

epartment of Industry, ience 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 <u>Dr Victoria A. Coleman</u> Nanometrology Section, Physical Metrology, NMI Australia

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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
- TiO₂ 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

n₂₀ = 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

n₂₀ = 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 (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

60

151

117

Technique	'x'	Traceability to SI?	'y'	Traceability to SI?	<i>x</i> -min	<i>x</i> -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	l~ <i>x⁶,</i> 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
Gl	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.



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.



P4 (DRAFT A2)

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



JRC-IRMM SiO₂ TiO₂







-irm m	Company Company	ERM			
CERT	IFICATE OF ANALYSIS			European Commission	
OLIVI					JOINT RESEARCH Reference Material
	ERM [®] - FD100				
			_	CERTIFIC	CATE O
					ERM [®] -FC
Intensity-weighted h Intensity-based m Number-based Intensity-weigh	CERTIFICATE O	FANAL	Y	Lungare Comparison	
¹⁾ As obtained by dynamic lig ²⁾ As obtained by centrifuc	ERM [®] - FI	0304		CONTROL OF	JOINT I
2.3 g/cm ³ . ³¹ As obtained by electron mi				Direc	torate F – Health,
⁴⁾ As obtained by small angle ⁵⁾ Unweighted mean value of	COLLOIDAL SILICA IN A		UT	CERT	FIFICA
with the method of determina traceable to the International		Equivalent s			ER
⁴ The certified uncertainty confidence of about 95 % es		Certified value 3)			
in Measurement (GUM:1995)	Scattering intensity-weighted harmonic mean			SILICA NA	NOPARTIC
This certificate is valid for o	diameter ¹)	42.1			Size
Sales date: The minimum amount of sa	Extinction intensity-based modal Stokes diameter ²⁾	33.0		Hydrodynamic diameter	Scattered ligh
NOTE	 As obtained by dynamic light scattering (DLS) according to according to ISO 13321:1996. 	5 ISO 22412:2008 apply	ing th	from DLS (cumulants method) ¹⁾	scattered ligh
European Reference Materi for Reference Materials and	 As obtained by centrifugal liquid sedimentation (CLS) accord an effective particle density of 2.305 g/cm³. 	ding to ISO 13318-1:200	1, line	Hydrodynamic diameter from DLS	Scattered lic
the principles laid down in agreement between BAM	 Unweighted mean value of the means of accepted sets of and with the method of determination indicated in the res 	data each set being obt	ained	(distribution calculation algorithms) ¹⁾	(arithmetic, ha
(http://www.erm-crm.org).	 uncertainty are traceable to the International System of Unit The certified uncertainty is the expanded uncertainty with 	s (SI).		Hydrodynamic diameter	Num
Accepted as an ERM [®] , Gee Latest revision: June 2011	 The centraled uncertainty is the expanded uncertainty with confidence of about 95 % estimated in accordance with IS Uncertainty in Measurement (GUM:1995) 			from PTA 1)	Number-v Num
	This certificate is valid for one year after purchase.			Stokes diameter from CLS ¹⁾ (turbidimetry)	Light ex
	Sales date: The minimum amount of sample to be used is 170 µL for C	P and DL 9 and 2 vi	for El	Area-equivalent diameter	Num
		Lo and DEo and 5 pE		from EM 1)	Numl
Condition Contraction	NOTE European Reference Material ERM [®] -FD304 was produced :	and contined under the		Mean particle diameter	Scattered X-
	for Reference Materials and Measurements of the European	Commission's Joint R	esearch Cent	from SAXS (model fitting) ¹⁾	Volu Num
	the principles laid down in the technical guidelines of agreement between BAM-IRMM-LGC. Information on	these guidelines is	available on	¹⁰ As obtained with the methods	described overleaf, i
	(http://www.erm-crm.org).			²⁾ Unweighted mean value of and/or with a different meth	od of determination
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		rof. Dr. Hendrik Emons	3	This certificate is valid for one	
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10 M 10 10		Institute for Reference M Reference M 2440 Gool Bolohum	laterials and N	Accepted as an ERM [®] , Geel,	October 2017

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	JOINT RESEARCH CENTRE		TITA		DIOXIDE NANORODS	IN 1-BUTANC	DL
	torate F Health, Consumers and Reference Mater		Size paramet	er	Weighting / Averaging	Certified value 2) [nm]	Uncertainty 3) [nm]
CERI	ERM [®] -FD101b	.13	Minimum Feret dia (F _{min}) Maximum Feret dia		Number-weighted / mode Number-weighted / median Number-weighted / mode	16.0 16.1 53.5	0.9 0.9 2.6
SILICA NA	NOPARTICLES IN AQUEOUS		(F _{max}) Maximum inscribe diameter ¹)	d circle	Number-weighted / median Number-weighted / mode Number-weighted / median	54.0 15.1 15.1	2.4 0.7 0.7
	Size distribution parameter: Weighting / Averaging	Certi valu [nr	Area-equivalent dia (ECD)	imeter 1)	Number-weighted / mode Number-weighted / mode	29.8	1.2
Hydrodynamic diameter from DLS (cumulants method) ¹⁾	Scattered light intensity-weighted / harmonic mean	89	Shape parame Aspect ratio		Weighting / Averaging Number-weighted / mode	Certified value 2) 0.298	Uncertainty 3) 0.018
(cumulants method) * Hydrodynamic diameter from DLS (distribution calculation algorithms) ¹¹	Scattered light intensity-weighted / mean (arithmetic, harmonic, geometric) and modal	93	(Fmin/Fmax)	mission and the ranges	Number-weighted / median d scanning electron microscopy and app c 5 nm – 35 nm (Fmi and maximum int	0.296 lying ISO 13322-1:2014	0.013 (image analysis),
Hydrodynamic diameter from PTA ¹⁾	Number-weighted / modal Number-weighted / arithmetic mean Number-weighted / median	82 87 82	²⁾ Unweighted mean va and/or with a different t Units (SI).	lue of the m schnique. T	teans of accepted sets of data; each se he certified value and its uncertainty and	e traceable to the Interr	ational System of
Stokes diameter from CLS ¹⁾ (turbidimetry)	Light extinction-weighted / modal	87	²⁾ The uncertainty of the level of confidence of at	out 95 % es	alue is the expanded uncertainty with a stimated in accordance with ISO 17034:2	coverage factor k = 2 c 016 and ISO Guide 35:2	orresponding to a 2017.
Area-equivalent diameter	Number-weighted / modal	83	This certificate is valid Sales date:	for one yea	ar after purchase.		
from EM ¹⁾	Number-weighted / median	83		of sample t	o be used is 5 uL, at least 100 partic	les have to be counte	d.
Mean particle diameter from SAXS	Scattered X-ray intensity-weighted / modal Volume-weighted / modal	82			· · · · ·		
(model fitting) ¹⁾	Number-weighted / modal	80	Geel, July 2019			0	
²¹ Unweighted mean value of t and/or with a different meth International System of Units (S ³⁰ The uncertainty of the certifi level of confidence of about 9 Uncertainty in Measurement (G	ed value is the expanded uncertainty with a coverage fa 15 % estimated in accordance with ISO/IEC Guide 98- SUM:1995), ISO, 2008.	tained in ertainty actor k =	Latest revision: May 20	21		on, Joint Research Cer h, Consumers and Re	
This certificate is valid for one	e year after purchase.						
Sales date: Accepted as an ERM [®] , Geel,	October 2017 Signed: Dr Doris Florian European Commission, Joint Res Directorate F - Health, Consume Retiesewee 111				crm.jrc	.ec.eu	ropa.eu
	B-2440 Geel, Belgium						

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 a/cm³.

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

⁴⁹ 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).

(i) 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.



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 Nanoparticle Populations
- 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 measured¹"



30 nm Au reference material

"particular quantity subject to measurement²"



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

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

Thank you

Dr Victoria Coleman

Section Manager, Nanometrology

NMI Australia

nano@measurement.gov.au

36 Bradfield Road

Lindfield, NSW 2070

measurement.gov.au

Malcolm Lawn Accurate nanoscale measurements (AFM)



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

Bakir Babic

mSPM