Australian Government
Department of Industry, Science and Resources

National Measurement Institute

Measurands and Method Dependency: Can One Size Fit All for Particles Suspended in Liquid?

Dr Åsa K. Jämting, Malcolm A Lawn, Sean Williams, Dr Bakir Babic and **Dr Victoria A. Coleman**
Nanometrology Section, Physical Metrology, NMI Australia

CCQM Particle Metrology Workshop – Breakout Session 2, 26 October 2022

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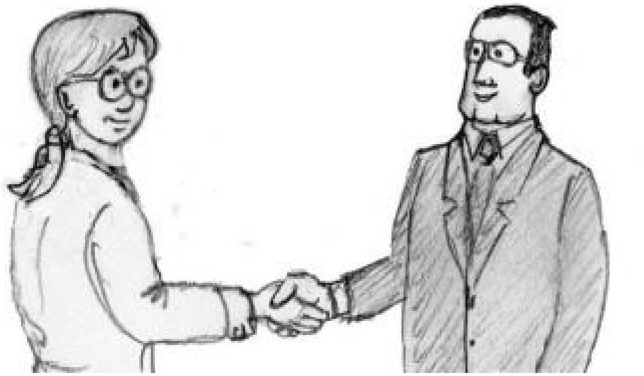
NMIA Nanometrology – drivers:
Accurate and reproducible measurements for nanotechnology

Research and Product Development

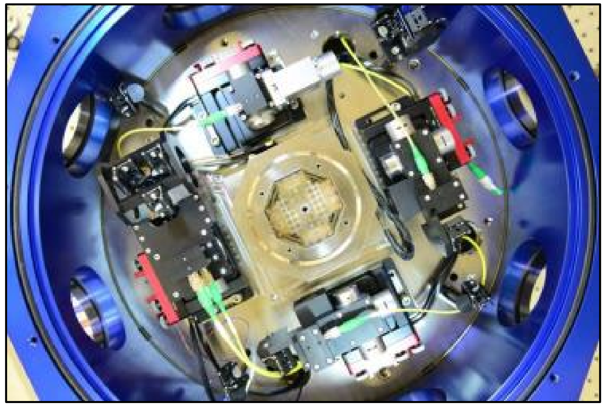


Trade

Quality Control

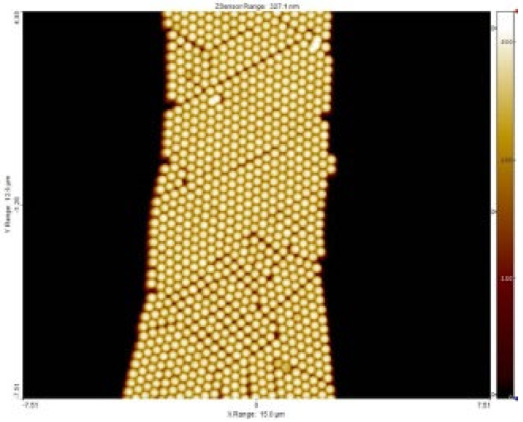
Safety and informed choice

NMIA Nanometrology – what we do:
Accurate and reproducible measurements for nanotechnology



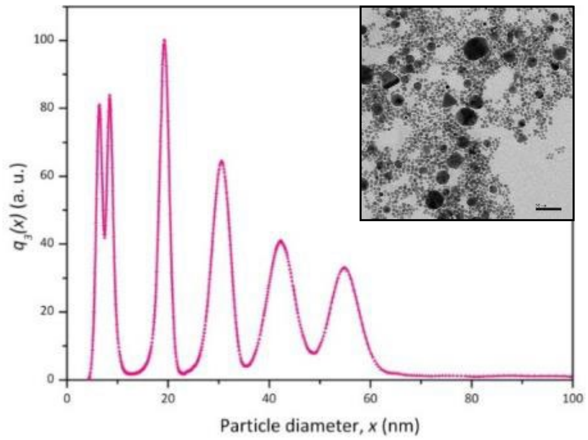
Primary Standard-
Metrological scanning probe microscope development and measurement (Traceability)

- Forces
- QTF
- FM non-contact



Accurate nanoscale measurements by atomic force microscopy

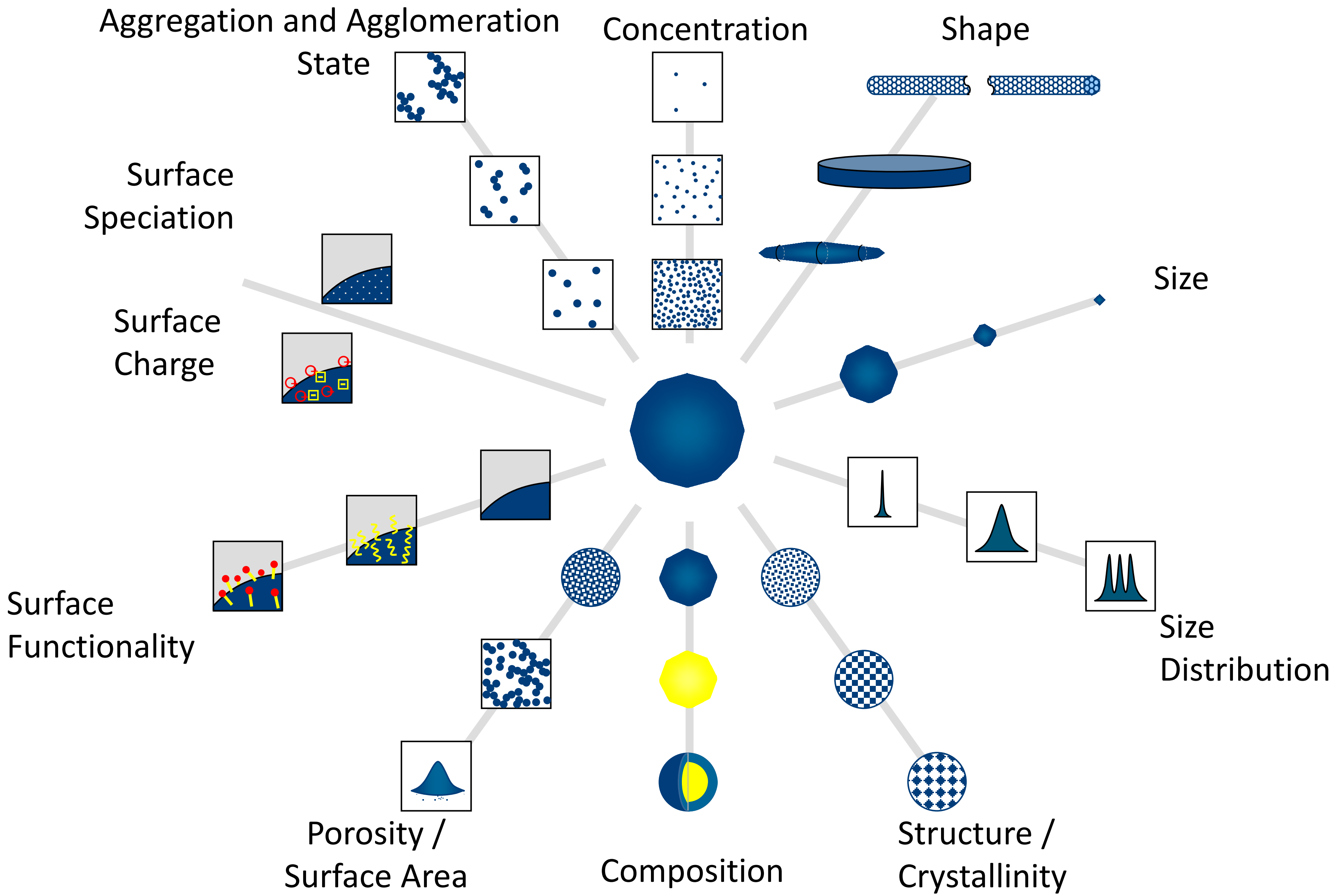
- Imaging forces
- Particle deformation
- Graphene
- CNCs



Accurate nanoscale measurements of particles in liquid

- Surface ligands
- TiO_2 pharmacokinetics
- Complex matricies (nano in food, products etc.)
- Microplastics
- Non-sphericity

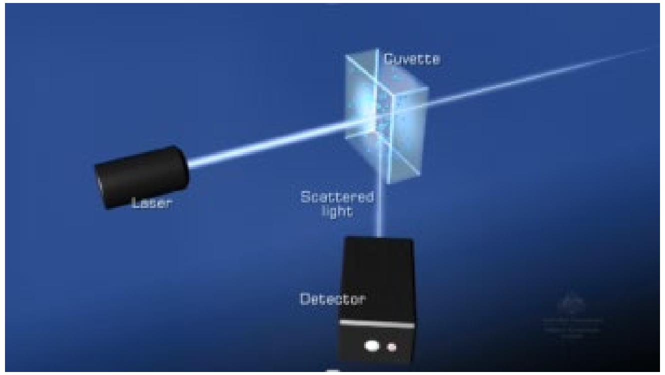
Active in: ISO TC229, TC24, TC281; APMP TCMM & TCL; CCL WGN; CCQM SAWG; VAMAS; OECD WPMN



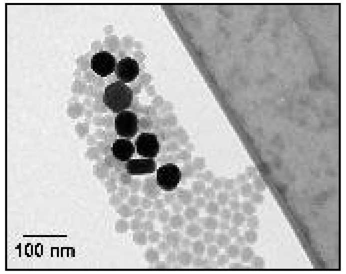
Hasselöv and Kaegi, 2009

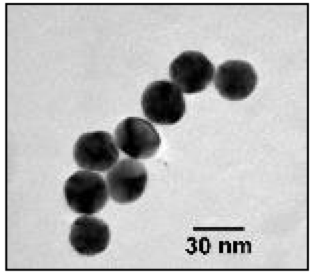
Understand your measurement
Looking under the hood – What assumptions are being made

Dynamic Light Scattering (DLS)

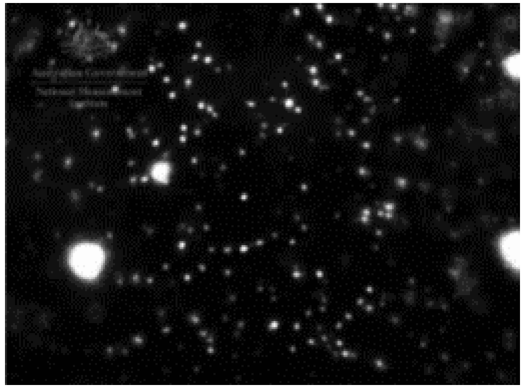


Electron Microscopy
(SEM and TEM)

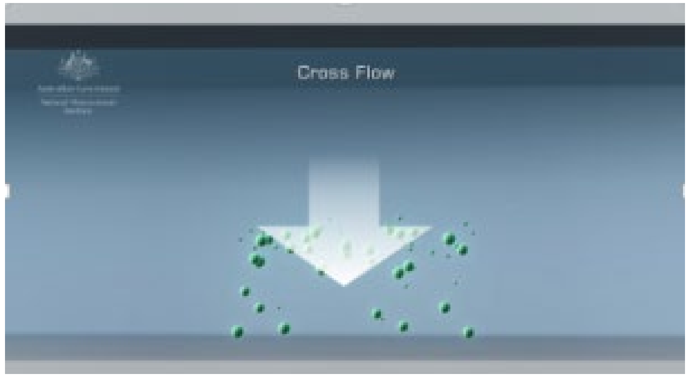




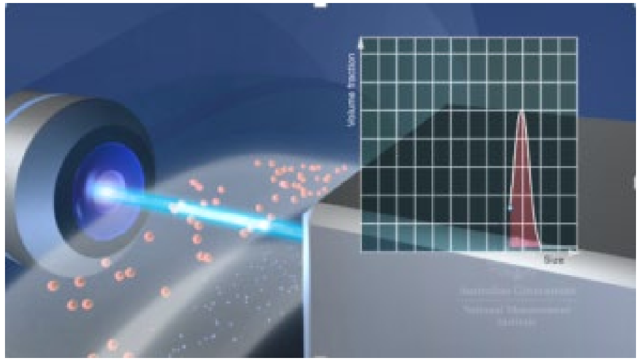
Particle tracking Analysis
(PTA)



Field flow fractionation
(FFF)

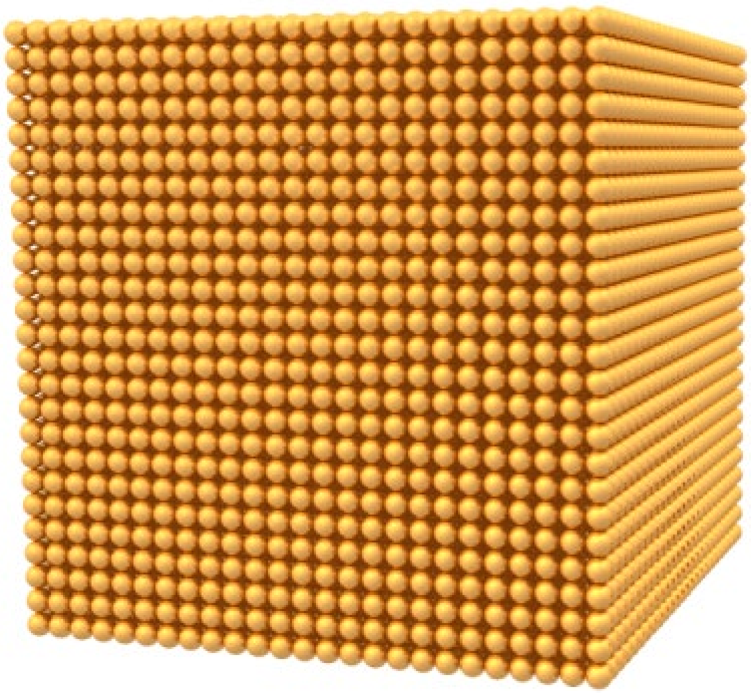


Differential Centrifugal
Sedimentation (DCS)



Understand your measurement
What is being measured (x- and y- axis!)

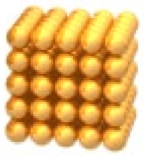
Example: 20 nm and 100 nm particles



Intensity

n_{20} = 15625

You can **convert** intensity data ('y') to volume/mass distributions using Mie theory **if** you know the *optical properties*, and volume/mass to number **if** you know *density*.

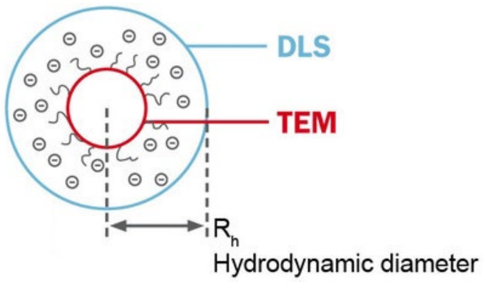


Volume/Mass

n_{20} = 125

Number

n_{100} = 1

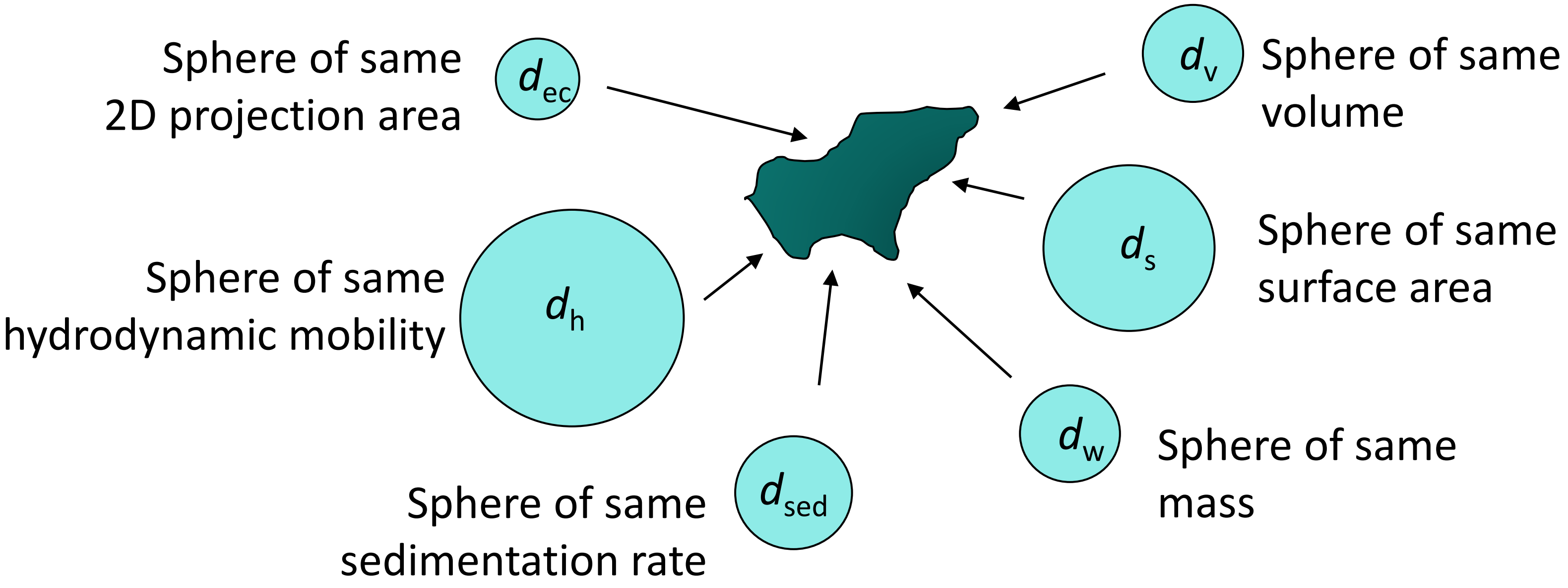


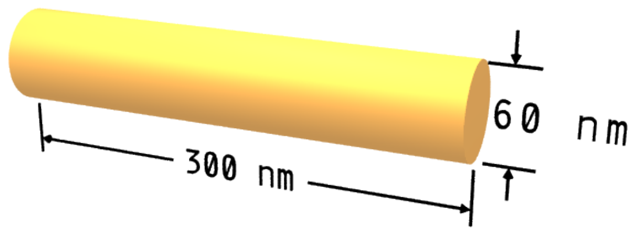
You can also convert between different 'x' diameters e.g. hydrodynamic diameter to 'hard sphere' diameter*

- width of particle size distribution (Q-correction)
- scattering angle and concentration dependence
- adsorbed water layer

*Takahashi K, Kato H, Kinugasa S. Development of a standard method for nanoparticle sizing by using the angular dependence of dynamic light scattering. Anal Sci. 2011;27(7):751. doi: 10.2116/analsci.27.751. PMID: 21747185.

Understand your measurement
Not all diameters are equal (to sphere or not to sphere, that is the question…)





Measurand	Size (nm)
Cross sectional diameter (of cross section perpendicular to axis)	60
Equivalent circle diameter derived from projected area (TEM)	151
Volume equivalent spherical diameter (Laser diffraction)	117

Measurand (VIM4):
Quantity intended to be measured

NOTE 4 In the past the term "measurand" was used to refer to both the quantity intended to be measured and the quantity being measured., i.e., the quantity with which the measuring system interacts. Given that, despite the best efforts of the measurer, the quantity intended to be measured might not be the same as the quantity being measured, this ambiguity was removed, by calling "measurand" only the former

Technique	*'x'*	Traceability to SI?	*'y'*	Traceability to SI?	*x*-min	*x*-max	Pros	Cons
DLS Dynamic light scattering	Hydrodynamic diameter	Partially, or via validation with a CRM	Intensity distribution	Unclear	Sub 1 nm *	~few µm*	Fast, Accurate for monodisperse	I~x^6, frequently misinterpreted
PTA Particle track analysis	Hydrodynamic diameter	Yes or via validation with a CRM	Number distribution	Yes	~20 nm*	~1 µm*	Single particle, Great for dynamics	Low statistics, Setting dependant
FFF Field flow fractionation	Elution time (detector dependant)	Detector dependant	Detector dependant	Detector dependant	0.1 nm	~2 µm	High resolution, Powerful Separation	Complex method development
DCS Differential centrifugal sedimentation	Stokes diameter	Partially, or via validation with a CRM	Scattering intensity	Unclear	~5-70 nm depending on density	5-20 µm depending on density	High resolution	Destructive, low density particles sediment slowly
EM Electron microscopy	2D diameter, Feret, equivalent area…	Yes	Intensity distribution	Yes	~0.1 nm	~few µm*	Seeing is believing, Possible to determine shape	Statistics and representative-ness
LD Laser diffraction	Volume-equivalent diameter	Via validation with a CRM	Volume distribution	Unclear	~60 nm	100 µm	Great for aggregation studies	Lower size limit. Small particles scatter weakly
RMM Resonant mass measurement	Mass - equivalent diameter	Via validation with a CRM	Mass and Number distribution	Yes	50 nm min density dependant	~2 µm	Measure density, Weigh particles	Sensitive to blockages, size limited

Case study 1: APMP L.-S5
Supplementary Comparison on Nanoparticle Size

Nanoparticle Characterization - Supplementary Comparison on Nanoparticle Size
H -L Lin *et al* 2019 *Metrologia* **56** 04004

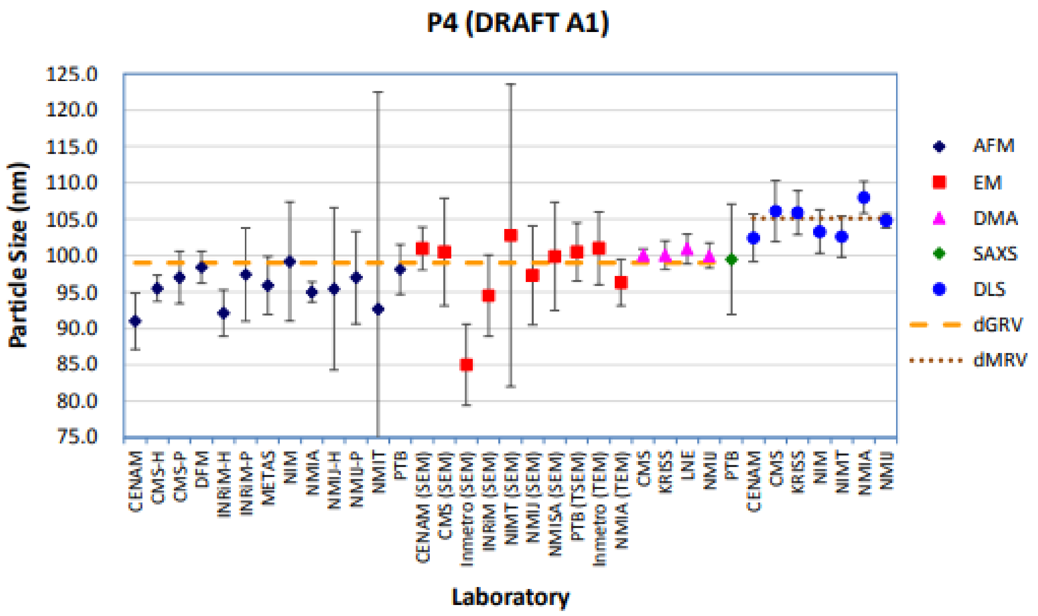
Particles shipped March 2012, Pilot labs CMS/ITRI, NMIJ

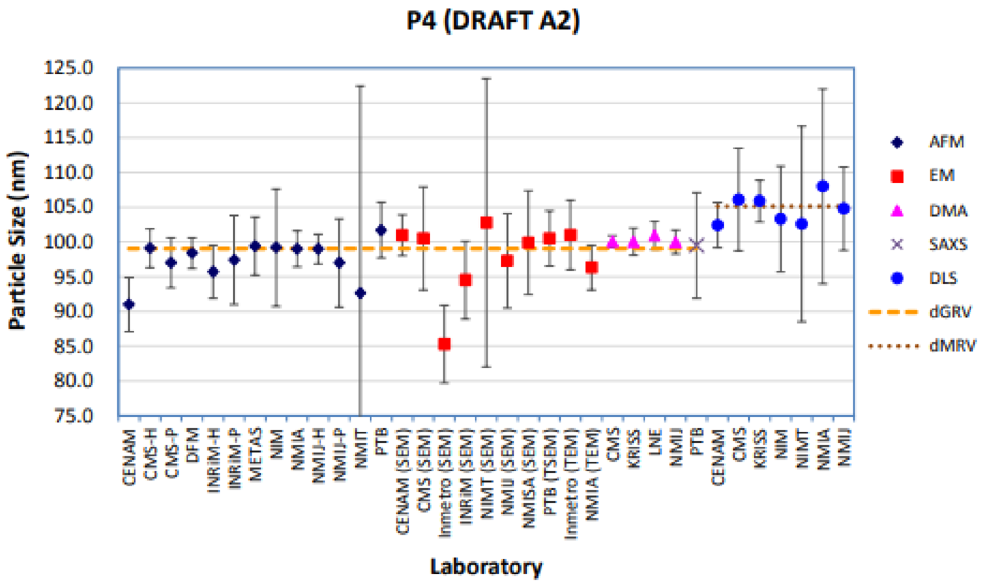
No.	Material	Nominal size nm	Volume mL	Number concentration particles/mL*	Manufacturer
G1	Nano gold	10	2	5.7×10^{12}	BBInternational
S2	Nano silver	20	2	4.0×10^{11}	nanoComposix
P3	Polystyrene latex	30	1	7.0×10^{14}	JSR
P4	Polystyrene latex	100	1	1.8×10^{13}	JSR
P5	Polystyrene latex	300	1	7.1×10^{11}	JSR

*Number concentration is provided by the manufacturers.

Method dependence observed in the results. Agreed to:
- Correct AFM measurements for deformation (due to particles adhering to substrate),
- modify DLS uncertainty to account for hydrodynamics.

Correction meant AFM values could be included in ‘Global’ RV, however DLS measurements were still too different and were compared to a ‘Method’ RV.





Case study 2: Australian interlab comparison 20 and 100 nm Gold Nanoparticles

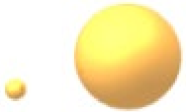
NPS 1: Monomodal Au; nominally 20 nm

NPS 2: Monomodal Au; nominally 100 nm

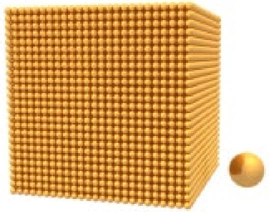
NPS 3: Bi-modal; mix of 20 nm and 100 nm Au, at a ratio designed to give equal intensity peaks in DLS

NPS 4: Bi-modal; mix of 20 nm and 100 nm Au, at a ratio designed to give equal number concentration using single-particle techniques

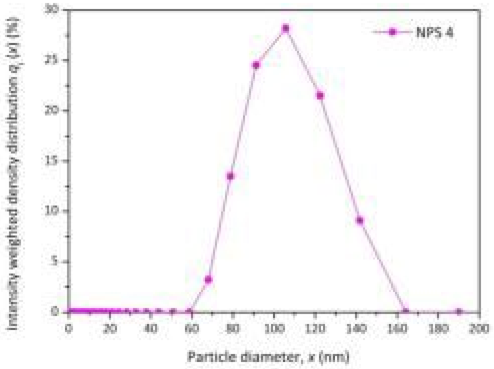
29 Laboratories participated



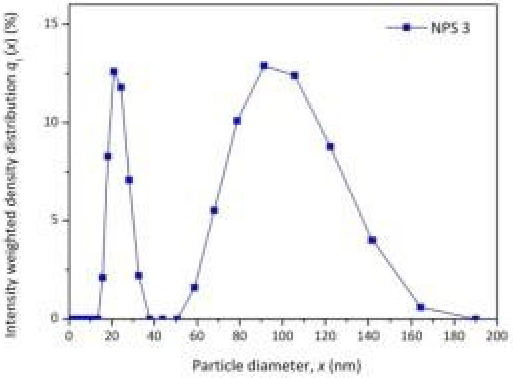
Equal number
1 : 1

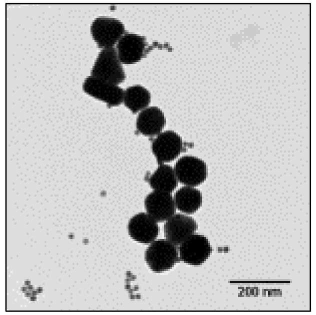


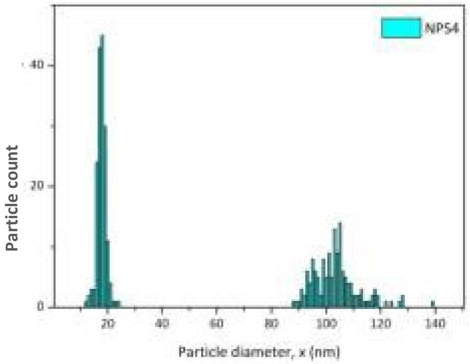
Equal light scattering intensity (I~d^6)
15625 : 1



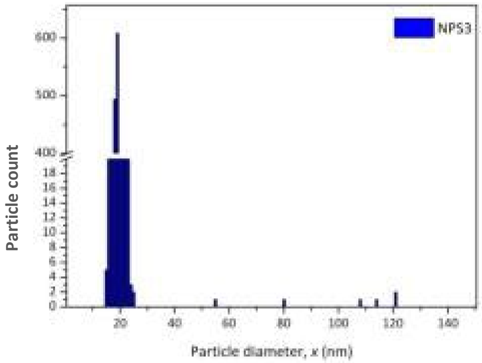
DLS

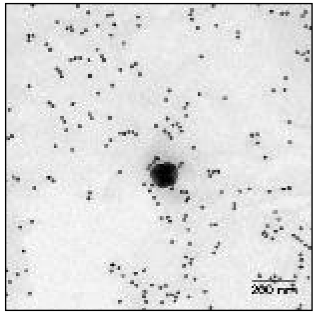






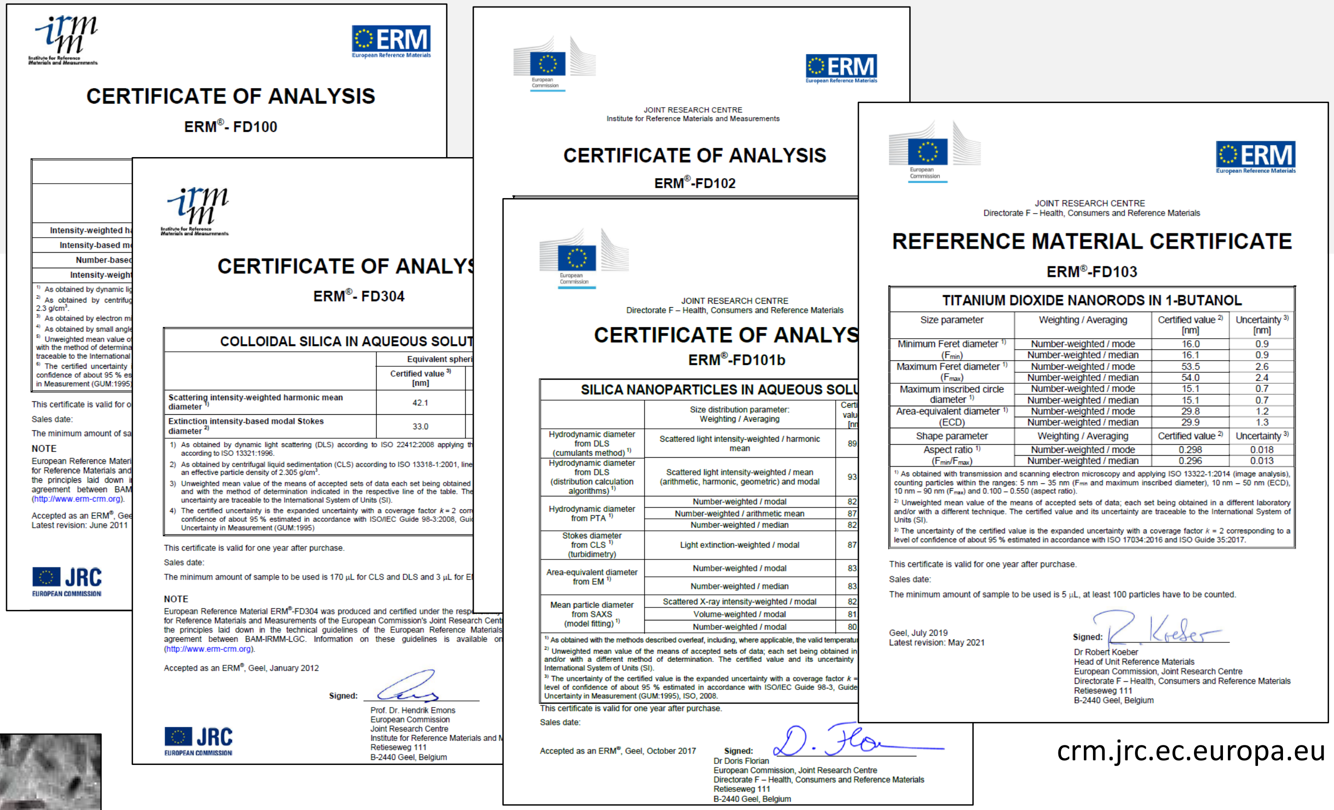
TEM





Certified Reference Materials

European Commission



JRC-IRMM

SiO_2 DLS

TiO_2 DCS

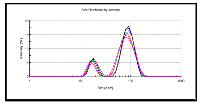
TEM

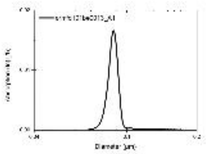
AFM

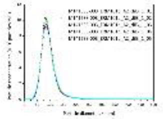
PTA

SEM

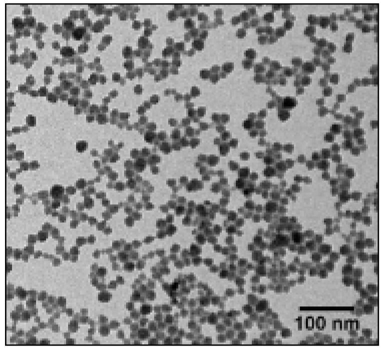
SAXS

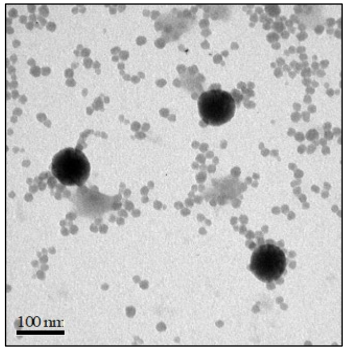


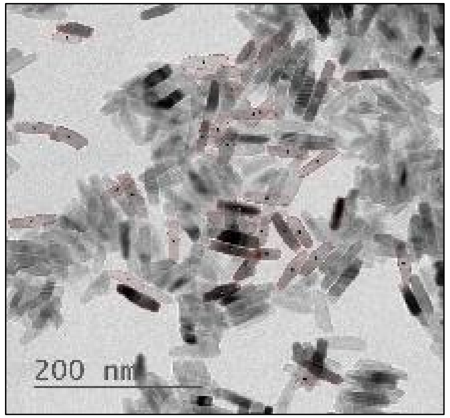


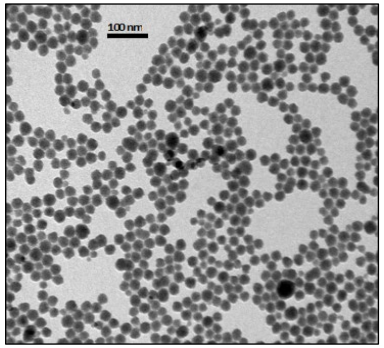


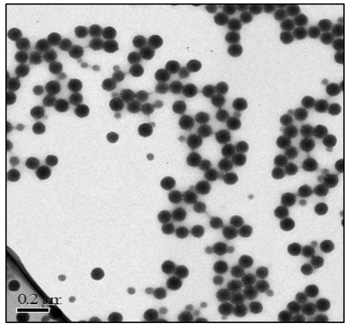
crm.jrc.ec.europa.eu

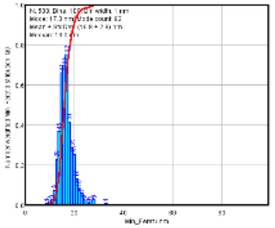


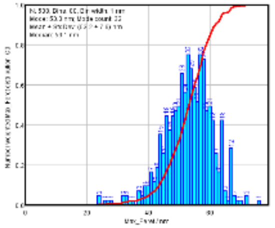












COLLOIDAL SILICA IN WATER

	Equivalent spherical diameter	
	Certified value [5] [nm]	Uncertainty [6] [nm]
Intensity-weighted harmonic mean diameter [1]	19.0	0.6
Intensity-based modal Stokes diameter [2]	20.1	1.3
Number-based modal diameter [3]	19.4	1.3
Intensity-weighted mean diameter [4]	21.8	0.7

[1] As obtained by dynamic light scattering according to ISO 22412:2008 (cumulants method).

[2] As obtained by centrifuge liquid sedimentation according to ISO 13318-1:2001 (line-start method); density 2.3 g/cm^3.

[3] As obtained by electron microscopy (transmission electron microscopy/scanning electron microscopy).

[4] As obtained by small angle X-ray scattering.

[5] Unweighted mean value of the means of accepted sets of data each set being obtained in a different laboratory and with the method of determination indicated in the respective line of the table. The certified value and its uncertainty are traceable to the International System of Units (SI).

[6] The certified uncertainty is the expanded uncertainty with a coverage factor $k = 2$ corresponding to a level of confidence of about 95 % estimated in accordance with ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement (GUM:1995), ISO, 2008.

VAMAS

www.vamas.org

Current active TWAs

- TWA 2 Surface Chemical Analysis
- TWA 5 Polymer Composites
- TWA 16 Superconducting Materials
- TWA 24 Performance Related Properties of Electroceramics
- TWA 31 Creep, Crack and Fatigue Growth in Weldments
- TWA 33 Polymer Nanocomposites
- TWA 34 Nanoparticle Populations
- TWA 36 Printed, flexible and stretchable electronics
- TWA 37 Quantitative Microstructural Analysis
- TWA 39 Solid Sorbents
- TWA 40 Synthetic Biomaterials
- TWA 41 Graphene and Related 2D Materials
- TWA 42 Raman Spectroscopy and Microscopy
- TWA 43 Thermal Properties
- TWA 44 ~~Self Healing Ceramics~~
- TWA 45 Micro and Nano Plastics in the Environment

Completed Projects

- **PROJECT 1:** Single-Wall Carbon Nanotube (SWCNT) Chiral Vector Distribution Determination [Complete]
- **PROJECT 2:** Titanium Dioxide (TiO_2) Nanopowder Surface Area Measurement
- **PROJECT 3:** Techniques for Characterizing Morphology of Airborne Nanoparticles
- **PROJECT 4:** Raman spectroscopy of fullerene nanofibers
- **PROJECT 5:** Method validation for determination of average aspect ratio of gold nanorods (GNRs) using UV-visible-NIR absorption spectrometry
- **PROJECT 6:** Primary particle size distribution measurements using transmission electron microscopy
- **PROJECT 7:** Requirements for describing materials on the nanoscale
- **PROJECT 8:** Determination of total sulfur and sulfate half ester content in cellulose nanocrystals
- **PROJECT 9:** Assessment of a quantitative nanomaterial definition
- **PROJECT 10:** Measurement of number concentration of colloidal nanoparticles
- **PROJECT 11:** Static Muliple Light Scattering (SMLS) - mean particle size evaluation
- **PROJECT 12:** Determination of particle size distribution for cellulose nanocrystals (CNCs)

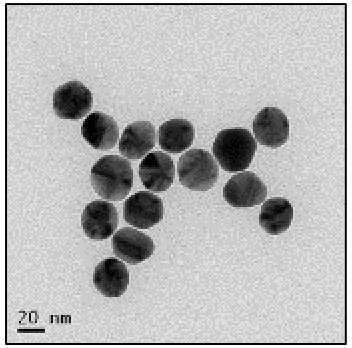
Active Projects

- **PROJECT 13:** Analysis of nano-objects using field flow fractionation
- **PROJECT 14:** Crystallinity of cellulose nanomaterials by Powder X-ray Diffraction and Rietveld Modelling
- **PROJECT 15:** Measurement of particle size and shape distribution of bipyramidal titania including deposition from liquid suspension
- **PROJECT 16:** Measurement of (relative) number concentration of bimodal silica nanoparticles including deposition from liquid suspension
- **PROJECT 17:** Line notation and unique identifiers for nanomaterials and groups of nanomaterials

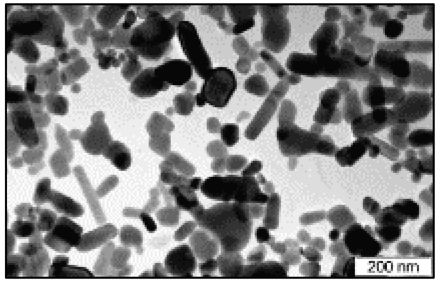
What helps the community?
How should NMIs respond?

“quantity intended to be measured[1]”

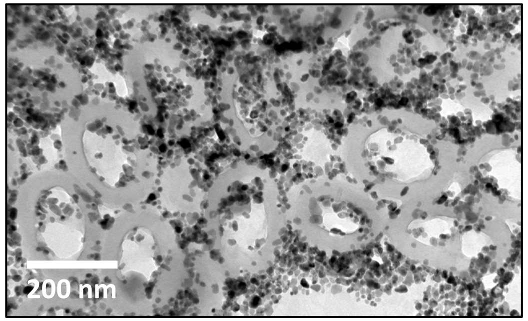
“particular quantity subject to measurement[2]”



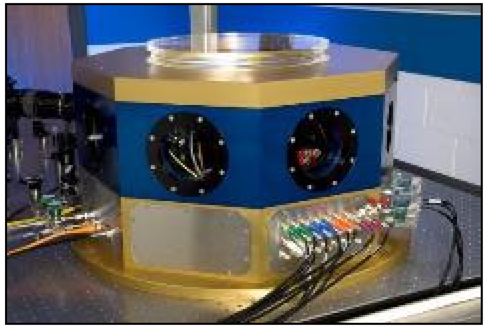
30 nm Au reference material



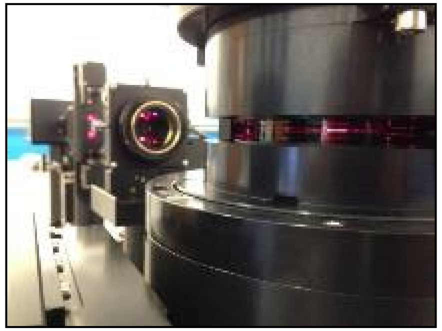
Commercial ZnO powder



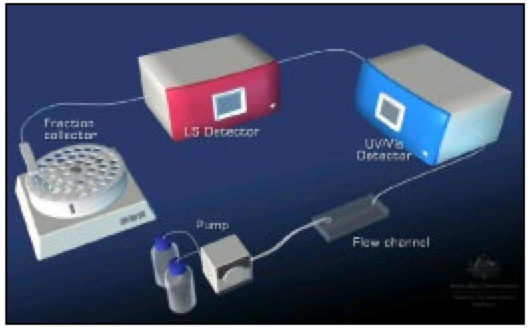
ZnO in sunscreen



Primary nanoscale standard



Commercial instrumentation



Multi (component and disciplinary) solution

Global reference values

$>> U_{meas}$ →

Method dependant reference values

- Large number of issues relating to:
  - method development
  - sample preparation/stabilisation
  - choice of measurement technique
- Standardised methods require experiments and statistical tests - work of VAMAS is key for development
- Method dependant RVs or global RVs?
- How should the metrology community respond in terms of e.g. CMCs? HFTLS for ‘particle diameter’
- Industrially relevant samples (complex matricies) is still a challenge
- Extremes (size, concentration and composition) is still a challenge
- More (certified) reference materials needed

[1] VIM3/4 definition of measurand
[2] VIM2 definition of measurand

Thank you

Malcolm Lawn
Accurate nanoscale measurements (AFM)

Bakir Babic
mSPM

Åsa Jämting
Victoria Coleman
Sean Williams
Accurate nanoscale measurements (other techniques)

Dr Victoria Coleman

Section Manager, Nanometrology

NMI Australia

nano@measurement.gov.au

36 Bradfield Road

Lindfield, NSW 2070

measurement.gov.au