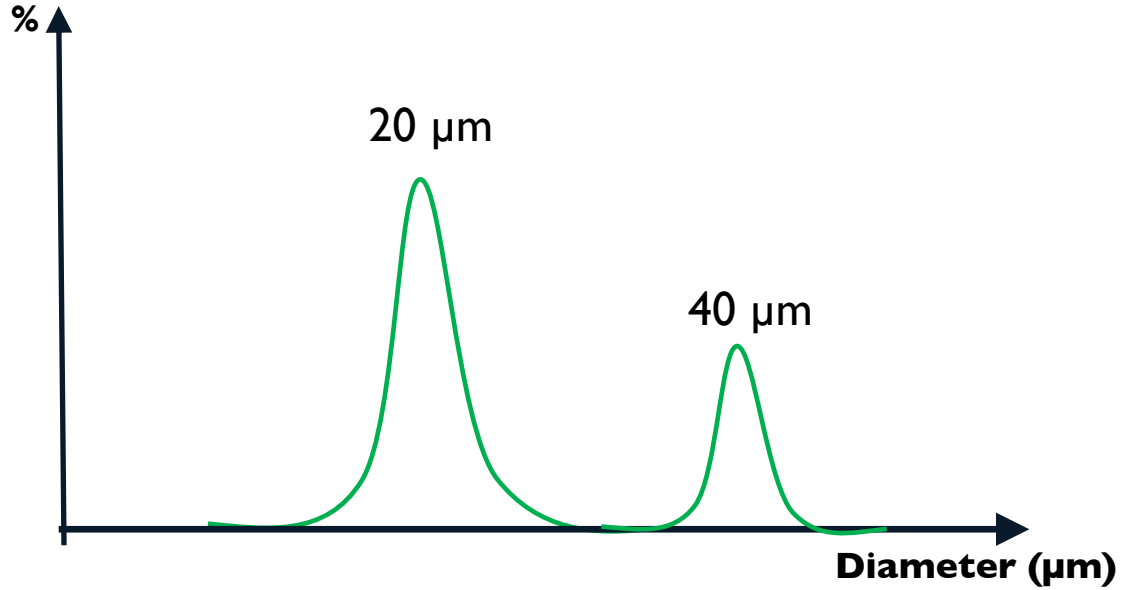
Particle size distribution



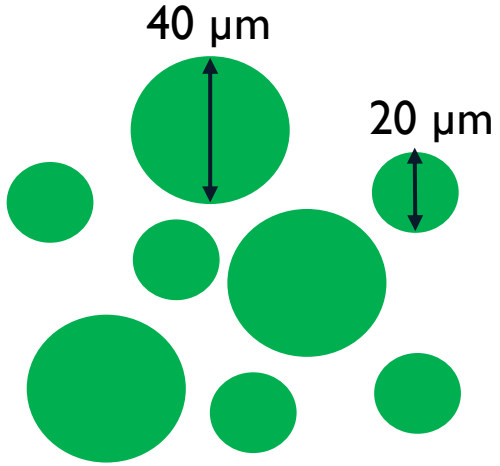


Microscopy helps elucidate Laser Diffraction particle size distribution with respect to particle morphology.

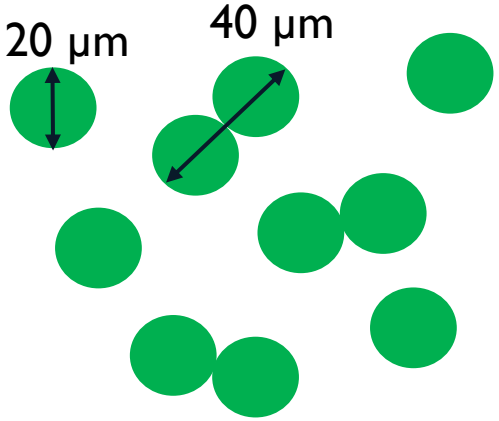
COVALENT METROLOGY



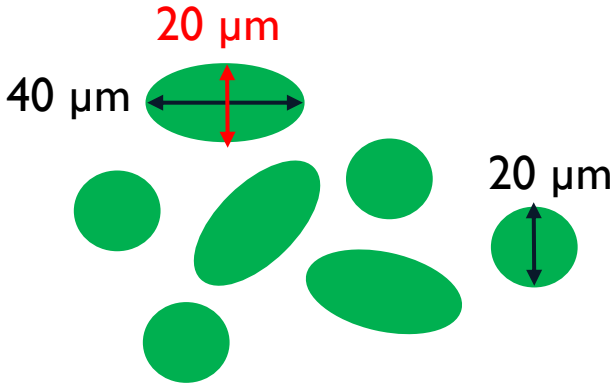
Possibility 1



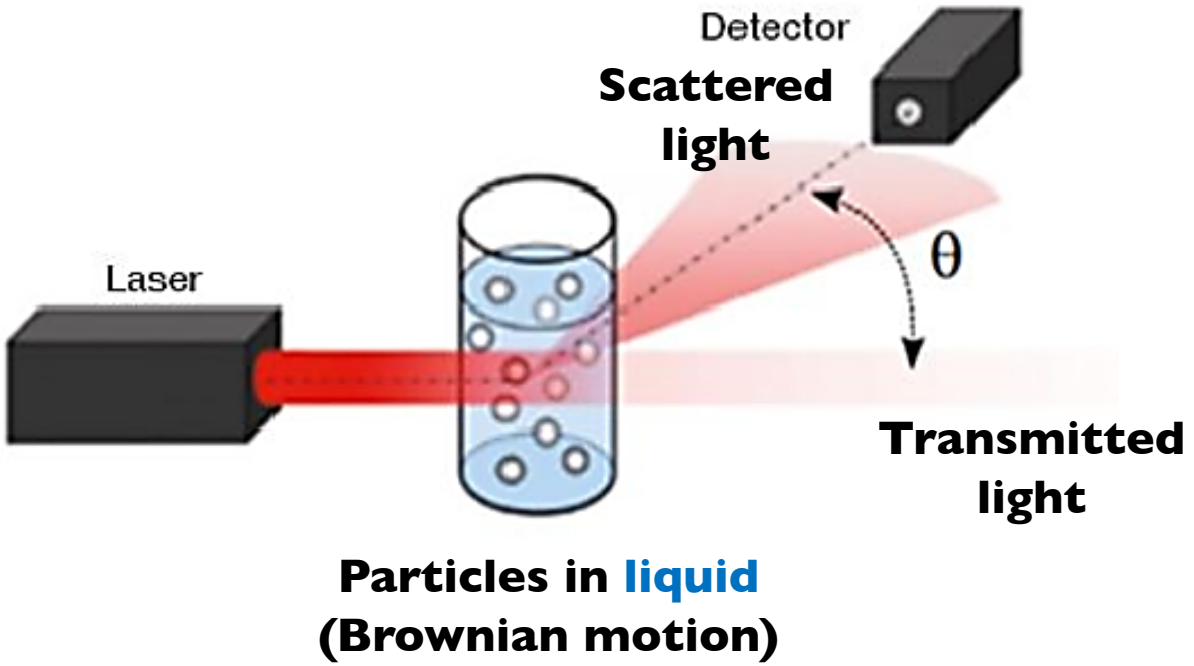
Possibility 2

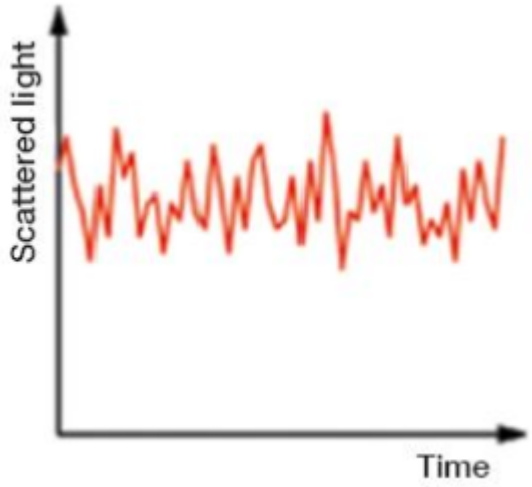


Possibility 3



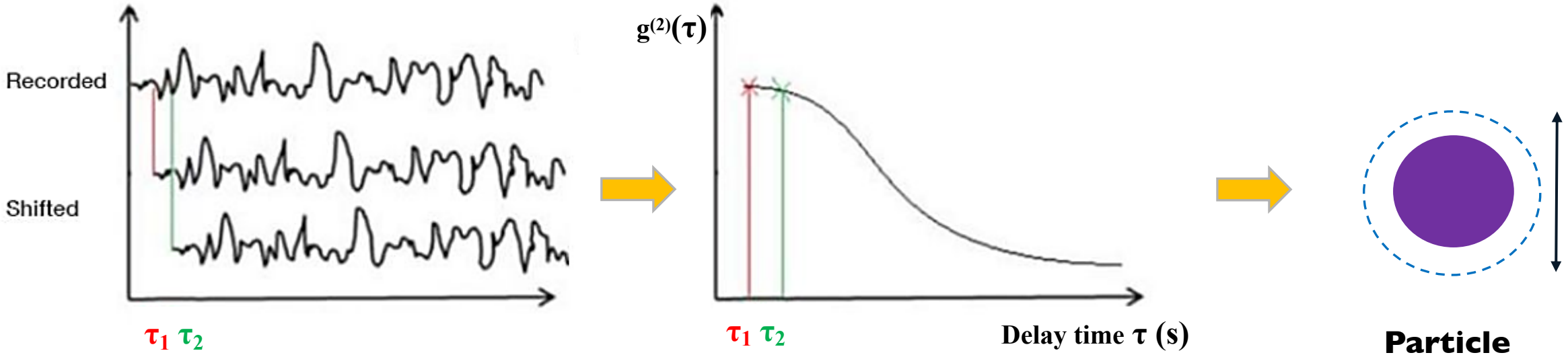
Dynamic light scattering (DLS) – instrument setup





https://wiki.anton-paar.com/us-en/the-principles-of-dynamic-light-scattering/

DLS for indirect particle size analysis



Particle hydrodynamic diameter: $2r_h$

Scattered light intensity I(t)

Correlation function

$$g^{(2)}(\tau) = \frac{\langle I(t)I(t+\tau)\rangle}{\langle I(t)\rangle^2} \rightarrow g^{(2)}(\tau) = B + \beta \exp(-2\Gamma\tau)$$

Decay rate Γ
Diffusion coefficient D

$$D = \frac{\Gamma}{q^2}$$

$$q = \frac{4\pi n_0}{\lambda_0} \sin(\theta/2)$$

$$r_k = \frac{kT}{6\pi\eta D}$$

https://wiki.anton-paar.com/us-en/the-principles-of-dynamic-light-scattering/

cf. Chu, B. *Laser Light Scattering: Basic Principles and Practice*; Academic Press: Boston, 1991

DLS for indirect particle size analysis

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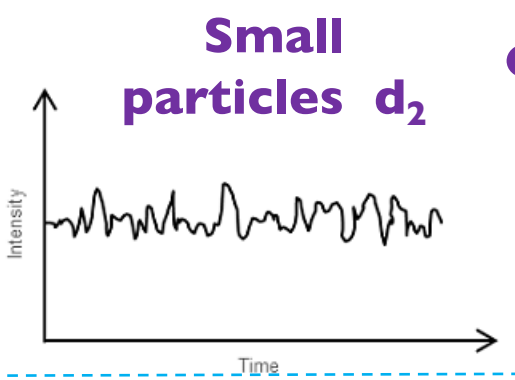
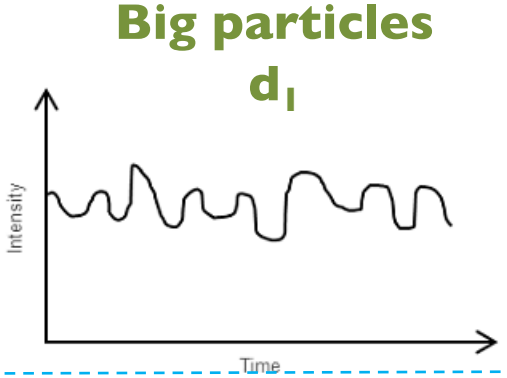
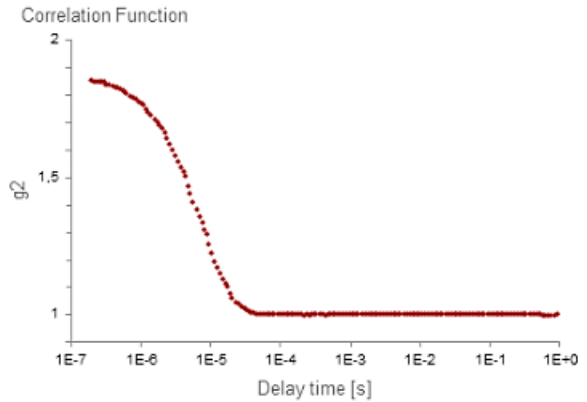
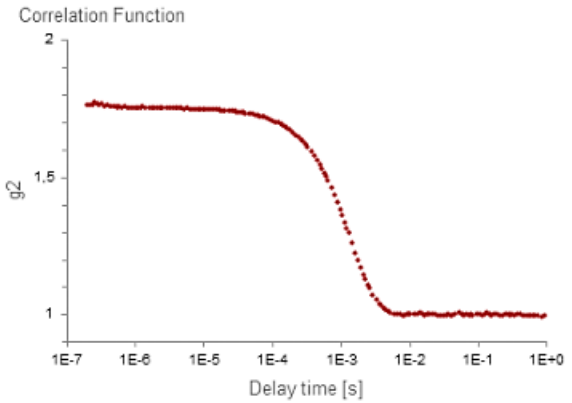
Scattered light intensity: I(t)



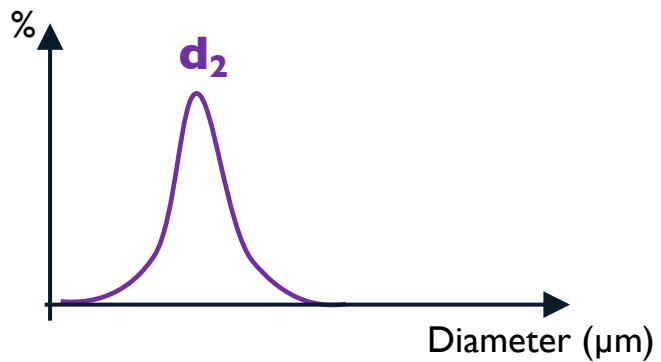


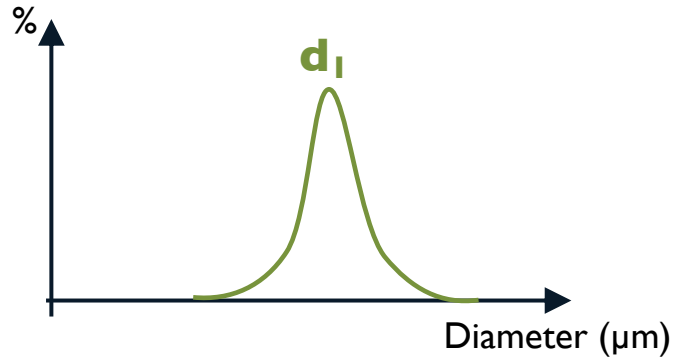
Correlation function



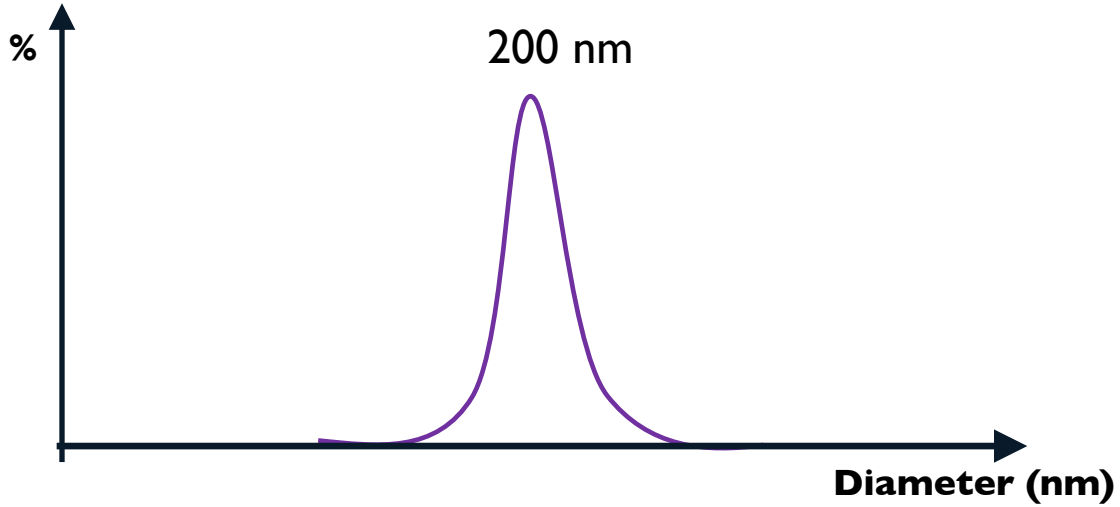


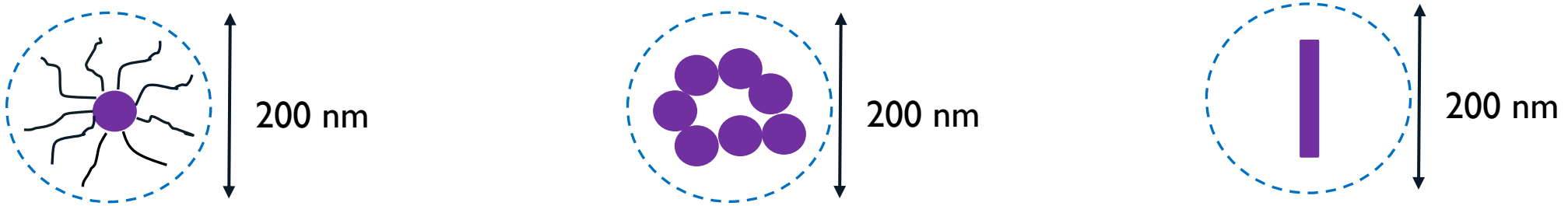
Particle size distribution





Microscopy helps elucidate DLS particle size distribution with respect to particle morphology.





Hydrodynamic diameter measured by DLS is diameter of a sphere that diffuses the same rate as particle under investigation.

Pusey PN. Correlation and light beating spectroscopy. In: Cummings HZ, Pike ER, editors. Photon correlation and light beating spectroscopy. New York: Plenum; 1972. pp. 387–428.

Laser diffraction/DLS for indirect particle size analysis: pros & cons

Pros

- Measure overall particle size distribution (LD, DLS)
- Fast automated data analysis (LD, DLS)

Cons

- Particle precipitation can impact result accuracy (DLS)
- Big particles can mask small particles (LD, DLS)
- Result may be tricky to interpret without knowing particle morphology (LD, DLS)

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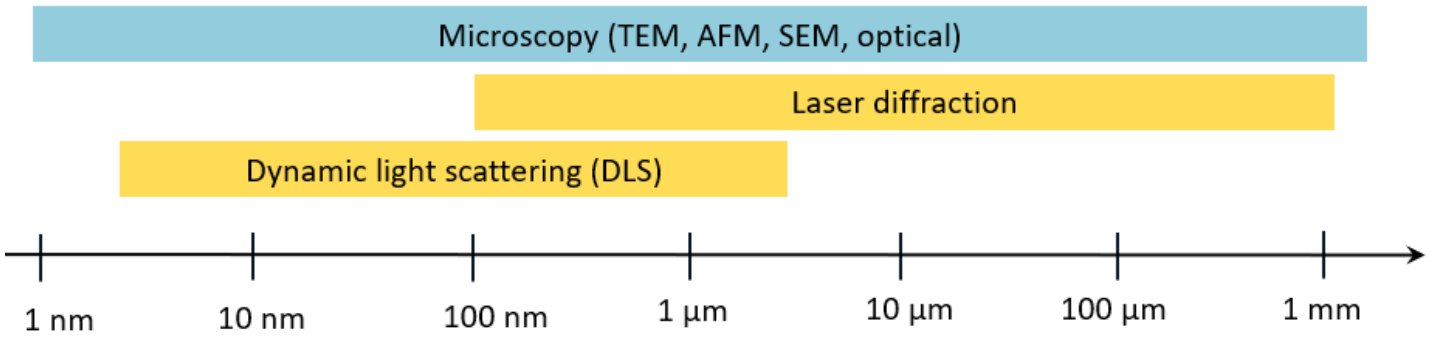
Which technique to pick for particle size analysis?

Factors to consider for technique selection

Factor	Microscopy	Laser Diffraction	DLS
Particle length scale	<1 nm - mm	100 nm - mm	< 10 nm – over 1 µm
Overall particle size distribution	No	Yes	Yes
Particle morphology	Yes	No	No
Low sample volume/concentration	Doable	No	Doable
Sample dispersion	Dry, wet	Dry, wet	Wet
Organic solvent tolerance	Yes	Limited	Yes



Particle size analysis capabilities at Covalent

DLS: Anton Paar Litesizer 500
- Particle size: 0.3 nm – 10 µm
- Resolution: 0.3 nm
- 220 nm particle size standard for precision check

Laser Diffraction: Anton Paar PSA 1190
- Particle size: 0.04 – 2500 µm
- Resolution: 40 nm
- 10-100 µm particle size standard for precision check

TEM: ThermoFisher
- Resolution: Å

SEM: ThermoFisher
- Resolution: nm

AFM: Anton Paar and Bruker
- Resolution: Å

Laser confocal microscope: Keyence
- Resolution: nm

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Why is particle size analysis (PSA) important?

Particle size is key to industrial product success

Particle size of quantum dots meeting target indicates success and reliability of wet chemistry preparation

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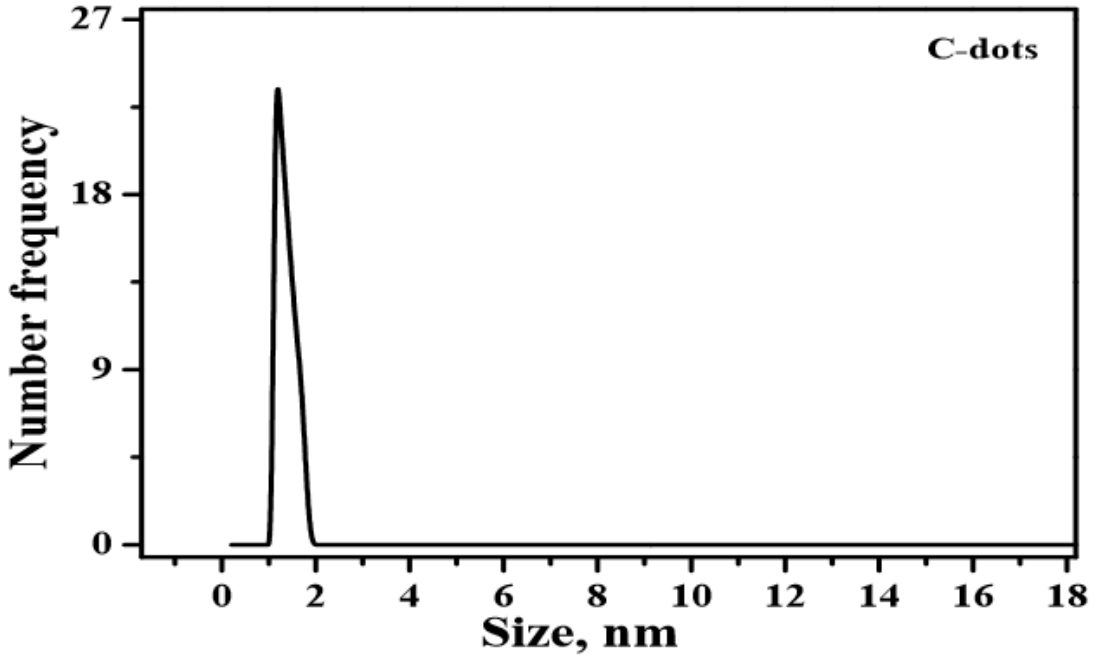

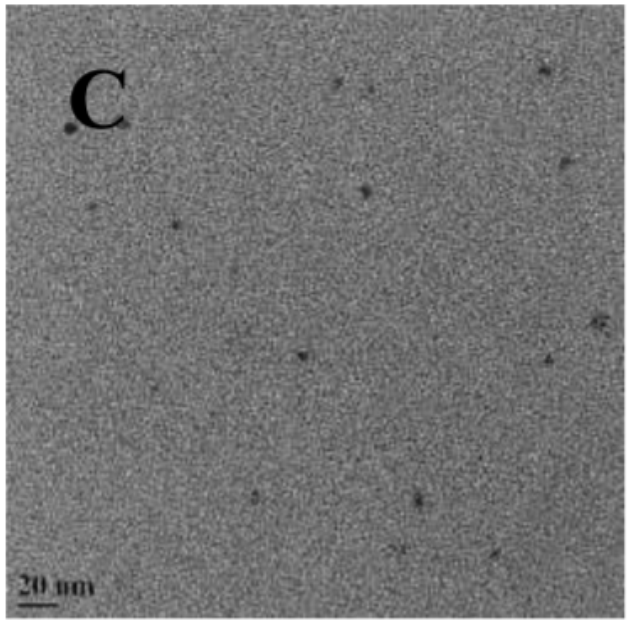

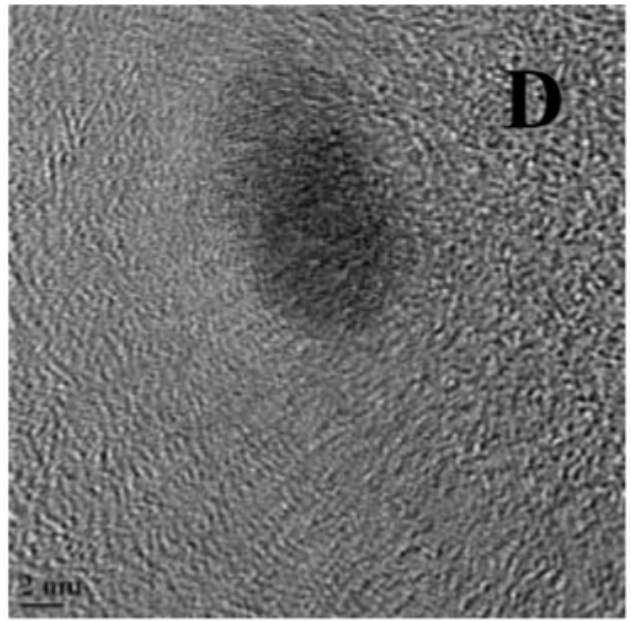

Both TEM and DLS were used for measuring QD particle size and morphology at nanometer scale.

Incorporation of Carbon Quantum Dots for Improvement of Supercapacitor Performance of Nickel Sulfide, ACS Omega 2018, 3, 17936−17946

Particle size analysis helps evaluate candidate electrode materials for use in lithium-ion battery

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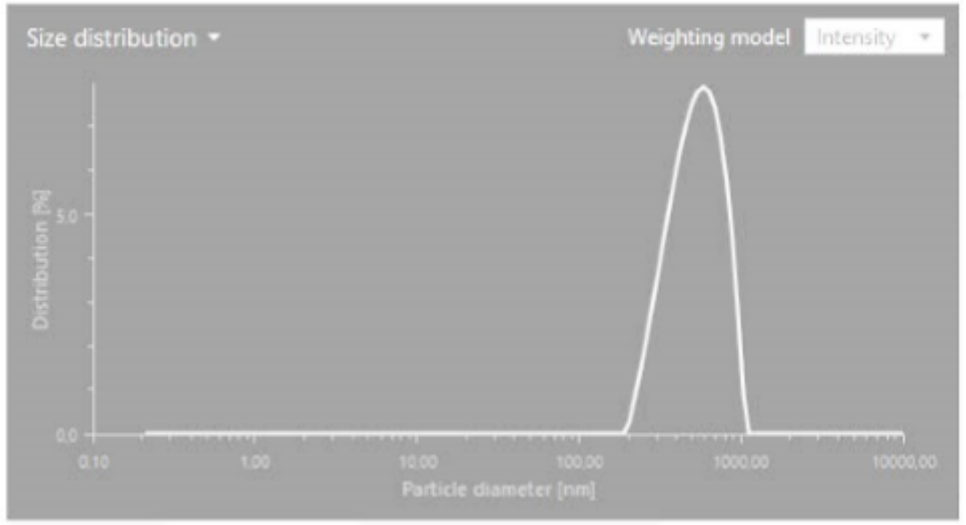


Figure 1 – Intensity-weighted particle size distribution of Super P® (carbon black) dispersed in deionized water

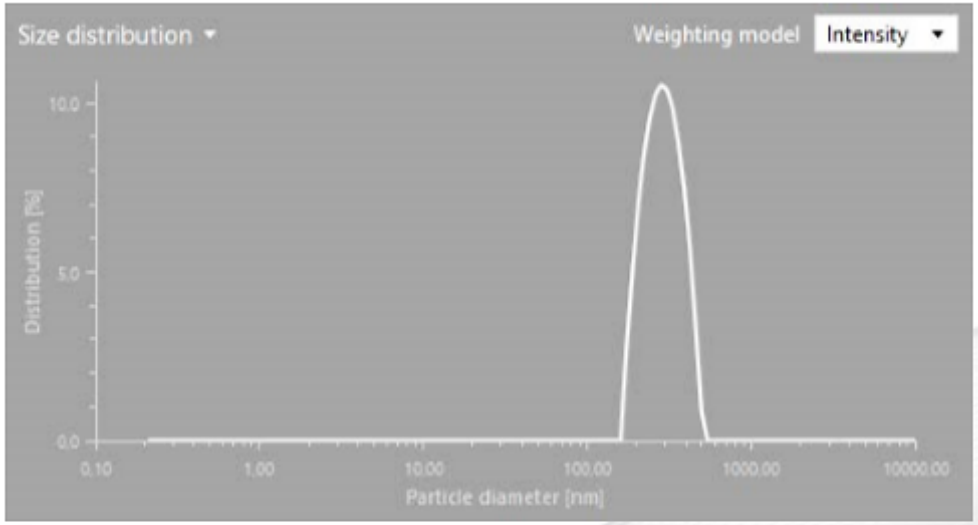


Figure 2 - Intensity-weighted particle size distribution of n-Si (crystalline silicon) dispersed in deionized water

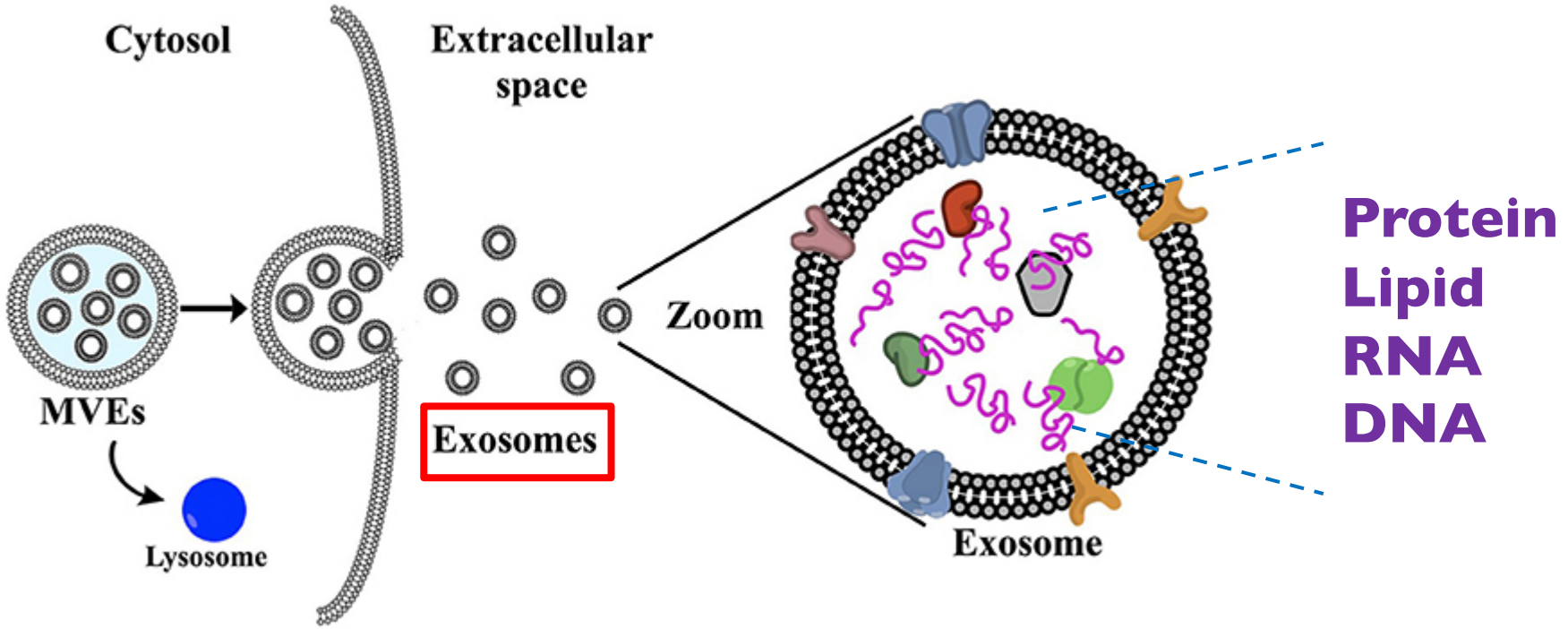
DLS was used for measuring electrode material particle size distribution at nanometer scale.

Sample	Polydispersity Index [%]	Hydrodynamic Diameter [nm]	Rel. Standard Deviation [%]
Super P	24.8	581.0	10.97
n-Si	19.4	318.6	1.29

Polydispersity index < 10 % for monodisperse sample

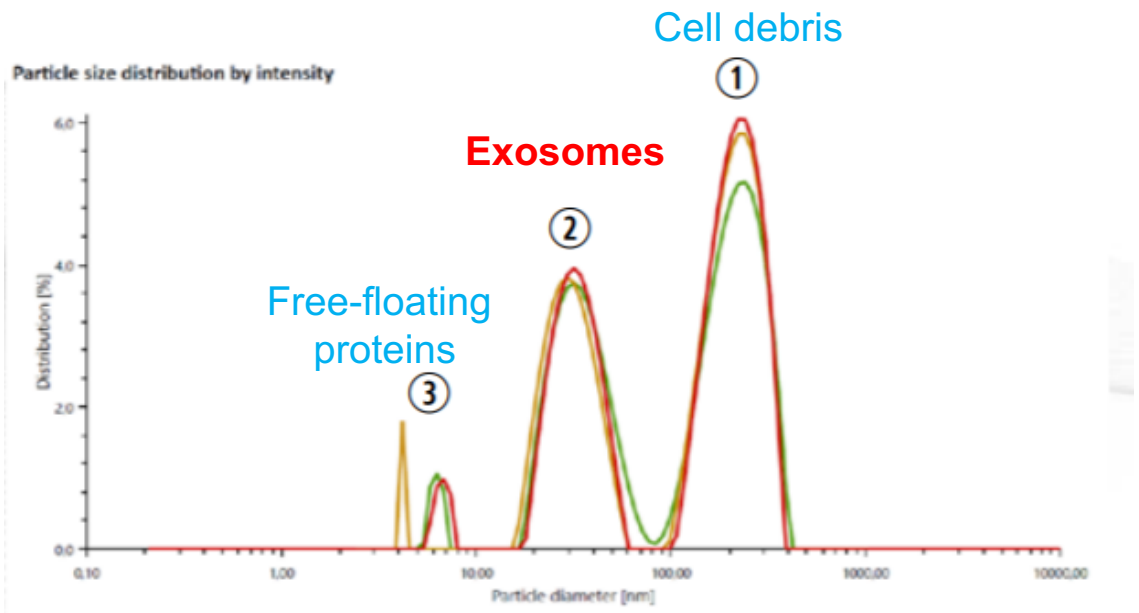
Power Tool: Investigating Battery Material with the Litesizer, Anton Paar application paper, D51IA045EN-B

Exosome particle size indicates cell viability and exosome stability



Biogenesis, secretion, and intercellular interactions of exosomes and other extracellular vesicles. *Annu. Rev. Cell Dev. Biol.* 2014, 30, 255–289.
Exosomes: Improved methods to characterize their morphology, RNA content, and surface protein biomarker. Analyst. 2015, 140(19): 6631–6642

PSA helped identify proper storage condition for better exosome stability



Time after isolation	Storage at 4 °C			Storage at 37 °C		
	Peak 1 [nm]	Peak 2 [nm]	Peak 3 [nm]	Peak 1 [nm]	Peak 2 [nm]	Peak 3 [nm]
0 hrs	218.6	33.3	3.1	165.8	36.1	
24 hrs	223.3	31.9	5.2	239.7	33.3	14.6
48 hrs	243.3	30.7	0.7	247.5	30.0	7.9
72 hrs	237.7	30.8	2.1	244.5	25.2	6.4
1 week	267.9	31.6	5.3	286.4	26.1	0.3

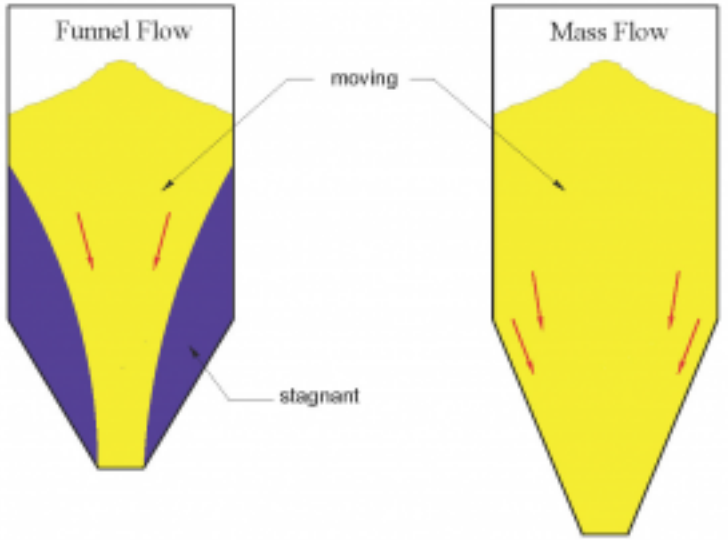
DLS used for measuring exosome particle size distribution at nanometer scale.

Characterization of Exosomes Isolated from Cell Culture Media, Anton Paar application paper D51IA047EN-A

Good powder flowability is desired for feeder efficiency at production line.

Poor flowability

Good flowability



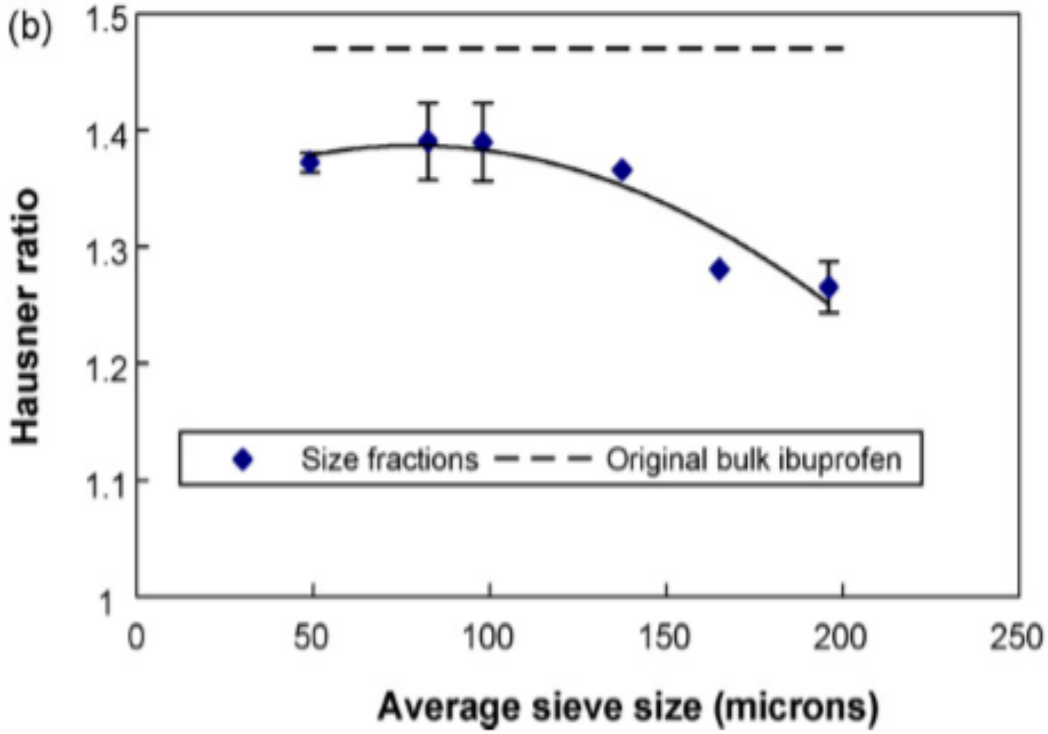
Hausner ratio $H = \frac{\rho_T}{\rho_B}$

ρ_B is freely settled bulk density of powder, ρ_T is the tapped bulk density of powder
The higher the Hausner ratio, the worse the powder flowability

http://rxtimes.com/improving-powder-flow-during-pharmaceutical-operations/

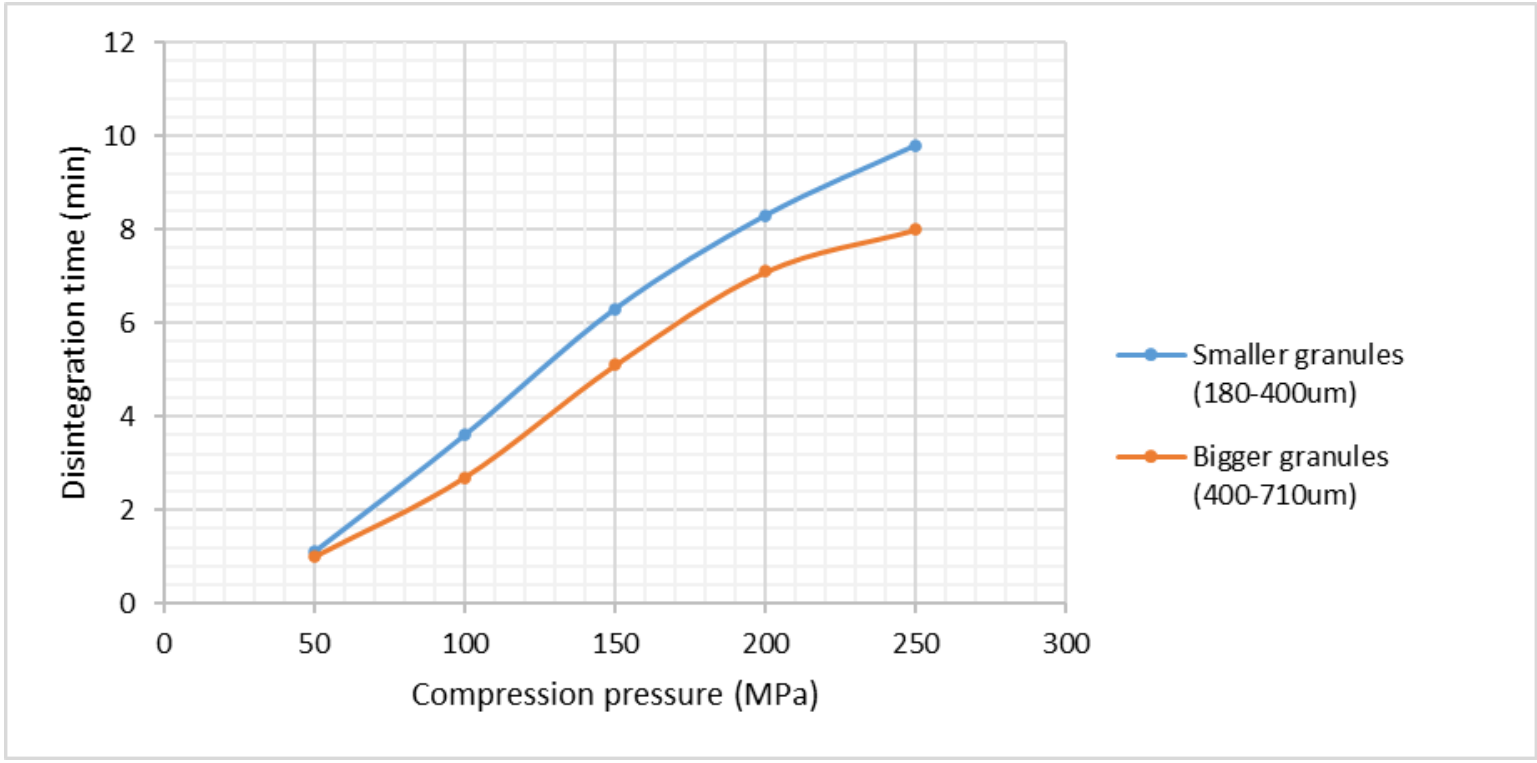
Bigger particle size can improve Ibuprofen powder flowability.

Particle size was measured by sieve analysis to fraction sample by particle size and directly apply each fraction to density test.



Effect of particle properties on the flowability of ibuprofen powders. International Journal of Pharmaceutics, 2008, 362, 109-117.

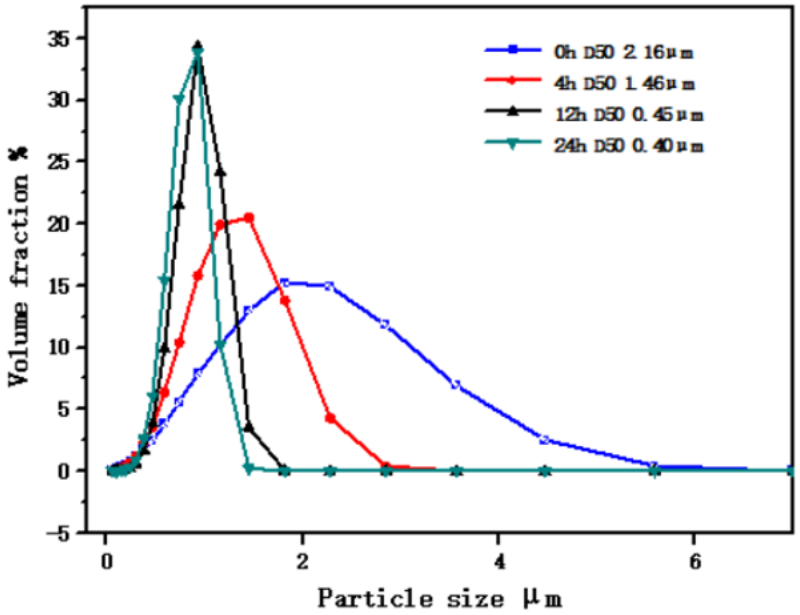
Tablet disintegration can be modulated by granule particle size



Particle size was measured by sieve analysis to fraction sample by particle size and apply each fraction directly to make tablet and evaluate disintegration.

A compressibility and compactibility study of real tableting mixtures: The effect of granule particle size. Acta Pharmaceutica 2012 62(3):325-40

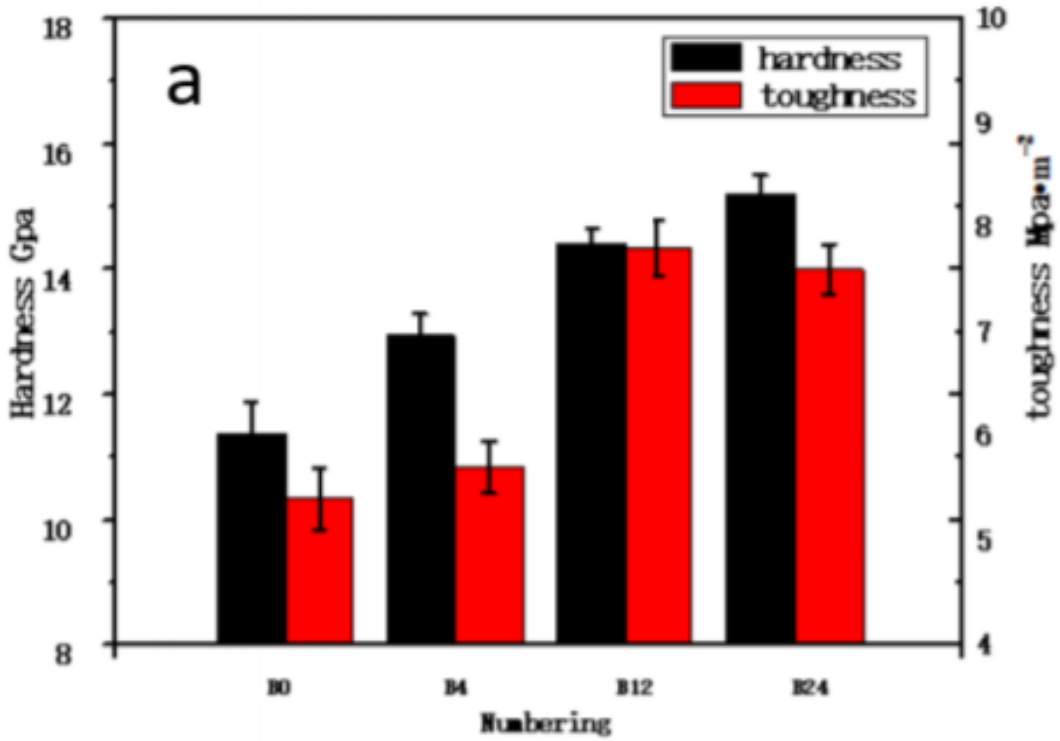
Press sintering is one way to make ceramic balls for bearing-rolling element

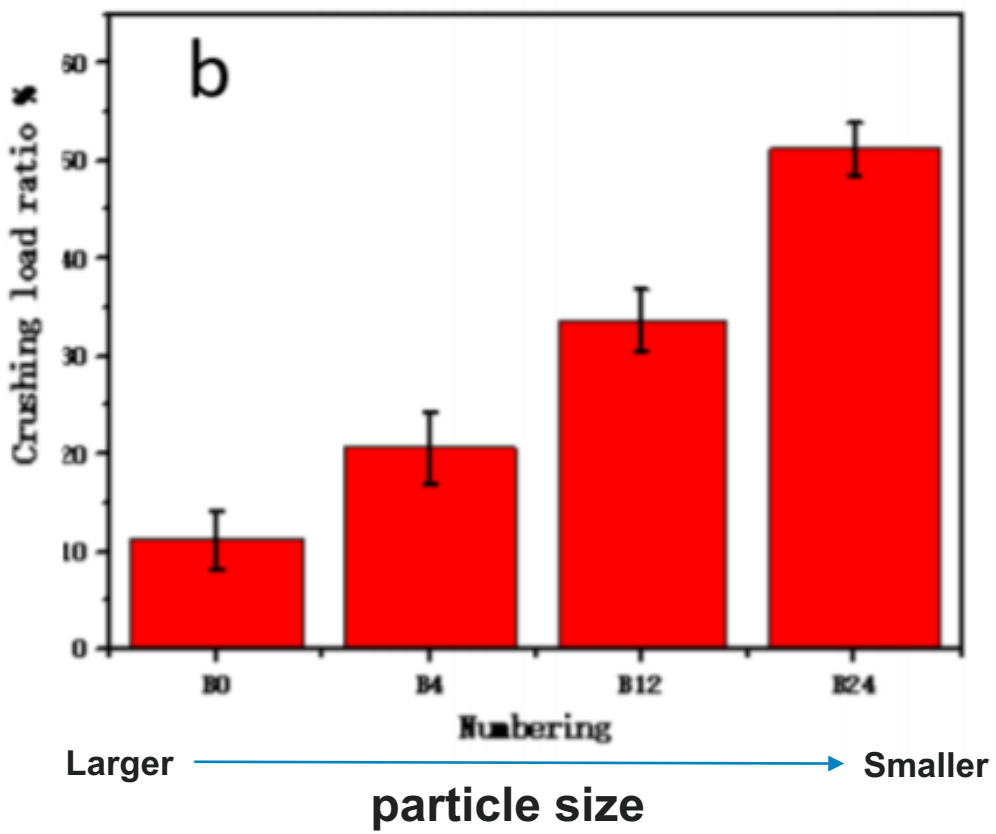


Particle size was measured by laser diffraction for particle size distribution of the ceramic powder at μm scale.

The Effect of Particle Size of Silicon Nitride Powder on Properties of Silicon Nitride Ceramic Balls
IOP Conf. Series: Materials Science and Engineering 678 (2019) 012041

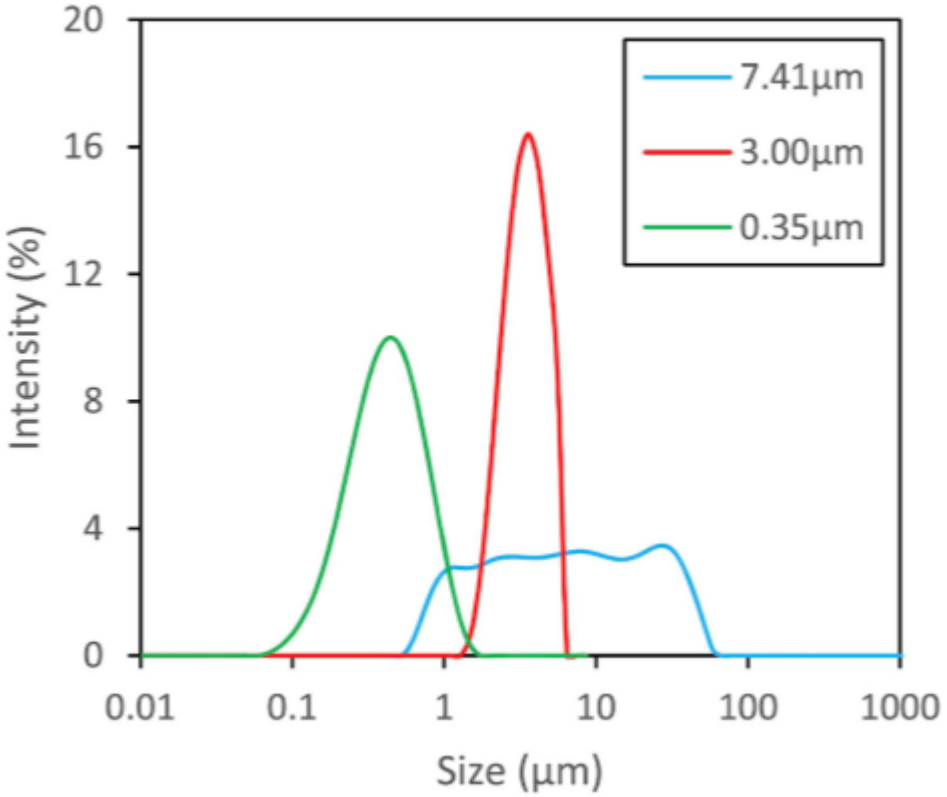
Mechanical properties of ceramic balls can enhance with smaller silicon nitride particle size





The Effect of Particle Size of Silicon Nitride Powder on Properties of Silicon Nitride Ceramic Balls
IOP Conf. Series: Materials Science and Engineering 678 (2019) 012041

Proper silica particle size and narrow distribution helps optimize slurry viscosity for 3D printing to prevent nozzle clogging



Alumina magnesia silicate particle size was measured by DLS for particle size distribution at μm scale in liquid dispersion.

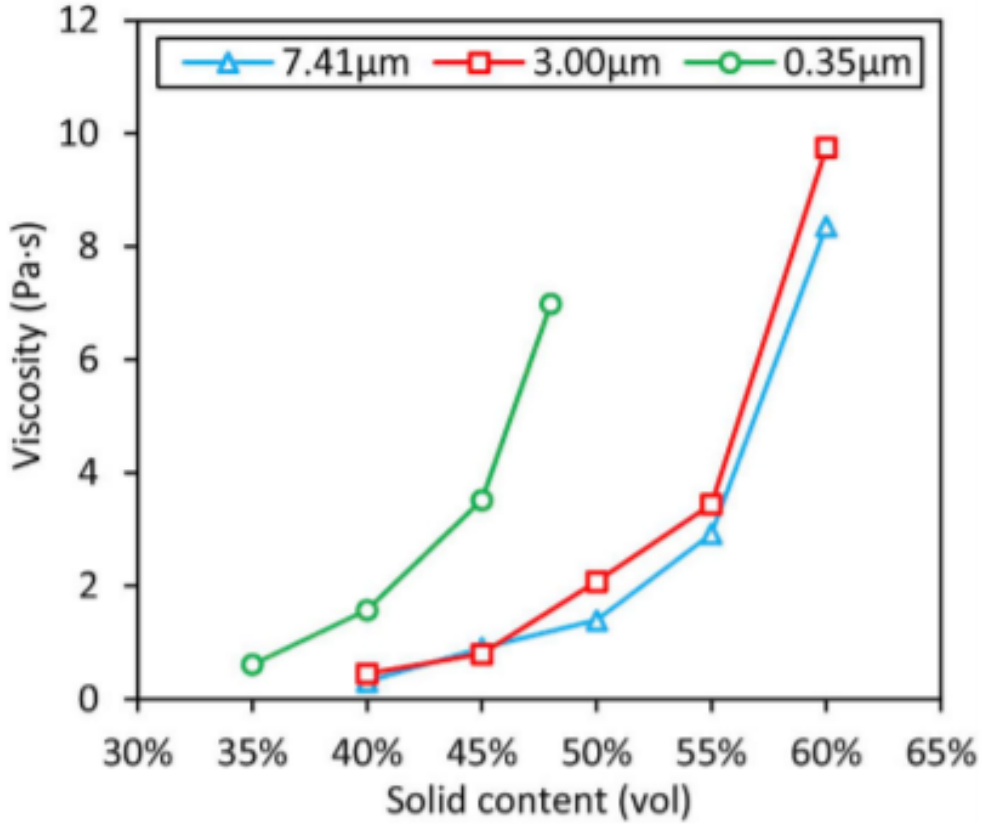


Fig. 8. Slurry viscosity as functions of solid content and particle size.

Preparation of high solid loading and low viscosity ceramic slurries for photopolymerization-based 3D printing
Ceramics International Volume 45, Issue 9, 15 June 2019, Pages 11549-11557

Bigger particles in silica slurry can cause wafer surface damage after chemical mechanical polishing

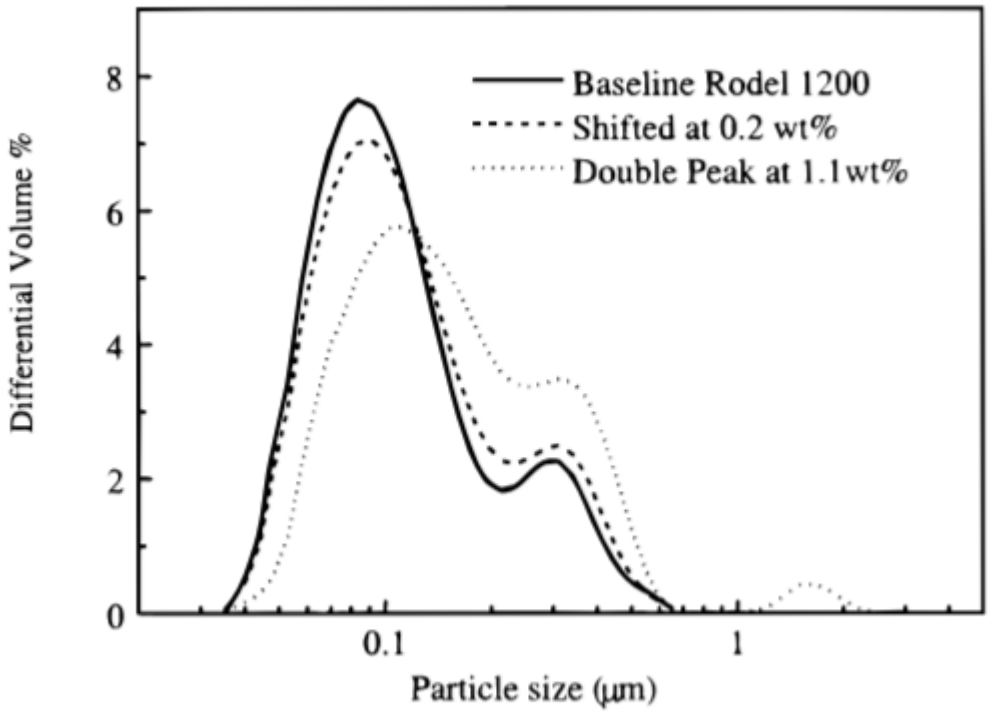
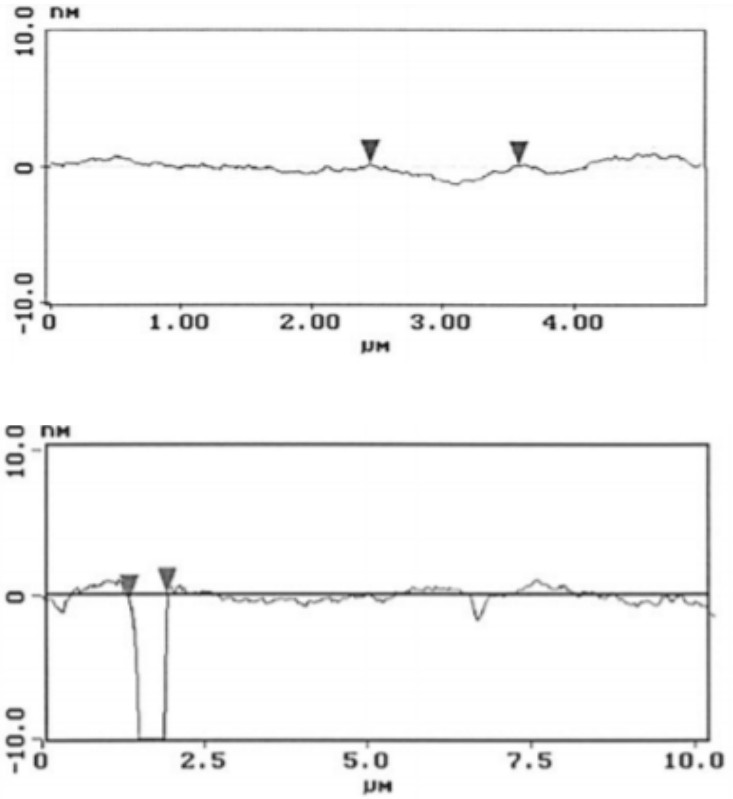


Figure 1. Particle size distributions for Rodel 1200 slurry spiked with Geltech 1.5 μm particles.



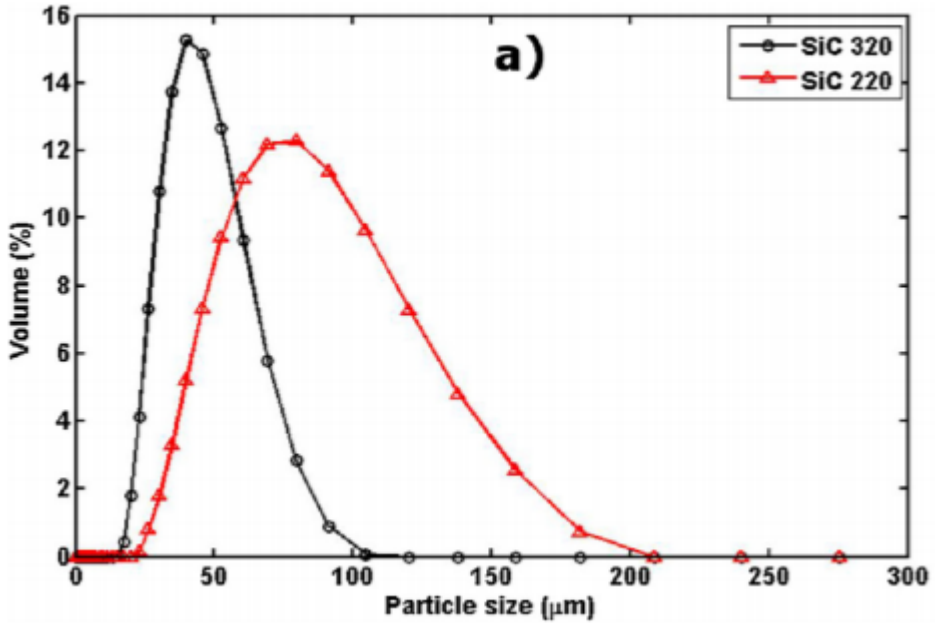
Base slurry – 0.2 μm particles
Acceptable polishing

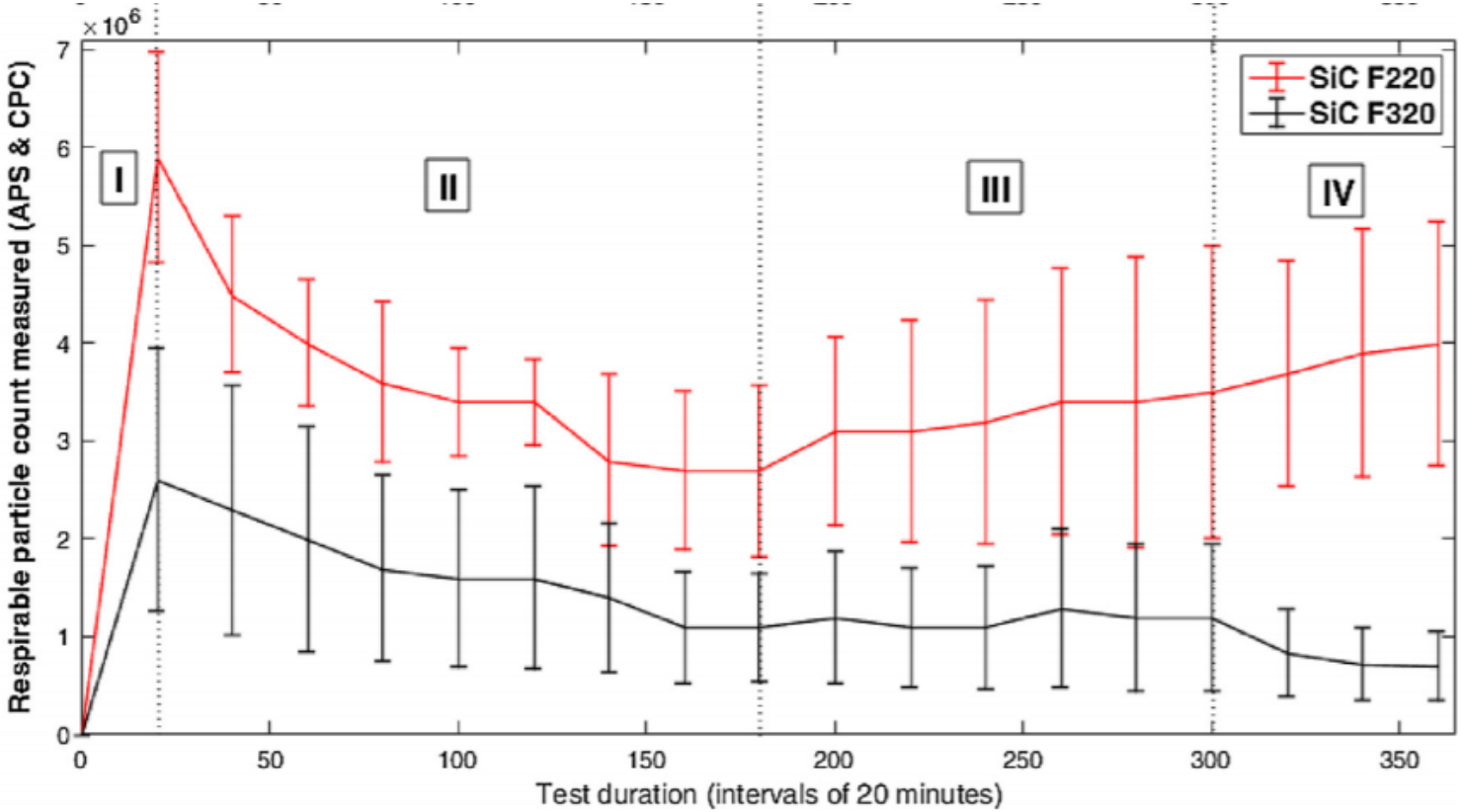
Base slurry spiked with 1.5 μm particles
Surface damage

Slurry silica particle size distribution was measured by DLS for both base slurry and base slurry spiked with bigger silica particles.

Effect of Particle Size of Chemical Mechanical Polishing Slurries for Enhanced Polishing with Minimal Defects, Journal of The Electrochemical Society, 2000, 147, 3523-3528.

SiC abrasive with bigger particle size can generate more respirable dust particles during handling.

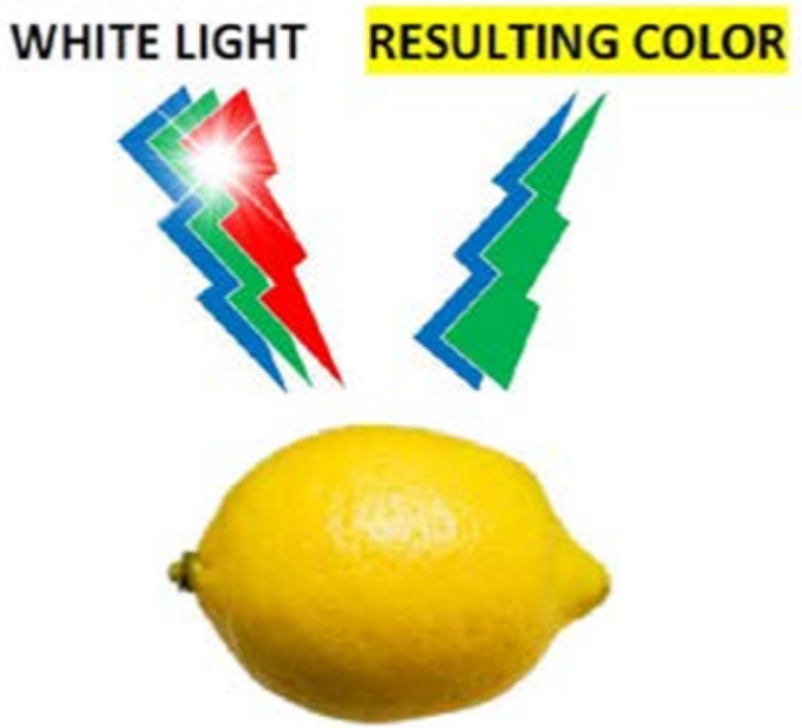


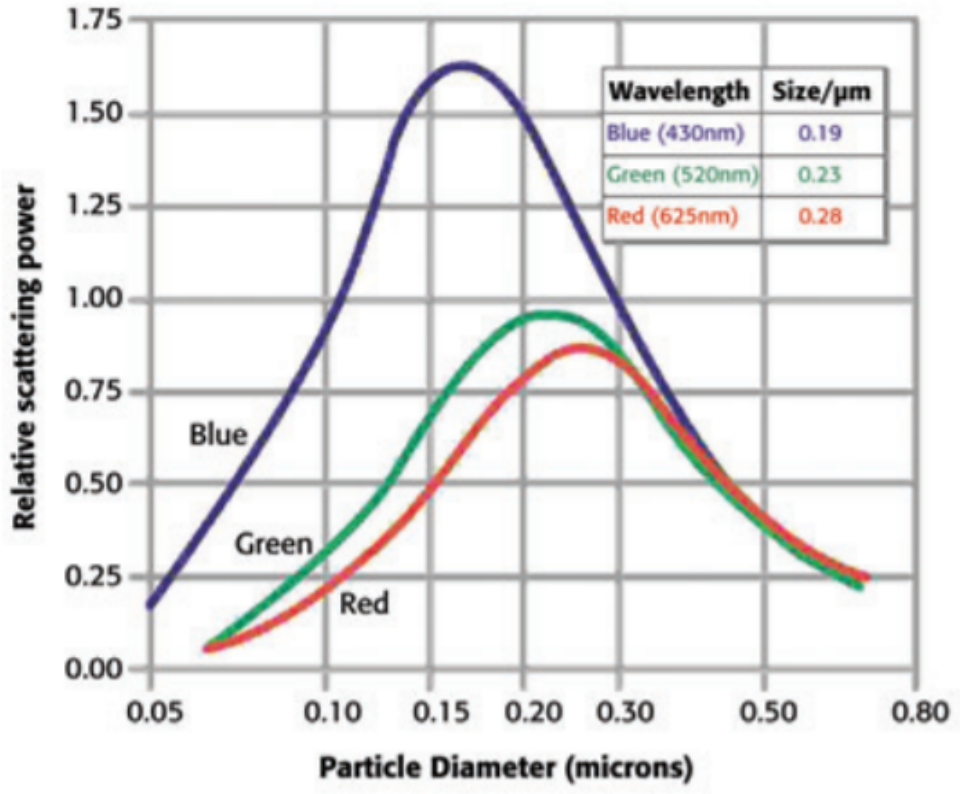


Particle size was measured by laser diffraction at μm scale for the dry abrasive powder.

Long-term dust generation from silicon carbide powders, Process Safety and Environmental Protection 2018, 116, 115-125.

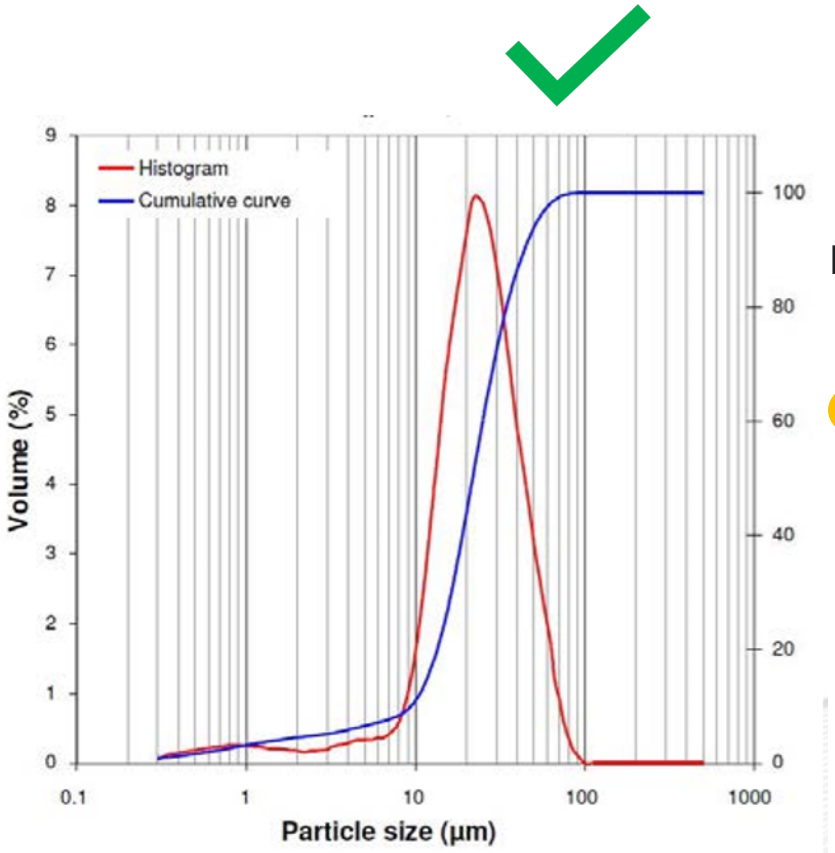
Pigment particle size determines its effectiveness to display color



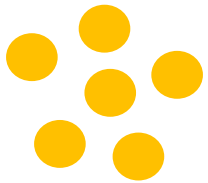


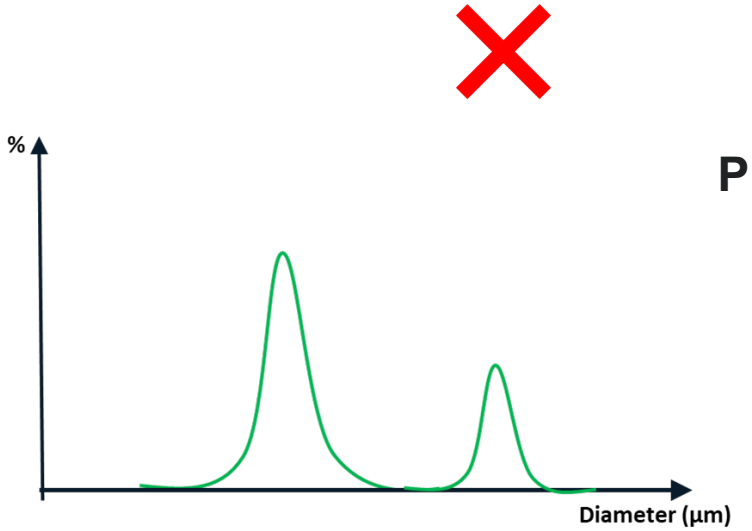
With Flying Colors: Pigment Size Analysis using Dry Jet Dispersion Technology. Anton Paar application paper, E27IA003EN-B
Pigments and Paint Dispersions. Henk G. Merkus. Particulate Products pp 343-370. Published by Springer in 2013.

Pigment particle size control is critical for paint quality

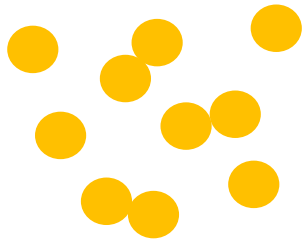


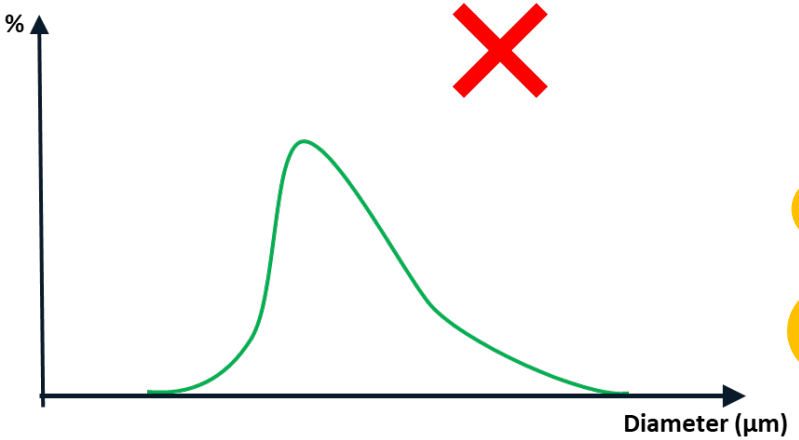
Monodisperse Pigment



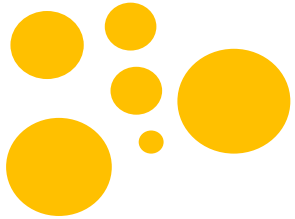


Pigment aggregate





Poor particle size control



Pigment particle size was measured by laser diffraction for particle size distribution of the dry powder at micron scale.

With Flying Colors: Pigment Size Analysis using Dry Jet Dispersion Technology. Anton Paar application paper, E27IA003EN-B

Pricing for particle size analysis by techniques

Technique	Laser Diffraction Particle size analyzer	Dynamic light scattering	Atomic Force Microscopy	Scanning Electron Microscopy	Transmission Electron Microscopy	Laser Scanning Confocal
You May Hear This Referred to As:	PSA or PSD	DLS	AFM or SPM	SEM or HRSEM	TEM	"Keyence"
Key Manufacturers	**Anton Paar**	**Anton Paar**	**Bruker**	**ThermoFisher**	**ThermoFisher**	**Keyence**
	Malvern	Malvern	Park Scientific	JEOL	JEOL	Zeiss
	Beckman Coulter	Beckman Coulter	Asylum Research	Zeiss	Hitachi	Leica
	Horiba	Horiba	**Anton Paar**	Hitachi		Olympus
	Sympatec	Wyatt	Molecular Vista	Tescan		Nikon
		Sympatec	Many others	Nikon		
Substrate Size Limitations			200mm max to reach edges; 300m in center	Most analytical services <200mm	Coupons	Flexible, with fixtures
Field of View - Min to Max			200nm to 70µm	1µm to 2mm	2nm to 10µm	100µm to 1mm
Particle size resolution	40 nm	0.3 nm	Å	nm	Å	nm
Particular challenges		Particle precipitation	Sample should be smooth	Non-conductive samples charging	Very small field of view	Reflectivity, Steep Slopes
Cost @ Covalent	**$300 / sample**	**$500 for 1 sample $800 for 2 samples $325 / sample for 3 or more samples**	**$175 / scan**	**$275 / hr (standard res) $375 / hr (hi-res)**	**$900 / sample (standard sample)**	**$300 / hr**

Acknowledgements

- **Anton Paar**

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- **Covalent Metrology**

Craig Hunter, Chris Moore, Jeff Sullivan, Warren Wong, Aleia Kim

Episode 7 recap and take-home message

- **Particle size analysis techniques**
  - Basics and technique selection
  - In-house capabilities at Covalent

- **Particle size analysis for industrial product success**
  - Quantum dots for use in capacitor
  - Battery electrode material
  - Therapeutic delivery carrier
  - Drug tablet
  - Ceramic for vehicle mechanical parts
  - Slurry for 3D printing and chemical mechanical polishing
  - Abrasive for dry polishing
  - Paint pigment

- **Next Episode**

- **Question and Answer**

Next episode

COVALENT METROLOGY

APPLICATIONS OF ATOMIC FORCE MICROSCOPY IN THE BIOSCIENCES

GUEST SPEAKER:

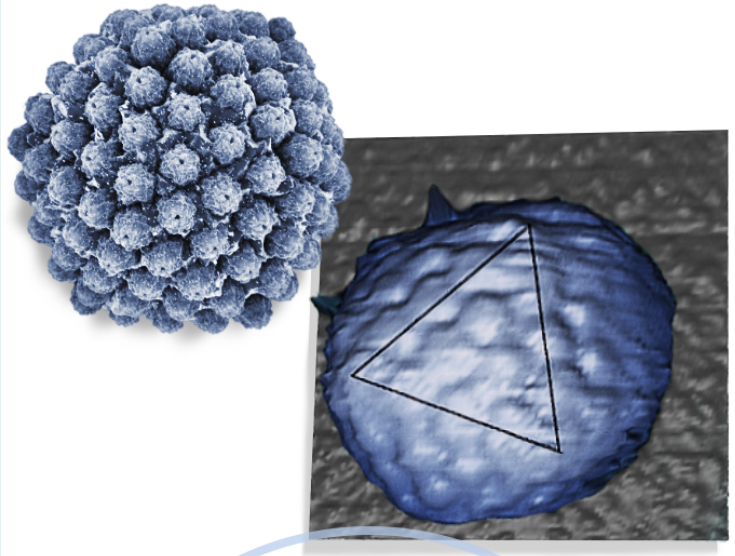
Sophia Hohlbauch
Senior Biological Applications Scientist, Asylum Research

May 21, 2020 11am PDT

COVALENT METROLOGY

OXFORD INSTRUMENTS

Asylum Research



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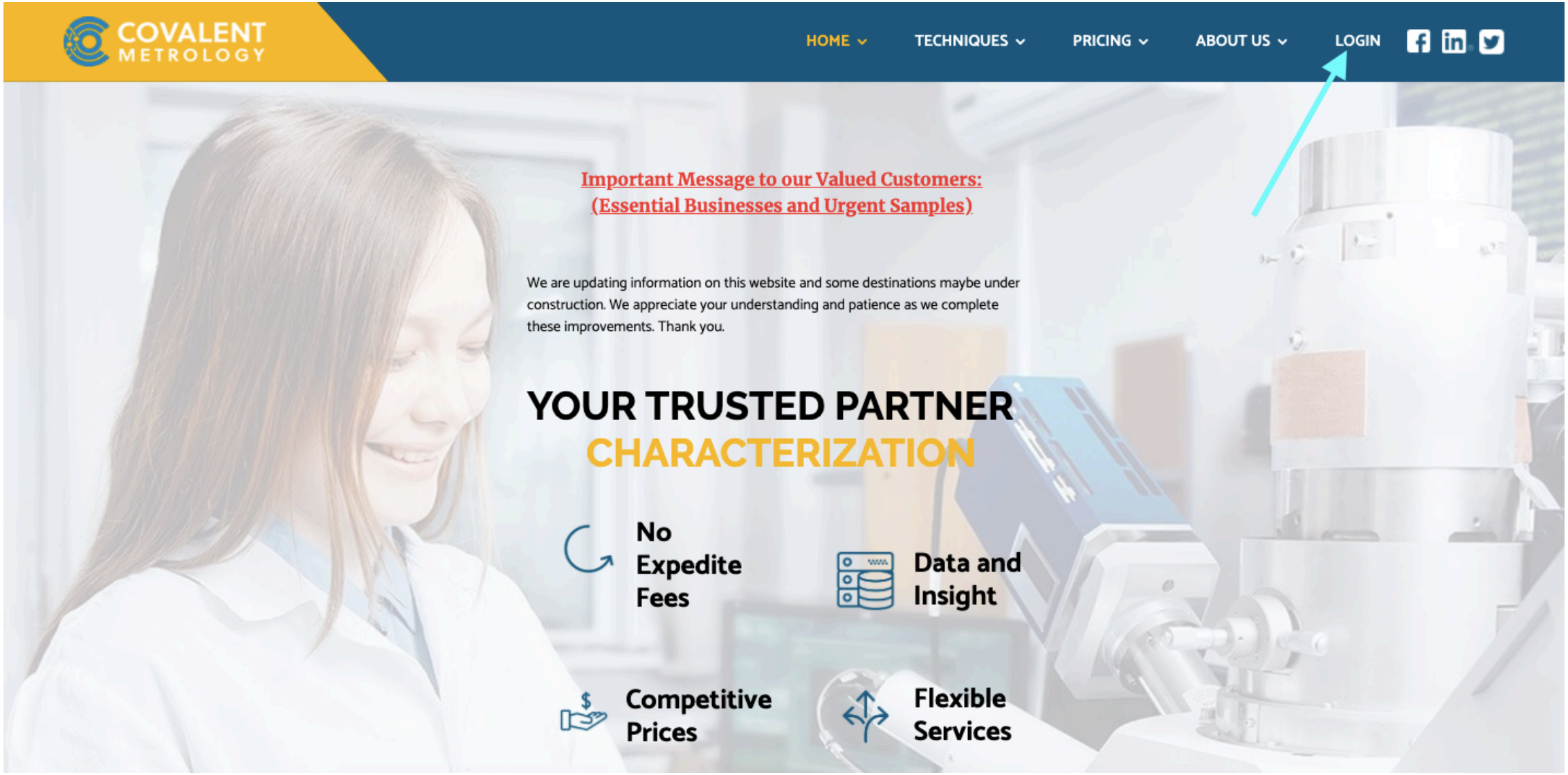

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