

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

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### NMIA Nanometrology – drivers:

Accurate and reproducible measurements for nanotechnology



Research and Product Development



Quality Control



Trade



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<sub>2</sub> pharmacokinetics
- Complex matricies (nano in food, products etc.)
- Microplastics
- Non-sphericity



### 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<sub>20</sub> = 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<sub>20</sub> = 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

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



	Measurand	Size (nm)
<u> </u>	Cross sectional diameter (of cross section perpendicular to axis)	60
60 ∩m 1↑	Equivalent circle diameter derived from projected area (TEM)	151
7	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?	<i>'y'</i>	Traceability to SI?	<i>x</i> -min	<i>x</i> -max	Pros	Cons
<b>DLS</b> 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 <sup>6</sup> , frequently misinterpreted
<b>PTA</b> 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
<b>FFF</b> 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
<b>EM</b> 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
<b>LD</b> 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
<b>RMM</b> 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
Gl	Nano gold	10	2	5.7×10 <sup>12</sup>	BBInternational
S2	Nano silver	20	2	4.0×10 <sup>11</sup>	nanoComposix
P3	Polystyrene latex	30	1	$7.0 \times 10^{14}$	JSR
P4	Polystyrene latex	100	1	$1.8 \times 10^{13}$	JSR
P5	Polystyrene latex	300	1	7.1×10 <sup>11</sup>	JSR

\*Number concentration is provided by the manufacturers.



P4 (DRAFT A1)

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



### **Certified Reference Materials**



100 mm

**JRC-IRMM** SiO<sub>2</sub> TiO<sub>2</sub>







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<sup>2)</sup> As obtained by centrifug	ERM <sup>®</sup> - FD	0304			JOINT RESEARCH CENTRE	
2.3 g/cm <sup>4</sup> . <sup>3)</sup> As obtained by electron mi				Direc	torate F – Health, Consumers and Reference Mate	rials
4 As obtained by small angle				CERI	ΓΙΕΙΟΑΤΕ ΟΕ ΑΝΑΙ	YS
with the method of determina	COLLOIDAL SILICA IN AC	QUEOUS SOLUT		OLIN		. 9
<sup>4</sup> The certified uncertainty		Equivalent spheri			ERM <sup>®</sup> -FD101b	
confidence of about 95 % es		Certified value 3)		r		
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I ne minimum amount of sa	1) As obtained by dynamic light scattering (DLS) according to	ISO 22412:2008 applying th		from DLS	Scattered light intensity-weighted / harmonic	89
NUTE Furnean Reference Materi	according to ISO 13321:1996.			(cumulants method) 1)	mean	_
for Reference Materials and	an effective particle density of 2.305 g/cm <sup>3</sup> .	ing to 150° 15516-1.2001, line		from DLS	Scattered light intensity-weighted / mean	93
agreement between BAM	<ol> <li>Unweighted mean value of the means of accepted sets of and with the method of determination indicated in the res</li> </ol>	data each set being obtained pective line of the table. The		(distribution calculation algorithms) <sup>1)</sup>	(anthmetic, narmonic, geometric) and modal	
(http://www.erm-crm.org).	uncertainty are traceable to the International System of Units 4) The certified uncertainty is the expanded uncertainty with	(SI). a coverage factor k = 2 com		Hydrodynamic diameter	Number-weighted / modal	82
Accepted as an ERM <sup>®</sup> , Gee Latest revision: June 2011	confidence of about 95 % estimated in accordance with IS	O/IEC Guide 98-3:2008, Guid		from PTA 1)	Number-weighted / anthmetic mean Number-weighted / median	87
	Undertainty in measurement (Grow, 1933)			Stokes diameter	Links affection unlabled (see det	
	This certificate is valid for one year after purchase.			(turbidimetry)	Light extinction-weighted / modal	87
	Sales date:			Area-equivalent diameter	Number-weighted / modal	83
JHC	The minimum amount of sample to be used is 170 µc for Ct	to and bits and 5 µc lor E		from EM <sup>1)</sup>	Number-weighted / median	83
EUROPEAN CONMISSION	NOTE			Mean particle diameter	Scattered X-ray intensity-weighted / modal	82
	European Reference Material ERM"-FD304 was produced a for Reference Materials and Measurements of the European	nd certified under the resp	h Cent	from SAXS	Volume-weighted / modal	81
	the principles laid down in the technical guidelines of t	he European Reference Ma	aterials	(moder intung)	Number-weighted / modal	80
	(http://www.erm-crm.org).	nese guidennes is availar		<sup>2)</sup> Unweighted mean value of 1	described overlear, including, where applicable, the valid to the means of accepted sets of data; each set being ob	tained in
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	Signed:	Chy		Uncertainty in Measurement (G	so w examined in accordance with ISOVIEC Guide 98- SUM:1995), ISO, 2008.	s, Guide
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M ERM JOINT RESEARCH CENTRE Directorate F – Health, Consumers and Reference Materials **REFERENCE MATERIAL CERTIFICATE** ERM<sup>®</sup>-FD103 TITANIUM DIOXIDE NANORODS IN 1-BUTANOL Size parameter Weighting / Averaging Certified value 2) Uncertainty Minimum Feret diameter Number-weighted / mode (I\*min) Maximum Feret diameter Number-weighted / mode (F<sub>max</sub>) Maximum inscrit diameter Number-weighted / mediar Number-weighted / mode Number-weighted / median rea-equivalent diameter (ECD) Number-weighted / mediar Weighting / Averaging Shape parameter Certified value 2) Uncertainty Aspect ratio 1 Number-weighted / mode (Fmin/Fmax) Number-weighted / median unting particles within the ranges nm – 90 nm (Fmax) and 0.100 – 0 - 35 nm (Errs and m rweighted mean value of the means of accepted sets of data; each se The uncertainty of the certified value is the expanded uncertainty with a coverage factor k = 2 corre-el of confidence of about 95 % estimated in accordance with ISO 17034:2016 and ISO Guide 35:2017 This certificate is valid for one year after purchase Sales date: The minimum amount of sample to be used is 5 µL, at least 100 particles have to be counted Geel, July 2019 Latest revision: May 2021 and of Linit Defen ctorate E = Health Consumers and Ref prence Materiak B-2440 Geel Belgiun crm.jrc.ec.europa.eu ctorate F B-2440 Geel, E

#### COLLOIDAL SILICA IN WATER

	Equivalent spherical diameter		
	Certified value <sup>5)</sup> [nm]	Uncertainty <sup>6}</sup> [nm]	
Intensity-weighted harmonic mean diameter 1)	19.0	0.6	
Intensity-based modal Stokes diameter 20	20.1	1.3	
Number-based modal diameter 3)	19.4	1.3	
Intensity-weighted mean diameter 4)	21.8	0.7	

<sup>1)</sup> As obtained by dynamic light scattering according to ISO 22412:2008 (cumulants method).

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

<sup>30</sup> As obtained by electron microscopy (transmission electron microscopy/scanning electron microscopy).

<sup>49</sup> As obtained by small angle X-ray scattering.

<sup>5)</sup> 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.



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#### **Current active TWAs**

- TWA 2 <u>Surface Chemical Analysis</u>
- TWA 5 <u>Polymer Composites</u>
- TWA 16 <u>Superconducting Materials</u>
- TWA 24 Performance Related Properties of Electroceramics
- TWA 31 Creep, Crack and Fatigue Growth in Weldments
- TWA 33 Polymer Nanocomposites
- TWA 34 <u>Nanoparticle Populations</u>
- TWA 36 Printed, flexible and stretchable electronics
- TWA 37 <u>Quantitative Microstructural Analysis</u>
- TWA 39 Solid Sorbents
- TWA 40 <u>Synthetic Biomaterials</u>
- TWA 41 Graphene and Related 2D Materials
- TWA 42 Raman Spectroscopy and Microscopy
- TWA 43 <u>Thermal Properties</u>
- 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 (TiO2) 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 UVvisible-NIR absorption spectrometry
- PROJECT 6: Primary particle size distribution measurements using transmission electron microscopy
- PROJECT 7: <u>Requirements for describing materials on the nanoscale</u>
- PROJECT 8: Determination of total sulfur and sulfate half ester content in cellulose nanocrystals
- PROJECT 9: Assessment of a quantitative nanomaterial definition
- **PROJECT 10:**<u>Measurement of number concentration of colloidal nanoparticles</u>
- PROJECT 11: <u>Static Muliple Light Scattering (SMLS) mean particle size evaluation</u>
- 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: <u>Crystallinity of cellulose nanomaterials by Powder X-ray Diffraction and Rietveld Modelling</u>
- PROJECT 15: <u>Measurement of particle size and shape distribution of bipyramidal titania including deposition</u>
   <u>from liquid suspension</u>
- PROJECT 16: <u>Measurement of (relative) number concentration of bimodal silica nanoparticles including</u>
   <u>deposition from liquid suspension</u>
- 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<sup>1</sup>"



30 nm Au reference material

### "particular quantity subject to measurement<sup>2</sup>"



ZnO in sunscreen



Primary nanoscale standard





Commercial instrumentation

Commercial ZnO powder





Multi (component and disciplinary) solution

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

<sup>1</sup> VIM3/4 definition of measurand <sup>2</sup> VIM2 definition of measurand

# Thank you

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Malcolm Lawn Accurate nanoscale measurements (AFM)



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

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