Characterisation of Nanomaterials for REACH and Beyond

24th October 2017

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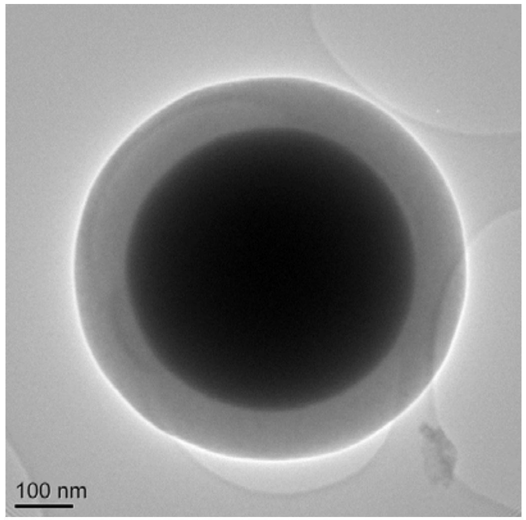
escubed limited



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Purpose

- The purpose of this presentation is to provide insight into how important physical properties of nanomaterials can be characterised for REACH and for wider applications.
- I'll discuss the challenges that characterisation of nanomaterials presents and how we at escubed can overcome them.
- We'll hopefully address some key questions:
  - What techniques are available for nanomaterial characterisation?
  - Which technique is best suited for a specific material?
  - What is the best way to prepare a material for nanomaterial characterisation?
  - How can we combine various techniques to give the best possible outcome?

About escubed limited

- Spin out - University of Leeds (Institute of Particle Science & Engineering)
- Specialist particle, powder and colloid analytical and R&D services
- Founders have over 60 years combined experience of particle, powder & colloidal characterisation and R&D
- [Access to] the widest range of particle analytical equipment in the UK
- Strategic business alliance with Malvern Instruments - sole UK supplier of all Malvern's UK contract analytical business in particle size, shape, zeta potential and rheology
- Standards/quality – GMP, BSI, ISO 17025 and Proficiency Testing

Malvern

UKAS TESTING 8467

Particle Size Analysis and REACH

- Particle size is a key parameter to assess when characterising nanomaterials.

- Definition of a nanomaterial (European Commission):

A natural, incidental or manufactured material containing particles, in an ***unbound state or as an aggregate or as an agglomerate*** *and where, for 50 % or more of the particles in* ***the number size distribution****, one or more external dimensions is in the size range* ***1 nm - 100 nm****.*

European Commission Definition of Nanomaterial, 2011/696/EU

This definition raises a number of points to be considered when measuring the particle size distribution of the nanomaterial in question:

- **#1 Types of particle present:** Unbound state, agglomerate or aggregate?
- **#2 Types of particle present:** How do we achieve dispersion?
- **#3 Which technique**: Particle size vs. particle size distribution? Type of size distribution available? Size capabilities of technique?

#1: Types of Particles/Particle Assemblages Present

- "Particle" means a minute piece of matter with defined physical boundaries

- "Agglomerate" - Collection of weakly-bound particles or aggregates or mixtures of the two where the resulting external surface area is similar to the sum of the surface areas of the individual components

- "Aggregate" - Particle comprising of strongly-bonded or fused particles *where the resulting external surface area may be significantly smaller than the sum of calculated surface areas of the individual components* (text in italics not included in in the commission definition)

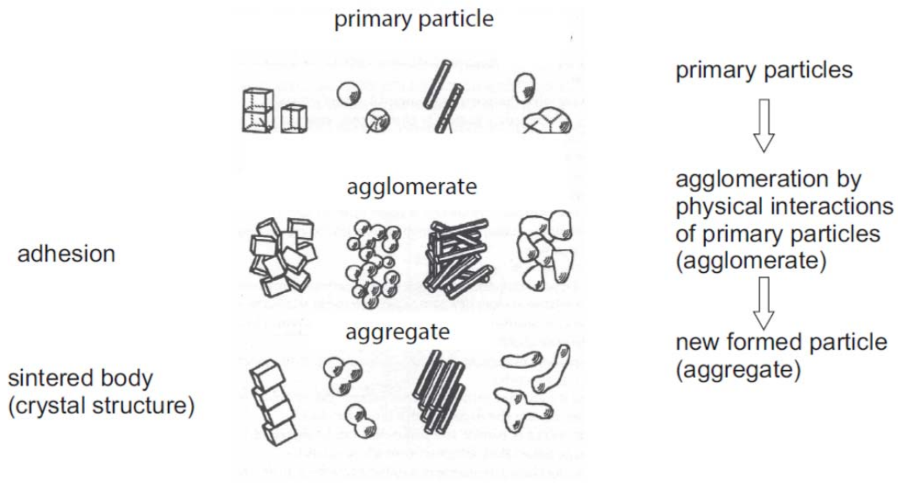
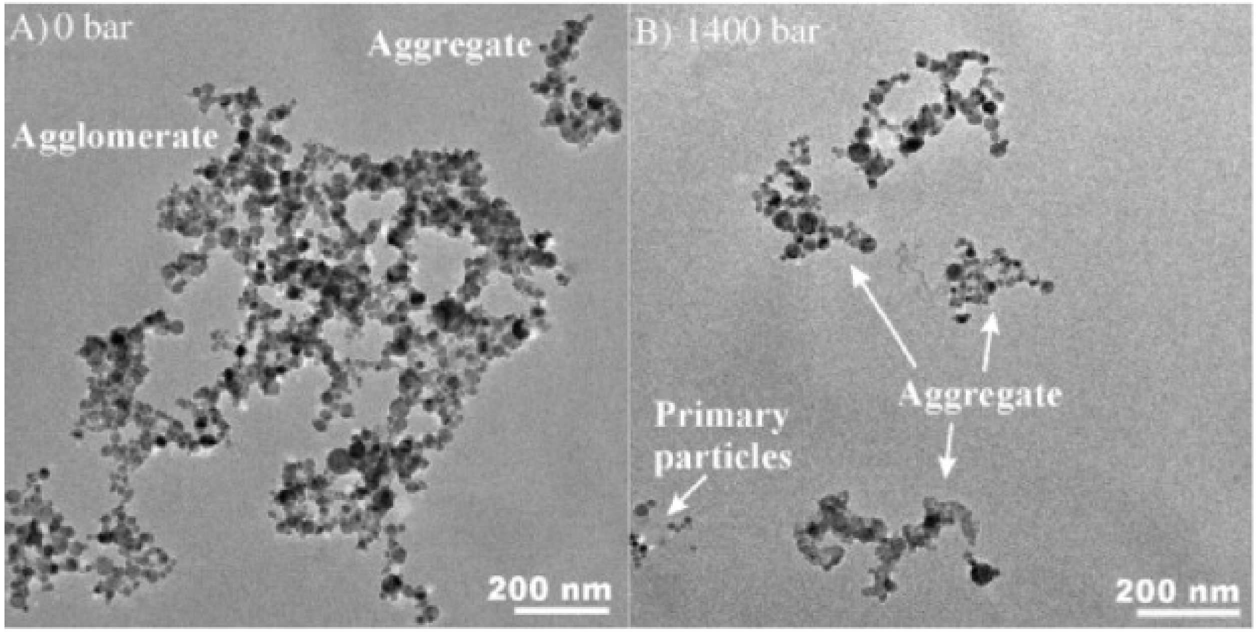


Figure 1: Relationships between primary particles, agglomerates and aggregates.

JRC Reference Reports. Requirements on measurements for the implementation of the European Commission definition of the term "nanomaterial", 2012.

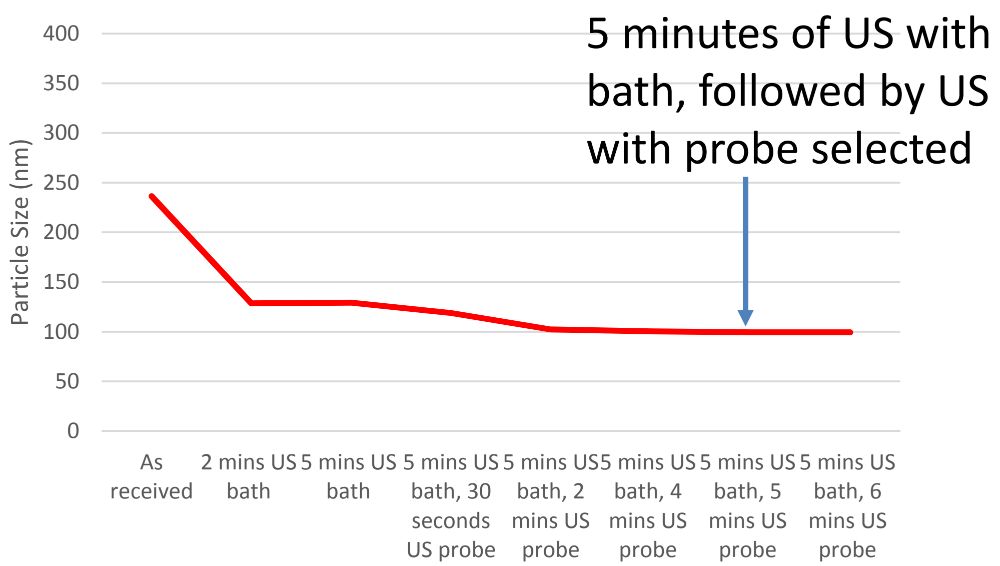
#1: Types of Particles/Particle Assemblages Present



The effect of high-pressure deagglomeration on morphology and size of TiO_2 assemblages
Faure et al, Sci. Technol. Adv. Mater. 14 (2013)

#1: Types of Particles/Particle Assemblages Present

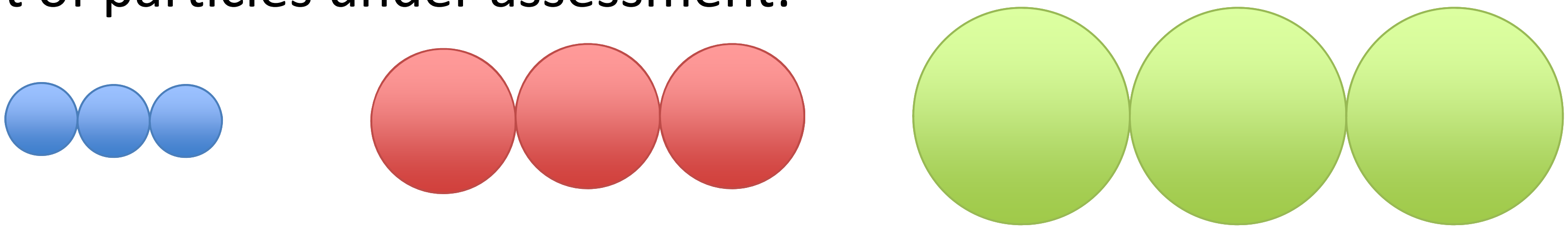
- It is required that the primary particle size distribution of the nanomaterial is measured.
- Application of ultrasound with ultrasonic bath and ultrasonic processor at varying durations.



Ultrasonication of a sample of commercially available TiO_2

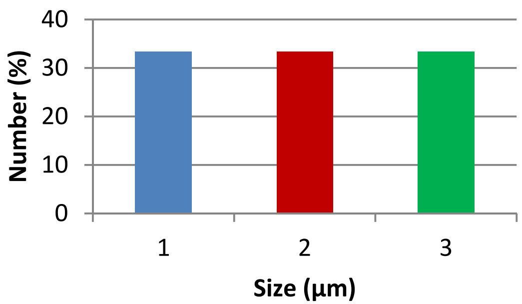
#2 Which Technique: Type of Distribution?

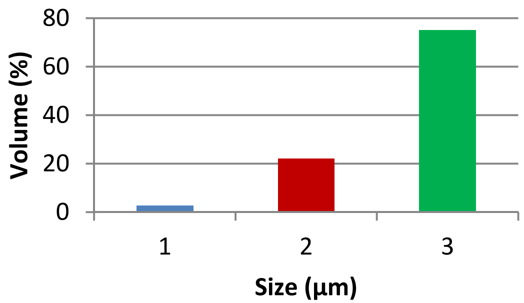
- Set of particles under assessment:

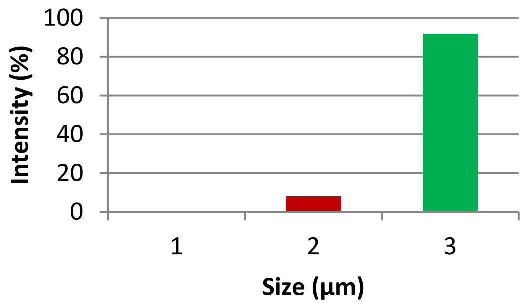


1 nm **2 nm** **3 nm**

Volume = $4\pi/3$ nm^3 (2.8%) Volume = $32\pi/3$ nm^3 (22.2%) Volume = 36π nm^3 (75%)

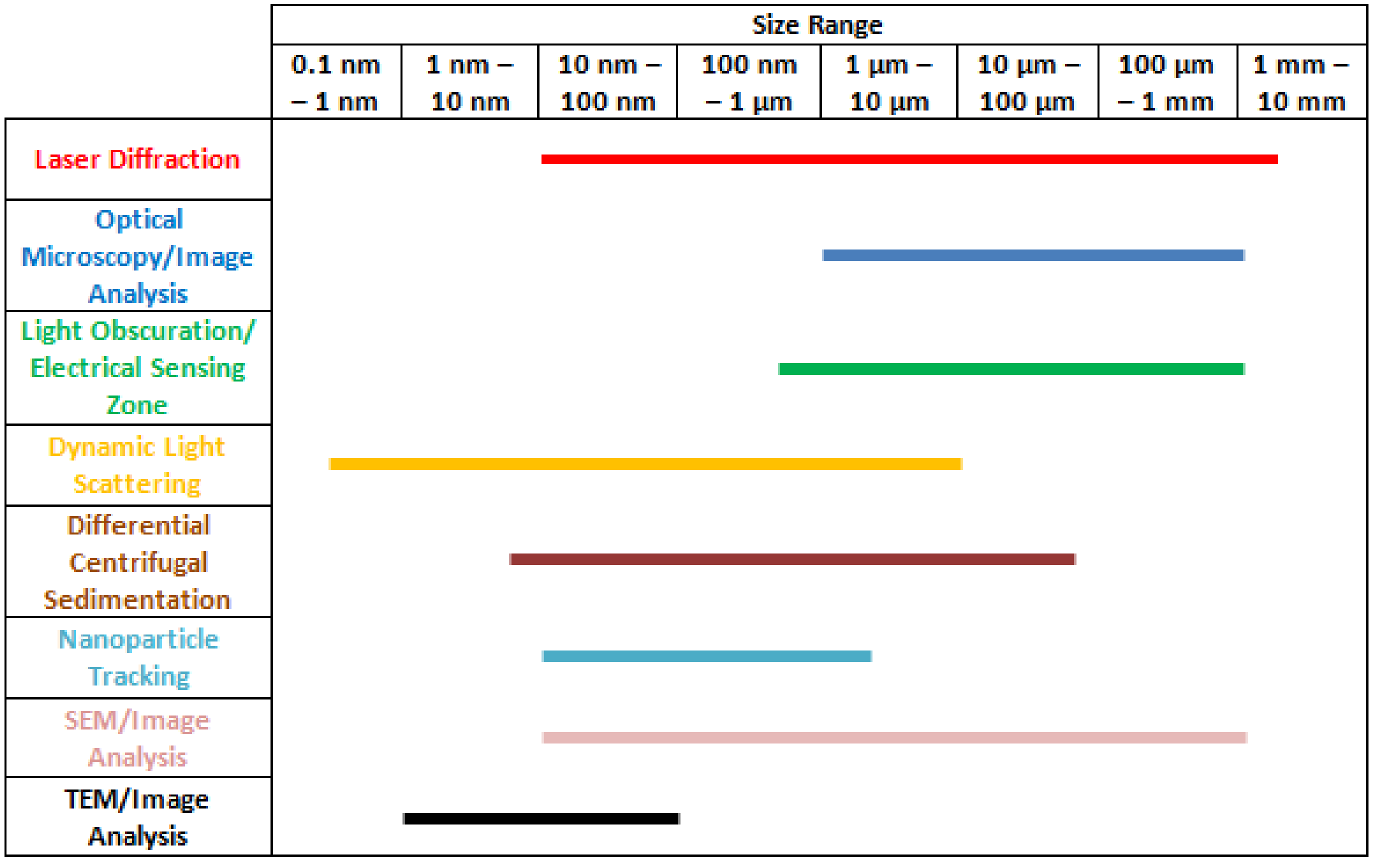




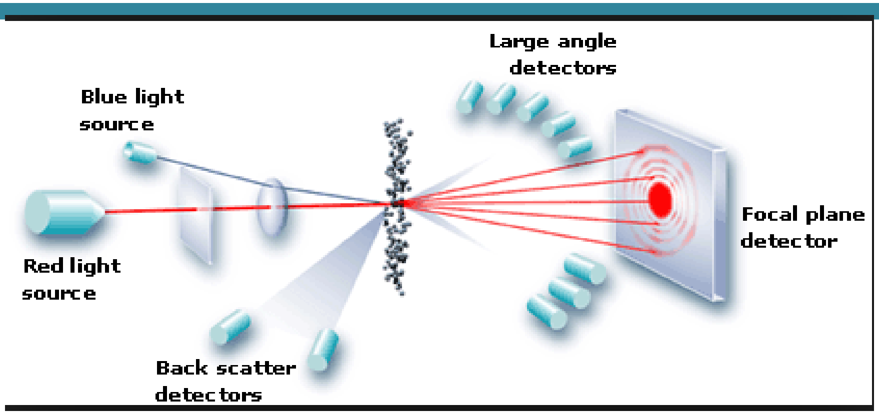


Number < **Volume** < **Intensity**

#2 Which Technique: Size Capabilities?



Particle Size by Laser Diffraction



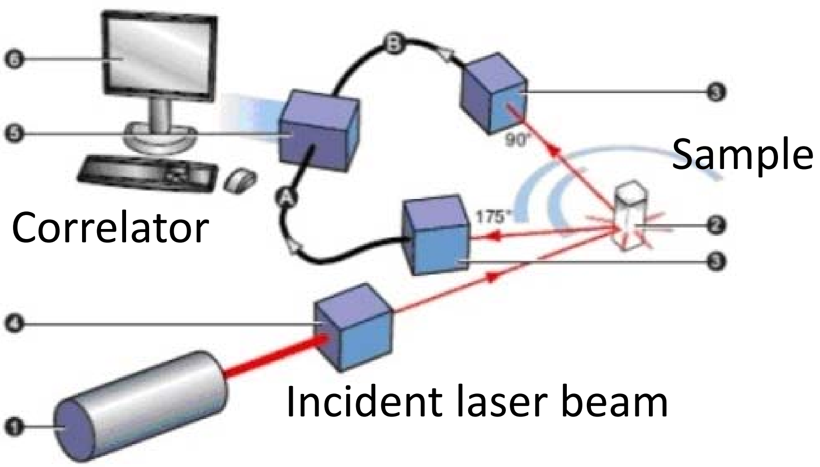
1. Sample is dispersed – wet or dry
2. Dispersed sample passes through the path of laser light - a diffraction pattern is generated.
3. The angle and intensity of scattered light is measured by an array of sensitive photodiodes
4. Raw data is inputted into algorithms (Mie or Fraunhofer theory based), which effectively work on this premise: **Large particles scatter intensely at narrow angles; small particles scatter weakly at wide angles**

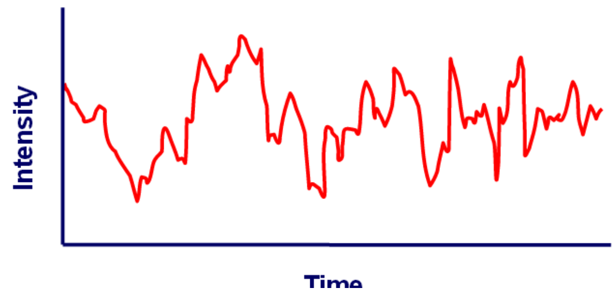
Particle Size by Laser Diffraction

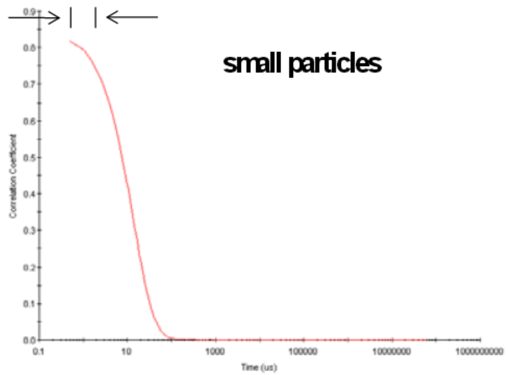
- Advantages:
  - Speed of measurements
  - Application flexibility
  - Very wide size range: 10 nm up to 3 mm
- Disadvantages:
  - Generates a volume distribution; transformation to a number distribution is prone to large errors. Cannot measure according to nanomaterial definition.

Particle Size by Dynamic Light Scattering

- Dynamic Light Scattering (DLS) measures hydrodynamic diameter of a particle.
- A laser beam passing through a dispersion of the nanoparticles is scattered.
- The intensity of scattered light at a fixed position is measured over time.
- Timescales for fluctuations in intensity depends on size of particles present.
- Process of correlation gives function which shows exponential decay; time constant is related to particle size







Particle Size by Dynamic Light Scattering

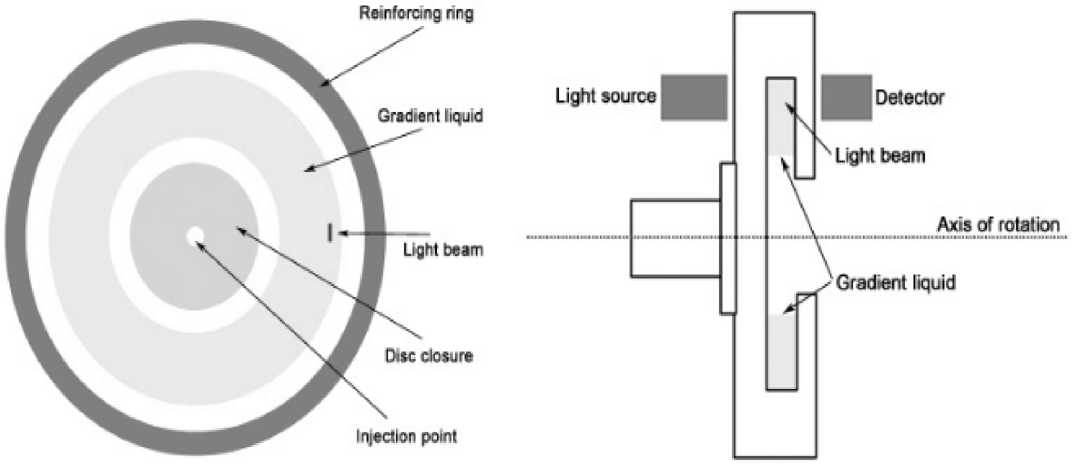
- Advantages:
  - Speed of measurements; small sample quantities
  - Performs well when measuring monodisperse sample with a known refractive index and nanoparticles are present in sufficient concentration.
- Disadvantages:
  - DLS does not generate particle size distribution in its standardised form, but a light scattering intensity weighted value. Generates an intensity distribution; strongly biased to the presence of large particles.
  - Transformation to number distribution relies on typically unrealistic assumptions

Particle Size Analysis by Differential Centrifugal Sedimentation

- Particles with larger diameters sediment at a faster rate than smaller particles.
- Sedimentation velocity increases as the square of the particle radius – Stokes' Equation.
- Sedimentation of particles achieved through centrifugation in a spinning disc. A density gradient within the spinning disc allows for more effective separation of fractions.
- Separated fractions are presented to an optics based detection system in decreasing size order.

$$V = \frac{2}{9}\frac{(\rho_p - \rho_f)}{\mu} g R^2$$

Stokes' Equation



Hollow Disc Centrifuge Design

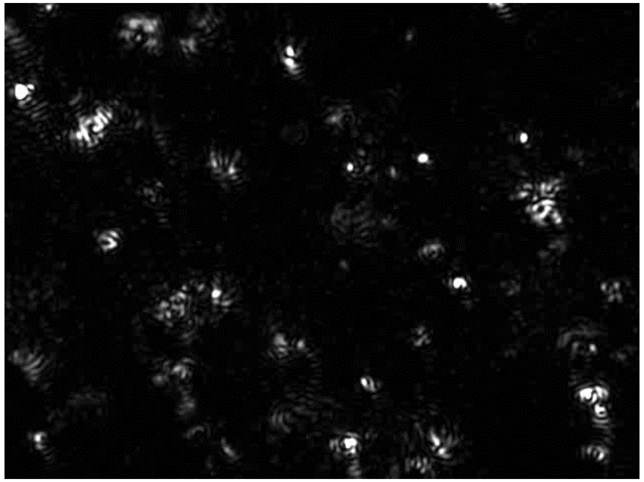
Particle Size Analysis by Differential Centrifugal Sedimentation

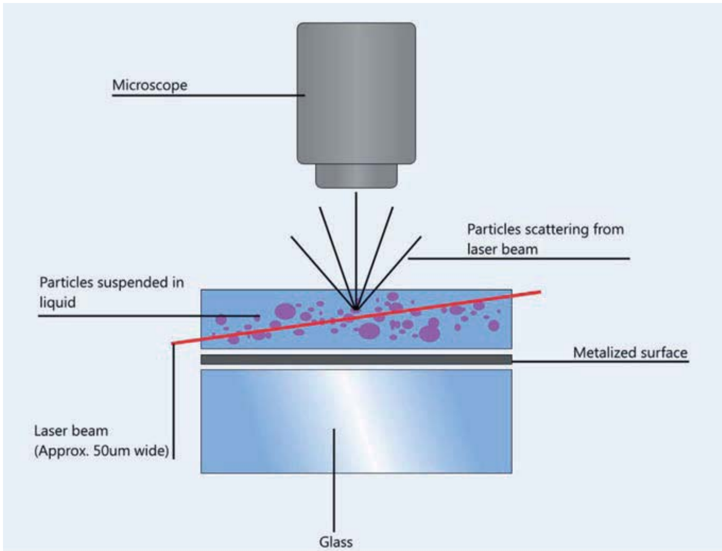
- Advantages:
  - Very high resolution – capable of separating particles with size difference as small as 2%.
  - Capable of reliably measuring polydisperse samples – separates different fractions before measurement so intensity-extinction based measurement is less biased to larger sizes and therefore closer to number-based distribution.
- Disadvantages:
  - Generates an intensity distribution; number distributions not usually produced.
  - Small band-width as difficult to select a disc speed that is appropriate for smaller and larger particles.
  - Relies on particle density being known and uniform

Particle Size Analysis by Nanoparticle Tracking – Malvern Nanosight

- Nanoparticle Tracking (NTA) relies on two phenomena of particles: the ability of individual particles to scatter light and the characteristic movement of particles due to Brownian motion.
- A laser beam passes through the dispersed sample. Each particle scatters light which is visualised using a 20x microscope with a CCD camera attached.

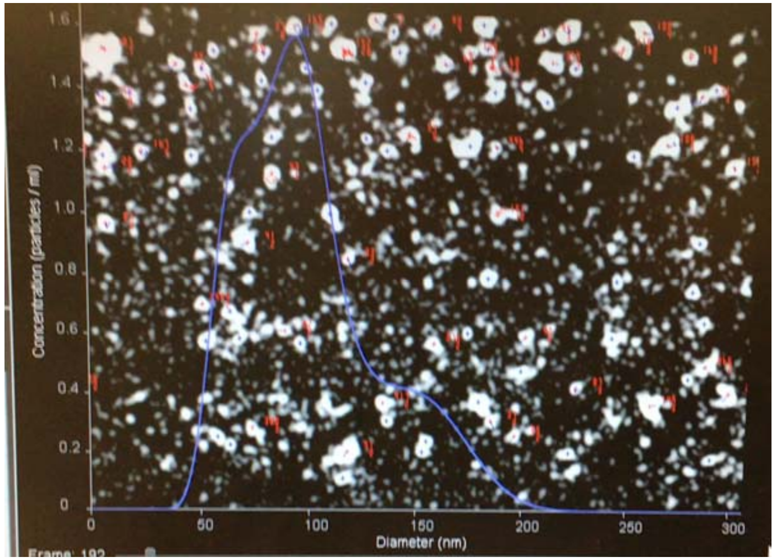
Diffracted light from TiO_2 particles undergoing Brownian motion





Particle Size Analysis by Nanoparticle Tracking

- A video of the motion of the various particles is captured.
- Software is able to analyse the video and track the motion of each individual particle and assign each particle with a diffusion coefficient and therefore a particle size.
- Particle size analysis on a particle-by-particle basis.

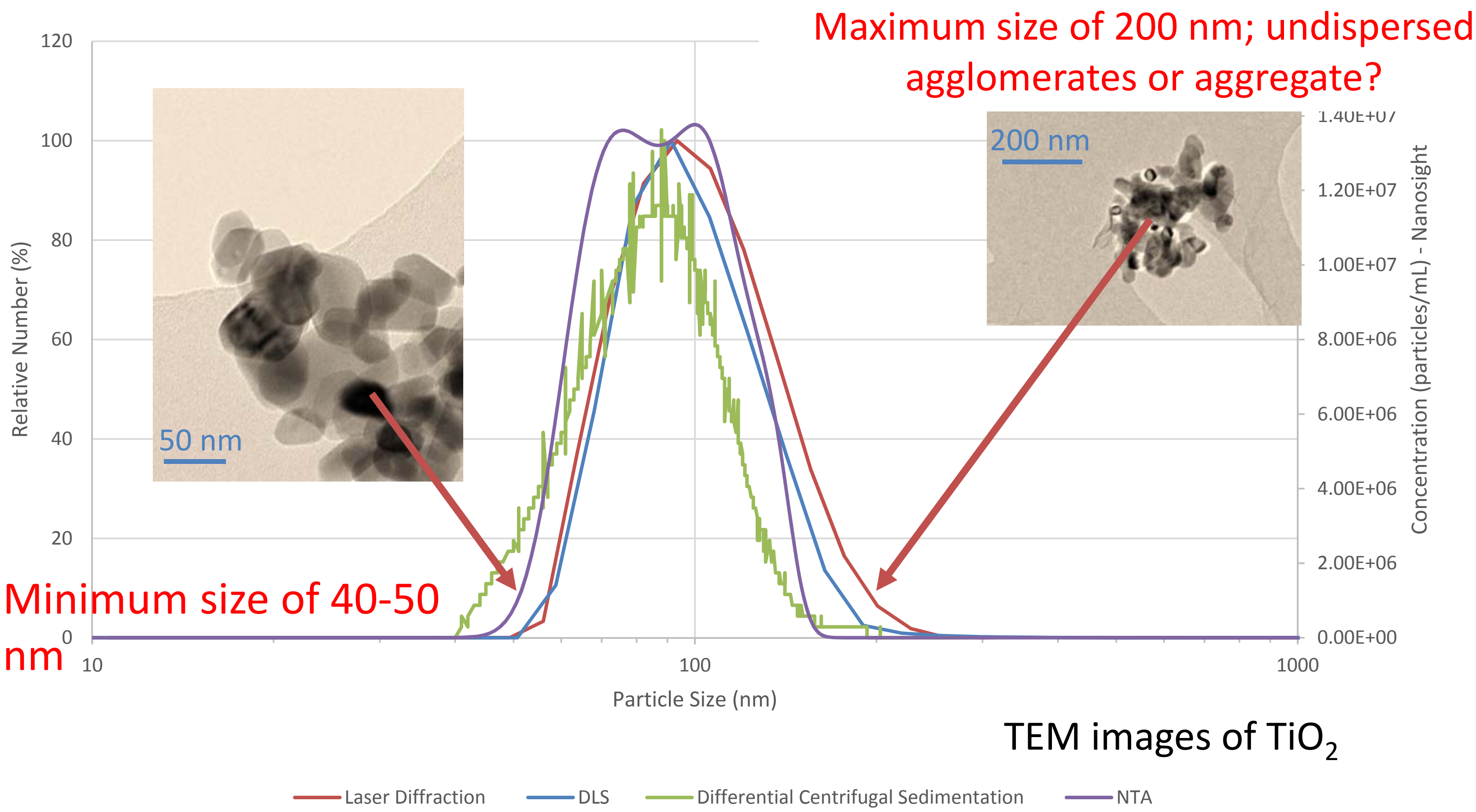


Real-time nanoparticle tracking analysis of TiO_2 particles

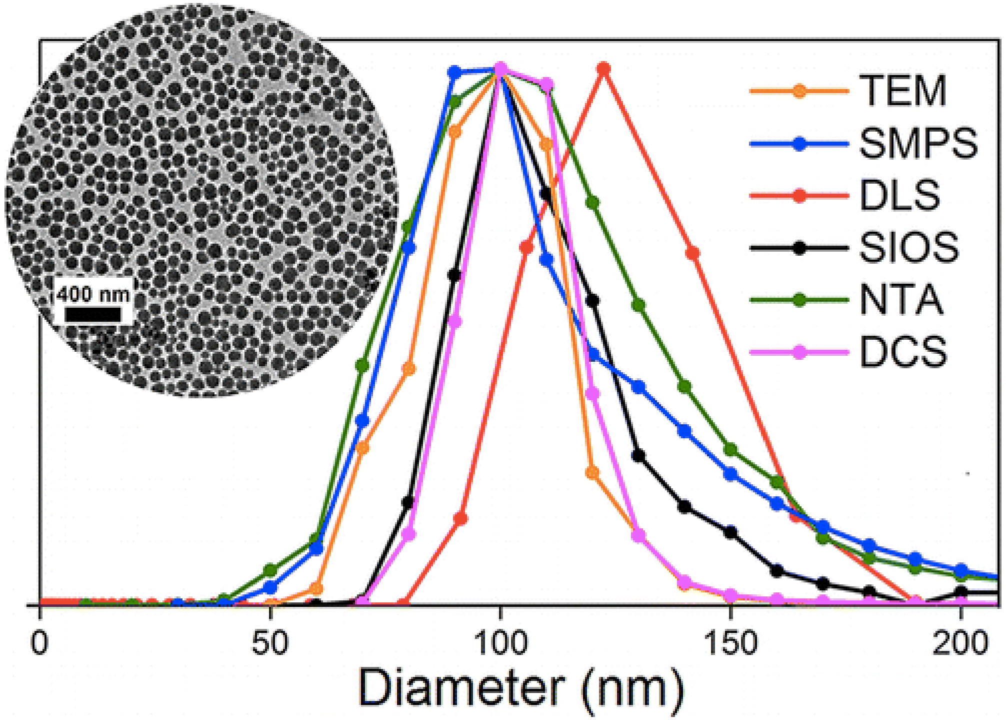
Particle Size Analysis by Nanoparticle Tracking

- Advantages:
  - Generates a number-based distribution – meets requirements for definition of a nanomaterial.
  - Particle size on a particle-by-particle basis – no bias from larger particles like with DLS
- Disadvantages:
  - Analysis of capture videos involves more operator input than other techniques.
  - Mostly limited to dispersion in solvent for which unit is calibrated.

Particle Size Analysis of TiO_2



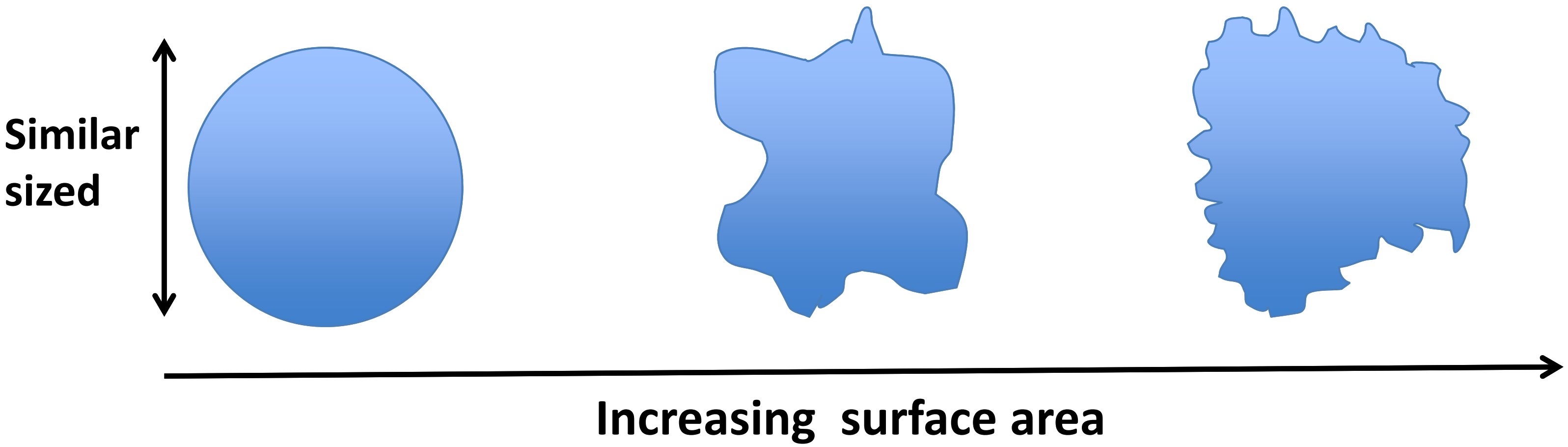
How do these techniques compare?



Emerging Techniques for Submicrometer Particle Sizing Applied to Stöber Silica, N. Bell et al., *Langmuir*, **2012**, *28* (29), pp 10860–10872

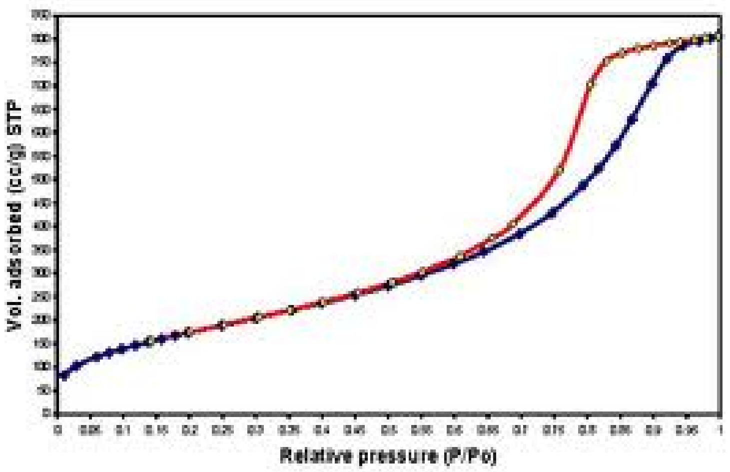
Specific Surface Area

- Surface area: a proxy for size or more?
- Same sized particles can have vastly different surface areas; effects on surface reactivity and toxicity.
- An alternative means of defining nanomaterials is through specifying that materials with a volume-specific surface area greater than 60 m^2/cm^3 shall be considered as nanomaterials.



Specific Surface Area- BET Analysis

- Common way of measuring the specific surface area is using a gas adsorption isotherm.
- The quantity of an analyte gas (e.g. nitrogen or krypton) adsorbed on particle surfaces is measured at a range of relative pressures.
- The quantity of gas required to form a monolayer over the external surface is calculated using BET theory.
- Mass specific surface area (MSSA, m^2/g) measured
- Use skeletal density (cm^3/g) to calculate the volume specific surface area (VSSA, m^2/cm^3)



Conclusions

- Particle size determination is method dependent – each method has pros and cons, so detailed information is required.
- Use microscopy with another technique (e.g. Nanosight) for particle size analysis to capture all required information.
- Surface area measurements build on particle size results – alternative route to defintion

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Services

Measure Particle Properties … Contract Analytical Service

- Particle size
- Shape/Morphology
- Surface Area
- Density
- Zeta Potential
- Rheology

Design Particles … R&D/CRO Service

1. Colloidal chemistry approaches – eg pickering emulsions (nm - µm - mm)
2. Encapsulation - drop-by-drop manufacture using membrane emulsification
3. Encapsulation – powdered water. (mattifying hair product)
4. Custom polymer synthesis – eg dust repellant coatings, engine oil additives
5. Ink Manufacture

REACH Analysis – helping companies meet physical data requirements for their materials, with a particular emphasis on nanomaterials, for REACH compliance. Particle size and morphology, BET surface area and density analyses.