Nanoparticle Characterization - Supplementary Comparison on Nanoparticle Size
APMP.L-S5

Final Report

Supplementary Comparison on Nanoparticle Size

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Technical Committee for Length (TCL)
Working Group for Material Metrology (WGMM)

Pilot Lab: Centre for Measurement Standards (CMS)
Industrial Technology Research Institute (ITRI)

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1 INTRODUCTION

Nanoparticle is one of the most promising creations of science. Numerous nanoproducts are developed globally to utilize the advantages of the nanoparticles for making daily lives more healthy and convenient [1]. However, the NPs could be hazardous to the environment, health and safety in some way. Thus, the harmonization of measurements and regulations for nanoparticle characterizations is highly demanded either to enhance the continuous development of nanoproducts and support the trade of the nanoproducts or to evaluate the possibility of hazard to environments, human health, and safety [2]. Among the characterizations identified in Organization for Economic Co-operation and Development (OECD), characterizing particle size is essential as a start to investigate the property characterization of nanoparticles. The proposed supplementary comparison for nanoparticle size was initiated by Technical Committee for Length (TCL) and Working Group for Materials Metrology (WGMM) at the Asia Pacific Metrology Programme (APMP) TCL meeting on 15 Nov 2010 in Pattaya, Thailand. According to the conclusions, the comparison is a joint effort between TCL and WGMM. Also, Centre for Measurement Standards of Industrial Technology Research Institute (CMS/ITRI) and National Metrology Institute of Japan (NMIJ) volunteered and were assigned for the pilot and co-pilot of the comparison, respectively. The supplementary comparison is opened primarily to APMP TCL members, APMP WGMM members, and other Regional metrology organization (RMO) TCL members. Additional requests may also be considered. The supplementary comparison result will serve as a harmonization of measurement capability for nanoparticle size, and a base for Calibration and Measurement Capabilities (CMC) submission.

2 DESCRIPTION OF THE REFERENCE NANOPARTICLES

Both size and material property of nanoparticles are especially important among many challenges for developments in nanotechnology, due to environmental and human health concerns over their frequent use in industries and laboratories. The harmonization of measurements and regulations are therefore required for nanoparticles. Thus, nanoparticles with size in the range from 10 nm to 300 nm, the last one being outside the nanoscale, this ranging until 100 nm according to its definition, and from three different materials (Au, Ag and PSL) were proposed in the 2011 Workshop on Nanoparticle Size Measurement held on April 14th to 15th in Taiwan for the supplementary comparison. The selected nanoparticles can meet the requirements of different measurement methods such as Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Dynamic Light Scattering (DLS), and Differential Mobility Analyzer (DMA). Since the choice of measurement methods is not limited, the participating laboratories can choose their own method to carry out the measurement. In general, the instruments

used shall be calibrated and capable of dimensional measurements in the nanometre-scale range to determine the nanoparticle sizes of the nanoparticles provided by the pilot laboratory. For this supplementary comparison, more detailed measurement instructions are provided for participants utilizing methods such as AFM, TEM, SEM, DLS and DMA. DLS is also known as Photon Correlation Spectroscopy (PCS) or Quasi-Elastic Light Scattering (QELS). The DMA is also known as Scanning Mobility Particle Sizer (SMPS).

The materials of the nanoparticles in this comparison include nano gold, nano silver and polystyrene latex. General information about the nanoparticles is listed in Table 1. Samples for this supplementary comparison were prepared by the pilot lab from the nanoparticles listed in Table 1 and distributed to each participating laboratory. The samples were subdivided from the nanoparticles and provided in suspension form of approximately one or two milliliters (mL) in quantity and stored in vials encased in a plastic enclosure. Homogeneity test was performed to ensure the consistency of the samples subdivided from the nanoparticles, before the start of the supplementary comparison.

Table 1. General information of nanoparticles

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.

3 PARTICIPANTS AND COMPARISON SCHEDULE

3.1 REQUIREMENTS FOR PARTICIPATION

Members from APMP TCL and WGMM and other RMOs were welcome to join this comparison. The participants (laboratories) who participate in this comparison agree to share the measurement results for analysis. The participants may carry out the measurement from the methods such as AFM, TEM, SEM, DLS and DMA. However, the instruments used shall be calibrated or capable of dimensional measurements in the nanoscale range for determining the nanoparticle diameters with uncertainty evaluation.

3.2 INFORMATION OF THE PARTICIPANTS

The participant information is listed in Table 2.

Table 2. Participant Information

Laboratory	Contact Person	Address	Phone/E-mail	Instrument
CENAM	Salas, Antonio	**Centro Nacional de Metrología** km 4.5 Carretera a Los Cues Municipio El Marques, Queretaro, C.P. 76246, Mexico	Tel:+524422110500 Fax:+524422110528 e-mail:jsalas@cenam.mx	SEM
CENAM	Salas, Antonio	**Centro Nacional de Metrología** km 4.5 Carretera a Los Cues Municipio El Marques, Queretaro, C.P. 76246, Mexico	Tel:+524422110500 Fax:+524422110528 e-mail:jsalas@cenam.mx	SPM
CENAM	Salas, Antonio	**Centro Nacional de Metrología** km 4.5 Carretera a Los Cues Municipio El Marques, Queretaro, C.P. 76246, Mexico	Tel:+52442110500 Fax:+524422110528 e-mail:jsalas@cenam.mx	DLS
DFM	Dirscherl, Kai	**Danish National Metrology Institute** Matematiktorvet 307, DK-2800 Kgs. Lyngby, Denmark	Tel:+4545255878 Fax:+4545931137 e-mail:kdi@dfm.dtu.dk	AFM
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CMS/ITRI	Weng, HanFu	**Center for Measurement Standards/ITRI** 321, Kuang fu Rd., Sec.2, Hsinchu, Taiwan 30011, ROC	Tel:+88635743871 Fax:+88635726445 e-mail:hfweng@itri.org.tw	SEM
CMS/ITRI	Weng, HanFu	**Center for Measurement Standards/ITRI** 321, Kuang fu Rd., Sec.2, Hsinchu, Taiwan 30011, ROC	Tel:+88635743871 Fax:+88635726445 e-mail:hfweng@itri.org.tw	AFM
CMS/ITRI	Weng, HanFu	**Center for Measurement Standards/ITRI** 321, Kuang fu Rd., Sec.2, Hsinchu, Taiwan 30011, ROC	Tel:+88635743871 Fax:+88635726445 e-mail:hfweng@itri.org.tw	DMA
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Inmetro	Damasceno, Jailton	**Instituto Nacional de Metrologia, Qualidade e Tecnologia** Av. Nossa Sra das Gracas, 50 – Predio 3 – Xerem, Duque de Caxias, RJ, 25250-020, Brazil	Tel:+552126799021 Fax:+552126799021 e-mail:jcdamasceno@inmetro.gov.br	TEM
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KRISS	Kim, Chang Soo	**Korea Research Institute of Standards and Science** 1 Doryong-Dong, Yuseong-Gu, Daejeon 305-340, Rep. of Korea	Tel: +82428685323 Fax: +82428685047 e-mail:kimcs@kriss.re.kr	DMA
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NIM	Gao, Sitian	**National Institute of Metrology** No. 18, Bei San Huan Dong Lu. Beijing 100013, China	Tel:+861064524903 Fax: +861084251574 e-mail:gaost@nim.ac.cn	XRD
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NMIA	Herrmann, Jan	**National Measurement Institute Australia** Bradfield Road West Lindfield NSW 2070, Australia	Tel:+61284673784 Fax:+61284673752 e-mail:jan.herrmann@measurement.gov.au	DLS
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NIMT	Buajarern, Jariya	**National Institute of Metrology(Thailand)** 3/4-5 Moo 3, Klong 5, Klong Luang, Pathumthani 12120, Thailand	Tel:+6625775100 ext. 1216 Fax:+6625775088 e-mail: jariya@nimt.or.th	DLS
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NMIJ	Takahata, Keiji	**National Metrology Institute of Japan, AIST** Tsukuba central 3 bldg., 1-1-1 Umezono, Tsukuba, Ibaraki 305-8563, Japan	Tel:+81298616808 Fax:+81298614070 e-mail:k.takahata@aist.go.jp	DMA
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NMIJ	Sugawara, Kentaro	**National Metrology Institute of Japan, AIST** Tsukuba central 3 bldg., 1-1-1 Umezono, Tsukuba, Ibaraki 305-8563, Japan	Tel:+81298614088 Fax:+81298614041 e-mail:sugawara.k@aist.go.jp	SEM
PTB	Buhr, Egbert	**Physikalisch-Technische Bundesanstalt** 4.2 Imaging and Wave Optics, Bundesallee 100, Braunschweig D-38116, Germany	Tel: +495315924200 Fax: +495315924205 e-mail: egbert.buhr@ptb.de	TSEM
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PTB	Krumrey, Michael	**Physikalisch-Technische Bundesanstalt** 7.11 X-ray Radiometry, Abbestraße 2-12, Berlin D-10587, Germany	Tel: +493063925085 Fax: +49303481697110 e-mail:Michael.Krumrey@ptb.de	SAXS

3.3 SCHEDULE

The subdivided samples were distributed to participating laboratories for measurement concurrently. Sample shipment was started during the first or second week of March 2012. Each laboratory was expected to finish the measurement within six weeks upon receipt of the samples. The comparison was originally scheduled to be finished by the end of May 2012, but was extended to November 2012, since part of participants required more time for data analysis and confirmation.

4 TRANSPORTATION, HANDLING, FINANCIAL ASPECTS

4.1 TRANSPORTATION

For delivery of the reference nanoparticles, every styrofoam box included one centrifuge tube box and cooling gel packs, see Figure 1. The centrifuge tube box included 5 tubes (6 tubes for DMA) and a label to identify the lab, person, and instrument, see Figure 2. The tube with red cap indicated the sample G1, the yellow cap indicated the sample S2, the white cap indicated the sample P3, the blue cap indicated the sample P4, the green cap indicated the sample P5, and the normal cap indicated the sample STADEX SC-010-S (for DMA only).

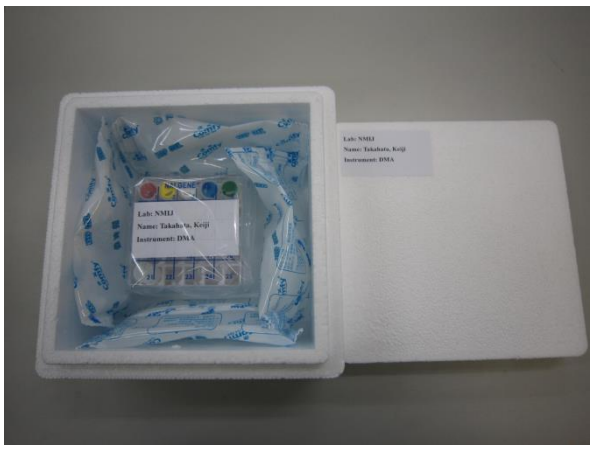

Figure 1. Transportation package of samples

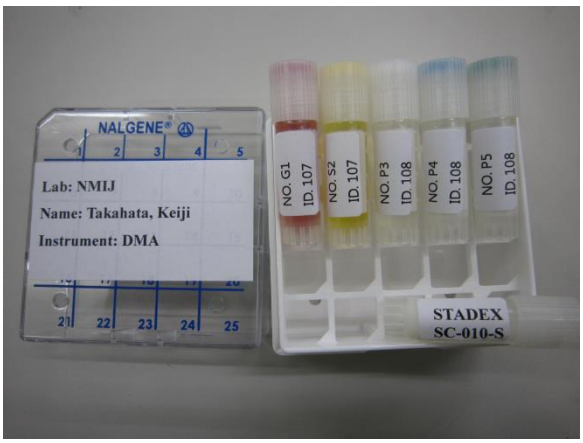

Figure 2**.** Centrifuge tube box with 5 tubes (or 6 tubes for DMA)

4.2 SAMPLE STORAGE AND HANDLING

From the day of receipt to the time of measurement, all samples should be stored at 4 °C, and prevented from direct exposure to intense light or ultraviolet radiation. All samples **should not be frozen**. The samples should be prepared in a clean bench (with a HEPA filter, high-efficiency particulate air filter) or a contamination-free environment. Trained scientific personnel was recommended to handle the sample at all times. Wearing appropriate personal protective gear (such as gloves, lab coat, goggles, etc.) and taking appropriate precautions when handling the samples were also recommended.

4.3 FINANCIAL ASPECT

Participation in this supplementary comparison was FREE OF CHARGE. The pilot and co-pilot covered the overall costs for the planning and organization of the comparison, including the preparation, supply, and shipping of the samples. Additional funding from 2010 APMP TC initiative was provided for preparation of samples in this comparison.

5 MEASURANDS

The measurement methods used in this comparison were not limited. Participants could choose methods such as AFM, SEM, TEM, DLS, DMA and etc. The different measurands to be determined on the reference nanoparticles by each method were described as follows. A complete description of the applied method and a detailed estimation of the measurement uncertainty according to the *ISO Guide to the Expression of Uncertainty in Measurement (GUM)* were required.

5.1 MEASURAND OF ATOMIC FORCE MICROSCOPY (AFM)

The following two methods for nanoparticle diameter measurement were recommended:

a. The diameter of the nanoparticle is defined D_h as the maximum height of a nanoparticle, as shown in Figure 3a.

b. The diameter of the nanoparticle is defined D_p as the pitch of any two adjacent nanoparticles, as shown in Figure 3b.

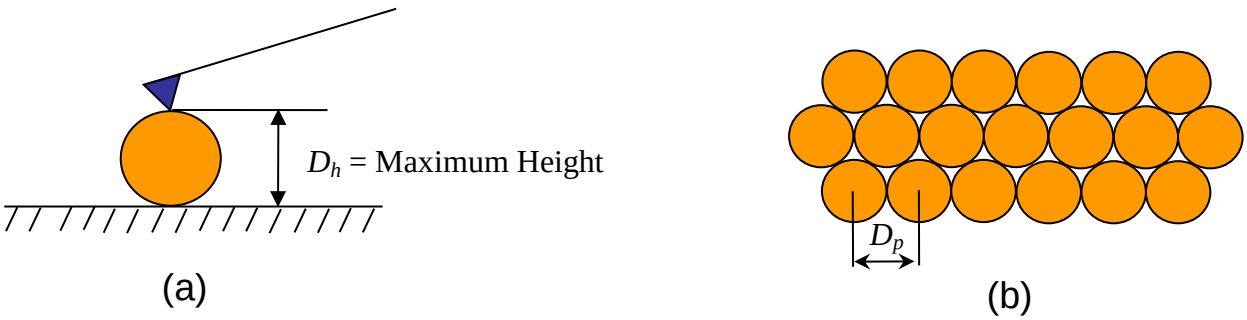

Figure 3**.** Measurement methods for nanoparticle diameter: (a) D_h as the maximum height of a nanoparticle (b) D_p as the pitch of any two adjacent nanoparticles

The scan parameters shown below in Table 3 (page 8) can be used as starting points. The mean diameters should be based on the analysis of at least 100 nanoparticles from at least 6 frames, each frame including at least 3 to 20 measurable nanoparticles.

5.2 MEASURAND OF ELECTRON MICROSCOPY (TEM AND SEM)

The equivalent diameter of projected area is used to determine nanoparticle diameter. The mean diameters should be based on the analysis of at least 100 nanoparticles from at least 10 frames, each

frame including at least 10 measurable nanoparticles.

Table 3. Scan parameters

Nominal diameter	Scan size
300 nm	9.0 μm × 9.0 μm and below
100 nm	3.0 μm × 3.0 μm and below
30 nm	1.5 μm × 1.5 μm and below
20 nm	1.0 μm × 1.0 μm and below
10 nm	0.5 μm × 0.5 μm and below

5.3 Measurand of Dynamic Light Scattering (DLS)

Intensity weighted mean diameter is used to determine the nanoparticle diameter. Properties of suspending medium (deionized water) at 20 °C were used to set up the instrument: medium viscosity, 1.002 mPa and medium refractive index, 1.332 (for laser wavelength 633 nm). If any other temperature or laser is used, these properties should be adjusted accordingly). At least 3 different concentrations of each sample were measured and recorded. For each concentration of the samples, at least 6 repeated measurements were performed.

5.4 Measurand of Differential Mobility Analyzer (DMA)

DMA measurement can be determined either by a relative measurement or an absolute measurement. In the relative measurement, additional polystyrene latex (PSL) nanoparticles approximately 100 nm in size, which is provided by the pilot laboratory, are used as a reference (refer to Table 4). In the absolute measurement, the reference PSL nanoparticles, in addition to samples G1 to P5, need to be measured as well.

Table 4. Reference particle

No	Certified number average diameter	Expanded uncertainty (k=2)	Manufacturer
STADEX SC-010-S	100.82 nm	0.66 nm	JSR

The measurement system, shown schematically in Figure 4, consists of an EAG, a charge neutralizer, a DMA, and a condensation particle counter (CPC). It is suggested to warm each instrument up for at least 30 min before taking measurements.

a. Conduct DMA measurement in the stepping mode.

As shown in Figure 5, at least eleven values of the DMA voltage were chosen to cover the whole particle peak. Each voltage was maintained for 30 seconds: using the first 20 seconds

for idling and the remaining 10 seconds for counting particles. The measurement started from the voltage which was expected to be near the centre of peak, and the voltage was changed alternately to the left and to the right of the first voltage as shown in Figure 5. The first and last voltages should be matched in order to check the stability of aerosol generation. The data was obtained and recorded in the measurement reports. Measurements of the DMA spectrum were repeated if the difference of particle counts of the first and last voltages is larger than 10 %. Curve fitting with vanishing tails on both sides of its peak was employed to interpolate the insufficient portion of data, if it is necessary. The peak is required to be clearly isolated from background particles.

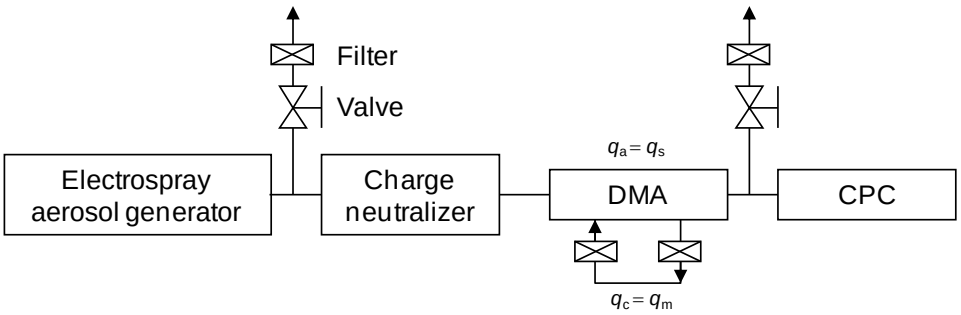

Figure 4. Schematic diagram of the measurement system

b. Determine the number mean diameter either by the moment method [3] or by the parameter fitting method [4]. In relative measurement, the certified diameter of the reference particles was used to correct possible errors in DMA electrode dimensions and other parameters.

c. For each sample, the measurements were repeated for three times a day on three different days.

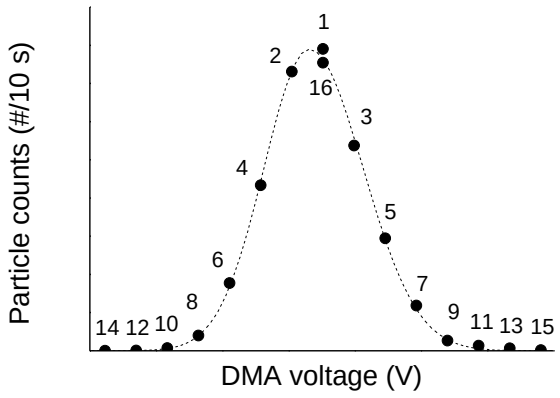

Figure 5**.** DMA spectrum obtained by stepping mode operation.

6 MEASUREMENT METHODS

6.1 OVERVIEW OF INSTRUMENTATION USED FOR AFM

In AFM measurement, tapping mode was applied by all participants. The participants were free to choose the height or pitch (or lateral) methods for nanoparticle diameter measurement with AFM. Most of the data sets were performed with height methods. NMIJ conducted height and pitch method for sample P3 and P4, and CMS and INRIM conducted both for sample P4 and P5. Considering the particle deformation, DFM provided two sets of the results with uncorrected and corrected data respectively. Table 5 gives a brief overview of AFM measuring condition.

Table 5. Overview of AFM measuring condition

LAB	Instrument and software	N.O.	Image resolution and frame size	Height/ pitch	Number of measured particles	Substrate
CENAM	JEOL™ instrument model JSPM 5200/WinSPM JEOL system™	G1	0.25 µm x 0.25 µm to 1.00 µm × 1.00 µm	Height	535	Mica
		S2	1.00 µm × 1.00 µm	Height	189	Mica
		P3	1.00 µm × 1.00 µm	Pitch	113	Mica
		P4	1.00 µm × 1.00 µm	Pitch	500	Mica
		P5	2.00 µm × 2.00 µm	Pitch	270	Mica
METAS	Metrology AFM based on a Dimension 3500 AFM from Digital Instruments	G1	512 × 512 pixels 0.5 µm × 0.5 µm	Height	653	Mica
		S2	512 × 512 pixels 1 µm × 1 µm	Height	349	Mica
		P3	512 × 512 pixels 1 µm × 1 µm	Height	398	Mica
		P4	512 × 512 pixels 2.2 µm × 2.2 µm	Height	875	Mica
		P5	512 × 512 pixels 6 µm × 6 µm	Height	1141	Mica
NMIJ	Metrological atomic force microscope (metrological AFM)	P3	512 × 512 pixels 512 nm × 512 nm	Height	263	Mica
				Pitch	199	Mica
		P4	1024 (Y) × 256 (X) pixels 4096 nm (Y) × 1024 nm (X)	Height	226	Mica
				Pitch	358	Mica
INRIM	Metrological atomic force microscope (metrological	G1	1024 × 1024 pixels 0.5 µm × 0.5 µm	Height	188	Mica

LAB	Instrument and software	N.O.	Image resolution and frame size	Height/ pitch	Number of measured particles	Substrate
	AFM); tips µmasch Hi'RES-C16/AIBS with G1, S2 and P3 samples, and Veeco NCHV-A with P4 and P5 samples	S2	1024 × 1024 pixels 0.8 µm × 0.8 µm	Height	215	Mica
		P3	1024 × 1024 pixels 1 µm × 1 µm	Height	115	Mica
		P4	1024 × 1024 pixels 2 µm × 2 µm	Height	156	Mica
				Pitch	26	Mica
		P5	1024 × 1024 pixels 5 µm × 5 µm	Height	63	Mica
				Pitch	136	Mica
PTB	SIS "Nanostation II" in the PTB cleanroom centre	G1	1024 × 1024 pixels mainly 0.8 µm × 0.8 µm, partly also 1.4 µm × 1.4 µm	Height	401	Glass
		S2	1024 × 1024 pixels 0.8 µm × 0.8 µm and 1.4 µm × 1.4 µm	Height	739	Silicon wafer
		P3	1024 × 1024 pixels 1 µm ×1 µm and 1.4 µm × 1.4 µm	Height	131	Glass
		P4	1024 × 1024 pixels 1.4 µm × 1.4 µm to 3 µm × 3 µm	Height	319	Glass
		P5	1024 × 1024 pixels mainly 10 µm × 10 µm, partly down to 2 µm × 2 µm	Height	300	Glass
NIM	Veeco Dimension ICON AFM / particle module of SPIP software	G1	1024 × 1024 pixels 0.5 µm × 0.5 µm	Height	138	Silicon wafer
		S2	1024 × 1024 pixels 1.0 µm × 1.0 µm	Height	123	Silicon wafer
		P3	1024 × 1024 pixels 1.5 µm × 1.5 µm	Height	145	Silicon wafer
		P4	1024 × 1024 pixels 3.0 µm × 3.0 µm	Height	126	Silicon wafer
		P5	1024 × 1024 pixels 9.0 µm × 9.0 µm	Height	114	Silicon wafer
NMIA	Asylum Research MFP-3D SA/SPIP software	G1	512 × 512 pixels 1 µm × 1 µm	Height	626	Mica
		S2	512 × 512 pixels 2 µm × 2 µm	Height	508	Mica
		P3	1024 × 1024 pixels 1 µm × 1 µm and 1.5µm × 1.5 µm	Height	1010	Mica

LAB	Instrument and software	N.O.	Image resolution and frame size	Height/ pitch	Number of measured particles	Substrate
		P4	2046 × 1411 pixels 15 μm × 10 μm	Height	6121	Mica
		P5	1024 × 852 pixels 15 μm × 12.5 μm	Height	810	Mica
NIMT	SEIKO SPA400 / AFM SPI Win Version 4.08F	G1	1 μm^2 and 1 Hz of scan speed	Height	100	Silicon wafer
		S2	1 μm^2 and 1 Hz of scan speed	Height	100	Silicon wafer
		P3	1 μm^2 and 1 Hz of scan speed	Pitch	100	Mica
		P4	1 μm^2 and 1 Hz of scan speed	Pitch	100	Mica
		P5	1 μm^2 and 1 Hz of scan speed	Pitch	100	Mica
DFM	Dimension 3100m(metrology head)	P4	512 × 512 pixels 3 μm × 3 μm	Height	2303	Mica
		P5	512 × 512 pixels 6 μm × 6 μm	Height	926	Mica
CMS	Dimension Icon /NanoScope Analysis software	G1	512 × 512 pixels 0.5 μm × 0.5 μm	Height	111	Mica
		S2	512 × 512 pixels 1 μm × 1 μm	Height	104	Mica
		P3	512 × 512 pixels 1 μm × 1 μm	Height	243	Silicon wafer
		P4	512 × 512 pixels 3 μm × 3 μm	Height	131	Silicon wafer
				Pitch	117	Silicon wafer
		P5	512 × 512 pixels 3 μm × 3 μm	Height	103	Silicon wafer
				Pitch	117	Silicon wafer

6.2 OVERVIEW OF INSTRUMENTATION USED FOR EM

Measurement conditions are summarized in Table 6 for the participants using SEM, TSEM and TEM methods. The equivalent diameter of projected area was used to determine nanoparticle diameter by most of the participants. Most of participants did not perform P3 results using TEMs.

Table 6. Measurement conditions of EM methods for each participant

LAB	Instrument/Software/Standard	N.O.	Measurement condition	Sample holder	Frame size	Particles numbers
CENAM	JXA-8200 EPMA / Scion image /SRM 1963a (101.8 ± 1.1)	P4	acceleration voltage: 30 kV, tilt angle: 0°, magnifications: 80k X	Aluminium	1.2 MB	**648**
		P5	acceleration voltage: 30 kV, tilt angle: 0°, magnifications: 40k X	Aluminium	1.2 MB	**510**
NMISA	LEO 1525 FE-SEM /Image J /NIST 484g line standard (500±34) nm	G1	acceleration voltage: 1 kV, tilt angle: 0°, magnifications: 100k X, 200k X, dilution ratio: none	Al stub	1024 × 768	**89**
		S2	acceleration voltage: 10 kV, tilt angle: 0°, magnifications: 100k X, 150k X, dilution ratio: none	Al stub	1024 × 768	**175**
		P3	acceleration voltage: 2 kV, tilt angle: 0°, magnifications: 150k X, dilution ratio: none	Al stub	1024 × 768	**100**
		P4	acceleration voltage: 5 kV, tilt angle: 0°, magnifications: 100k X, number of measurement ,dilution ratio: none	Al stub	1024 × 768	**88**
		P5	acceleration voltage: 10 kV, tilt angle: 0°, magnifications: 50k X, dilution ratio: none	Al stub	1024 × 768	**92**
PTB	Zeiss Leo Supra 35VP (used in TSEM mode) /home-made Matlab program using ImageJ particle analysis routines /144 nm and 700 nm grating PTB VIS/UV laser diffractometer	G1	bright field imaging mode and stored as 16 bit files acceleration voltage: 30 kV, tilt angle: 0°, values of the magnifications: 150k X, dilution ratio: undiluted	Carbon film supported by a copper grid	770 nm × 570 nm	**2394**
		S2	bright field imaging mode and stored as 16 bit files, acceleration voltage: 30 kV, tilt angle: 0°, values of the magnifications: 100k X, dilution ratio: undiluted	Carbon film supported by a copper grid	1.1 µm × 0.9 µm	**4283**
		P3	bright field imaging mode and stored as 16 bit files, acceleration voltage: 30 kV, tilt angle: 0°, values of the magnifications: 100k X, dilution ratio: undiluted	Thin carbon film supported by a copper grid	1.1 µm × 0.9 µm	**2941**
		P4	bright field imaging mode and stored as 16 bit files, acceleration voltage: 30 kV, tilt angle: 0°, values of the magnifications: 20k X, dilution ratio: undiluted	Thin carbon film supported by a copper grid	5.9 µm × 4.4 µm	**4432**

LAB	Instrument/Software/Standard	N.O.	Measurement condition	Sample holder	Frame size	Particles numbers
CMS	Zeiss SUPRA 60VP /SmartSEM FESEM software/SRM NIST 8011 (9.9 ± 0.1) nm and 70 nm pitch grating traced to PTB	G1	2.6 s/frame, acceleration voltage: 10 kV, tilt angle: 0°, values of the magnifications: 100k X, dilution ratio: undiluted	Al stub	1024 × 768, 1142 × 795 nm^2	**112**
		S2	2.6 s/frame, acceleration voltage: 10 kV, tilt angle: 0°, values of the magnifications: 100k X, dilution ratio: undiluted	Al stub	1024 × 768, 1142 × 795 nm^2	**116**
		P3	2.6 s/frame, acceleration voltage: 10 kV, tilt angle: 0°, values of the magnifications: 100k X, dilution ratio: undiluted	Al stub	1024 × 768, 1142 × 795 nm^2	**104**
		P4	2.6 s/frame, acceleration voltage: 10 kV, tilt angle: 0°, values of the magnifications: 100k X, dilution ratio: undiluted	Al stub	1024 × 768, 2280 × 1585 nm^2	**119**
		P5	2.6 s/frame, acceleration voltage: 10 kV, tilt angle: 0°, values of the magnifications: 100k X, number of measured particles: 109, dilution ratio: undiluted	Al stub	1024 × 768, 11.39 × 7.95 μm^2	**109**
NMIJ	Hitachi S-4300SE/image processing of pattern matching/He-Ne laser interferometer	P4	acceleration voltage: 1.5 kV, tilt angle: 0°, values of the magnifications: 30k X, dilution ratio: 1:10	Al stub	2560 × 1920	**129**
		P5	acceleration voltage: 2 kV, tilt angle: 0°, values of the magnifications: 10k X, dilution ratio: 1:10	Al stub	2560 × 1920	**158**
INRiM	FEI Quanta 3D FEG/ ImageJ/ two dimensional grating from Agar, a SIRA standard specimen with a 462,92 +/- 0,05 nm pitch, traceably measured at INRiM by optical diffraction.	G1	acceleration voltage: 30 kV, tilt angle: 0°, values of the magnifications: 800k X, dilution ratio: undiluted	Al stub	340 nm	**100**
		S2	acceleration voltage: 30 kV, tilt angle: 0°, values of the magnifications: 300k X, dilution ratio: undiluted	Al stub	1000 nm	**100**
		P4	acceleration voltage: 30 kV, tilt angle: 0°, values of the magnifications: 500k X, dilution ratio: undiluted	Al stub	600 nm	**100**
		P5	acceleration voltage: 30 kV, tilt angle: 0°, values of the magnifications: 150k X, dilution ratio: undiluted	Al stub	2000 nm	**100**
NIMT	Hitachi S-3400N/ SEM data management/ 2-dimensional grating, 144 nm, traceable to NIST	P4	acceleration voltage: 30 kV, tilt angle: 0°, values of the magnifications: 50k X, dilution ratio: undiluted	Al stub	2.5 × 1.6 μm	**100**
		P5	acceleration voltage: 30 kV, tilt angle: 0°, values of the magnifications: 25k X, dilution ratio: undiluted	Al stub	5.0 × 3.2 μm	**100**
KRISS	TEM/ ImageJ/ Lattice constants of Si and GaAs	G1	acceleration voltage: 300 kV, tilt angle: 0°, values of the magnifications: 75k X, dilution ratio: undiluted	Copper grids with thin carbon film	2048 × 2048 pixels	**118**
		S2	acceleration voltage: 300 kV, tilt angle: 0°, values of the magnifications: 75k X, dilution ratio: undiluted	Copper grids with thin carbon film	2048 × 2048 pixels	**101**
Inmetro	SEM/ Nova Nanolab/Image J/ 8013 NIST Reference Material – 60 nm gold Nanoparticles	G1	acceleration voltage: 15 kV, tilt angle: 0°, values of the magnifications: 500k X, dilution ratio: undiluted	Stub	0.5968 μm	**90**
		S2	acceleration voltage: 10 kV, tilt angle: 0°, values of the magnifications: 200k X, dilution ratio: 50%	Stub	1.492 μm	**107**

LAB	Instrument/Software/Standard	N.O.	Measurement condition	Sample holder	Frame size	Particles numbers
		P3	acceleration voltage: 10 kV, tilt angle: 0°, values of the magnifications: 300k X, dilution ratio: 80 %	Stub	0.9946 µm	**225**
		P4	acceleration voltage: 15 kV, tilt angle: 0°, values of the magnifications: 400k X, dilution ratio: 50%	Stub	0.746 µm	**100**
		P5	acceleration voltage: 15 kV, tilt angle: 0°, values of the magnifications: 200k X, dilution ratio: undiluted	Stub	1.492 µm	**93**
Inmetro	TEM / A probe-corrected FEG Titan 80-300 (FEI) / Image J/ Mag*I*Cal	G1	acceleration voltage: 300 kV, tilt angle: 0°, values of the magnifications: 490k X, dilution ratio: undiluted, Image J "Straight line measure"	Copper grid	56,93 nm × 56,93 nm	**209**
		S2	acceleration voltage: 300 kV, tilt angle: 0°, values of the magnifications: 87 k X, dilution ratio: undiluted, Image J "Straight line measure"	Copper grid	258,98 nm × 258,98 nm	**193**
		P4	acceleration voltage: 300 kV, tilt angle: 0°, values of the magnifications: 43 k X, dilution ratio: 80 %, Image J "Make Binary" and "Analyze Particles"	Copper grid	495,52 nm × 495,52 nm	**218**
		P5	acceleration voltage: 300 kV, tilt angle: 0°, values of the magnifications: 21 k X, dilution ratio: 50 %, Image J "Straight line measure"	Copper grid	1035,65 nm × 1035,65 nm	**223**
NMIA	Jeol 2100 TEM // Image J G1 and S2 - Silica particle 21 nm, ERM-FD 100P4 – PSL 100, Thermo Scientific,P5 - PSL 300, Thermo Scientific	G1	acceleration voltage: 200 kV, tilt angle: 0°, values of the magnifications: 400k X, dilution ratio: 1:33	Copper grid	1024 × 1024 pixels	**5499**
		S2	acceleration voltage: 200 kV, tilt angle: 0°, values of the magnifications: 400k X, dilution ratio: 1:12.5	Copper grid	1024 × 1024 pixels	**314**
		P4	acceleration voltage: 200 kV, tilt angle: 0°, values of the magnifications: 50k X, dilution ratio: 1:200	Copper grid	672 × 578 pixels	**365**
		P5	acceleration voltage: 200 kV, tilt angle: 0°, values of the magnifications: 50k X, dilution ratio: 1:200	Copper grid	672 × 578 pixels	**160**

6.3 Overview of instrumentation used for DLS

Measurement conditions for light scattering method are summarized in Table 7. For comparable results, all participants performed the measurements with a diluted sample using deionised water. In Table 7, all laboratories used Cumulants method to estimate particle sizes. The selected scattering angles were either at 173° or 90°. NMIJ performed two measurement results: one with 90° and the other one was the extrapolation of angles respectively. Two wavelengths of the lasers were used as 632.8 nm and 532 nm.

Table 7. Measurement conditions of DLS for each participant

LAB	Measurement Instruments	Instrument setup	Analysis type	Estimation method
CENAM	Malvern Zetasizer Nano S	Wavelength of laser: 633 nm, Scattering angle: 173°, Temperature of sample holder: 20.0 °C, Viscosity: 1.003 mPa·s, Refractive index (medium): 1.330	Frequency	**Cumulants**
CMS	Sympatec NanoPhox	Wavelength of laser: 632.8 nm, Scattering angle: 90°, Temperature of sample holder: 20.0 °C, Viscosity: 1.002 mPa·s, Refractive index (medium): 1.332	Cross correlation	**Cumulants**
NIM	Sympatec NANOPHOX PARTICLE ANALYSER NX0059	Wavelength of laser: 632.8 nm, Scattering angle: 90°, Temperature of sample holder: 20.0 °C, Viscosity: 1.002 mPa·s, Refractive index (medium): 1.332	Autocorrelation cross-correlation	**NNLS**
NIMA	Malvern Zetasizer Nano ZS	Wavelength of laser: 633 nm, Scattering angle: 173°, Temperature of sample holder: 20.0 °C, Viscosity: 1.002 mPa·s, Refractive index (medium): 1.332	Autocorrelation	**Cumulants**
NIMT	Malvern ZetasizerNanoseries model S4700	Wavelength of laser: 633 nm, Scattering angle: 173°, Temperature of sample holder: 20.0 °C, Viscosity: 1.002 mPa·s, Refractive index (medium): 1.332	Autocorrelation	**Cumulants**
NMIJ	ALV goniometer system	Wavelength of laser: 532 nm, Scattering angle: 90° and extrapolation of angles, Temperature of sample holder: 20.0 °C, Viscosity: 1.002 mPa s, Refractive index (medium): 1.335	Autocorrelation	**Cumulants**
KRISS	Brookhaven BI-200SM	Wavelength of laser: 632.8 nm, Scattering angle: 173° Temperature of sample holder: 20.0 °C, Viscosity: 1.002 mPa·s, Refractive index (medium): 1.332	Autocorrelation	**Cumulants**

6.4 OVERVIEW OF INSTRUMENTATION USED FOR DMA

DMA measurements were performed in two methods: one is the relative method (CMS, LNE, NMIJ and KRISS) and the other one is the absolute method (KRISS). Measurement conditions are summarized in Table 8 for participants using DMA.

Table 8. Measurement conditions of DMA for each participant

LAB	Relative / absolute	Aerosol generator, DMA and CPC	Samples	Sheath/Aerosol flow rate (L/min)
CMS	Relative	Electrospray Aerosol Generator TSI 3480 Long DMA: TSI 3081 CPC TSI 3776	P3	**19.0/1.0**
			P4	**19.0/1.0**
			P5	**6.0/0.6**
KRISS	Absolute	Electrospray Aerosol Generator TSI 3480 for G1, P3, P4 Atomizer TSI 3076 for P5 Long DMA : TSI 3081 for P3, P4, P5 Nano DMA : TSI 3085 for G1 CPC : TSI 3776	G1	**15/1.5**
	Relative		P3	**10/1**
			P4	**10/1**
	Absolute		P5	**3/0.3**
LNE	Relative	Atomizer TSI 30776 Long DMA : TSI 3081 CPC: TSI 30226	P4	**18.50/1.00**
			P5	**6.00/0.60**
NMIJ	Relative	Electrospray Aerosol Generator TSI 3480 Long DMA: TSI 3081 CPC TSI 3025	G1	**19.5/1.0**
			P3	**19.5/1.0**
			P4	**19.5/1.0**
			P5	**6.0/0.6**

6.5 OVERVIEW OF INSTRUMENTATION USED FOR SAXS

Small-angle X-ray scattering (SAXS) was the method used by PTB in this comparison.

Measurement conditions are summarized in Table 9.

Table 9. Measurement conditions of SAXS

LAB	Measurement instruments	Samples	Instrument setup	Analysis type
PTB	Four-crystal monochromator at BESSY II, HZB SAXS	G1	Photon energy : 10 keV Sample detector distance: 2433 mm Detector pixel size: 78.94 µm Scattering angle range: 0.11° - 1.83° Analysis type: hard spheres, Gaussian distribution	**Hard spheres, Gaussian distribution**
		S2	Photon energy : 8 keV Sample detector distance: 2433 mm Detector pixel size: 78.94 µm Scattering angle range: 0.25° - 1.92°	
		P3	Photon energy : 8 keV Sample detector distance: 2433 mm Detector pixel size: 78.94 µm Scattering angle range: 0.11° - 0.71°	
		P4	Photon energy : 10 keV Sample detector distance: 2433 mm Detector pixel size: 78.94 µm Scattering angle range: 0.07° - 1.04	
		P5	Photon energy : 8 keV Sample detector distance: 4582 mm Detector pixel size: 78.94 µm Scattering angle range: 0.05° - 0.41°	

7 UNCERTAINTY ESTIMATIONS

7.1 UNCERTAINTY OF MEASUREMENT

The uncertainty of measurement was evaluated according to the ISO/IEC Guide 98-3:2008[5]. The uncertainty sources were divided into components associated with the realisation of the object compared, and those associated with the comparison method.

E_n numbers were adopted for determining the consistency of the participants' results. The reference value (d_{ref}) used for the determination of the E_n numbers was calculated with the inverse-variance weighted mean of the participants' measurement data based on Equation (1) and (2), below:

$$d_{ref} = \sum_{i=1}^{n} w_i d_i \tag{1}$$

$$w_i = \frac{u^{-2}(d_i)}{\sum_{i=1}^{n} u^{-2}(d_i)} \tag{2}$$

where the inverse-variance weights w_i were calculated with the combined standard uncertainty, $u(d_i)$, which is obtained from the participants' results d_i.

The associated standard uncertainty is presented as Equation (3):

$$u_c(d_{ref}) = [\sum_{i=1}^{n} u^{-2}(d_i)]^{-0.5} \tag{3}$$

The effective degrees of freedom for the reference value were calculated by Equation (4):

$$\nu_{eff}(d_{ref}) = \frac{u_c^4(d_{ref})}{\sum_{i=1}^{n} \frac{u_i^4(d_{ref})}{\nu_{eff}(d_i)}} \text{ with } u_i(d_{ref}) = |c_i| \cdot u(d_i) = \frac{u^{-1}(d_i)}{\sum_{i=1}^{n} u^{-2}(d_i)} \tag{4}$$

Then E_n numbers with a critical value of 1.0 were calculated by Equation (5) [6]:

$$E_n = \frac{d_i - d_{ref}}{\sqrt{U_k^2 - U_{ref}^2}} \tag{5}$$

where U_k is the expanded uncertainty of the participant's result, and U_{ref} is the expanded uncertainty of the reference values. Since correlation effects exist when the participant's results contribute to the reference value, the minus sign ("-") was used in the denominator for the

calculation of the E_n numbers.[1] Otherwise, the plus sign ("+") was used when the reference value does not depend on the participants' results.

7.2 CONSIDERATIONS OF ADDITIONAL METHOD ASSOCIATED UNCERTAINTIES

In order to decide the degree of equivalence (DOE) in next section, reference values are required to be determined first. Two possible reference values are considered here: the method dependent reference value (MRV) and the global reference value (GRV). The MRVs are decided for different measurement methods according to the corresponding reported uncertainties and measurement values from the participants. Each measurement method owns its own reference value. In contrast, the GRV is the only value for all methods from all the reported values and uncertainties. The decisions of using MRVs and GRV for DOEs are discussed in Section 8. In order to calculate the MRVs and the GRV, some key uncertainties were studied and prepared for participants to consider and revise the reported measurement uncertainties. The modified uncertainty with measurement results were NOT used for the evaluations of the DOEs, but would be used for the determination of the reference values only. The suggested uncertainties include the following:

Atomic Force Microscope (AFM)

If the participants used the particle height for the diameter of the particles, the particle deformation due to particle-substrate adhesion should be estimated and corrected. Thus, the diameter and uncertainty due to the deformation should be revised as:

$$y_i = x_i + \hat{\delta}_i \tag{6}$$

$$u^2(y_i) = u^2(x_i) + u^2\left(\hat{\delta}_i\right) \tag{7}$$

Dynamic light scattering (DLS)

Additional uncertainties associated with the effects of finite width of size distribution, scattering-angle and particle-concentration dependences of measurement results, and thickness of water molecule layer adsorbed on particle surfaces were considered. Thus, the uncertainty for the DLS measurements would be changed as:

$$y_i = x_i \tag{8}$$

[1] Note that the expression of E_n given in Equation (5) needs to be modified as given in Equation (20) owing to the data revision described in 7.2

$$u^2(y_i) = u^2(x_i) + \Delta u^2_{DLS_i} \quad (9)$$

Differential mobility analyzer (DMA)

Additional uncertainty associated with non-sphericity of particles was considered. Thus, the uncertainty for the DMA measurements would be changed as:

$$y_i = x_i \quad (10)$$

$$u^2(y_i) = u^2(x_i) + \Delta u^2_{DMA_i} \quad (11)$$

A list of possible uncertainty sources for the instruments mentioned above was given in **Appendix A**. The participating laboratories were encouraged to list all uncertainty sources for their applied method. The list in **Appendix A** was only a reference, but not a completed list.

To reflect the preparations of the comparison report, the following draft versions were described briefly, as:

Table 10. History of the different Draft-versions with their dates of preparation

Version	Circulation Date	Notes
Draft A	2013-01-11	● First collection of reported data from participants
Draft A_01 (Draft A1)	2014-02-06	● After minor corrections from participants for obvious typing errors, formats, and so forth
Draft A2	2014-05-09	● Only shared with co-pilot (NMIJ) ● Revised uncertainties for AFM and DLS
Draft A3	2017-08-15	● Reported with calculated reference values and analysis results
Draft A4	2018-03-22	● Modifications in responded to participants' comments of the Draft A3
Draft A5	2018-05-18	● Corrections in responded to participants' comments of Table 5 and Table B15 in the Draft A4, without any changes on the E_n results
Draft B	2018-06-11	● A summary was reported in "Consultative Committee for Length – CCL" Working Group Meetings (WG-MRA, WG-S, WG-N) from 2018-06-11 ~ 15.

Both the measurement results with originally reported uncertainties (Draft A1) and the revised measurement results with modified uncertainties (Draft A2) are listed in **Appendix B**. The measurement results with originally reported uncertainties in the Draft A1 are indicated as x_l and $u(x_l)$. The revised data and uncertainty were arranged and summarized in Draft A2. The symbols used to indicate the revised versions are y_l and $u(y_l)$ for clarification. In a brief note here, symbols for the three versions of data related to the uncertainties reported from the participants are explained

as below.

Draft A1: $[x_i, u(x_i)]$

- Data that reflect the original capability of each lab
- DOE will be calculated for this data

Draft A2: $[y_i, u(y_i)]$

- Considered scientifically more reasonable than the originally reported data of each lab in Draft A1
- Used to calculate MRVs and GRVs

Draft A2, but with Paule-Mandel adjustment: $[z_i, u(z_i)]$

- $z_i = y_i$
- $u^2(z_i) = u^2(y_i) + u_{PM}^2$

8 DEGREE OF EQUIVALENCE (DOE)

8.1 METHOD ADOPTED FOR DECIDING REFERENCE VALUES

A 3-step method was used to decide the degree of equivalence (DOE) of the size measurements for nanoparticles in this comparison. The analysis flow chart is summarized and shown in Figure 6. The 3-step method was proposed and discussed in the 'International Workshop on Nanoparticle Size Measurement' held in 2014 and 2015 at Taiwan. Before the calculations of the DOEs, two terms are defined for this comparison. The first one is MRV (method dependent reference value), which is obtained by the same method. GRV (global reference value) is also considered to include all the measurement results for each particle type. The 3-step method for the DOE is described below:

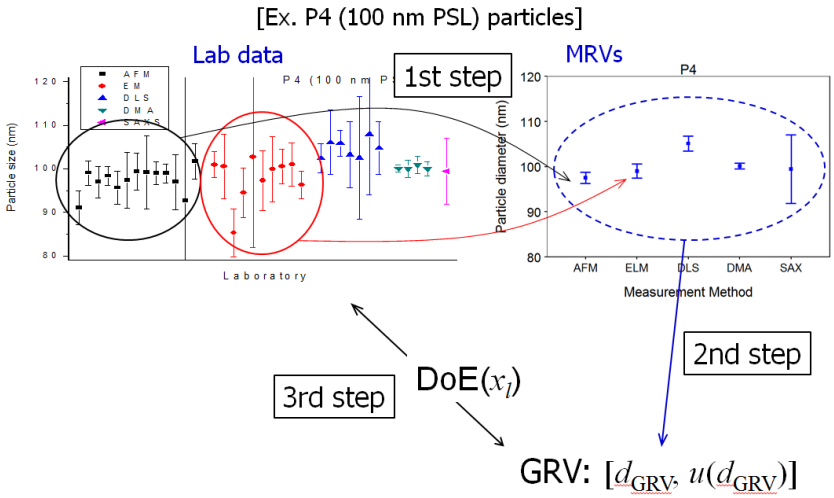

Figure 6**.** the schematic description of the 3-step method for the DOE

Step 1: Intra-method analysis for consistency check

To perform the 'consistency check' within a method for each particle type, the Chi-square (χ^2) test is applied. The set $[y_l, u(y_l)]$ is considered consistent, if Chi-square (χ^2) test is fulfilled, as:

$$\chi^2_{obs} \leq \chi^2(L-1, 0.95), \text{ where } (l = 1,2, \dots, L) \quad (12)$$

Here, the y_l is the data reported by laboratory l, and the $u(y_l)$ is the correlated uncertainty for the reported data **in the Draft A2**. If the χ^2 test failed, the largest consistent subset (LCS)[7, 8] method is used to find a consistent subset of $[y_l, u(y_l)]$. The final MRV, d_{MRV}, is determined from the consistent subset and referred to Equation (1) to (3), as:

$$d_{MRV} = \sum_l w_l y_l \quad (13)$$

$$u^2(d_{MRV}) = \frac{1}{\sum u^{-2}(y_l)} \quad (14)$$

$$w_l = \frac{u^{-2}(y_l)}{\sum u^{-2}(y_l)} \quad (15)$$

Here, the formula for a weighted mean is used when data is mutually independent.[2] Figure 7 shows the consistency results of the MRVs for all 5 nanoparticles based on the largest consistent subset method. It can be found that the MRVs were found not consistent for all 5 nanoparticles in the χ^2 tests. The MRV of the DLS is consistently larger than the other 4 MRVs in all nanoparticles. As a result, if the LCS method is applied when we attempt to construct a GRV from the MRVs, the MRV of the DLS is always excluded.

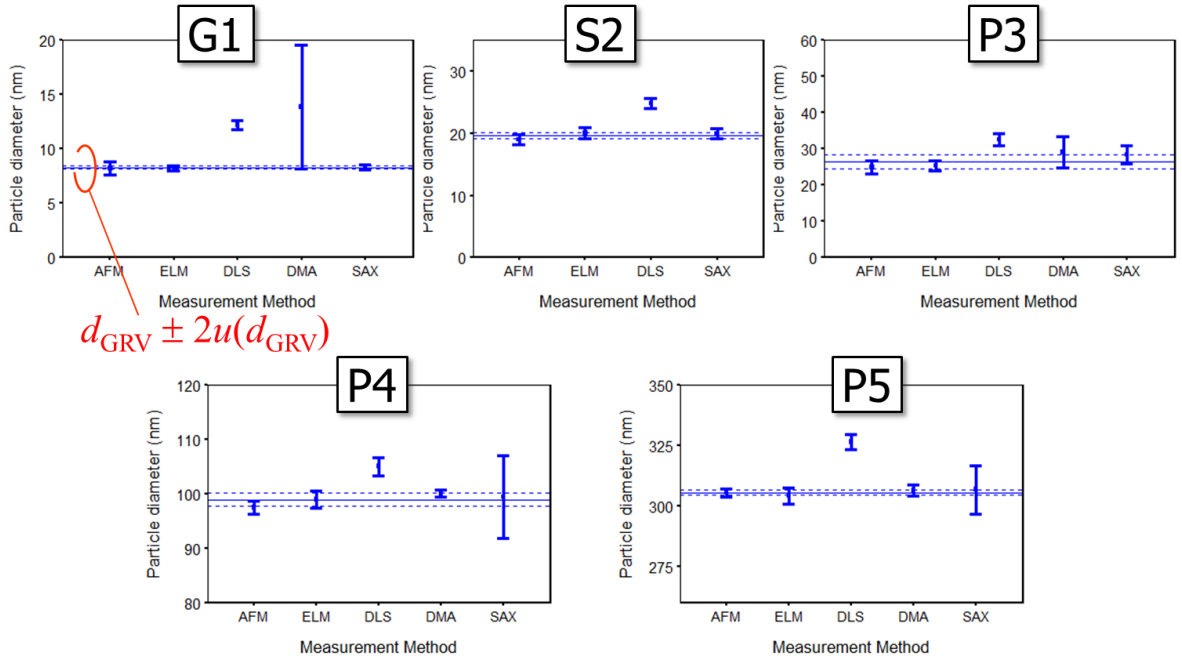

Figure 7**.** Method dependent reference values (MRVs) for all 5 nanoparticles

Step 2: Inter-method analysis for GRVs

With the MRVs in hand from the previous paragraphs (step 1), the consistency check was performed between the MRVs. The procedure is the same as the one described in step 1. Once the inconsistent MRV is recognized, the inconsistent MRV is excluded for calculating GRVs. In other words, the GRVs are calculated from the consistent MRVs for each particle type. Based on the reported data, we have the following:

[2] There can be correlations between y_l's of different laboratories stemming from the data revision described in 7.2. When such correlations exist, Equations (14) and (15) need to be replaced with expressions involving the variance-covariance matrix for y_l's. A detailed description of the data analysis including the treatment of between-laboratory correlations is to be given in a paper which is currently being prepared and will be submitted to a scientific journal.

- The MRVs were found not consistent for all five particles in the χ^2 tests.
- The MRV of DLS is consistently larger than the other MRVs. If the LCS method is applied, it is always excluded from the LCS.
- For P3 and P4 particles, the remaining four MRVs are still not consistent, but the inconsistency is minor.
- Exclude DLS from the onset. This does not mean that the DLS gives incorrect results. It just means that it gives consistently different results from the other measurement methods.
- When the remaining MRVs are found still inconsistent, the Paule-Mandel adjustment [9] is applied to recover consistency between them.

To apply Paule-Mandel adjustment for P3 and P4 particles, all the MRVs except for DLS were included. The revised uncertainties in the Draft A2 were used for Paule-Mandel adjustment, as:

$$u^2(d_m) \rightarrow \tilde{u}^2(d_m) = u^2(d_m) + u_{PM}^2 \tag{16}$$

where u_{PM} indicates the additional uncertainty needed to make the MRVs consistent in the Paule-Mandel adjustment.

Because of the MRV's, d_m (m = 1, 2, ... M), are mutually independent, the GRV can be determined from the usual formula as:

$$d_{GRV} = \sum_m^M w_m d_m \tag{17}$$

$$\frac{1}{u^2(d_{GRV})} = \sum_m \frac{1}{\tilde{u}^2(d_m)} \tag{18}$$

$$w_m = \frac{\tilde{u}^{-2}(d_m)}{\sum_{m'} \tilde{u}^{-2}(d_{m'})} \tag{19}$$

Step 3: Evaluation of degree of equivalence (DOE)

From step 1 and 2, both MRVs and GRVs were obtained. The DOE is obtained to check the consistency of each lab data x_l with the GRVs. The E_n number is often used as a quantitative measure of the DOE, which is defined as Equation (5) and revised as below:

$$E_n(x_l) = \frac{x_l - d_{GRV}}{2 \times u(x_l - d_{GRV})} \tag{20}$$

where $x_l - d_{GRV}$ is the deviation of the reported data compared with a GRV.[3] At a confidence level of 95 %, the coverage factor of 2 is used in Equation (4). If $|E_n(x_l)| \leq 1$, it indicates that x_l is considered consistent with d_{GRV}.

8.2 RESULTS OF E_N CALCULATIONS

The data in the Draft A2 (after modification) reported from each laboratory was listed in **Appendix B** and used to calculate the reference values (RV) following the 3-step method, and then, the calculated RVs were applied to calculate E_n numbers with the data in the Draft A1 (before modification). Since the measurement data from DLS is very different than the measurement data from the other methods, MRVs for DLS were used in the E_n number calculation for the measurement data reported from the DLS method. The GRVs were applied in the E_n numbers calculations for the measurement data reported from AFM, EM, DMA and SAXS methods. The RVs are listed in the below Table 11.

Table 11. Global reference values (GRVs) for AFM, EM, DMA, and SAXS; method dependent reference value (MRV) for DLS

Reference Values										
Method	**G1**		**S2**		**P3**		**P4**		**P5**	
AFM EM DMA SAXS	d_{GRV}	$u(d_{GRV})$	d_{GRV}	$u(d_{GRV})$	d_{GRV}	$u(d_{GRV})$	d_{GRV}	$u(d_{GRV})$	d_{GRV}	$u(d_{GRV})$
	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
	8.30	**0.08**	**19.66**	**0.23**	**26.49**	**0.99**	**99.03**	**0.63**	**305.73**	**0.59**
DLS	d_{MRV}	$u(d_{MRV})$	d_{MRV}	$u(d_{MRV})$	d_{MRV}	$u(d_{MRV})$	d_{MRV}	$u(d_{MRV})$	d_{MRV}	$u(d_{MRV})$
	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
	12.21	**0.23**	**24.84**	**0.42**	**32.68**	**0.83**	**105.13**	**0.84**	**326.6**	**1.6**

[3] While we reasonably assume that x_l's are mutually independent, there can be correlations between y_l's as noted in footnote 2. It should be noted that the determination of d_{GRV} is based on y_l's, and not on x_l's. Therefore, even if data y_l of laboratory l contributes to d_{GRV}, the correlation coefficient $r(x_l, d_{GRV})$ is not equal to $u(d_{GRV})/u(x_l)$ as is expected in cases where data are mutually independent. As a consequence, the expression $u(x_l - d_{GRV}) = \sqrt{u^2(x_l) \pm u^2(d_{GRV})}$ is no longer valid in general, and consideration to the variance-covariance matrix among y_l's is needed in calculating $u(x_l - d_{GRV})$. Details of this analysis will be described in a paper mentioned in footnote 2.

8.2.1 Nano gold with 10 nm nominal diameter (G1)

As shown in Figure 8, the E_n numbers for the total of 8 measurement results from AFM, 8 measurement results from EM, one from DMA and one from SAXS were summarized in Tables 12 ~15. The GRV of 8.30 nm with the uncertainty of 0.08 nm was used in the calculation. Three sets of measurement results (AFM from NMIA, SEM from Inmetro, and DMA from NMIJ) were considered not consistent with the d_{GRV}, since their $|E_n| > 1$. If the data of the Draft A2 (after modifications with certain uncertainties) was used for further analysis, the E_n number for DMA was smaller than 1 and considered consistent with d_{GRV}, as shown in Figure C2 (page 69).

For the calculations of the E_n numbers for the 7 DLS results, the MRV of 12.21 nm with 0.23 nm uncertainty was used. Table 16 (page 29) shows the results of the E_n numbers of DLS results. It indicates that only two (NIMT and NMIA) were consistent with the d_{MRV}, as shown in Figure 8. However, if the data of the Draft A2 (after modifications with certain uncertainties) was used for further analysis, four (CMS, NIMT, NMIA, and NMIJ) out the 7 data sets were consistent with the d_{MRV}, as shown in Figure C2 (page 68).

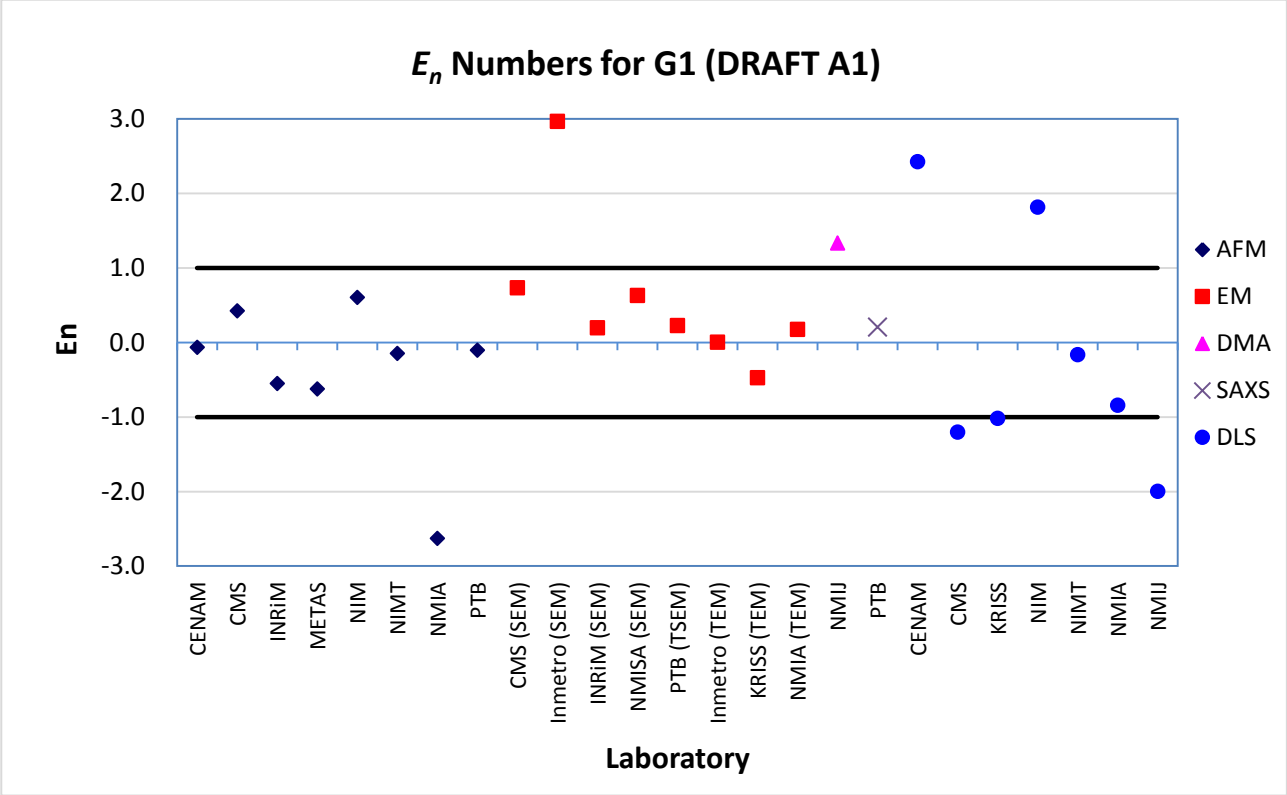

Figure 8. E_n numbers of all participants for G1 (Draft A1)

Table 12. AFM results for G1 based on Draft A1

AFM results for G1							
LAB	**Measurement results**		**Reference values**		**Degrees of equivalence**		
	d_x	$u(d_x)$	d_{GRV}	$u(d_{GRV})$	$d_x - d_{GRV}$	$u(d_x - d_{GRV})$	E_n
	nm	**nm**	**nm**	**nm**	**nm**	**nm**	
CENAM	8.2	0.74	8.30	0.08	-0.10	0.74	-0.07
CMS	8.8	0.6	8.30	0.08	0.50	0.59	0.42
INRiM	7.2	1.0	8.30	0.08	-1.10	1.00	-0.55
METAS	7.3	0.8	8.30	0.08	-1.00	0.80	-0.62
NIM	9.68	1.15	8.30	0.08	1.38	1.15	0.60
NIMT	7.875	1.43	8.30	0.08	-0.42	1.43	-0.15
NMIA	6.2	0.4	8.30	0.08	-2.10	0.40	-2.63
PTB	8.0	1.4	8.30	0.08	-0.30	1.40	-0.11

Table 13. EM results for G1 based on Draft A1

EM results for G1							
LAB	**Measurement results**		**Reference values**		**Degrees of equivalence**		
	d_x	$u(d_x)$	d_{GRV}	$u(d_{GRV})$	$d_x - d_{GRV}$	$u(d_x - d_{GRV})$	E_n
	nm	**nm**	**nm**	**nm**	**nm**	**nm**	
CMS(SEM)	10.2	1.3	8.30	0.08	1.90	1.30	0.73
Inmetro(SEM)	11.3	0.5	8.30	0.08	3.00	0.51	2.97
INRiM(SEM)	9.2	2.3	8.30	0.08	0.90	2.30	0.20
NMISA(SEM)	11.3	2.39	8.30	0.08	3.00	2.39	0.63
PTB(TSEM)	8.7	0.9	8.30	0.08	0.40	0.90	0.22
Inmetro(TEM)	8.3	0.4	8.30	0.08	0.00	0.39	0.00
KRISS(TEM)	8.191	0.137	8.30	0.08	-0.11	0.11	-0.48
NMIA(TEM)	8.4	0.3	8.30	0.08	0.10	0.29	0.18

Table 14. DMA results for G1 based on Draft A1

DMA results for G1							
LAB	**Measurement results**		**Reference values**		**Degrees of equivalence**		
	d_x	$u(d_x)$	d_{GRV}	$u(d_{GRV})$	$d_x - d_{GRV}$	$u(d_x - d_{GRV})$	E_n
	nm	**nm**	**nm**	**nm**	**nm**	**nm**	
NMIJ	13.9	2.1	8.30	0.08	5.60	2.10	1.33

Table 15. SAXS results for G1 based on Draft A1

SAXS results for G1							
LAB	**Measurement results**		**Reference values**		**Degrees of equivalence**		
	d_x	$u(d_x)$	d_{GRV}	$u(d_{GRV})$	$d_x - d_{GRV}$	$u(d_x - d_{GRV})$	E_n
	nm	**nm**	**nm**	**nm**	**nm**	**nm**	
PTB	8.33	0.11	8.30	0.08	0.03	0.08	0.20

Table 16. DLS results for G1 based on Draft A1

DLS results for G1							
LAB	**Measurement results**		**Reference values**		**Degrees of equivalence**		
	d_x	$u(d_x)$	d_{MRV}	$u(d_{MRV})$	$d_x - d_{MRV}$	$u(d_x - d_{MRV})$	E_n
	nm	**nm**	**nm**	**nm**	**nm**	**nm**	
CENAM	14.52	0.42	12.21	0.23	2.31	0.48	2.42
CMS	10.4	0.7	12.21	0.23	-1.81	0.75	-1.21
KRISS	9.8	1.2	12.21	0.23	-2.41	1.18	-1.02
NIM	14.74	0.66	12.21	0.23	2.53	0.70	1.81
NIMT	11.81	1.2	12.21	0.23	-0.40	1.20	-0.17
NMIA	12.1	0.2	12.21	0.23	-0.11	0.07	-0.85
NMIJ	10.6	0.3	12.21	0.23	-1.61	0.40	-2.00

8.2.2 Nano silver with 20 nm nominal diameter (S2)

As shown in Figure 9 for the case of nano silver S2, the E_n numbers for the total of 8 measurement results from AFM, 8 measurement results from EM, one result from DMA and one from SAXS were summarized in Tables 17 ~ 19. The GRV of 19.66 nm with the uncertainty of 0.23 nm was used in the calculation of E_n numbers. Five sets of measurement results (AFM from INRiM and NMIA, and SEM from CMS, Inmetro and INRiM) were considered not consistent with the d_{GRV}, since their $|E_n| > 1$.

For the calculations of the E_n numbers for the 7 DLS results, the MRV of 24.84 nm with 0.42 nm uncertainty was used. Table 20 (page 32) and Figure 9 show the results of the E_n numbers of DLS results. It indicates that two (CENAM and NIM) were not consistent with the d_{MRV}.

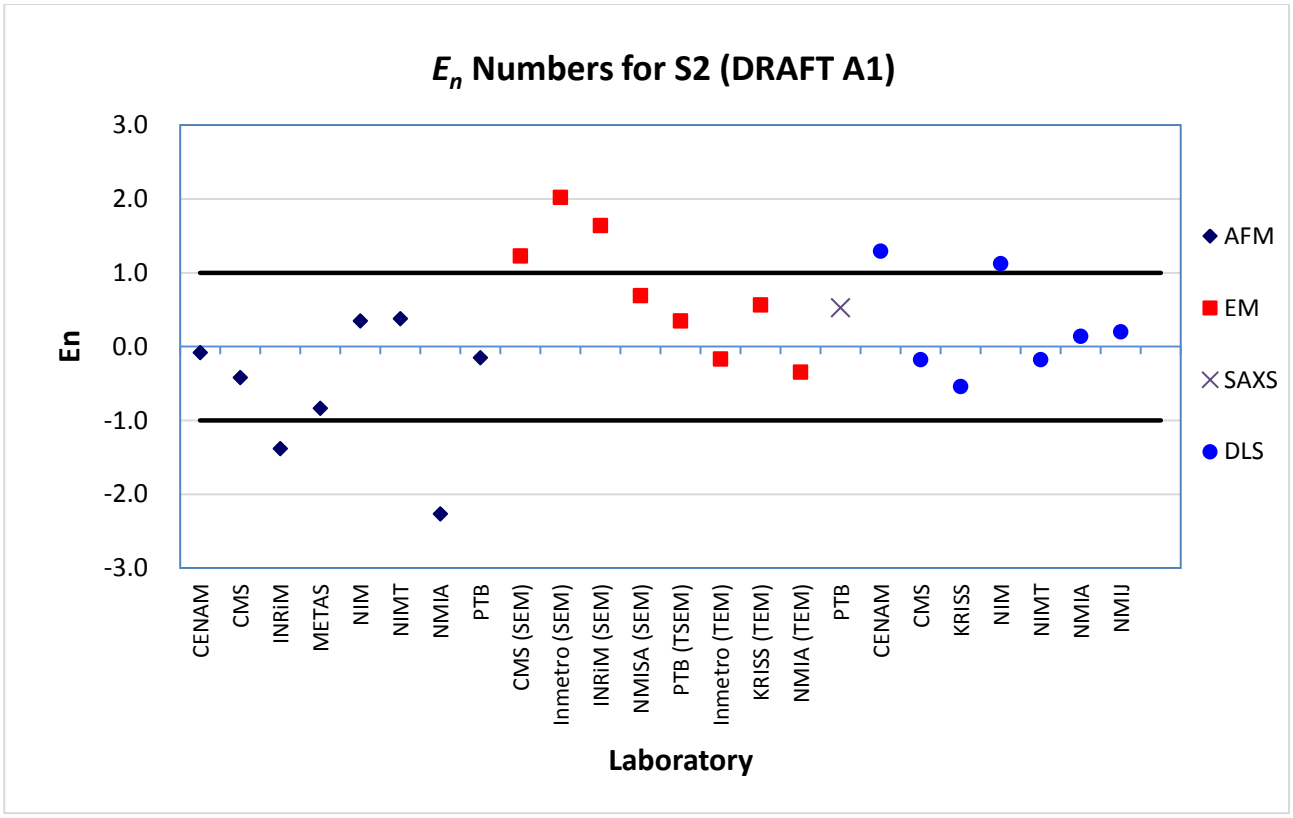

Figure 9**.** E_n numbers of all participants for S2 (Draft A1)

Table 17. AFM results for S2 based on Draft A1

AFM results for S2							
LAB	**Measurement results**		**Reference values**		**Degrees of equivalence**		
	d_x	$u(d_x)$	d_{GRV}	$u(d_{GRV})$	$d_x - d_{GRV}$	$u(d_x - d_{GRV})$	E_n
	nm	**nm**	**nm**	**nm**	**nm**	**nm**	
CENAM	19.3	2.15	19.66	0.23	-0.36	2.14	-0.08
CMS	19.1	0.7	19.66	0.23	-0.56	0.66	-0.42
INRiM	16.9	1	19.66	0.23	-2.76	1.00	-1.38
METAS	18.2	0.9	19.66	0.23	-1.46	0.87	-0.84
NIM	21.3	2.38	19.66	0.23	1.64	2.37	0.35
NIMT	21.023	1.81	19.66	0.23	1.37	1.80	0.38
NMIA	17.0	0.6	19.66	0.23	-2.66	0.59	-2.27
PTB	19.3	1.2	19.66	0.23	-0.36	1.18	-0.15

Table 18. EM results for S2 based on Draft A1

EM results for S2							
LAB	**Measurement results**		**Reference values**		**Degrees of equivalence**		
	d_x	$u(d_x)$	d_{GRV}	$u(d_{GRV})$	$d_x - d_{GRV}$	$u(d_x - d_{GRV})$	E_n
	nm	**nm**	**nm**	**nm**	**nm**	**nm**	
CMS(SEM)	22.8	1.3	19.66	0.23	3.14	1.28	1.23
Inmetro(SEM)	24.2	1.1	19.66	0.23	4.54	1.12	2.02
INRiM(SEM)	33.1	4.1	19.66	0.23	13.44	4.11	1.64
NMISA(SEM)	23.3	2.66	19.66	0.23	3.64	2.65	0.69
PTB (TSEM)	20.4	1.1	19.66	0.23	0.74	1.08	0.35
Inmetro (TEM)	19.4	0.8	19.66	0.23	-0.26	0.77	-0.17
KRISS (TEM)	21.323	1.494	19.66	0.23	1.67	1.48	0.56
NMIA (TEM)	19.2	0.7	19.66	0.23	-0.46	0.66	-0.35

Table 19. SAXS results for S2 based on Draft A1

SAXS results for S2							
LAB	**Measurement results**		**Reference values**		**Degrees of equivalence**		
	d_x	$u(d_x)$	d_{GRV}	$u(d_{GRV})$	$d_x - d_{GRV}$	$u(d_x - d_{GRV})$	E_n
	nm	**nm**	**nm**	**nm**	**nm**	**nm**	
PTB	20.0	0.4	19.66	0.23	0.34	0.33	0.52

Table 20. DLS results for S2 based on Draft A1

DLS results for S2							
LAB	**Measurement results**		**Reference values**		**Degrees of equivalence**		
	d_x	$u(d_x)$	d_{MRV}	$u(d_{MRV})$	$d_x - d_{MRV}$	$u(d_x - d_{MRV})$	E_n
	nm	**nm**	**nm**	**nm**	**nm**	**nm**	
CENAM	28.39	1.31	24.84	0.42	3.55	1.37	1.29
CMS	24.3	1.4	24.84	0.42	-0.54	1.50	-0.18
KRISS	23.5	1.3	24.84	0.42	-1.34	1.23	-0.54
NIM	26.9	0.89	24.84	0.42	2.06	0.92	1.12
NIMT	24.4	1.2	24.84	0.42	-0.44	1.22	-0.18
NMIA	24.9	0.3	24.84	0.42	0.06	0.22	0.14
NMIJ	25.1	0.4	24.84	0.42	0.26	0.66	0.20

8.2.3 PSL with 30 nm nominal diameter (P3)

As shown in Figure 10 for the case of PSL P3, the E_n numbers for the total of 10 measurement results from AFM, 4 measurement results from EM, 3 measurement results from DMA and one result from SAXS were summarized in Tables 21 ~24. The GRV of 26.49 nm with the uncertainty of 0.99 nm was used in the calculation for the E_n numbers. Four sets of measurement results (AFM from CMS, METAS and NMIA, and SEM from Inmetro) were considered not consistent with d_{GRV}, since their $|E_n| > 1$. Additionally, all DMA values were larger than 1 and considered not consistent with d_{GRV}, either. However, if the data of the Draft A2 (after modifications with certain uncertainties) was used for further analysis, all DMA values were smaller than 1 and considered consistent with d_{GRV}, as shown in Figure C6 (page 72).

For the calculations of the E_n numbers for the DLS results (7 sets), the MRV of 32.68 nm with 0.83 nm uncertainty was used. Table 25 (page 35) and Figure 10 show the results of the E_n numbers of DLS results. It indicates that 3 (KRISS, NIMT and NMIA) were not consistent with the d_{MRV}.

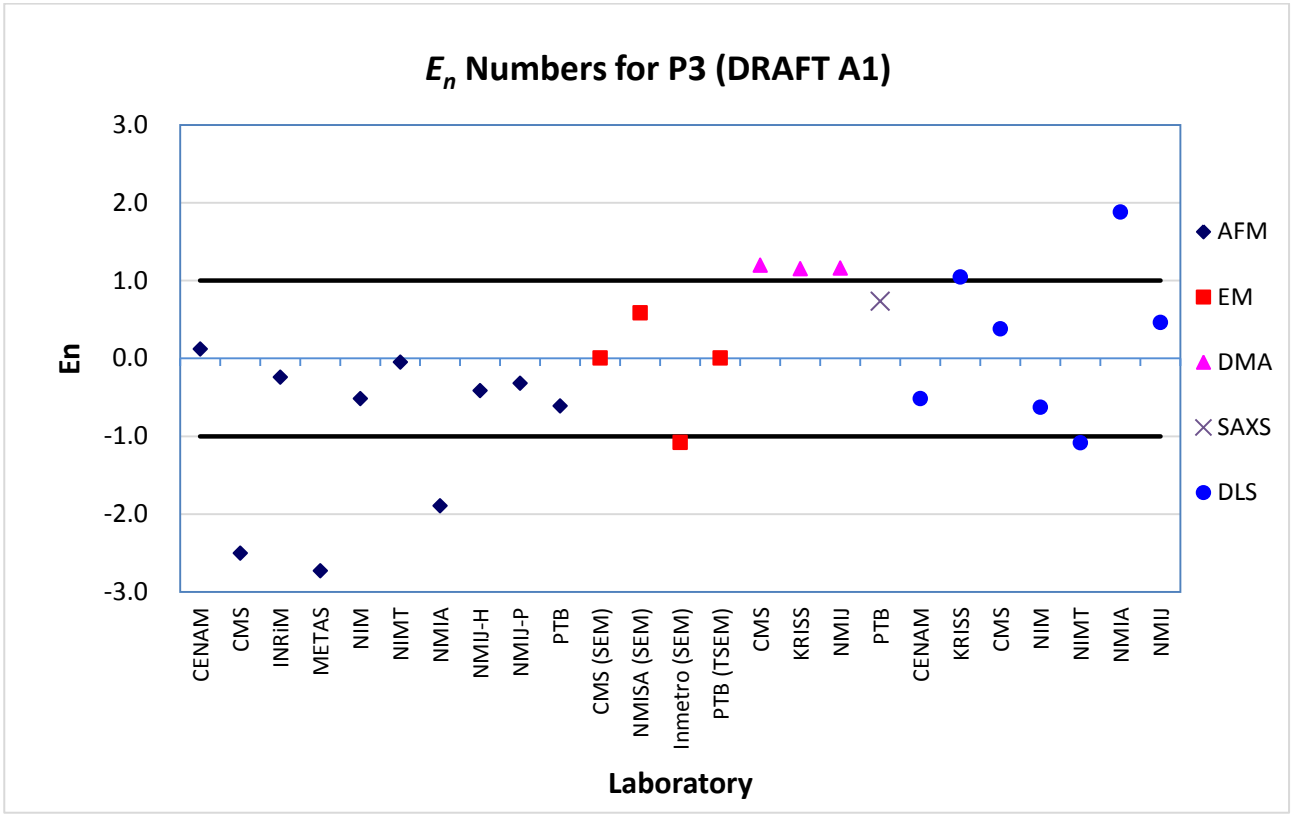

Figure 10. E_n numbers of all participants for P3 (Draft A1)

Table 21. AFM results for P3 based on Draft A1

AFM results for P3							
LAB	**Measurement results**		**Reference values**		**Degrees of equivalence**		
	d_x	$u(d_x)$	d_{GRV}	$u(d_{GRV})$	$d_x - d_{GRV}$	$u(d_x - d_{GRV})$	E_n
	nm	**nm**	**nm**	**nm**	**nm**	**nm**	
CENAM	27.1	2.42	26.49	0.99	0.61	2.52	0.12
CMS	20.6	0.7	26.49	0.99	-5.89	1.18	-2.50
INRiM	25.7	1.3	26.49	0.99	-0.79	1.63	-0.24
METAS	19.6	0.9	26.49	0.99	-6.89	1.26	-2.73
NIM	23.5	2.72	26.49	0.99	-2.99	2.89	-0.52
NIMT	25.017	14.83	26.49	0.99	-1.48	14.85	-0.05
NMIA	21.7	0.8	26.49	0.99	-4.79	1.27	-1.89
NMIJ-H	23.3	3.71	26.49	0.99	-3.19	3.84	-0.42
NMIJ-P	25.05	2.13	26.49	0.99	-1.44	2.24	-0.32
PTB	23.1	2.6	26.49	0.99	-3.39	2.76	-0.61

Table 22. EM results for P3 based on Draft A1

EM results for P3							
LAB	**Measurement results**		**Reference values**		**Degrees of equivalence**		
	d_x	$u(d_x)$	d_{GRV}	$u(d_{GRV})$	$d_x - d_{GRV}$	$u(d_x - d_{GRV})$	E_n
	nm	**nm**	**nm**	**nm**	**nm**	**nm**	
CMS(SEM)	26.5	1.4	26.49	0.99	0.01	1.62	0.00
NMISA(SEM)	30.1	2.98	26.49	0.99	3.61	3.09	0.58
Inmetro(SEM)	23.7	1.0	26.49	0.99	-2.79	1.29	-1.08
PTB (TSEM)	26.5	1.3	26.49	0.99	0.01	1.54	0.00

Table 23. DMA results for P3 based on Draft A1

DMA results for P3							
LAB	**Measurement results**		**Reference values**		**Degrees of equivalence**		
	d_x	$u(d_x)$	d_{GRV}	$u(d_{GRV})$	$d_x - d_{GRV}$	$u(d_x - d_{GRV})$	E_n
	nm	**nm**	**nm**	**nm**	**nm**	**nm**	
CMS	29.04	0.44	26.49	0.99	2.55	1.07	1.19
KRISS	29.13	0.61	26.49	0.99	2.64	1.15	1.15
NMIJ	29.16	0.62	26.49	0.99	2.67	1.15	1.16

Table 24. SAXS results for P3 based on Draft A1

SAXS results for P3							
LAB	**Measurement results**		**Reference values**		**Degrees of equivalence**		
	d_x	$u(d_x)$	d_{GRV}	$u(d_{GRV})$	$d_x - d_{GRV}$	$u(d_x - d_{GRV})$	E_n
	nm	**nm**	**nm**	**nm**	**nm**	**nm**	
PTB	28.4	1.2	26.49	0.99	1.91	1.30	0.73

Table 25. DLS results for P3 based on Draft A1

DLS results for P3							
LAB	**Measurement results**		**Reference values**		**Degrees of equivalence**		
	d_x	$u(d_x)$	d_{MRV}	$u(d_{MRV})$	$d_x - d_{MRV}$	$u(d_x - d_{MRV})$	E_n
	nm	**nm**	**nm**	**nm**	**nm**	**nm**	
CENAM	31.49	1.41	32.68	0.83	-1.19	1.14	-0.52
KRISS	34.5	1.2	32.68	0.83	1.82	0.87	1.04
CMS	34.2	1.9	32.68	0.83	1.52	2.02	0.38
NIM	31.3	1.19	32.68	0.83	-1.38	1.10	-0.63
NIMT	28.58	1.7	32.68	0.83	-4.10	1.89	-1.08
NMIA	36.3	0.5	32.68	0.83	3.62	0.96	1.88
NMIJ	33.4	0.4	32.68	0.83	0.72	0.78	0.46

8.2.4 PSL with 100 nm nominal diameter (P4)

As shown in Figure 11 for the case of PSL P4, the E_n numbers for the total of 13 measurement results from AFM, 10 measurement results from EM, 4 results from DMA and one result from SAXS were summarized in Tables 26 ~29. The GRV of 99.03 nm with the uncertainty of 0.63 nm was used in the calculation of the E_n numbers. Four sets of measurement results from AFM (CENAM, CMS-H, INRiM-H and NMIA) and one set from EM (Inmetro) were considered not consistent with the d_{GRV}, since their $|E_n| > 1$.

For the calculations of the E_n numbers for the 7 DLS results, the MRV of 105.13 nm with 0.84 nm uncertainty was used. Table 30 (page 38) and Figure 11 show the results of the E_n numbers of DLS results. It indicates that one (NMIA) was not consistent with the d_{MRV}.

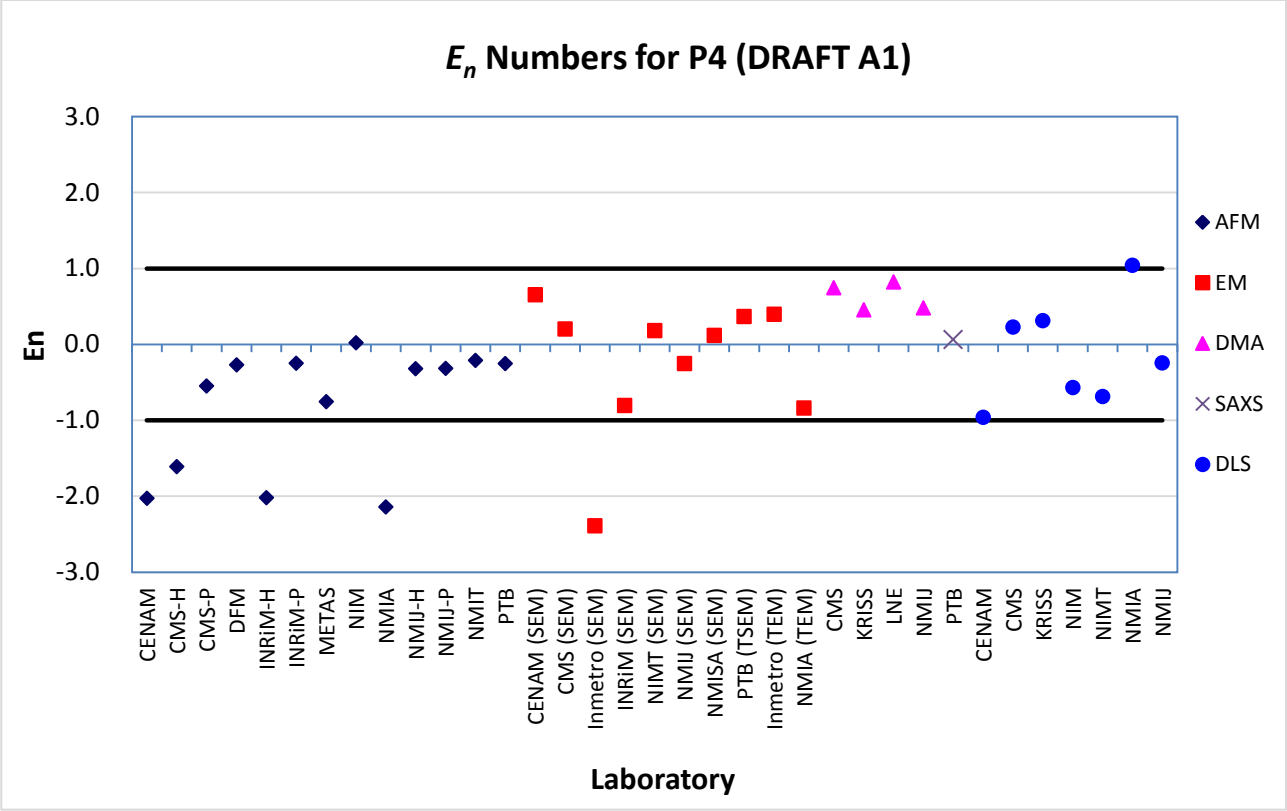

Figure 11. E_n numbers of all participants for P4 (Draft A1)

Table 26. AFM results for P4 based on Draft A1

AFM results for P4							
LAB	**Measurement results**		**Reference values**		**Degrees of equivalence**		
	d_x	$u(d_x)$	d_{GRV}	$u(d_{GRV})$	$d_x - d_{GRV}$	$u(d_x - d_{GRV})$	E_n
	nm	**nm**	**nm**	**nm**	**nm**	**nm**	
CENAM	91.0	1.94	99.03	0.63	-8.03	1.98	-2.03
CMS-H	95.5	0.9	99.03	0.63	-3.53	1.09	-1.61
CMS-P	97.0	1.8	99.03	0.63	-2.03	1.84	-0.55
DFM	98.4	1.1	99.03	0.63	-0.63	1.17	-0.27
INRiM-H	92.1	1.6	99.03	0.63	-6.93	1.71	-2.02
INRiM-P	97.4	3.2	99.03	0.63	-1.63	3.22	-0.25
METAS	95.9	2.0	99.03	0.63	-3.13	2.07	-0.76
NIM	99.2	4.09	99.03	0.63	0.17	4.14	0.02
NMIA	95.0	0.7	99.03	0.63	-4.03	0.94	-2.15
NMIJ-H	95.42	5.57	99.03	0.63	-3.61	5.60	-0.32
NMIJ-P	96.99	3.17	99.03	0.63	-2.04	3.19	-0.32
NMIT	92.637	14.9	99.03	0.63	-6.39	14.90	-0.21
PTB	98.1	1.7	99.03	0.63	-0.93	1.81	-0.26

Table 27. EM results for P4 based on Draft A1

EM results for P4							
LAB	**Measurement results**		**Reference values**		**Degrees of equivalence**		
	d_x	$u(d_x)$	d_{GRV}	$u(d_{GRV})$	$d_x - d_{GRV}$	$u(d_x - d_{GRV})$	E_n
	nm	**nm**	**nm**	**nm**	**nm**	**nm**	
CENAM(SEM)	100.97	1.47	99.03	0.63	1.94	1.49	0.65
CMS(SEM)	100.5	3.7	99.03	0.63	1.47	3.71	0.20
Inmetro(SEM)	85.3	2.8	99.03	0.63	-13.73	2.87	-2.39
INRiM(SEM)	94.5	2.8	99.03	0.63	-4.53	2.81	-0.81
NIMT(SEM)	102.77	10.37	99.03	0.63	3.74	10.37	0.18
NMIJ(SEM)	97.3	3.4	99.03	0.63	-1.73	3.41	-0.25
NMISA(SEM)	99.9	3.73	99.03	0.63	0.87	3.74	0.12
PTB (TSEM)	100.5	2.0	99.03	0.63	1.47	2.02	0.36
Inmetro (TEM)	101.0	2.5	99.03	0.63	1.97	2.51	0.39
NMIA (TEM)	96.3	1.6	99.03	0.63	-2.73	1.62	-0.84

Table 28. DMA results for P4 based on Draft A1

DMA results for P4							
LAB	**Measurement results**		**Reference values**		**Degrees of equivalence**		
	d_x	$u(d_x)$	d_{GRV}	$u(d_{GRV})$	$d_x - d_{GRV}$	$u(d_x - d_{GRV})$	E_n
	nm	**nm**	**nm**	**nm**	**nm**	**nm**	
CMS	100.07	0.43	99.03	0.63	1.04	0.70	0.74
KRISS	100.05	0.98	99.03	0.63	1.02	1.12	0.45
LNE	100.93	1.02	99.03	0.63	1.90	1.16	0.82
NMIJ	100.00	0.85	99.03	0.63	0.97	1.01	0.48

Table 29. SAXS results for P4 based on Draft A1

SAXS results for P4							
LAB	**Measurement results**		**Reference values**		**Degrees of equivalence**		
	d_x	$u(d_x)$	d_{GRV}	$u(d_{GRV})$	$d_x - d_{GRV}$	$u(d_x - d_{GRV})$	E_n
	nm	**nm**	**nm**	**nm**	**nm**	**nm**	
PTB	99.5	3.8	99.03	0.63	0.47	3.75	0.06

Table 30. DLS results for P4 based on Draft A1

DLS results for P4							
LAB	**Measurement results**		**Reference values**		**Degrees of equivalence**		
	d_x	$u(d_x)$	d_{MRV}	$u(d_{MRV})$	$d_x - d_{MRV}$	$u(d_x - d_{MRV})$	E_n
	nm	**nm**	**nm**	**nm**	**nm**	**nm**	
CENAM	102.43	1.63	105.13	0.84	-2.70	1.40	-0.97
CMS	106.1	2.1	105.13	0.84	0.97	2.15	0.22
KRISS	105.9	1.5	105.13	0.84	0.77	1.25	0.31
NIM	103.3	1.49	105.13	0.84	-1.83	1.61	-0.57
NIMT	102.61	1.4	105.13	0.84	-2.52	1.83	-0.69
NMIA	108	1.1	105.13	0.84	2.87	1.38	1.04
NMIJ	104.8	0.5	105.13	0.84	-0.33	0.67	-0.25

8.2.5 PSL with 300 nm nominal diameter (P5)

As shown in Figure 12 for the case of PSL P5, the E_n numbers for the total of 11 measurement results from AFM, 9 measurement results from EM, 3 results from DMA and one result from SAXS were summarized in Tables 31 ~ 34. The GRV of 305.73 nm with the uncertainty of 0.59 nm was used in the calculation of the E_n numbers. Four sets of measurement results (AFM from PTB, NMIA and NIMT, and SEM from Inmetro) were considered not consistent with the d_{GRV}, since their $|E_n| > 1$.

For the calculations of the E_n numbers for the 7 DLS results, the MRV of 326.6 nm with the uncertainty of 1.6 nm uncertainty was used. Table 35 (page 41) and Figure 12 show the results of the E_n numbers of DLS results. It indicates that one (NMIA) was not consistent with the d_{MRV}.

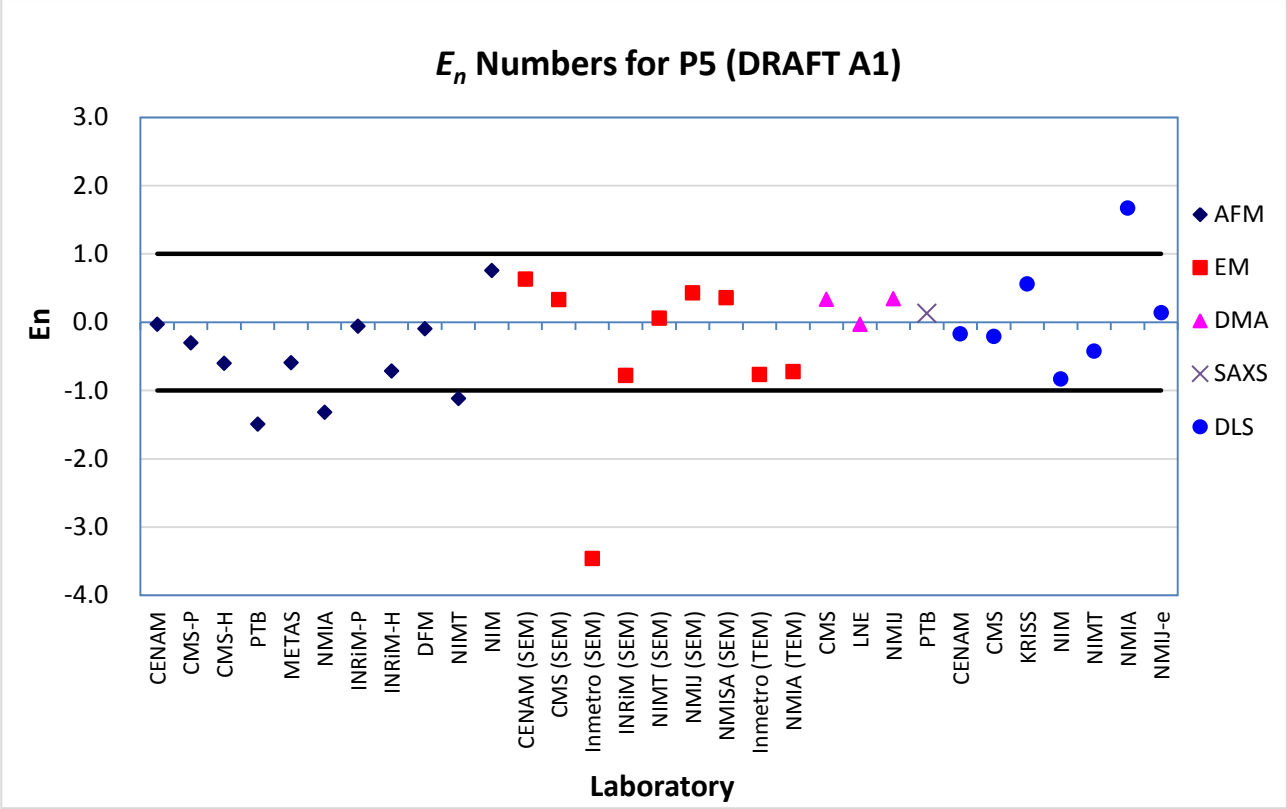

Figure 12. E_n numbers of all participants for P5 (Draft A1)

Table 31. AFM results for P5 based on Draft A1

AFM results for P5							
LAB	**Measurement results**		**Reference values**		**Degrees of equivalence**		
	d_x	$u(d_x)$	d_{GRV}	$u(d_{GRV})$	$d_x - d_{GRV}$	$u(d_x - d_{GRV})$	E_n
	nm	**nm**	**nm**	**nm**	**nm**	**nm**	
CENAM	305.6	2.09	305.73	0.59	-0.13	2.01	-0.03
CMS-P	304.5	2.1	305.73	0.59	-1.23	2.02	-0.30
CMS-H	302.9	2.3	305.73	0.59	-2.83	2.34	-0.61
PTB	298.5	2.4	305.73	0.59	-7.23	2.42	-1.50
METAS	302.4	2.8	305.73	0.59	-3.33	2.80	-0.60
NMIA	303	1	305.73	0.59	-2.73	1.03	-1.32
INRiM-P	305.2	4.4	305.73	0.59	-0.53	4.36	-0.06
INRiM-H	300.3	3.8	305.73	0.59	-5.43	3.80	-0.71
DFM	305.5	1.3	305.73	0.59	-0.23	1.16	-0.10
NIMT	269.76	16.11	305.73	0.59	-35.97	16.10	-1.12
NIM	314.6	5.88	305.73	0.59	8.87	5.89	0.75

Table 32. EM results for P5 based on Draft A1

EM results for P5							
LAB	**Measurement results**		**Reference values**		**Degrees of equivalence**		
	d_x	$u(d_x)$	d_{GRV}	$u(d_{GRV})$	$d_x - d_{GRV}$	$u(d_x - d_{GRV})$	E_n
	nm	**nm**	**nm**	**nm**	**nm**	**nm**	
CENAM(SEM)	312.25	5.23	305.73	0.59	6.52	5.20	0.63
CMS(SEM)	312.1	9.7	305.73	0.59	6.37	9.68	0.33
Inmetro(SEM)	268.8	5.3	305.73	0.59	-36.93	5.33	-3.46
INRiM(SEM)	300.5	3.4	305.73	0.59	-5.23	3.35	-0.78
NIMT(SEM)	307.88	17.97	305.73	0.59	2.15	17.96	0.06
NMIJ(SEM)	308.5	3.3	305.73	0.59	2.77	3.25	0.43
NMISA(SEM)	313.1	10.3	305.73	0.59	7.37	10.28	0.36
Inmetro (TEM)	297.8	5.2	305.73	0.59	-7.93	5.17	-0.77
NMIA (TEM)	300	4	305.73	0.59	-5.73	3.96	-0.72

Table 33. DMA results for P5 based on Draft A1

DMA results for P5							
LAB	**Measurement results**		**Reference values**		**Degrees of equivalence**		
	d_x	$u(d_x)$	d_{GRV}	$u(d_{GRV})$	$d_x - d_{GRV}$	$u(d_x - d_{GRV})$	E_n
	nm	**nm**	**nm**	**nm**	**nm**	**nm**	
CMS	306.5	1.3	305.73	0.59	0.77	1.16	0.33
LNE	305.56	2.92	305.73	0.59	-0.17	2.86	-0.03
NMIJ	307.6	2.8	305.73	0.59	1.87	2.74	0.34

Table 34. SAXS results for P5 based on Draft A1

SAXS results for P5							
LAB	**Measurement results**		**Reference values**		**Degrees of equivalence**		
	d_x	$u(d_x)$	d_{GRV}	$u(d_{GRV})$	$d_x - d_{GRV}$	$u(d_x - d_{GRV})$	E_n
	nm	**nm**	**nm**	**nm**	**nm**	**nm**	
PTB	307	5	305.73	0.59	1.27	4.97	0.13

Table 35. DLS results for P5 based on Draft A1

DLS results for P5							
LAB	**Measurement results**		**Reference values**		**Degrees of equivalence**		
	d_x	$u(d_x)$	d_{MRV}	$u(d_{MRV})$	$d_x - d_{MRV}$	$u(d_x - d_{MRV})$	E_n
	nm	**nm**	**nm**	**nm**	**nm**	**nm**	
CENAM	325.15	4.54	326.6	1.6	-1.48	4.25	-0.17
CMS	324.3	5.8	326.6	1.6	-2.33	5.62	-0.21
KRISS	331.1	4.3	326.6	1.6	4.47	4.00	0.56
NIM	319.7	4.31	326.6	1.6	-6.93	4.16	-0.83
NIMT	316.69	11.2	326.6	1.6	-9.94	11.72	-0.42
NMIA	341	4	326.6	1.6	14.37	4.30	1.67
NMIJ	327	2	326.6	1.6	0.37	1.37	0.14

9 SUMMARY

Nanoparticles with size in the range from 10 nm to 300 nm and from three different materials (Au 10 nm, Ag 20 nm, and PSL 30 nm, 100 nm and 300 nm) were used in this supplementary comparison. The selected nanoparticles meet the requirements of different measurement methods such as Atomic Force Microscopy (AFM), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Dynamic Light Scattering (DLS), and Differential Mobility Analyzer (DMA), Small Angle X-Ray Scattering and for forth. Since the choice of measurement methods was not limited, the participating laboratories could choose their own method to carry out the measurement.

Most results were received between May and July 2012, a few were received during October and November. All 37 participating laboratories returned results, which were summarized in the Draft A1 and listed in the **Appendix B** of the present draft. However, not all laboratories were able to perform measurement of all 5 nanoparticles. The measurement methods were grouped into 5 methods such as AFM, EM (SEM and TEM), DMA, SAXS, and DLS for further analysis. The different measurands determined on the nanoparticles were specified and discussed based on each method. For the DLS method, the possible definition of the measurand was 'intensity-weighted harmonic diameter of particles of a specific material based on the diffusion process of particles.'

In order to decide the degree of equivalence (DOE), two reference values were considered in this comparison: the method dependent reference value (MRV) and the global reference value (GRV). The MRVs were decided for different measurement methods according to the corresponding reported uncertainties and measurement values from the participants. Each measurement method owns its own reference value. In contrast, the GRV was the only value for all methods from all the reported values and uncertainties.

In order to calculate the MRVs and the GRV, some key uncertainties were studied and prepared for participants to consider and revise the reported measurement uncertainties. The revised data (indicated as 'after modification') were listed in the Draft A2 and also in the **Appendix B**. The modified uncertainty with measurement results were NOT used for the evaluations of the DOEs, but only for the determination of the reference values following the 3-step method. The MRVs and GRVs were then used for calculating E_n numbers for the data (Draft A1) before modification. The E_n numbers after data modification in Draft A2 were also calculated, but were listed and plotted in the informative **Appendix B** and **C**.

This is a common observation that the DLS gives consistently different results from the other measurement methods. This is possibly because the DLS observes diffusion process of particles and does not directly observe particle diameters, with DLS measurement being affected by the scattering angle, particle concentration, absorbed molecules on particle surfaces, and diffusion

weighted populations. The assumption that the particles are spherical was commonly made in the nanoparticle measurements. It is important to make clear the distinction that the methods used are measuring the mean diameter of a population of particles, not just a single particle. Probably if participants include a different specific contribution to the uncertainty for, in same way, consider the non-cancelled "systematic" errors depending on the methods, it may be easier to compare the results.

Since the measurement data from DLS are very different than the measurement data from the other methods, MRVs for DLS were used in the E_n number calculation for the measurement data reported from the DLS method. The GRVs were applied in the E_n numbers calculations for the measurement data reported from AFM, EM, DMA and SAXS methods. The main objective of the data modification for DLS was to make the result consistent with others. This objective is no longer meaningful once we decided not to use DLS in the calculation of GRV. Nevertheless, this modification was interesting from the scientific point of view. A scientific paper was suggested to detail the 3-step method and the use of Paule-Mandel adjustment in the calculation of GRV.

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APPENDIX A: POSSIBLE UNCERTAINTIES OF MEASUREMENT METHODS

Atomic Force Microscope (AFM):

- Metrological traceability
- Measurement repeatability
- Thermal effects
- System linearity
- Drift of mechanical frame
- Surface roughness effect (height measurement)
- Tip shape error (spacing measurement)
- Segregation (spacing measurement, [A1])
- Particle deformation (vertical and/or lateral)
- Others

Transmission Electron Microscopy (TEM):

- Metrological traceability
- Measurement repeatability
- Edge effects
- Abbe errors due to the unwanted tilt and rotation angles of stages
- Measurement noise
- Others

Scanning Electron Microscopy (SEM):

- Metrological traceability
- Measurement repeatability
- Edge effects
- Image drift due to charging effect, mechanical unstable and so on
- Abbe errors due to the unwanted tilt and rotation angles of stages
- Measurement noise
- Others

Dynamic Light Scattering (DLS):

- Boltzmann constant
- Absolute temperature
- Refractive index of dispersant
- Viscosity
- Scattering angle
- Decay rate

- Laser wavelength
- Effects of analysis type
- Others

Differential Mobility Analyzer (DMA) - relative measurement):

- Repeatability
- Reproducibility
- Reference PSL particles
- Data analysis methodology (choice of a fitting function, accuracy in the moment method, etc.)
- Voltage (offset)
- Formula of charge distribution
- Slip correction
- Effect of Brownian motion
- Effect of evaporation residues
- Others

Differential Mobility Analyzer (DMA) - absolute measurement:

- Repeatability
- Reproducibility
- Outer and inner radii, and length of electrodes
- Sheath air flow rate
- Effect of aerosol flow rate on apparent size [A2]
- Slip correction
- Data analysis methodology
- Temperature and pressure
- Viscosity of air
- Voltage
- Formula of charge distribution
- Effect of Brownian motion
- Effect of evaporation residues
- Others

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APPENDIX B: SUMMARY OF GRVS, MRVS AND E_N NUMBERS

The following tables (Table B1 ~ B24) and figures (Figure B1 ~ B10) in this section summarize all reported results d_i (Draft A1 and A2) from all participants. Correspondingly, the combined standard uncertainties u_c , GRVs, MRVs and E_n numbers were then calculated and listed for all measurement methods, respectively.

G1 Nano gold 10 nm

Table B1. Reported AFM results for G1

AFM results for G1																	
LAB	Draft A1		Draft A2			Draft A2 with Paule-Mandel adjustment			Degrees of equivalence based on Draft A1			Degrees of equivalence based on Draft A2			Degrees of equivalence based on Draft A2 with Paule-Mandel adjustment		
	d_x	$u(d_x)$	Deformation	d_y	$u(d_y)$	u_{PM}	d_z	$u(d_z)$	$d_x - d_{GRV}$	$u(d_x - d_{GRV})$	E_n	$d_y - d_{GRV}$	$u(d_y - d_{GRV})$	E_n	$d_z - d_{GRV}$	$u(d_z - d_{GRV})$	E_n
	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm		nm	nm		nm	nm	
CENAM	8.2	0.74	-	8.2	0.74	0	8.2	0.74	-0.10	0.74	-0.07	-0.10	0.74	-0.07	-0.10	0.74	-0.07
CMS	8.8	0.6	0.715	9.5	0.6	0	9.5	0.6	0.50	0.60	0.42	1.20	0.60	1.01	1.20	0.60	1.01
INRiM	7.2	1.0	0.7	7.9	1.0	0	7.9	1.0	-1.10	1.00	-0.55	-0.40	1.00	-0.20	-0.40	1.00	-0.20
METAS	7.3	0.8	0.74	8.0	0.85	0	8.0	0.85	-1.00	0.80	-0.62	-0.30	0.85	-0.18	-0.30	0.85	-0.18
NIM	9.68	1.15	-	9.68	1.17	0	9.68	1.17	1.38	1.15	0.60	1.38	1.17	0.59	1.38	1.17	0.59
NIMT	7.875	1.43	0.688	8.563	1.44	0	8.563	1.44	-0.42	1.43	-0.15	0.26	1.44	0.09	0.26	1.44	0.09
NMIA	6.2	0.4	0.8	7.0	0.5	0	7.0	0.5	-2.10	0.40	-2.63	-1.30	0.49	-1.31	-1.30	0.49	-1.31
PTB	8.0	1.4	0.715	8.7	1.4	0	8.7	1.4	-0.30	1.40	-0.11	0.40	1.40	0.14	0.40	1.40	0.14

d_x : diameter of particles reported at Draft A1

$u(d_x)$: combined standard uncertainty reported at Draft A1

d_y : diameter of particles reported at Draft A2

$u(d_y)$: combined standard uncertainty reported at Draft A2

u_{PM} : uncertainty added for Paule-Mandel adjustment

d_z : diameter of particles reported at Draft A2 with Paule-Mandel adjustment

$u(d_z)$: combined standard uncertainty reported at Draft A2 with Paule-Mandel adjustment

d_{GRV} : global reference value of diameter of particles

Table B2. Reported EM results for G1

EM results for G1																
LAB	Draft A1		Draft A2		Draft A2 with Paule-Mandel adjustment			Degrees of equivalence at Draft A1			Degrees of equivalence at Draft A2			Degrees of equivalence at Draft A2 with Paule-Mandel adjustment		
	d_x	$u(d_x)$	d_y	$u(d_y)$	u_{PM}	d_z	$u(d_z)$	$d_x - d_{GRV}$	$u\,(d_x - d_{GRV})$	E_n	$d_y - d_{GRV}$	$u\,(d_y - d_{GRV})$	E_n	$d_z - d_{GRV}$	$u\,(d_z - d_{GRV})$	E_n
	nm	nm	nm	nm	nm	nm	nm	nm	nm		nm	nm		nm	nm	
CMS (SEM)	10.2	1.3	10.2	1.3	0	10.2	1.3	1.90	1.30	0.73	1.90	1.30	0.73	1.90	1.30	0.73
Inmetro (SEM)	11.3	0.5	11.3	0.5	0	11.3	0.5	3.00	0.51	2.97	3.00	0.51	2.97	3.00	0.51	2.97
INRiM (SEM)	9.2	2.3	9.2	2.3	0	9.2	2.3	0.90	2.30	0.20	0.90	2.30	0.20	0.90	2.30	0.20
NMISA (SEM)	11.3	2.39	11.3	2.39	0	11.3	2.39	3.00	2.39	0.63	3.00	2.39	0.63	3.00	2.39	0.63
PTB (TSEM)	8.7	0.9	8.7	0.9	0	8.7	0.9	0.40	0.90	0.22	0.40	0.90	0.22	0.40	0.90	0.22
Inmetro (TEM)	8.3	0.4	8.3	0.4	0	8.3	0.4	0.00	0.39	0.00	0.00	0.39	0.00	0.00	0.39	0.00
KRISS (TEM)	8.191	0.137	8.191	0.137	0	8.191	0.137	-0.11	0.11	-0.48	-0.11	0.11	-0.48	-0.11	0.11	-0.48
NMIA (TEM)	8.4	0.3	8.4	0.3	0	8.4	0.3	0.10	0.29	0.18	0.10	0.29	0.18	0.10	0.29	0.18

Table B3. Reported DMA results for G1

DMA results for G1																
LAB	Draft A1		Draft A2		Draft A2 with Paule-Mandel adjustment			Degrees of equivalence at Draft A1			Degrees of equivalence at Draft A2			Degrees of equivalence at Draft A2 with Paule-Mandel adjustment		
	d_x	$u(d_x)$	d_y	$u(d_y)$	u_{PM}	d_z	$u(d_z)$	$d_x - d_{GRV}$	$u\,(d_x - d_{GRV})$	E_n	$d_y - d_{GRV}$	$u\,(d_y - d_{GRV})$	E_n	$d_z - d_{GRV}$	$u\,(d_z - d_{GRV})$	E_n
	nm	nm	nm	nm	nm	nm	nm	nm	nm		nm	nm		nm	nm	
NMIJ	13.9	2.1	13.9	2.8	0	13.9	2.8	5.60	2.10	1.33	5.60	2.84	0.98	5.60	2.84	0.98

Table B4. Reported SAXS results for G1

SAXS results for G1																
LAB	Draft A1		Draft A2		Draft A2 with Paule-Mandel adjustment			Degrees of equivalence at Draft A1			Degrees of equivalence at Draft A2			Degrees of equivalence at Draft A2 with Paule-Mandel adjustment		
	d_x	$u(d_x)$	d_y	$u(d_y)$	u_{PM}	d_z	$u(d_z)$	$d_x - d_{GRV}$	$u\,(d_x - d_{GRV})$	E_n	$d_y - d_{GRV}$	$u\,(d_y - d_{GRV})$	E_n	$d_z - d_{GRV}$	$u\,(d_z - d_{GRV})$	E_n
	nm	nm	nm	nm	nm	nm	nm	nm	nm		nm	nm		nm	nm	
PTB	8.33	0.11	8.33	0.11	0	8.33	0.11	0.03	0.08	0.20	0.03	0.08	0.20	0.03	0.08	0.20

Table B5. Reported DLS results for G1

DLS results for G1										
LAB	Draft A1		Draft A2		Degrees of equivalence at Draft A1			Degrees of equivalence at Draft A2		
	d_x	$u(d_x)$	d_y	$u(d_y)$	$d_x - d_{MRV}$	$u(d_x - d_{MRV})$	E_n	$d_y - d_{MRV}$	$u(d_y - d_{MRV})$	E_n
	nm	nm	nm	nm	nm	nm		nm	nm	
CENAM	14.52	0.42	14.52	0.42	2.31	0.48	2.42	2.31	0.48	2.42
CMS	10.4	0.7	10.4	3.0	-1.81	0.75	-1.21	-1.81	2.99	-0.30
KRISS	9.8	1.2	9.8	1.2	-2.41	1.18	-1.02	-2.41	1.18	-1.02
NIM	14.74	0.66	14.74	0.79	2.53	0.70	1.81	2.53	0.82	1.54
NIMT	11.81	1.2	11.81	1.56	-0.40	1.20	-0.17	-0.40	1.54	-0.13
NMIA	12.1	0.2	12.1	0.4	-0.11	0.07	-0.85	-0.11	0.33	-0.17
NMIJ	10.6	0.3	10.6	2.9	-1.61	0.40	-2.00	-1.61	2.89	-0.28

d_x : diameter of particles reported at Draft A1

$u(d_x)$: combined standard uncertainty reported at Draft A1

d_y : diameter of particles reported at Draft A2

$u(d_y)$: combined standard uncertainty reported at Draft A2

d_{MRV} : method-dependent reference value of diameter of particles

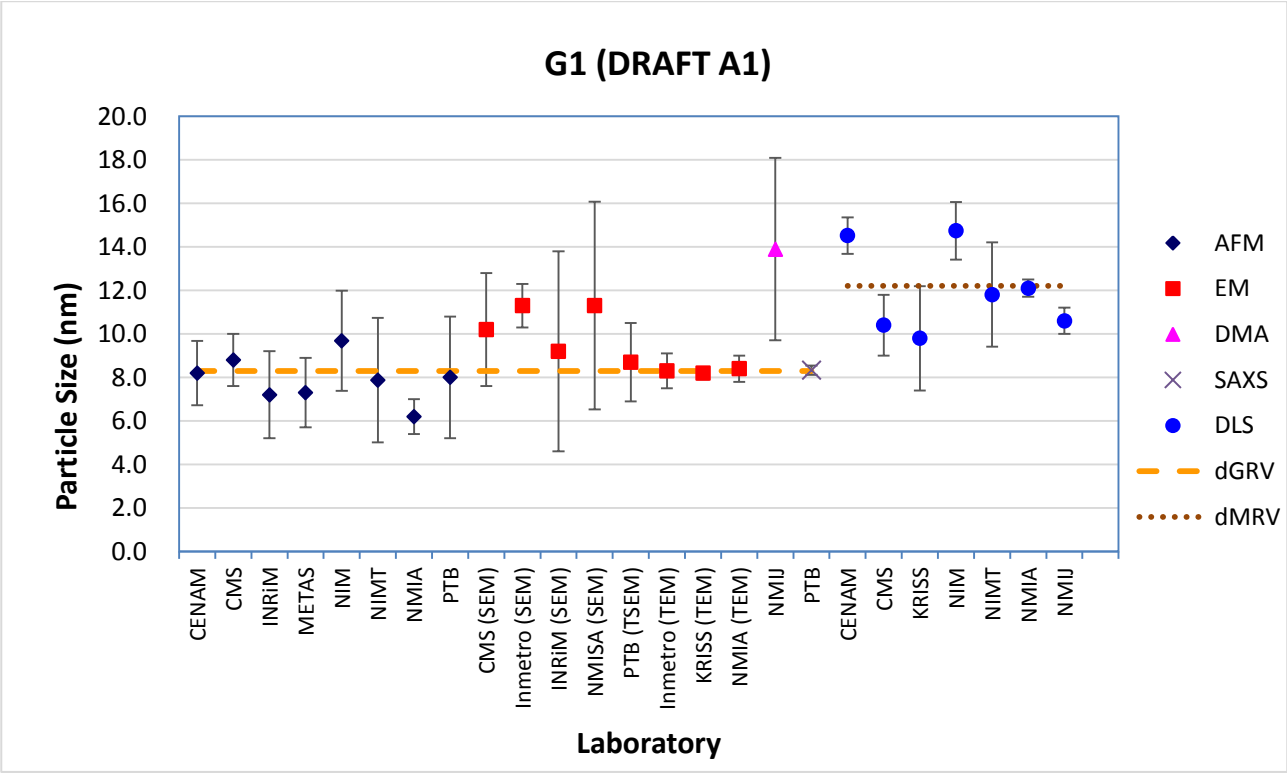

Figure B1. Measurement results and uncertainties reported by participants for G1 (Draft A1)

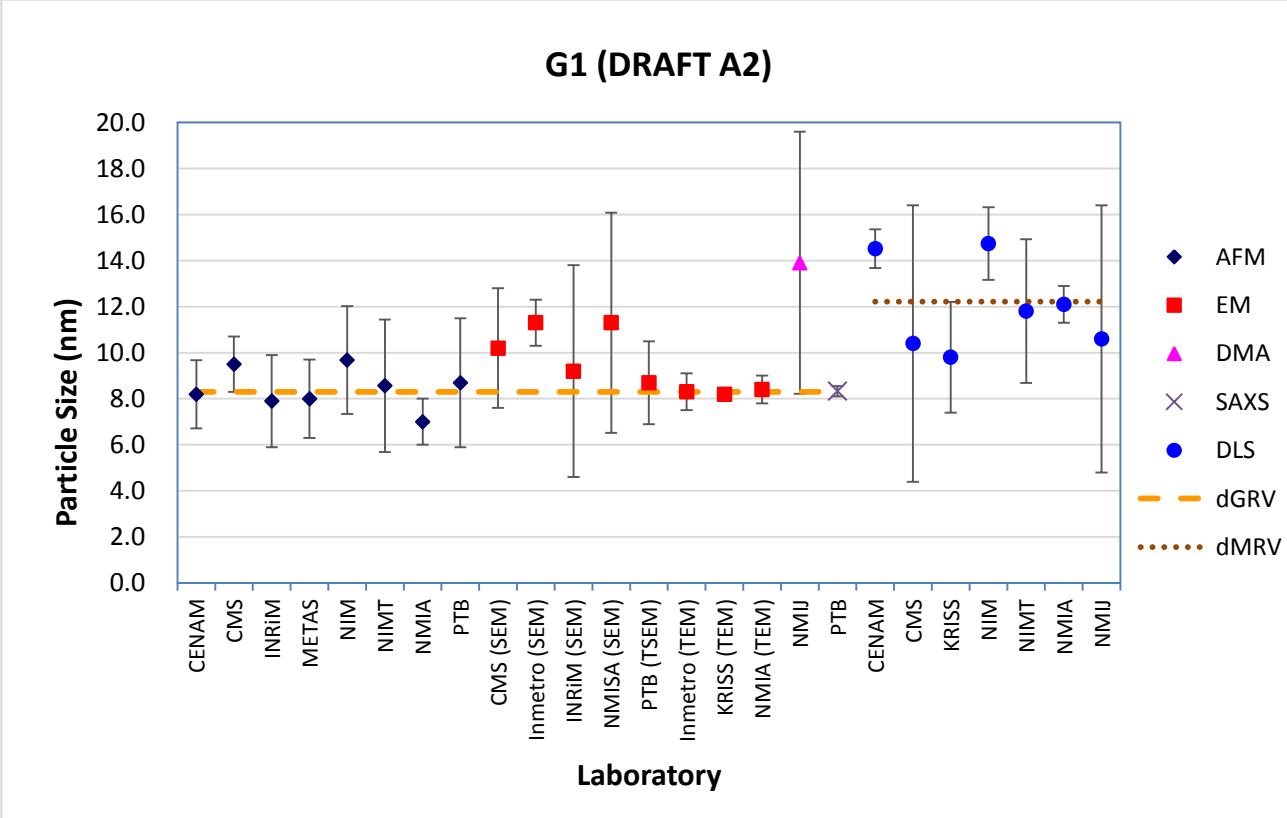

Figure B2. Measurement results and uncertainties reported by participants for G1 (Draft A2)

S2 Nano silver 20 nm

Table B6. Reported AFM results for S2

AFM results for S2																		
LAB	Draft A1		Draft A2			Draft A2 with Paule-Mandel adjustment			Degrees of equivalence based on Draft A1			Degrees of equivalence based on Draft A2			Degrees of equivalence based on Draft A2 with Paule-Mandel adjustment		
	d_x	$u(d_x)$	Deformation	d_y	$u(d_y)$	u_{PM}	d_z	$u(d_z)$	$d_x - d_{GRV}$	$u\,(d_x - d_{GRV})$	E_n	$d_y - d_{GRV}$	$u(d_y - d_{GRV})$	E_n	$d_z - d_{GRV}$	$u(d_z - d_{GRV})$	E_n
	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm		nm	nm		nm	nm	
CENAM	19.3	2.15	-	19.3	2.15	0	19.3	2.15	-0.36	2.14	-0.08	-0.36	2.14	-0.08	-0.36	2.14	-0.08
CMS	19.1	0.7	0.688	19.8	0.7	0	19.8	0.7	-0.56	0.66	-0.42	0.14	0.66	0.11	0.14	0.66	0.11
INRiM	16.9	1	0.7	17.6	1.1	0	17.6	1.1	-2.76	1.00	-1.38	-2.06	1.08	-0.96	-2.06	1.08	-0.96
METAS	18.2	0.9	-	18.2	0.9	0	18.2	0.9	-1.46	0.87	-0.84	-1.46	0.87	-0.84	-1.46	0.87	-0.84
NIM	21.3	2.38	-	21.3	2.38	0	21.3	2.38	1.64	2.37	0.35	1.64	2.37	0.35	1.64	2.37	0.35
NIMT	21.023	1.81	0.675	21.698	1.82	0	21.698	1.82	1.37	1.80	0.38	2.04	1.81	0.57	2.04	1.81	0.57
NMIA	17.0	0.6	1.1	18.1	0.7	0	18.1	0.7	-2.66	0.59	-2.27	-1.56	0.66	-1.18	-1.56	0.66	-1.18
PTB	19.3	1.2	0.688	20.0	1.2	0	20	1.2	-0.36	1.18	-0.15	0.34	1.18	0.15	0.34	1.18	0.15

Table B7. Reported EM results for S2

EM results for S2																	
LAB	Draft A1		Draft A2		Draft A2 with Paule-Mandel adjustment			Degrees of equivalence at Draft A1			Degrees of equivalence at Draft A2			Degrees of equivalence at Draft A2 with Paule-Mandel adjustment		
	d_x	$u(d_x)$	d_y	$u(d_y)$	u_{PM}	d_z	$u(d_z)$	$d_x - d_{GRV}$	$u\,(d_x - d_{GRV})$	E_n	$d_y - d_{GRV}$	$u\,(d_y - d_{GRV})$	E_n	$d_z - d_{GRV}$	$u\,(d_z - d_{GRV})$	E_n
	nm	nm	nm	nm	nm	nm	nm	nm	nm		nm	nm		nm	nm	
CMS(SEM)	22.8	1.3	22.8	1.3	0	22.8	1.3	3.14	1.28	1.23	3.14	1.28	1.23	3.14	1.28	1.23
Inmetro(SEM)	24.2	1.1	24.2	1.1	0	24.2	1.1	4.54	1.12	2.02	4.54	1.12	2.02	4.54	1.12	2.02
INRiM(SEM)	33.1	4.1	33.1	4.1	0	33.1	4.1	13.44	4.11	1.64	13.44	4.11	1.64	13.44	4.11	1.64
NMISA(SEM)	23.3	2.66	23.3	2.66	0	23.3	2.66	3.64	2.65	0.69	3.64	2.65	0.69	3.64	2.65	0.69
PTB (TSEM)	20.4	1.1	20.4	1.1	0	20.4	1.1	0.74	1.08	0.35	0.74	1.08	0.35	0.74	1.08	0.35
Inmetro (TEM)	19.4	0.8	19.4	0.8	0	19.4	0.8	-0.26	0.77	-0.17	-0.26	0.77	-0.17	-0.26	0.77	-0.17
KRISS (TEM)	21.323	1.494	21.323	1.494	0	21.323	1.494	1.67	1.48	0.56	1.67	1.48	0.56	1.67	1.48	0.56
NMIA (TEM)	19.2	0.7	19.2	0.7	0	19.2	0.7	-0.46	0.66	-0.35	-0.46	0.66	-0.35	-0.46	0.66	-0.35

Table B8. SAXS results for S2

SAXS results for S2																
LAB	Draft A1		Draft A2		Draft A2 with Paule-Mandel adjustment			Degrees of equivalence at Draft A1			Degrees of equivalence at Draft A2			Degrees of equivalence at Draft A2 with Paule-Mandel adjustment		
	d_x	$u(d_x)$	d_y	$u(d_y)$	u_{PM}	d_z	$u(d_z)$	$d_x - d_{GRV}$	$u\,(d_x - d_{GRV})$	E_n	$d_y - d_{GRV}$	$u\,(d_y - d_{GRV})$	E_n	$d_z - d_{GRV}$	$u\,(d_z - d_{GRV})$	E_n
	nm	nm	nm	nm	nm	nm	nm	nm	nm		nm	nm		nm	nm	
PTB	20.0	0.4	20.0	0.4	0	20.0	0.4	0.34	0.33	0.52	0.34	0.33	0.52	0.34	0.33	0.52

Table B9. DLS results for S2

DLS results for S2										
LAB	Draft A1		Draft A2		Degrees of equivalence at Draft A1			Degrees of equivalence at Draft A2		
	d_x	$u(d_x)$	d_y	$u(d_y)$	$d_x - d_{MRV}$	$u(d_x - d_{MRV})$	E_n	$d_y - d_{MRV}$	$u\,(d_y - d_{MRV})$	E_n
	nm	nm	nm	nm	nm	nm		nm	nm	
CENAM	28.39	1.31	28.39	1.31	3.55	1.37	1.29	3.55	1.37	1.29
CMS	24.3	1.4	24.3	4.0	-0.54	1.50	-0.18	-0.54	3.98	-0.07
KRISS	23.5	1.3	23.5	1.3	-1.34	1.23	-0.54	-1.34	1.23	-0.54
NIM	26.9	0.89	26.9	2.0	2.06	0.92	1.12	2.06	1.96	0.53
NIMT	24.4	1.2	24.4	2.1	-0.44	1.22	-0.18	-0.44	2.06	-0.11
NMIA	24.9	0.3	24.9	1.1	0.06	0.22	0.14	0.06	1.02	0.03
NMIJ	25.1	0.4	25.1	3.7	0.26	0.66	0.20	0.26	3.68	0.04

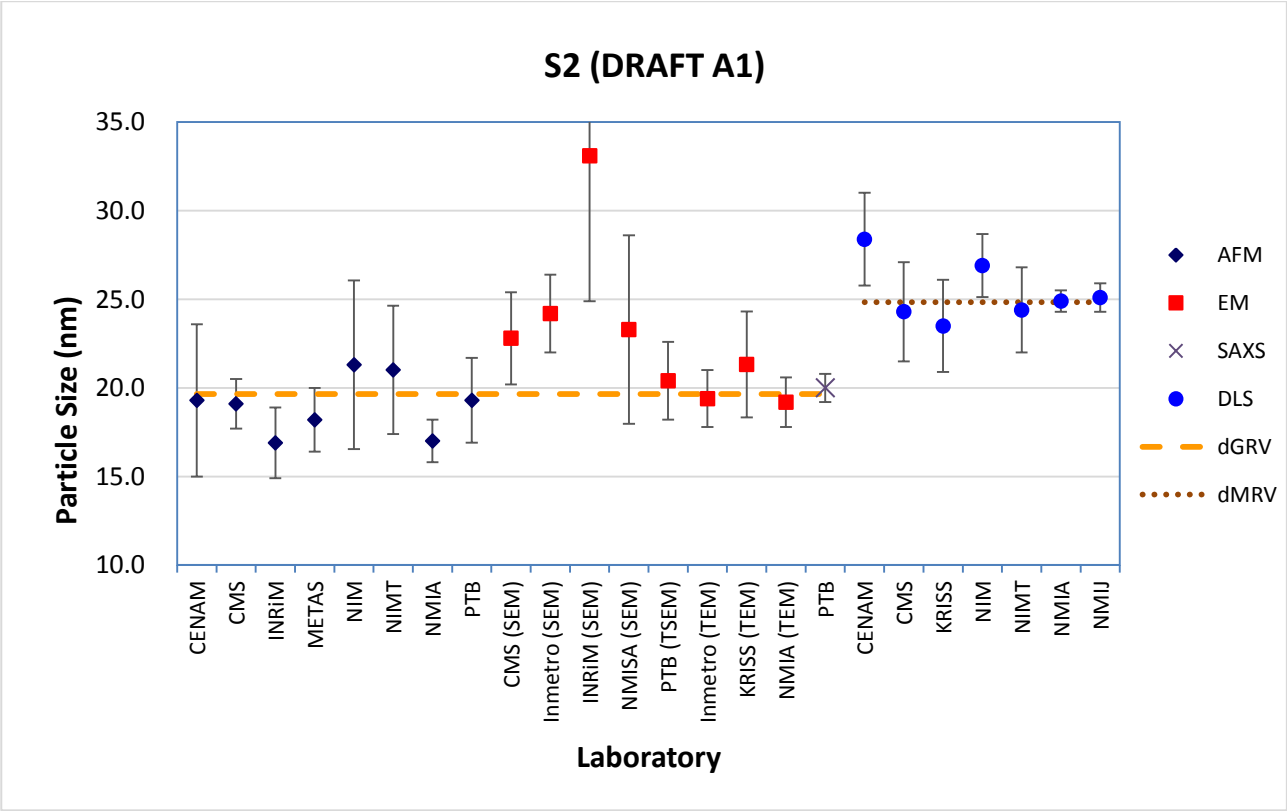

Figure B3. Measurement results and uncertainties reported by participants for S2 (Draft A1)

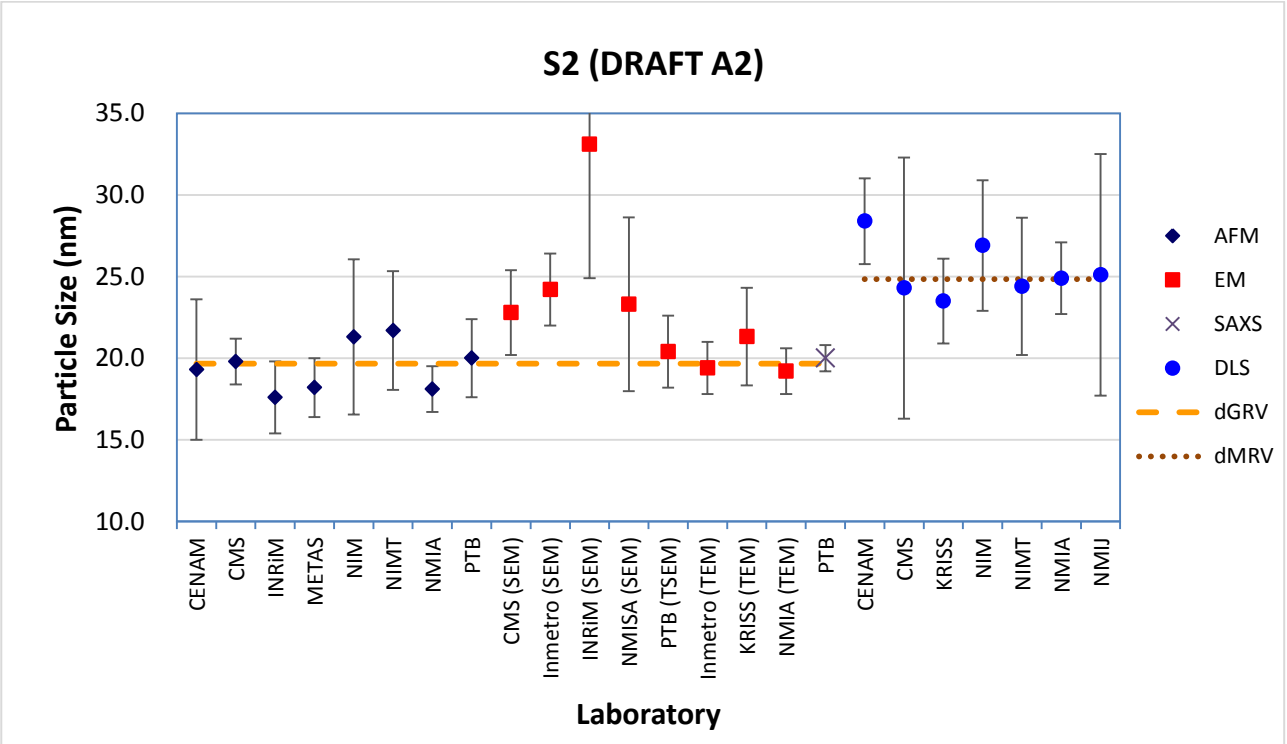

Figure B4. Measurement results and uncertainties reported by participants for S2 (Draft A2)

P3 Polystyrene latex 30 nm

Table B10. AFM results for P3

AFM results for P3																		
LAB	Draft A1		Draft A2			Draft A2 with Paule-Mandel adjustment			Degrees of equivalence based on Draft A1			Degrees of equivalence based on Draft A2			Degrees of equivalence based on Draft A2 with Paule-Mandel adjustment		
	d_x	$u(d_x)$	Deformation	d_y	$u(d_y)$	u_{PM}	d_z	$u(d_z)$	$d_x - d_{GRV}$	$u\,(d_x - d_{GRV})$	E_n	$d_y - d_{GRV}$	$u(d_y - d_{GRV})$	E_n	$d_z - d_{GRV}$	$u(d_z - d_{GRV})$	E_n
	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm		nm	nm		nm	nm	
CENAM	27.1	2.42	-	27.1	2.42	1.581	27.1	2.89	0.61	2.52	0.12	0.61	2.52	0.12	0.61	2.72	0.11
CMS	20.6	0.7	3.953	24.6	1.3	1.581	24.6	2.05	-5.89	1.18	-2.50	-1.89	1.48	-0.64	-1.89	1.79	-0.53
INRiM	25.7	1.3	4.0	29.7	1.7	1.581	29.7	2.32	-0.79	1.63	-0.24	3.21	1.86	0.86	3.21	2.12	0.76
METAS	19.6	0.9	4.43	24.1	1.2	1.581	24.1	1.98	-6.89	1.26	-2.73	-2.39	1.39	-0.86	-2.39	1.72	-0.69
NIM	23.5	2.72	-	23.5	2.98	1.581	23.5	3.37	-2.99	2.89	-0.52	-2.99	3.06	-0.49	-2.99	3.23	-0.46
NIMT	25.017	14.83	-	25.017	14.83	1.581	25.017	14.91	-1.48	14.85	-0.05	-1.48	14.85	-0.05	-1.48	14.88	-0.05
NMIA	21.7	0.8	4.3	26	1.5	1.581	26	2.18	-4.79	1.27	-1.89	-0.49	1.66	-0.15	-0.49	1.94	-0.13
NMIJ-H	23.3	3.71	3.95	27.25	1.25	1.581	27.25	2.02	-3.19	3.84	-0.42	0.76	1.45	0.26	0.76	1.77	0.21
NMIJ-P	25.05	2.13	-	25.05	2.13	1.581	25.05	2.65	-1.44	2.24	-0.32	-1.44	2.24	-0.32	-1.44	2.46	-0.29
PTB	23.1	2.6	3.95	27.1	2.8	1.581	27.1	3.22	-3.39	2.76	-0.61	0.61	2.89	0.11	0.61	3.06	0.10

Table B11. EM results for P3

EM results for P3																	
LAB	Draft A1		Draft A2		Draft A2 with Paule-Mandel adjustment			Degrees of equivalence at Draft A1			Degrees of equivalence at Draft A2			Degrees of equivalence at Draft A2 with Paule-Mandel adjustment		
	d_x	$u(d_x)$	d_y	$u(d_y)$	u_{PM}	d_z	$u(d_z)$	$d_x - d_{GRV}$	$u\,(d_x - d_{GRV})$	E_n	$d_y - d_{GRV}$	$u\,(d_y - d_{GRV})$	E_n	$d_z - d_{GRV}$	$u\,(d_z - d_{GRV})$	E_n
	nm	nm	nm	nm	nm	nm	nm	nm	nm		nm	nm		nm	nm	
CMS(SEM)	26.5	1.4	26.5	1.4	1.581	26.5	2.11	0.01	1.62	0.00	0.01	1.62	0.00	0.01	1.87	0.00
NMISA(SEM)	30.1	2.98	30.1	2.98	1.581	30.1	3.37	3.61	3.09	0.58	3.61	3.09	0.58	3.61	3.23	0.56
Inmetro(SEM)	23.7	1.0	23.7	1.0	1.581	23.7	1.87	-2.79	1.29	-1.08	-2.79	1.29	-1.08	-2.79	1.59	-0.88
PTB (TSEM)	26.5	1.3	26.5	1.3	1.581	26.5	2.05	0.01	1.54	0.00	0.01	1.54	0.00	0.01	1.79	0.00

Table B12. DMA results for P3

DMA results for P3																	
LAB	Draft A1		Draft A2		Draft A2 with Paule-Mandel adjustment			Degrees of equivalence at Draft A1			Degrees of equivalence at Draft A2			Degrees of equivalence at Draft A2 with Paule-Mandel adjustment		
	d_x	$u(d_x)$	d_y	$u(d_y)$	u_{PM}	d_z	$u(d_z)$	$d_x - d_{GRV}$	$u\,(d_x - d_{GRV})$	E_n	$d_y - d_{GRV}$	$u\,(d_y - d_{GRV})$	E_n	$d_z - d_{GRV}$	$u\,(d_z - d_{GRV})$	E_n
	nm	nm	nm	nm	nm	nm	nm	nm	nm		nm	nm		nm	nm	
CMS	29.04	0.44	29.04	2.20	1.581	29.04	2.71	2.55	1.07	1.19	2.55	2.13	0.60	2.55	2.53	0.50
KRISS	29.13	0.61	29.13	2.24	1.581	29.13	2.75	2.64	1.15	1.15	2.64	2.18	0.61	2.64	2.56	0.51
NMIJ	29.16	0.62	29.16	2.25	1.581	29.16	2.75	2.67	1.15	1.16	2.67	2.18	0.61	2.67	2.57	0.52

Table B13. SAXS results for P3

SAXS results for P3																	
LAB	Draft A1		Draft A2		Draft A2 with Paule-Mandel adjustment			Degrees of equivalence at Draft A1			Degrees of equivalence at Draft A2			Degrees of equivalence at Draft A2 with Paule-Mandel adjustment		
	d_x	$u(d_x)$	d_y	$u(d_y)$	u_{PM}	d_z	$u(d_z)$	$d_x - d_{GRV}$	$u\,(d_x - d_{GRV})$	E_n	$d_y - d_{GRV}$	$u\,(d_y - d_{GRV})$	E_n	$d_z - d_{GRV}$	$u\,(d_z - d_{GRV})$	E_n
	nm	nm	nm	nm	nm	nm	nm	nm	nm		nm	nm		nm	nm	
PTB	28.4	1.2	28.4	1.2	1.581	28.4	1.98	1.91	1.30	0.73	1.91	1.30	0.73	1.91	1.72	0.55

Table B14. DLS results for P3

DLS results for P3										
LAB	Draft A1		Draft A2		Degrees of equivalence at Draft A1			Degrees of equivalence at Draft A2		
	d_x	$u(d_x)$	d_y	$u(d_y)$	$d_x - d_{MRV}$	$u(d_x - d_{MRV})$	E_n	$d_y - d_{MRV}$	$u\,(d_y - d_{MRV})$	E_n
	nm	nm	nm	nm	nm	nm		nm	nm	
CENAM	31.49	1.41	31.49	1.41	-1.19	1.14	-0.52	-1.19	1.14	-0.52
KRISS	34.5	1.2	34.5	1.2	1.82	0.87	1.04	1.82	0.87	1.04
CMS	34.2	1.9	34.2	5.9	1.52	2.02	0.38	1.52	5.84	0.13
NIM	31.3	1.19	31.3	2.6	-1.38	1.10	-0.63	-1.38	2.47	-0.28
NIMT	28.58	1.7	28.58	9.68	-4.10	1.89	-1.08	-4.10	9.72	-0.21
NMIA	36.3	0.5	36.3	7.9	3.62	0.96	1.88	3.62	7.94	0.23
NMIJ	33.4	0.4	33.4	5.6	0.72	0.78	0.46	0.72	5.54	0.07

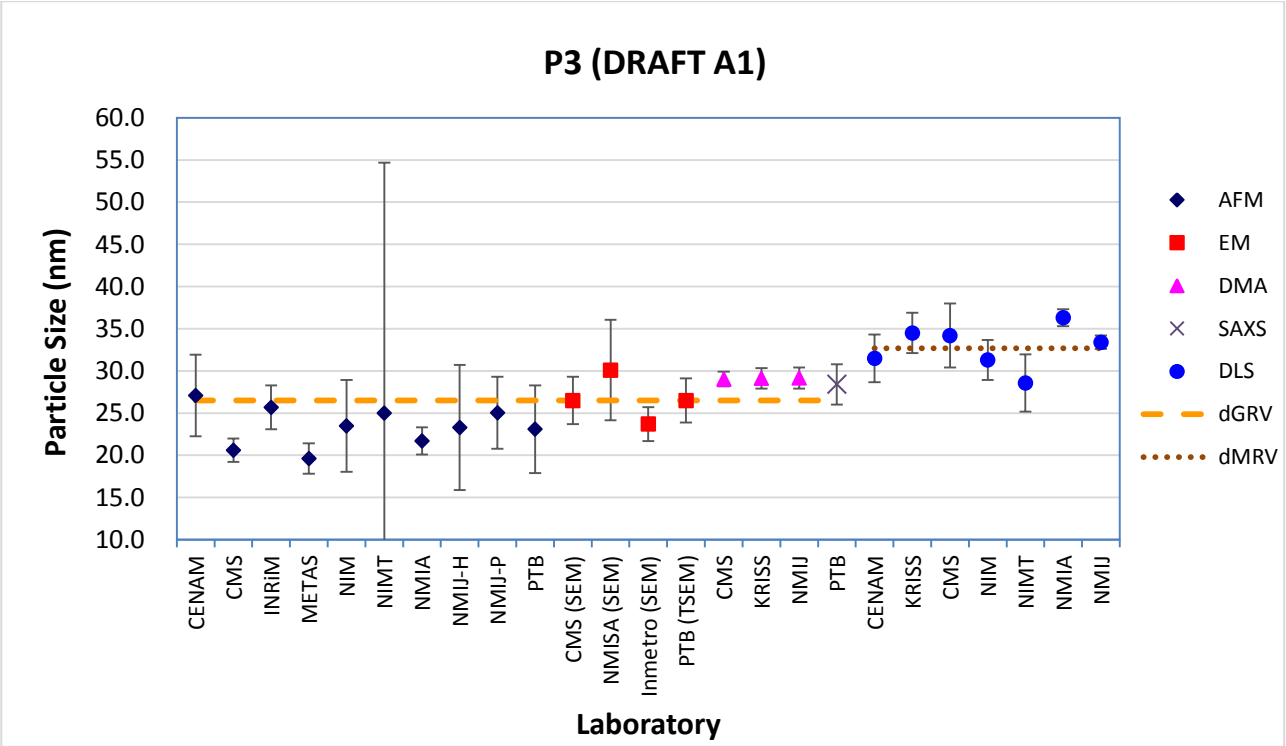

Figure B5. Measurement results and uncertainties reported by participants for P3 (Draft A1)

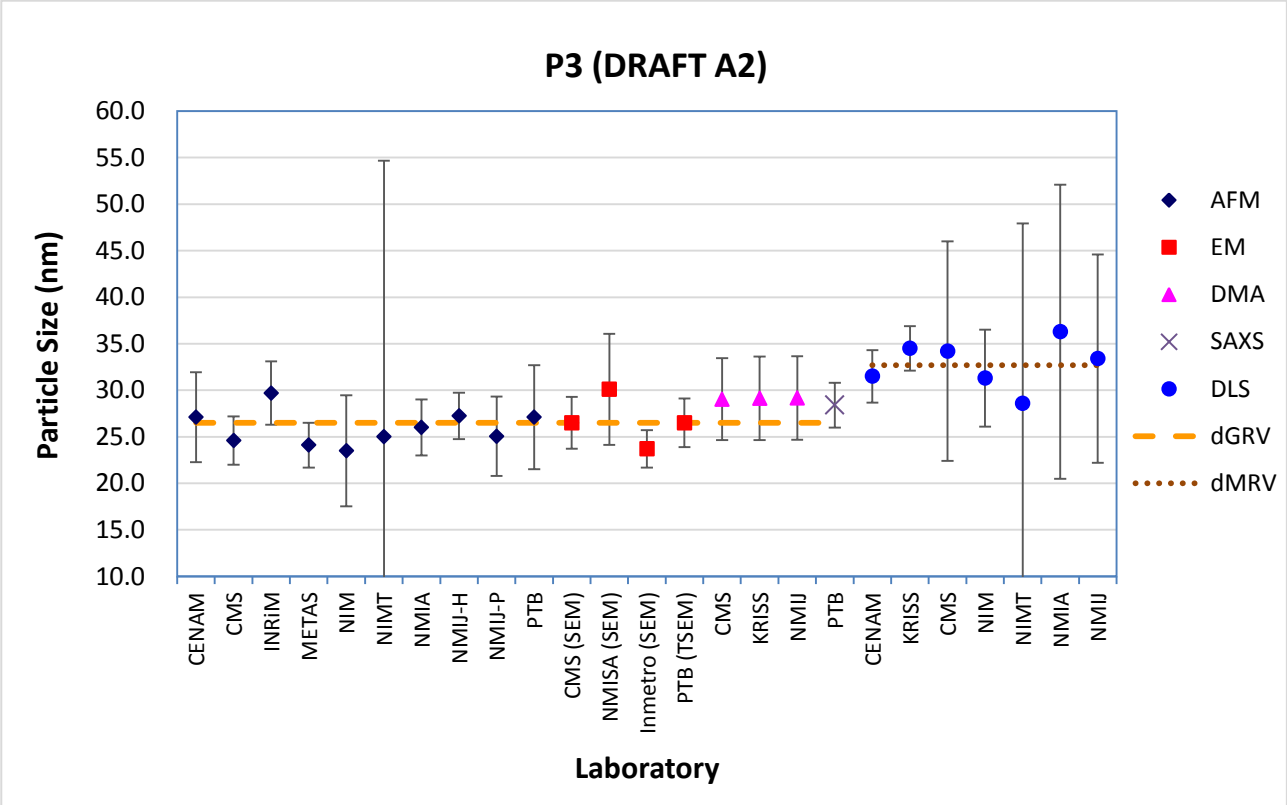

Figure B6. Measurement results and uncertainties reported by participants for P3 (Draft A2)

P4 Polystyrene latex 100 nm

Table B15. AFM results for P4

AFM results for P4																	
LAB	**Draft A1**		**Draft A2**			**Draft A2 with Paule-Mandel adjustment**			**Degrees of equivalence based on Draft A1**			**Degrees of equivalence based on Draft A2**			**Degrees of equivalence based on Draft A2 with Paule-Mandel adjustment**		
	d_x	$u(d_x)$	Deformation	d_y	$u(d_y)$	u_{PM}	d_z	$u(d_z)$	$d_x - d_{GRV}$	$u\,(d_x - d_{GRV})$	E_n	$d_y - d_{GRV}$	$u(d_y - d_{GRV})$	E_n	$d_z - d_{GRV}$	$u(d_z - d_{GRV})$	E_n
	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm		nm	nm		nm	nm	
CENAM	91.0	1.94	-	91.0	1.94	0.934	91	2.15	-8.03	1.98	-2.03	-8.03	1.98	-2.03	-8.03	2.06	-1.95
CMS-H	95.5	0.9	3.559	99.1	1.4	0.934	99.1	1.68	-3.53	1.09	-1.61	0.07	1.45	0.02	0.07	1.56	0.02
CMS-P	97.0	1.8	-	97.0	1.8	0.934	97.0	2.03	-2.03	1.84	-0.55	-2.03	1.84	-0.55	-2.03	1.93	-0.53
DFM	98.4	1.1	-	98.4	1.1	0.934	98.4	1.44	-0.63	1.17	-0.27	-0.63	1.17	-0.27	-0.63	1.30	-0.24
INRiM-H	92.1	1.6	3.6	95.7	1.9	0.934	95.7	2.12	-6.93	1.71	-2.02	-3.33	1.94	-0.86	-3.33	2.02	-0.82
INRiM-P	97.4	3.2	-	97.4	3.2	0.934	97.4	3.33	-1.63	3.22	-0.25	-1.63	3.22	-0.25	-1.63	3.27	-0.25
METAS	95.9	2.0	3.56	99.4	2.1	0.934	99.4	2.30	-3.13	2.07	-0.76	0.37	2.13	0.09	0.37	2.21	0.08
NIM	99.2	4.09	-	99.2	4.22	0.934	99.2	4.32	0.17	4.14	0.02	0.17	4.24	0.02	0.17	4.28	0.02
NMIA	95.0	0.7	3.6	99.0	1.3	0.934	99	1.60	-4.03	0.94	-2.15	-0.03	1.36	-0.01	-0.03	1.47	-0.01
NMIJ-H	95.42	5.57	3.56	98.98	1.07	0.934	98.98	1.42	-3.61	5.60	-0.32	-0.05	1.14	-0.02	-0.05	1.27	-0.02
NMIJ-P	96.99	3.17	-	96.99	3.17	0.934	96.99	3.30	-2.04	3.19	-0.32	-2.04	3.19	-0.32	-2.04	3.24	-0.31
NMIT	92.637	14.9	-	92.637	14.9	0.934	92.637	14.93	-6.39	14.90	-0.21	-6.39	14.90	-0.21	-6.39	14.92	-0.21
PTB	98.1	1.7	3.56	101.7	2.0	0.934	101.7	2.21	-0.93	1.81	-0.26	2.67	2.04	0.66	2.67	2.12	0.63

Table B16. EM results for P4

EM results for P4																
LAB	Draft A1		Draft A2		Draft A2 with Paule-Mandel adjustment			Degrees of equivalence at Draft A1			Degrees of equivalence at Draft A2			Degrees of equivalence at Draft A2 with Paule-Mandel adjustment		
	d_x	$u(d_x)$	d_y	$u(d_y)$	u_{PM}	d_z	$u(d_z)$	$d_x - d_{GRV}$	$u\,(d_x - d_{GRV})$	E_n	$d_y - d_{GRV}$	$u\,(d_y - d_{GRV})$	E_n	$d_z - d_{GRV}$	$u\,(d_z - d_{GRV})$	E_n
	nm	nm	nm	nm	nm	nm	nm	nm	nm		nm	nm		nm	nm	
CENAM (SEM)	100.97	1.47	100.97	1.47	0.934	100.97	1.74	1.94	1.49	0.65	1.94	1.49	0.65	1.94	1.62	0.60
CMS (SEM)	100.5	3.7	100.5	3.7	0.934	100.5	3.82	1.47	3.71	0.20	1.47	3.71	0.20	1.47	3.76	0.20
Inmetro (SEM)	85.3	2.8	85.3	2.8	0.934	85.3	2.95	-13.73	2.87	-2.39	-13.73	2.87	-2.39	-13.73	2.94	-2.34
INRiM (SEM)	94.5	2.8	94.5	2.8	0.934	94.5	2.95	-4.53	2.81	-0.81	-4.53	2.81	-0.81	-4.53	2.88	-0.79
NIMT (SEM)	102.77	10.37	102.77	10.37	0.934	102.77	10.41	3.74	10.37	0.18	3.74	10.37	0.18	3.74	10.39	0.18
NMIJ (SEM)	97.3	3.4	97.3	3.4	0.934	97.3	3.53	-1.73	3.41	-0.25	-1.73	3.41	-0.25	-1.73	3.47	-0.25
NMISA (SEM)	99.9	3.73	99.9	3.73	0.934	99.9	3.85	0.87	3.74	0.12	0.87	3.74	0.12	0.87	3.79	0.11
PTB (TSEM)	100.5	2.0	100.5	2.0	0.934	100.5	2.21	1.47	2.02	0.36	1.47	2.02	0.36	1.47	2.12	0.35
Inmetro (TEM)	101.0	2.5	101.0	2.5	0.934	101.0	2.67	1.97	2.51	0.39	1.97	2.51	0.39	1.97	2.59	0.38
NMIA (TEM)	96.3	1.6	96.3	1.6	0.934	96.3	1.85	-2.73	1.62	-0.84	-2.73	1.62	-0.84	-2.73	1.74	-0.78

Table B17. DMA results for P4

DMA results for P4																
LAB	Draft A1		Draft A2		Draft A2 with Paule-Mandel adjustment			Degrees of equivalence at Draft A1			Degrees of equivalence at Draft A2			Degrees of equivalence at Draft A2 with Paule-Mandel adjustment		
	d_x	$u(d_x)$	d_y	$u(d_y)$	u_{PM}	d_z	$u(d_z)$	$d_x - d_{GRV}$	$u\,(d_x - d_{GRV})$	E_n	$d_y - d_{GRV}$	$u\,(d_y - d_{GRV})$	E_n	$d_z - d_{GRV}$	$u\,(d_z - d_{GRV})$	E_n
	nm	nm	nm	nm	nm	nm	nm	nm	nm		nm	nm		nm	nm	
CMS	100.07	0.43	100.07	0.43	0.934	100.07	1.03	1.04	0.70	0.74	1.04	0.70	0.74	1.04	0.81	0.64
KRISS	100.05	0.98	100.05	0.98	0.934	100.05	1.35	1.02	1.12	0.45	1.02	1.12	0.45	1.02	1.20	0.42
LNE	100.93	1.02	100.93	1.02	0.934	100.93	1.38	1.90	1.16	0.82	1.90	1.16	0.82	1.90	1.23	0.77
NMIJ	100.00	0.85	100.00	0.85	0.934	100.00	1.26	0.97	1.01	0.48	0.97	1.01	0.48	0.97	1.10	0.44

Table B18. SAXS results for P4

SAXS results for P4																
LAB	Draft A1		Draft A2		Draft A2 with Paule-Mandel adjustment			Degrees of equivalence at Draft A1			Degrees of equivalence at Draft A2			Degrees of equivalence at Draft A2 with Paule-Mandel adjustment		
	d_x	$u(d_x)$	d_y	$u(d_y)$	u_{PM}	d_z	$u(d_z)$	$d_x - d_{GRV}$	$u\,(d_x - d_{GRV})$	E_n	$d_y - d_{GRV}$	$u\,(d_y - d_{GRV})$	E_n	$d_z - d_{GRV}$	$u\,(d_z - d_{GRV})$	E_n
	nm	nm	nm	nm	nm	nm	nm	nm	nm		nm	nm		nm	nm	
PTB	99.5	3.8	99.5	3.8	0.934	99.5	3.91	0.47	3.75	0.06	0.47	3.75	0.06	0.47	3.86	0.06

Table B19. DLS results for P4

DLS results for P4										
LAB	Draft A1		Draft A2		Degrees of equivalence at Draft A1			Degrees of equivalence at Draft A2		
	d_x	$u(d_x)$	d_y	$u(d_y)$	$d_x - d_{MRV}$	$u(d_x - d_{MRV})$	E_n	$d_y - d_{MRV}$	$u\,(d_y - d_{MRV})$	E_n
	nm	nm	nm	nm	nm	nm		nm	nm	
CENAM	102.43	1.63	102.43	1.63	-2.70	1.40	-0.97	-2.70	1.40	-0.97
CMS	106.1	2.1	106.1	3.7	0.97	2.15	0.22	0.97	3.60	0.13
KRISS	105.9	1.5	105.9	1.5	0.77	1.25	0.31	0.77	1.25	0.31
NIM	103.3	1.49	103.3	3.8	-1.83	1.61	-0.57	-1.83	3.71	-0.25
NIMT	102.61	1.4	102.61	7.04	-2.52	1.83	-0.69	-2.52	6.99	-0.18
NMIA	108	1.1	108	7	2.87	1.38	1.04	2.87	7.05	0.20
NMIJ	104.8	0.5	104.8	3.0	-0.33	0.67	-0.25	-0.33	2.88	-0.06

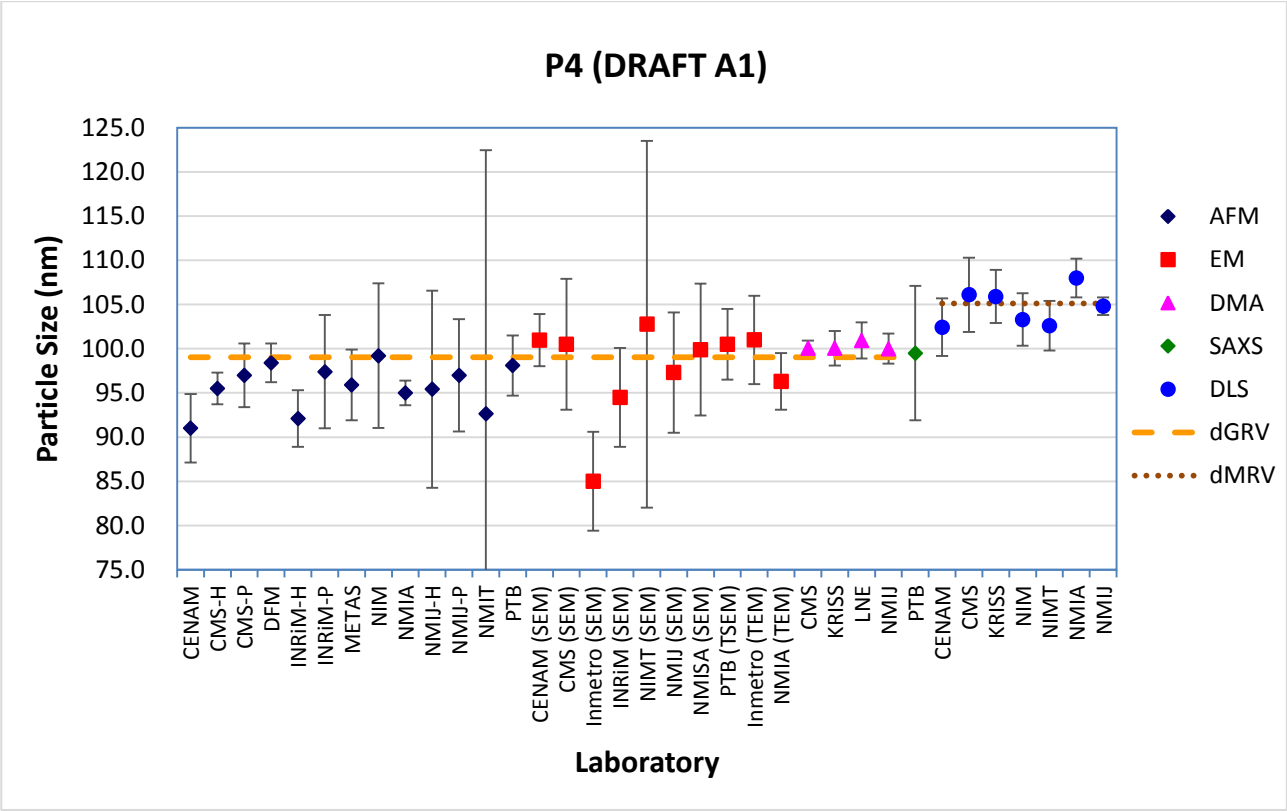

Figure B7. Measurement results and uncertainties reported by participants for P4 (Draft A1)

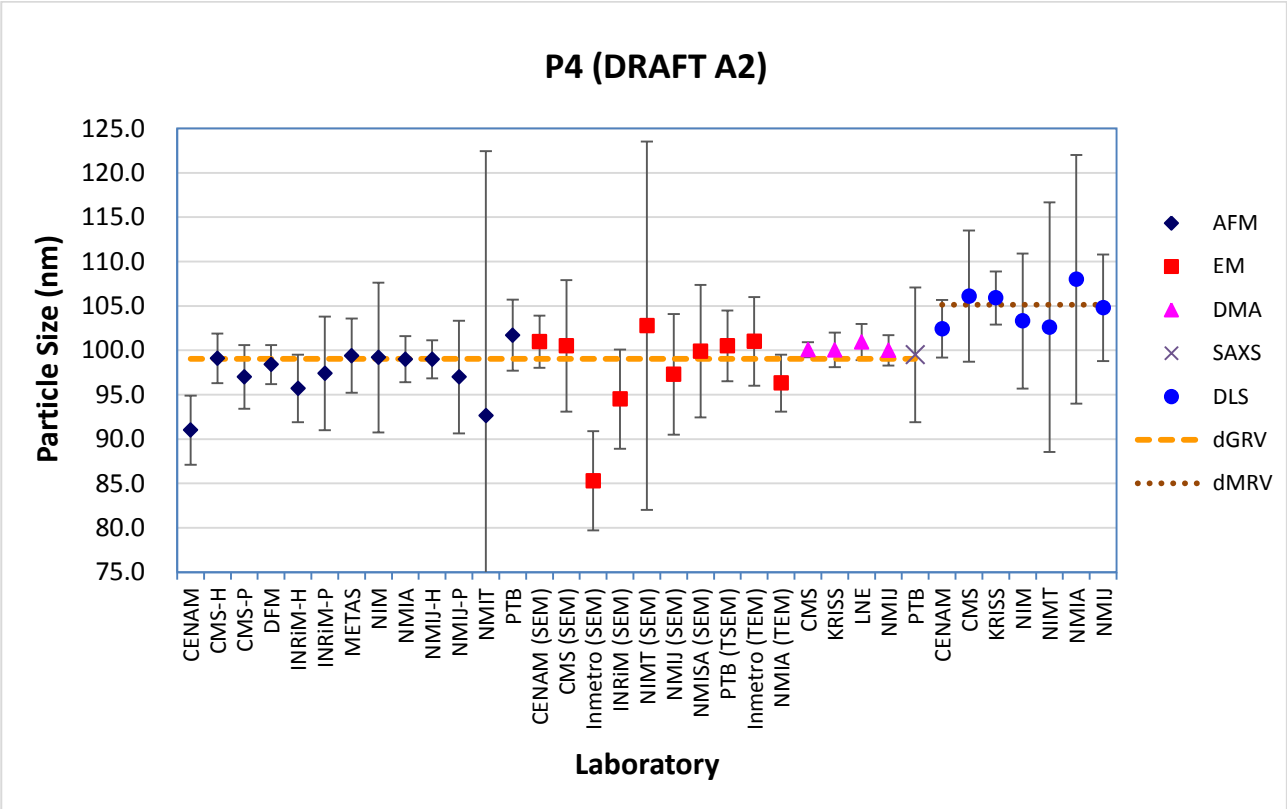

Figure B8. Measurement results and uncertainties reported by participants for P4 (Draft A2)

P5 Polystyrene latex 300 nm

Table B20. AFM results for P5

AFM results for P5																	
LAB	Draft A1		Draft A2			Draft A2 with Paule-Mandel adjustment			Degrees of equivalence based on Draft A1			Degrees of equivalence based on Draft A2			Degrees of equivalence based on Draft A2 with Paule-Mandel adjustment		
	d_x	$u(d_x)$	Deformation	d_y	$u(d_y)$	u_{PM}	d_z	$u(d_z)$	$d_x - d_{GRV}$	$u(d_x - d_{GRV})$	E_n	$d_y - d_{GRV}$	$u(d_y - d_{GRV})$	E_n	$d_z - d_{GRV}$	$u(d_z - d_{GRV})$	E_n
	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm		nm	nm		nm	nm	
CENAM	305.6	2.09	-	305.6	2.09	0	305.6	2.09	-0.13	2.01	-0.03	-0.13	2.01	-0.03	-0.13	2.01	-0.03
CMS-P	304.5	2.1	-	304.5	2.1	0	304.5	2.1	-1.23	2.02	-0.30	-1.23	2.02	-0.30	-1.23	2.02	-0.30
CMS-H	302.9	2.3	3.472	306.4	2.6	0	306.4	2.6	-2.83	2.34	-0.61	0.67	2.53	0.13	0.67	2.53	0.13
PTB	298.5	2.4	3.47	302.0	2.6	0	302.0	2.6	-7.23	2.42	-1.50	-3.73	2.53	-0.74	-3.73	2.53	-0.74
METAS	302.4	2.8	3.47	305.9	2.9	0	305.9	2.9	-3.33	2.80	-0.60	0.17	2.84	0.03	0.17	2.84	0.03
NMIA	303	1	3.5	307	1.4	0	307	1.4	-2.73	1.03	-1.32	1.27	1.27	0.50	1.27	1.27	0.50
INRiM-P	305.2	4.4	-	305.2	4.4	0	305.2	4.4	-0.53	4.36	-0.06	-0.53	4.36	-0.06	-0.53	4.36	-0.06
INRiM-H	300.3	3.8	3.5	303.8	3.9	0	303.8	3.9	-5.43	3.80	-0.71	-1.93	3.86	-0.25	-1.93	3.86	-0.25
DFM	305.5	1.3	-	305.5	1.3	0	305.5	1.3	-0.23	1.16	-0.10	-0.23	1.16	-0.10	-0.23	1.16	-0.10
NIMT	269.76	16.11	-	269.758	16.11	0	269.76	16.11	-35.97	16.10	-1.12	-35.97	16.10	-1.12	-35.97	16.10	-1.12
NIM	314.6	5.88	-	314.6	5.96	0	314.6	5.96	8.87	5.89	0.75	8.87	5.93	0.75	8.87	5.93	0.75

Table B21. EM results for P5

EM results for P5																
LAB	Draft A1		Draft A2		Draft A2 with Paule-Mandel adjustment			Degrees of equivalence at Draft A1			Degrees of equivalence at Draft A2			Degrees of equivalence at Draft A2 with Paule-Mandel adjustment		
	d_x	$u(d_x)$	d_y	$u(d_y)$	u_{PM}	d_z	$u(d_z)$	$d_x - d_{GRV}$	$u\,(d_x - d_{GRV})$	E_n	$d_y - d_{GRV}$	$u\,(d_y - d_{GRV})$	E_n	$d_z - d_{GRV}$	$u\,(d_z - d_{GRV})$	E_n
	nm	nm	nm	nm	nm	nm	nm	nm	nm		nm	nm		nm	nm	
CENAM (SEM)	312.25	5.23	312.25	5.23	0	312.25	5.23	6.52	5.20	0.63	6.52	5.20	0.63	6.52	5.20	0.63
CMS (SEM)	312.1	9.7	312.1	9.7	0	312.1	9.7	6.37	9.68	0.33	6.37	9.68	0.33	6.37	9.68	0.33
Inmetro (SEM)	268.8	5.3	268.8	5.3	0	268.8	5.3	-36.93	5.33	-3.46	-36.93	5.33	-3.46	-36.93	5.33	-3.46
INRiM (SEM)	300.5	3.4	300.5	3.4	0	300.5	3.4	-5.23	3.35	-0.78	-5.23	3.35	-0.78	-5.23	3.35	-0.78
NIMT (SEM)	307.88	17.97	307.88	17.97	0	307.88	17.97	2.15	17.96	0.06	2.15	17.96	0.06	2.15	17.96	0.06
NMIJ (SEM)	308.5	3.3	308.5	3.3	0	308.5	3.3	2.77	3.25	0.43	2.77	3.25	0.43	2.77	3.25	0.43
NMISA (SEM)	313.1	10.3	313.1	10.3	0	313.1	10.3	7.37	10.28	0.36	7.37	10.28	0.36	7.37	10.28	0.36
Inmetro (TEM)	297.8	5.2	297.8	5.2	0	297.8	5.2	-7.93	5.17	-0.77	-7.93	5.17	-0.77	-7.93	5.17	-0.77
NMIA (TEM)	300	4	300	4	0	300	4	-5.73	3.96	-0.72	-5.73	3.96	-0.72	-5.73	3.96	-0.72

Table B22. DMA results for P5

DMA results for P5																
LAB	Draft A1		Draft A2		Draft A2 with Paule-Mandel adjustment			Degrees of equivalence at Draft A1			Degrees of equivalence at Draft A2			Degrees of equivalence at Draft A2 with Paule-Mandel adjustment		
	d_x	$u(d_x)$	d_y	$u(d_y)$	u_{PM}	d_z	$u(d_z)$	$d_x - d_{GRV}$	$u\,(d_x - d_{GRV})$	E_n	$d_y - d_{GRV}$	$u\,(d_y - d_{GRV})$	E_n	$d_z - d_{GRV}$	$u\,(d_z - d_{GRV})$	E_n
	nm	nm	nm	nm	nm	nm	nm	nm	nm		nm	nm		nm	nm	
CMS	306.5	1.3	306.5	1.3	0	306.5	1.3	0.77	1.16	0.33	0.77	1.16	0.33	0.77	1.16	0.33
LNE	305.56	2.92	305.56	2.92	0	305.56	2.92	-0.17	2.86	-0.03	-0.17	2.86	-0.03	-0.17	2.86	-0.03
NMIJ	307.6	2.8	307.6	2.8	0	307.6	2.8	1.87	2.74	0.34	1.87	2.74	0.34	1.87	2.74	0.34

Table B23. SAXS results for P5

SAXS results for P5																
LAB	Draft A1		Draft A2		Draft A2 with Paule-Mandel adjustment			Degrees of equivalence at Draft A1			Degrees of equivalence at Draft A2			Degrees of equivalence at Draft A2 with Paule-Mandel adjustment		
	d_x	$u(d_x)$	d_y	$u(d_y)$	u_{PM}	d_z	$u(d_z)$	$d_x - d_{GRV}$	$u\,(d_x - d_{GRV})$	E_n	$d_y - d_{GRV}$	$u\,(d_y - d_{GRV})$	E_n	$d_z - d_{GRV}$	$u\,(d_z - d_{GRV})$	E_n
	nm	nm	nm	nm	nm	nm	nm	nm	nm		nm	nm		nm	nm	
PTB	307	5	307	5	0	307	5	1.27	4.97	0.13	1.27	4.97	0.13	1.27	4.97	0.13

Table B24. DLS results for P5

DLS results for P5										
LAB	Draft A1		Draft A2		Degrees of equivalence at Draft A1			Degrees of equivalence at Draft A2		
	d_x	$u(d_x)$	d_y	$u(d_y)$	$d_x - d_{MRV}$	$u(d_x - d_{MRV})$	E_n	$d_y - d_{MRV}$	$u\ (d_y - d_{MRV})$	E_n
	nm	nm	nm	nm	nm	nm		nm	nm	
CENAM	325.15	4.54	325.15	4.54	-1.48	4.25	-0.17	-1.48	4.25	-0.17
CMS	324.3	5.8	324.3	6.4	-2.33	5.62	-0.21	-2.33	6.20	-0.19
KRISS	331.1	4.3	331.1	4.3	4.47	4.00	0.56	4.47	4.00	0.56
NIM	319.7	4.31	319.7	9.1	-6.93	4.16	-0.83	-6.93	8.96	-0.39
NIMT	316.69	11.2	316.69	95.21	-9.94	11.72	-0.42	-9.94	95.20	-0.05
NMIA	341	4	341	10	14.37	4.30	1.67	14.37	10.13	0.71
NMIJ	327	2	327	3.3	0.37	1.37	0.14	0.37	2.89	0.06

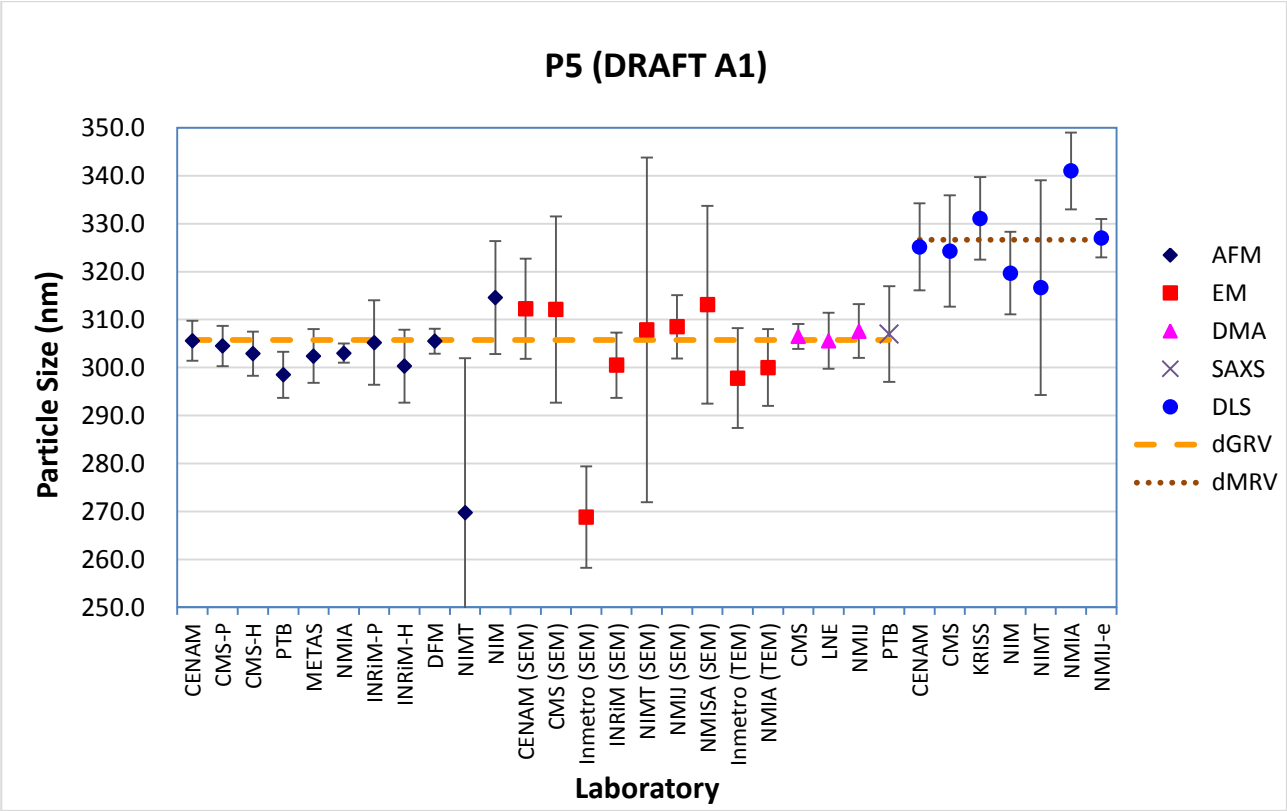

Figure B9. Measurement results and uncertainties reported by participants for P5 (Draft A1)

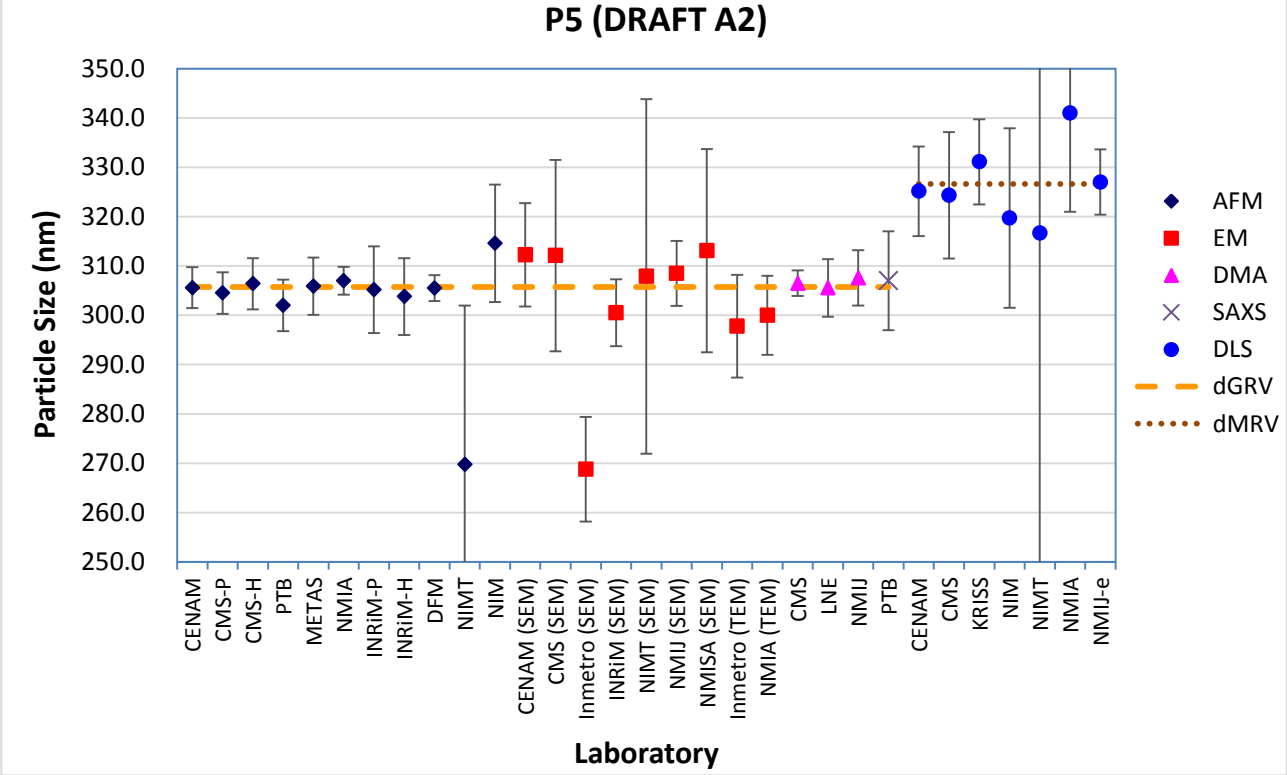

Figure B10. Measurement results and uncertainties reported by participants for P5 (Draft A2)

APPENDIX C: E_N NUMBER EVALUATIONS BASED ON DRAFT A1 AND DRAFT A2

As discussed in Section 8, the data in the Draft A2 (after modification) reported from each laboratory were used to calculate the reference values (RV) following the 3-step method, and then, the calculated RVs were applied to calculate E_n numbers with the data in the Draft A1 (before modification). In this appendix C, we summarize the calculation of E_n numbers with the data in the Draft A2 (after modification). Since the measurement data from DLS is very different than the measurement data from the other methods, MRVs for DLS were used in the E_n number calculation for the measurement data reported from the DLS method. The GRVs were applied in the E_n numbers calculations for the measurement data reported from AFM, EM, DMA and SAXS methods. The RVs are listed in the Table 11 (page 26) and re-listed in the Table C1 below. The MRVs for AFM, EM, DMA and SAXS methods are also listed in the Table C2 for references. The MRVs for AFM, EM, DMA, and SAXS after Paule-Mandel adjustment are summarized in the Table C3 (page 66).

It can be noticed that the measurement value and the associated uncertainties for G1 from the DMA were significantly larger than the measurement reults and their associated uncertainties from other methods. Additionally, the corresponding MRV for the DMA was much larger than the MRVs for AFM, EM, and SAXS. However, the analysis results from the 3-step method described in section 8 showed that the 4 measurement results from the 4 methods for G1 were consistent, beased on the MRVs and uncertainties. Thus, eventually, the GRV of 8.30 was applied to calculate the DOE for G1 as listed in Table C1. This is also the case with the DMA measurents of P3.

Table C1. Global reference values (GRVs) for AFM, EM, DMA, and SAXS; method dependent reference value (MRV) for DLS (same as Table 11)

Reference Values										
Method	**G1**		**S2**		**P3**		**P4**		**P5**	
AFM EM DMA SAXS	d_{GRV}	$u(d_{GRV})$	d_{GRV}	$u(d_{GRV})$	d_{GRV}	$u(d_{GRV})$	d_{GRV}	$u(d_{GRV})$	d_{GRV}	$u(d_{GRV})$
	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
	8.30	**0.08**	**19.66**	**0.23**	**26.49**	**0.99**	**99.03**	**0.63**	**305.73**	**0.59**
DLS	d_{MRV}	$u(d_{MRV})$	d_{MRV}	$u(d_{MRV})$	d_{MRV}	$u(d_{MRV})$	d_{MRV}	$u(d_{MRV})$	d_{MRV}	$u(d_{MRV})$
	nm	nm	nm	nm	nm	nm	nm	nm	nm	nm
	12.21	**0.23**	**24.84**	**0.42**	**32.68**	**0.83**	**105.13**	**0.84**	**326.6**	**1.6**

Table C2. Method dependent reference values (MRVs) for all measurement techniques of AFM, EM, DMA, and SAXS before Paule-Mandel adjustment

Method Dependent Reference Values – before Paule-Mandel Adjustment										
Method	**G1**		**S2**		**P3**		**P4**		**P5**	
	d_{MRV} nm	$u(d_{MRV})$ nm	d_{MRV} nm	$u(d_{MRV})$ nm	d_{MRV} nm	$u(d_{MRV})$ nm	d_{MRV} nm	$u(d_{MRV})$ nm	d_{MRV} nm	$u(d_{MRV})$ nm
AFM	**8.21**	**0.30**	**19.01**	**0.38**	**24.91**	**0.90**	**97.56**	**0.63**	**305.58**	**0.76**
EM	**8.27**	**0.12**	**20.08**	**0.43**	**25.42**	**0.68**	**99.02**	**0.79**	**304.3**	**1.8**
DMA	**13.9**	**2.9**	**--**	**--**	**29.1**	**2.2**	**100.15**	**0.34**	**306.5**	**1.1**
SAXS	**8.33**	**0.11**	**20.00**	**0.40**	**28.4**	**1.2**	**99.5**	**3.8**	**307.0**	**5.0**

Table C3. Method dependent reference values (MRVs) for all measurement techniques of AFM, EM, DMA, and SAXS after Paule-Mandel adjustment

Method Dependent Reference Values – after Paule-Mandel Adjustment										
Method	**G1**		**S2**		**P3**		**P4**		**P5**	
	d_{MRV} nm	$u(d_{MRV})$ nm	d_{MRV} nm	$u(d_{MRV})$ nm	d_{MRV} nm	$u(d_{MRV})$ nm	d_{MRV} nm	$u(d_{MRV})$ nm	d_{MRV} nm	$u(d_{MRV})$ nm
AFM	**8.21**	**0.30**	**19.01**	**0.38**	**24.9**	**1.9**	**97.6**	**1.2**	**305.58**	**0.76**
EM	**8.27**	**0.12**	**20.08**	**0.43**	**25.4**	**1.8**	**99.0**	**1.3**	**304.3**	**1.8**
DMA	**13.9**	**2.9**	**--**	**--**	**29.1**	**2.7**	**100.2**	**1.0**	**306.5**	**1.1**
SAXS	**8.33**	**0.11**	**20.00**	**0.40**	**28.4**	**2.0**	**99.5**	**4.0**	**307.0**	**5.0**

C1. *NANO GOLD WITH 10 NM NOMINAL DIAMETER (G1)*

The E_n numbers for the total of 8 measurement results from AFM, 8 measurement results from EM, one from DMA and one from SAXS were listed in Tables 12 ~15. The GRV of 8.30 nm with the uncertainty of 0.08 nm was used in the calculation. Three sets of measurement results (AFM from NMIA, SEM from Inmetro, and DMA from NMIJ) were considered not consistent with the d_{GRV}, since their $|E_n| > 1$. The E_n numbers for all participants based on Draft A1 are plotted in Figure 8 and re-plotted in Figure C1 (page 68).

When the reported data listed in the Draft A2 was considered, the E_n numbers were re-calculated for the DOE. The E_n numbers for all participants based on Draft A2 are plotted in Figure C2 (page 68). The results were also summarized in Tables B1 ~ B4. It can be found that three sets of measurement results (AFM from CMS and NMIA, and SEM from Inmetro) were considered not consistent with the d_{GRV}, since their $|E_n| > 1$. Compared the results from the previous paragraph, it can be noticed that the E_n number for the DMA (NMIJ) was improved to within $|E_n| \leq 1$, but the E_n number for the AFM from CMS was drop out for $|E_n| > 1$. The Paule-Mandel adjustment among the four methods (AFM, EM, DMA and SAXS) was not needed for G1 particles. The change for the DMA analysis was due to the uncertainty modification for adding the type B uncertainty associated with possible non-sphericity of the particles into draft A2. The uncertainty of the DMA measurments was up from 2.1 of Draft A1 to 2.8 for the Draft A2, so that the E_n number for the DMA (NMIJ) was improved to within $|E_n| \leq 1$.

For the calculations of the E_n numbers for the 7 DLS results, the MRV 12.21 nm with 0.23 nm uncertainty was used. Table 16 (page 29) in Section 8 and Table B5 (page 49) showed the results of the E_n numbers of DLS results. It indicates that only two (NIMT and NMIA) were consistent with the d_{MRV}, as shown in Figure C1 (page 68). However, if the data of the Draft A2 (after modifications with certain uncertainties) was used for further analysis, four (CMS, NIMT, NMIA, and NMIJ) out the 7 data sets were now consistent with the d_{MRV}, as shown in Figure C2 (page 68).

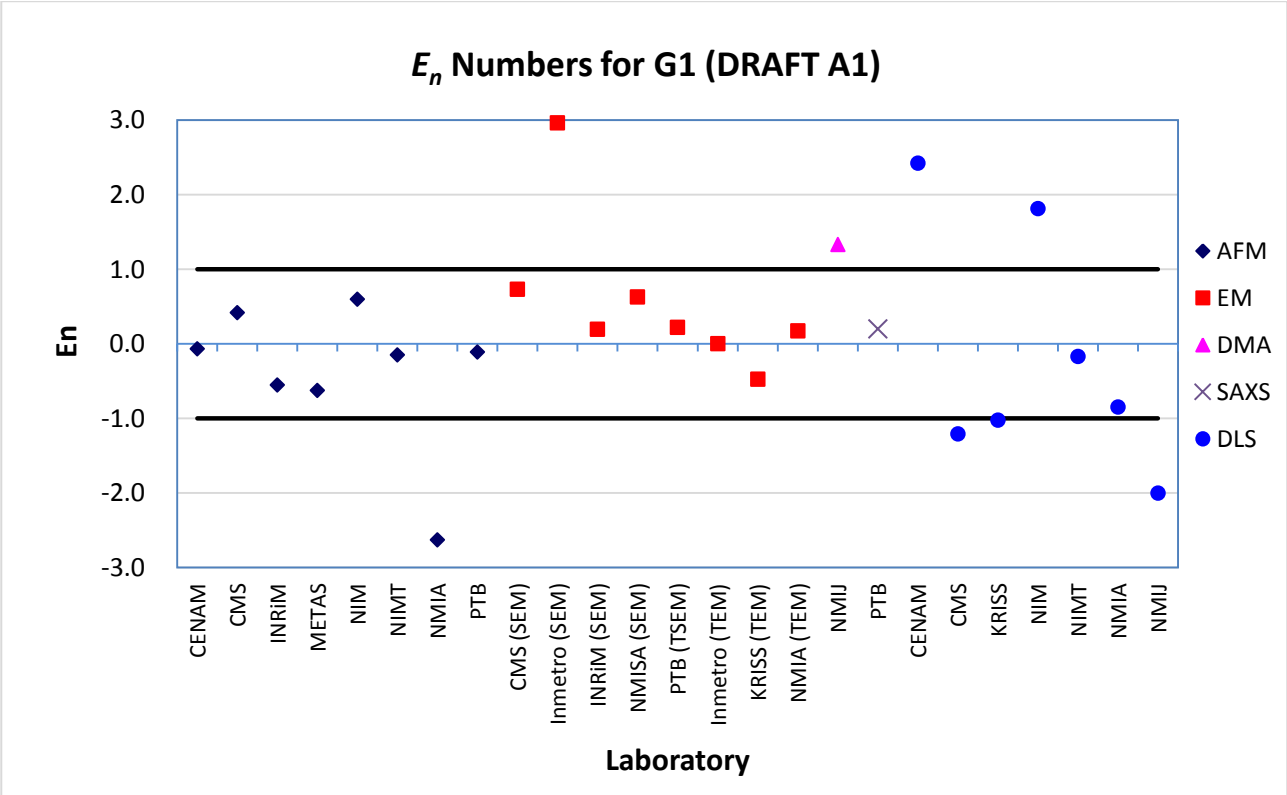

Figure C1. E_n numbers of all participants for G1 (Draft A1)

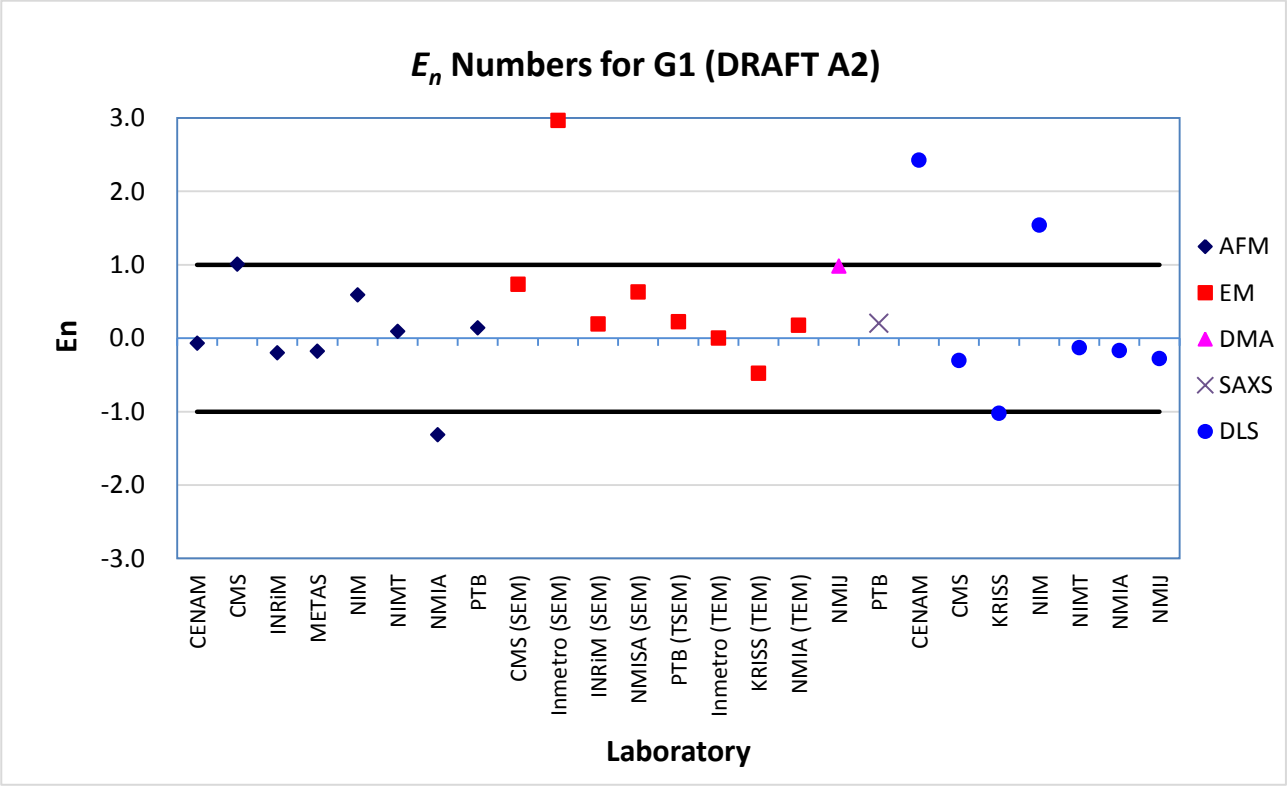

Figure C2. E_n numbers of all participants for G1 (Draft A2)

C2. *NANO SILVER WITH 20 NM NOMINAL DIAMETER (S2)*

From Section 8, for nano silver S2, the E_n numbers for the total of 8 measurement results from AFM, 8 measurement results from EM, one result from DMA and one from SAXS were summarized in Tables 17 ~ 19. The GRV of 19.66 nm with the uncertainty of 0.23 nm was used in the calculation for the E_n numbers. Five sets of measurement results (AFM from INRiM and NMIA, and SEM from CMS, Inmetro and INRiM) were considered not consistent with the d_{GRV}, since their $|E_n| > 1$, as shown in Figure C3 (page 70) (same as Figure 9 in section 8).

When the reported data listed in the Draft A2 was considered, the E_n numbers were re-calculated for the DOE. The E_n numbers for all participants based on Draft A2 are plotted in Figure C4 (page 70). The results were summarized in Tables B6 ~ B8. It can be found that 4 sets of measurement results (AFM from NMIA, and SEM from CMS, Inmetro and INRiM) were considered not consistent with the d_{GRV}, since their $|E_n| > 1$. Compared the results from the previous paragraph, it can be noticed that the E_n number for the AFM from INRiM was improved to within $|E_n| \leq 1$ and the E_n numbers for the AFM from NIMA were also improved. The Paule-Mandel adjustment among the three methods (AFM, EM, and SAXS) was not needed for S2 particles.

For the calculations of the E_n numbers for the 7 DLS results, the MRV of 24.84 nm with 0.42 nm uncertainty was used. Table 20 (page 32) in Section 8 shows the results of the E_n numbers of DLS results. It indicates that two (CENAM and NIM) were not consistent with the d_{MRV}. However, if the data of the Draft A2 (after modifications with certain uncertainties) in the Table B9 (page 52) was used for further analysis, only one measurement result from CENAM was considered not consistent with the d_{MRV}, as shown in Figure C4 (page 70).

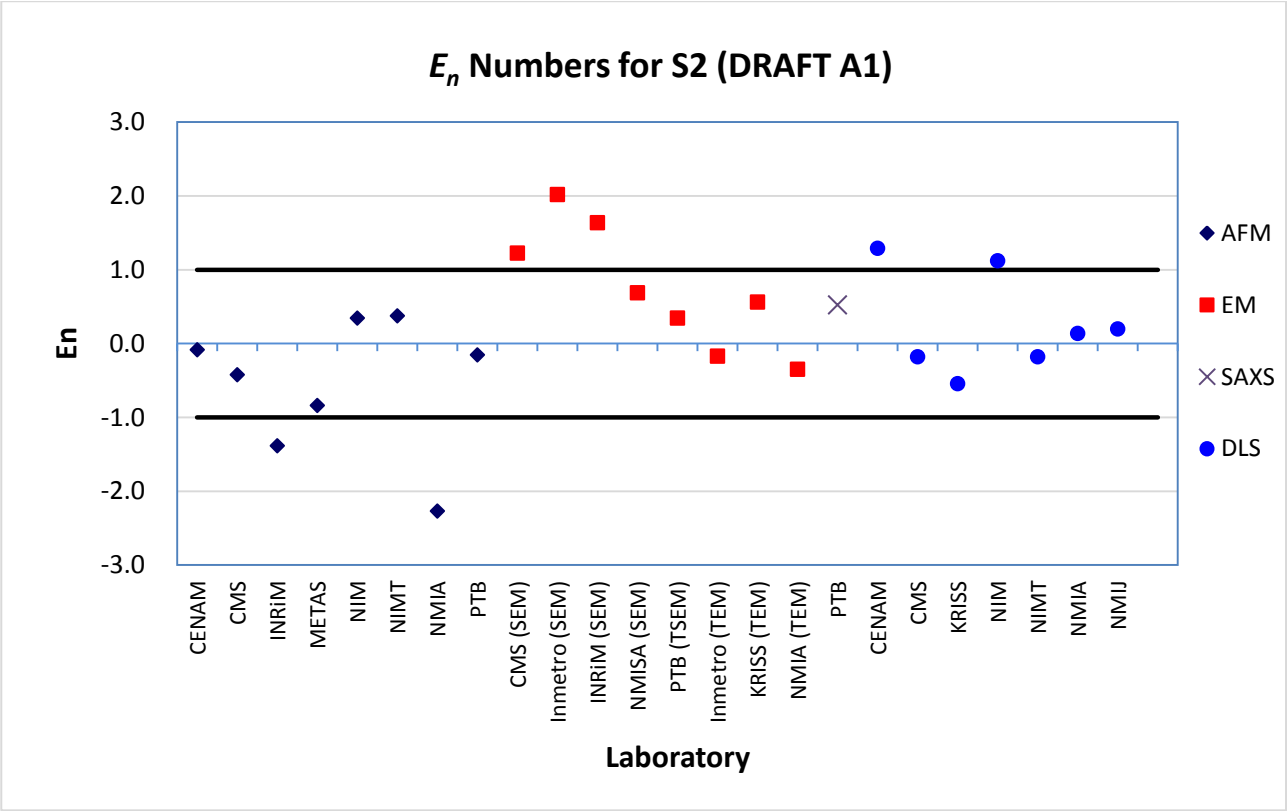

Figure C3. E_n numbers of all participants for S2 (Draft A1)

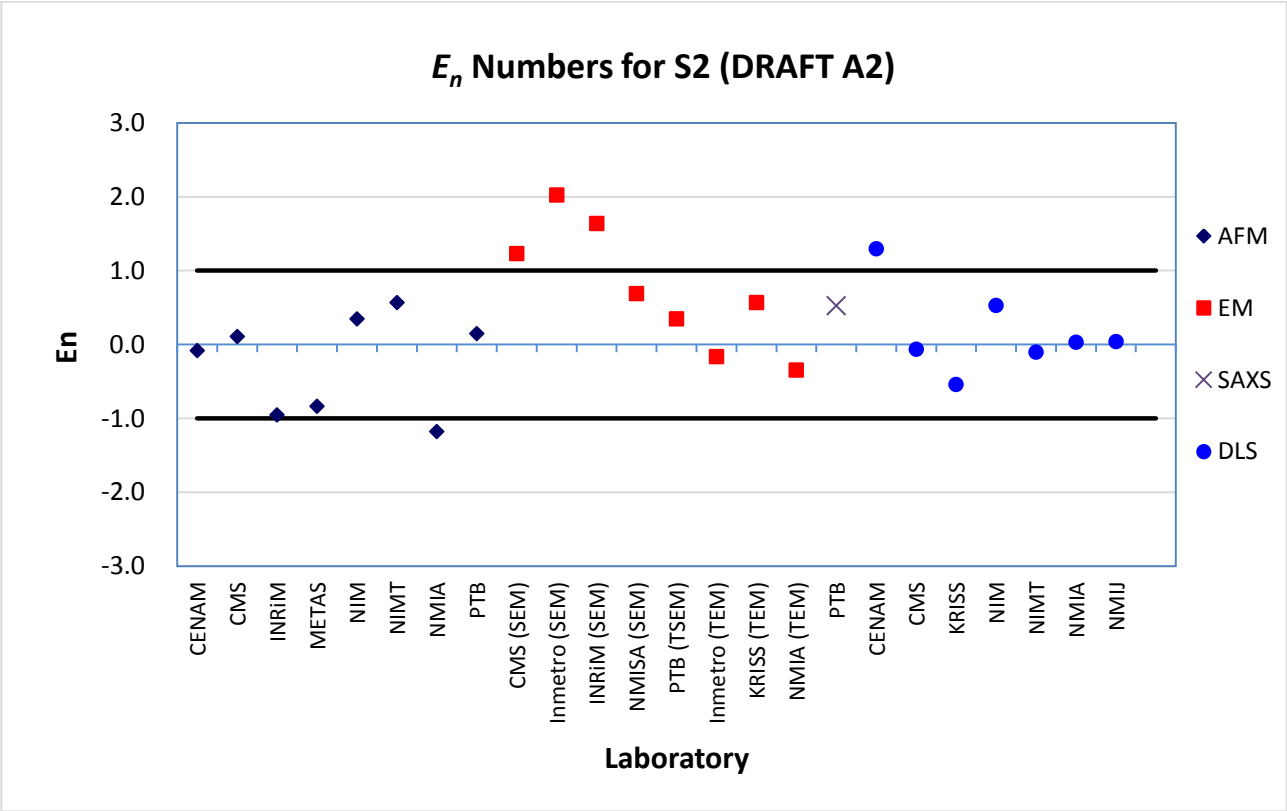

Figure C4. E_n numbers of all participants for S2 (Draft A2)

C3. *PSL WITH 30 NM NOMINAL DIAMETER (P3)*

For the PSL P3 from Section 8, the E_n numbers for the total of 10 measurement results from AFM, 4 measurement results from EM, 3 measurement results from DMA and one result from SAXS were summarized in Tables 21 ~24. The GRV of 26.49 nm with the uncertainty of 0.99 nm was used in the calculation. As shown in Figure C5 (page 72) (same as Figure 10 in section 8), four sets of measurement results (AFM from CMS, METAS and NMIA, and SEM from Inmetro) were considered not consistent with d_{GRV}, since their $|E_n| > 1$. Additionally, all DMA values (CMS, KRISS and NMIJ) were larger than 1 and considered not consistent with d_{GRV}, either.

When the reported data listed in the Draft A2 was considered, the E_n numbers were re-calculated for the DOE. The E_n numbers for all participants based on Draft A2 are plotted in Figure C6 (page 72). The results were summarized in Tables B10 ~B13. It can be found that only one set of measurement results (SEM from Inmetro) was considered not consistent with the d_{GRV}, since their $|E_n| > 1$. Compared the results from the previous section, the 3 sets of measurement results (AFM from CMS, METAS and NMIA) and the 3 sets of measurement results for DMA measurements (CMS, KRISS and NMIJ) were all improved to within $|E_n| \leq 1$. If the DOE at Draft A2 with Paule-Mandel adjustment was applied, as shown in Figure C7 (page 73), all measurement results were all improved to within $|E_n| \leq 1$ and considered consistent with the d_{GRV}.

For the calculations of the E_n numbers for the DLS results (7 sets), the MRV of 32.68 nm with 0.83 nm uncertainty was used. Table 25 (page 35) and Figure C5 (page 72) show the results of the E_n numbers of DLS results. It indicates that 3 (KRISS, NIMT and NMIA) were not consistent with the d_{MRV}. However, if the data of the Draft A2 (after modification with certain uncertainties) in the Table B14 (page 55) was used for further analysis, 2 measurement results (NIMT and NMIA) were improved to within $|E_n| \leq 1$, only one measurement result from KRISS was considered not consistent with the d_{MRV} with $E_n = 1.04$, as shown in Figure C6 (page 72).

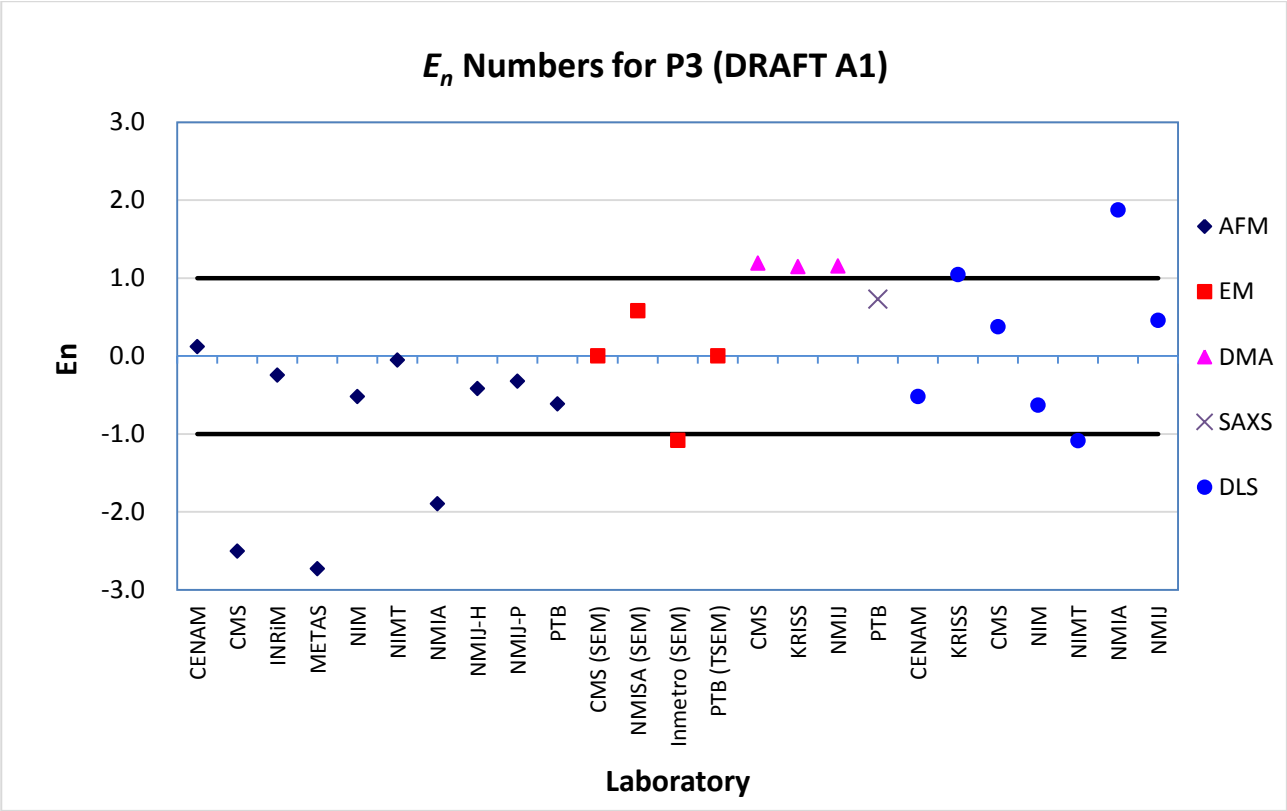

Figure C5. E_n numbers of all participants for P3 (Draft A1)

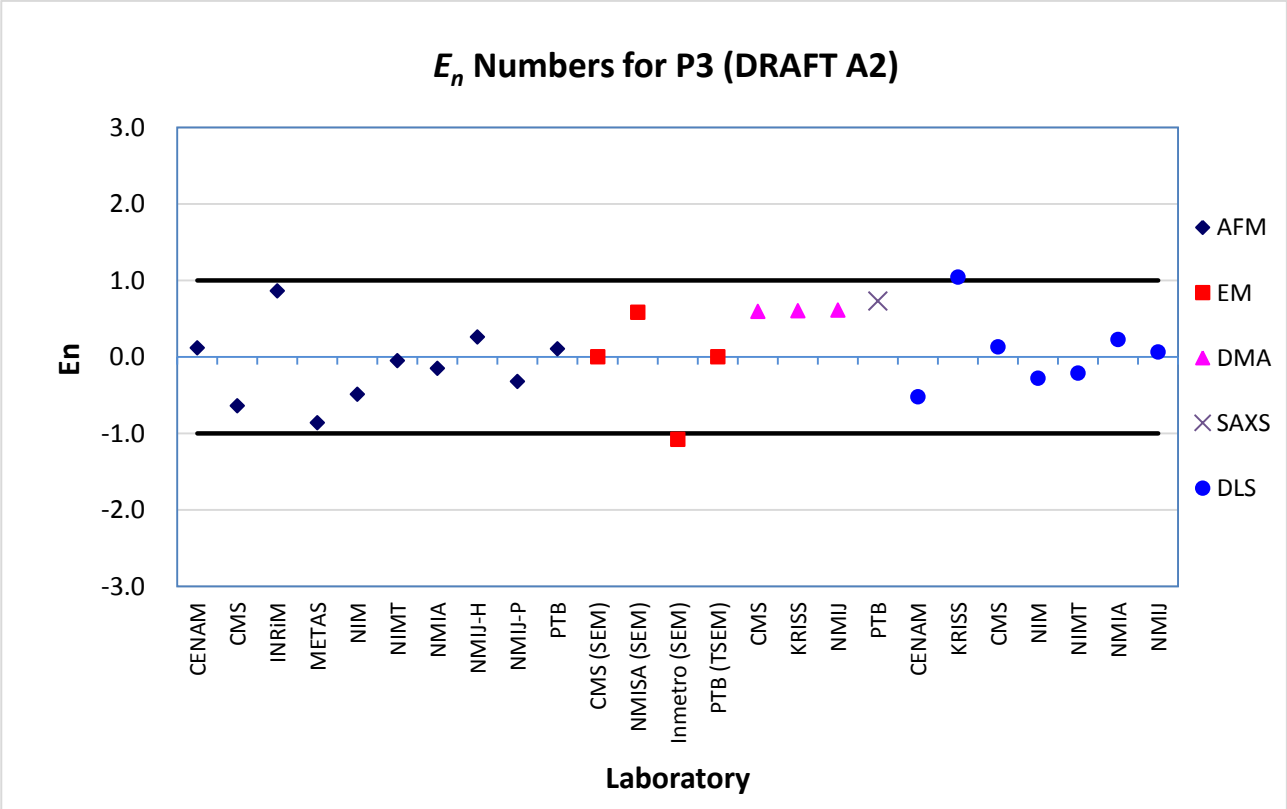

Figure C6. E_n numbers of all participants for P3 (Draft A2)

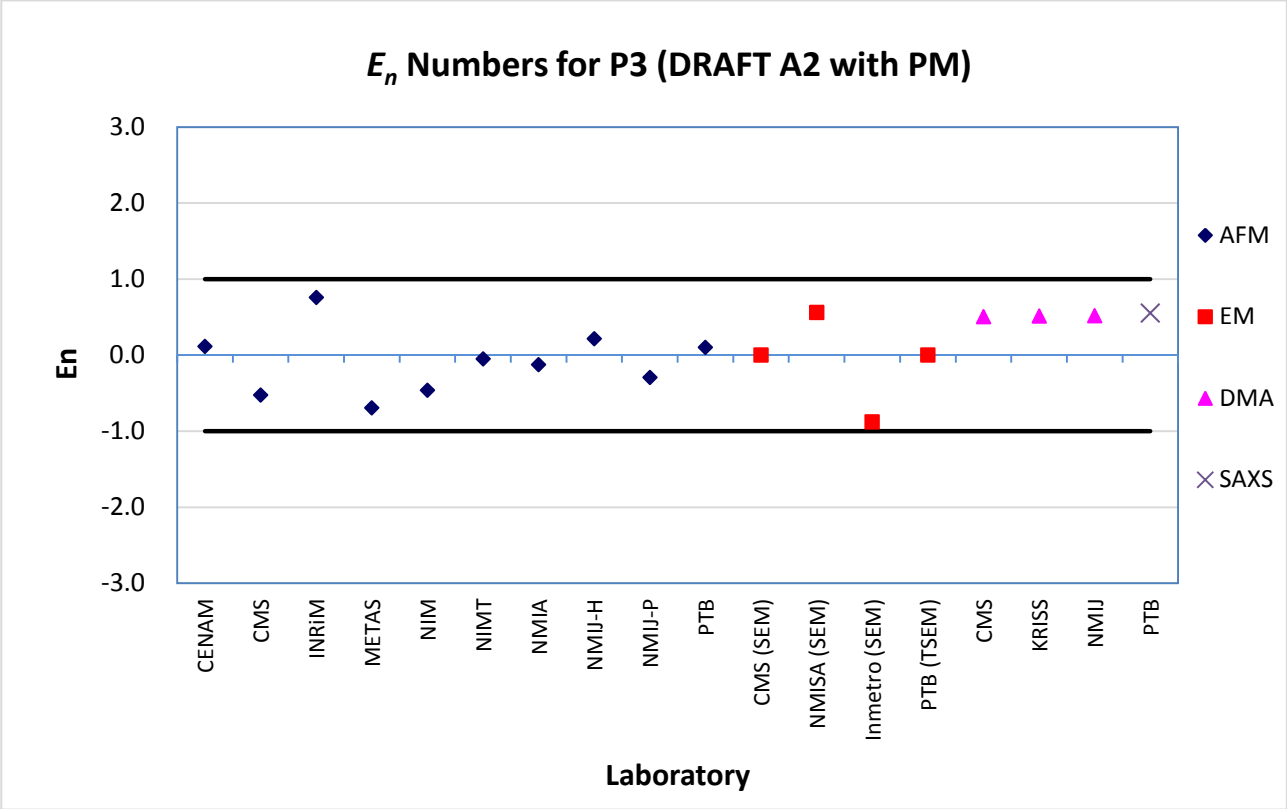

Figure C7. E_n numbers with Paule-Mandel adjustment of all participants for P3 (Draft A2)

C4. *PSL WITH 100 NM NOMINAL DIAMETER (P4)*

For the PSL P4, the E_n numbers for the total of 13 measurement results from AFM, 10 measurement results from EM, 4 results from DMA and one result from SAXS were summarized in Tables 26 ~29. The GRV of 99.03 nm with the uncertainty of 0.63 nm was used in the calculation. As shown in Figure C8 (page 75) (same as Figure 11 in section 8), four sets of measurement results from AFM (CENAM, CMS-H, INRiM-H and NMIA) and one set from EM (Inmetro) were considered not consistent with the d_{GRV}, since their $|E_n| > 1$.

When the reported data listed in the Draft A2 were considered, the E_n numbers were re-calculated for the DOE. The E_n numbers for all participants based on Draft A2 are plotted in Figure C9 (page 75). The results were summarized in Tables B15 ~B18. It can be found that only 2 sets of measurement results (AFM from CENAM and SEM from Inmetro) were considered not consistent with the d_{GRV}, since their $|E_n| > 1$. Compared the results from the previous paragraph, the 3 sets of measurement results (AFM from CMS-H, INRiM-H and NMIA) were all improved to within $|E_n| \leq 1$. The DOE at Draft A2 with Paule-Mandel adjustment showed the same results, as shown in Figure C10 (page 76): 2 sets of measurement results (AFM from CENAM and SEM from Inmetro) were considered not consistent with the d_{GRV}, since their $|E_n| > 1$.

For the calculations of the E_n numbers for the 7 DLS results, the MRV of 105.13 nm with 0.84 nm uncertainty was used. Table 30 (page 38) shows the results of the E_n numbers of DLS results. It indicates that one (NMIA) was not consistent with the d_{MRV}. However, if the data of the Draft A2 (after modifications with certain uncertainties) in the Table B19 (page 59) was used for further analysis, all measurement results were improved to within $|E_n| \leq 1$ and was considered consistent with the d_{MRV}, as shown in Figure C9 (page 75).

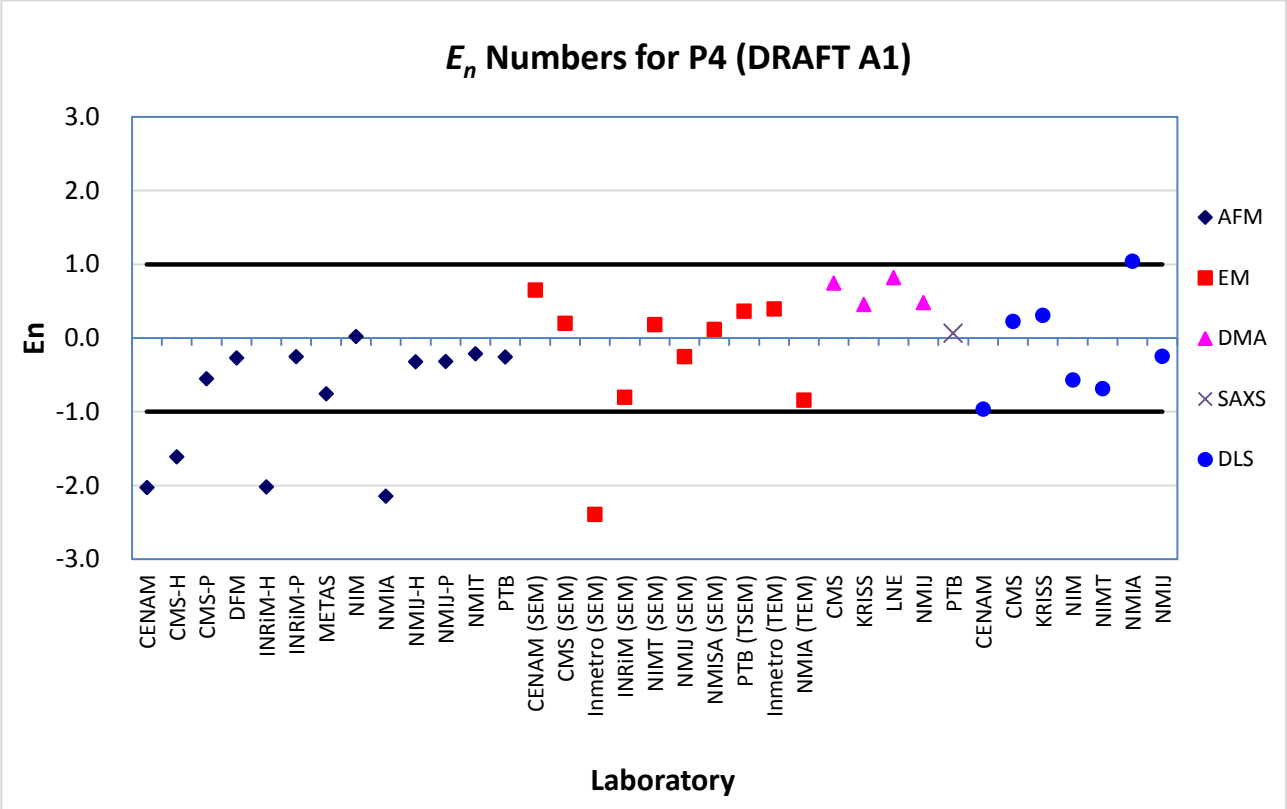

Figure C8. E_n numbers of all participants for P4 (Draft A1)

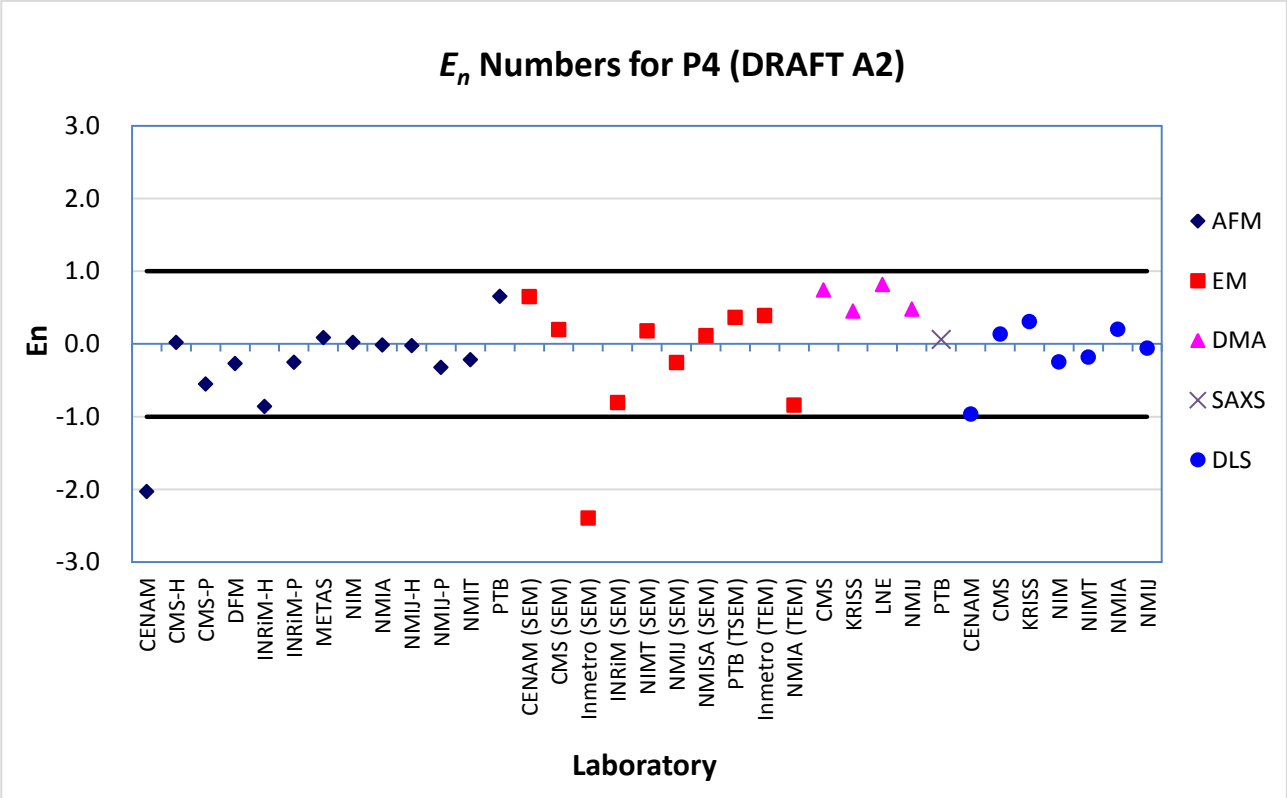

Figure C9. E_n numbers of all participants for P4 (Draft A2)

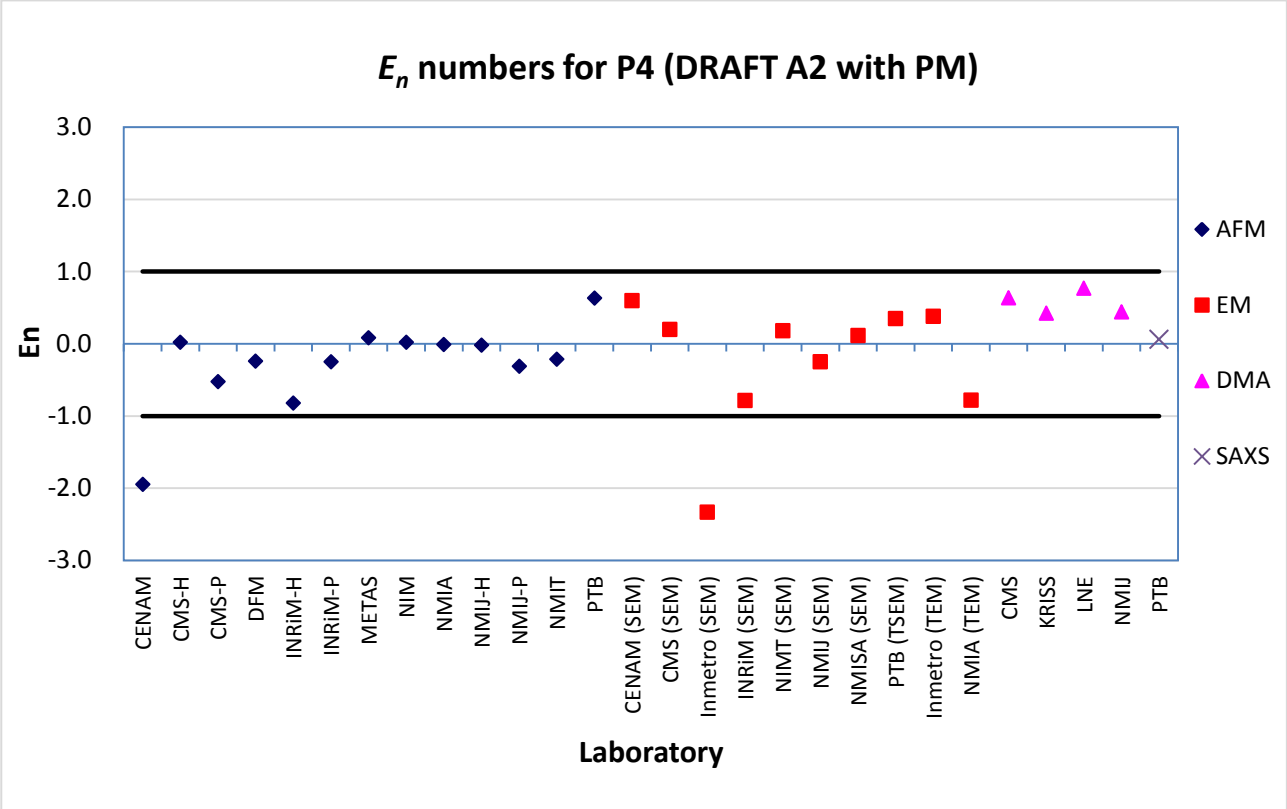

Figure C10**.** E_n numbers with Paule-Mandel adjustment of all participants for P4 (Draft A2)

C5. *PSL WITH 300 NM NOMINAL DIAMETER (P5)*

For the PSL P5, the E_n numbers for the total of 11 measurement results from AFM, 9 measurement results from EM, 3 results from DMA and one result from SAXS were summarized in Tables 31 ~ 33. The GRV 305.73 nm with the uncertainty of 0.59 nm was used in the calculation. As shown in Figure C11 (page 78) (same as Figure 12 in section 8), four sets of measurement results (AFM from PTB, NMIA and NIMT, and SEM from Inmetro) were considered not consistent with the d_{GRV}, since their $|E_n| > 1$.

When the reported data listed in the Draft A2 were considered, the E_n numbers were re-calculated for the DOE. The E_n numbers for all participants based on Draft A2 are plotted in Figure C12 (page 78). The results were summarized in Tables B20 ~ B23. It can be found that only 2 sets of measurement results (AFM from NIMT, and SEM from Inmetro) were considered not consistent with the d_{GRV}, since their $|E_n| > 1$. Compared the results from previous paragraph, the 2 sets of measurement results (AFM from PTB and NMIA) were all improved to within $|E_n| \leq 1$. The Paule-Mandel adjustment among the four methods (AFM, EM, DMA and SAXS) was not needed for P5 particles.

For the calculations of the E_n numbers for the 7 DLS results, the MRV of 326.6 nm with uncertainty of 1.6 nm uncertainty was used. Table 34 (page 41) shows the results of the E_n numbers of DLS results. It indicates that one (NMIA) was not consistent with the d_{MRV}. However, if the data of the Draft A2 (after modifications with certain uncertainties) in the Table B24 (page 63) was used for further analysis, all measurement results were improved to within $|E_n| \leq 1$ and was considered consistent with the d_{MRV}, as shown in Figure C12 (page 78).

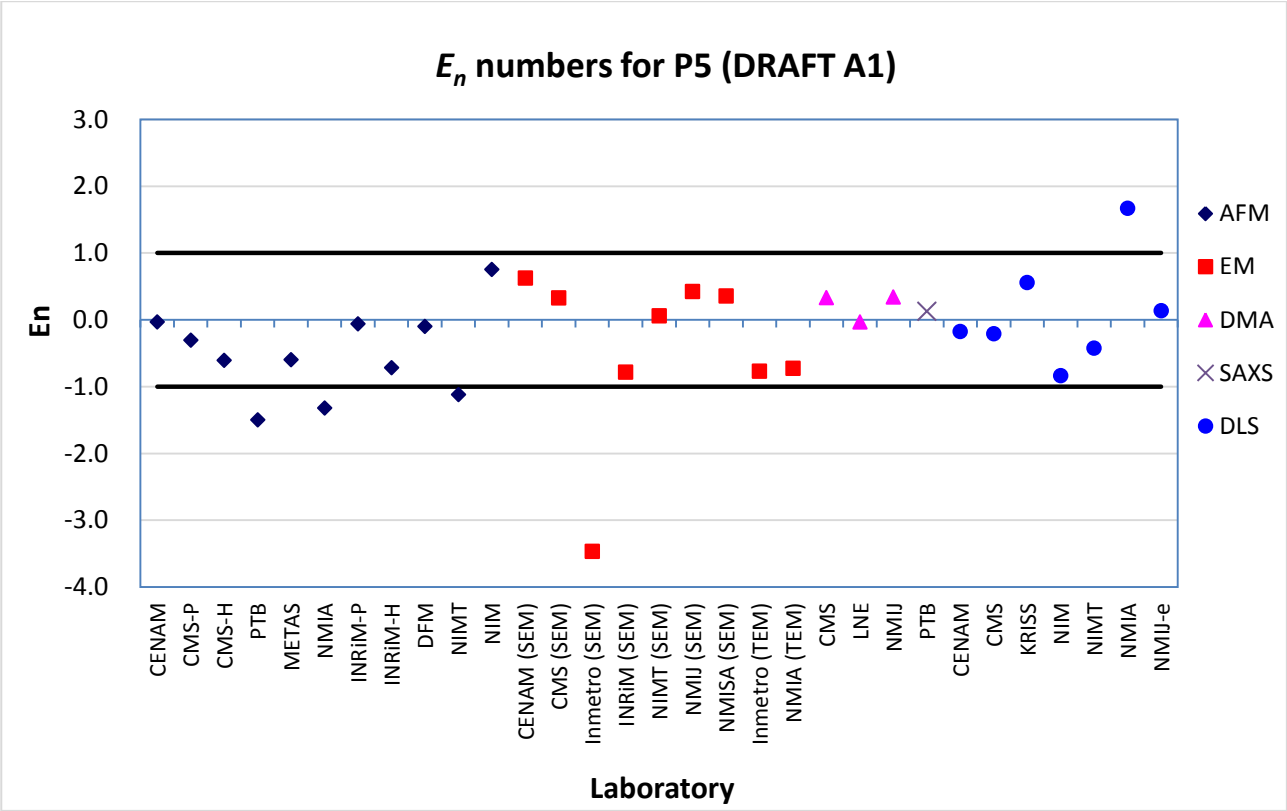

Figure C11. E_n numbers of all participants for P5 (Draft A1)

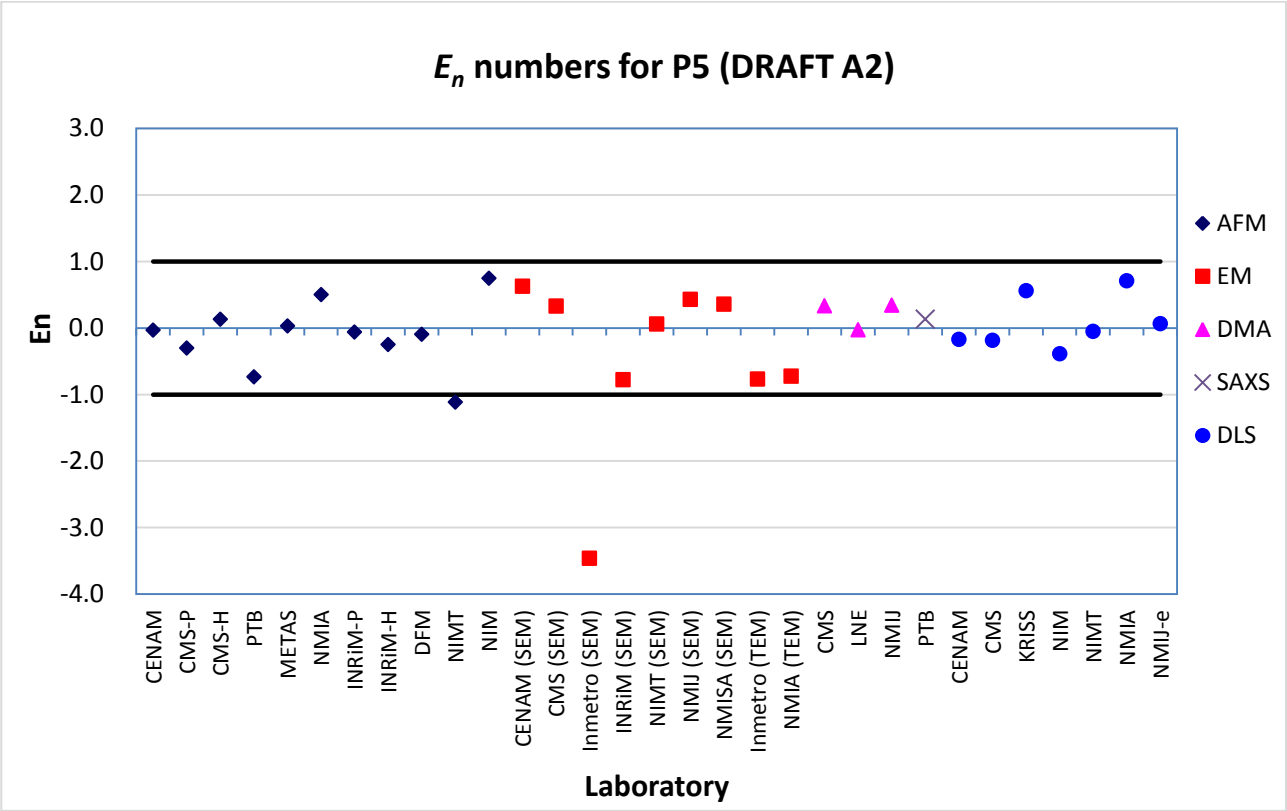

Figure C12. E_n numbers of all participants for P5 (Draft A2)

APPENDIX D: SUGGESTIONS OF UNCERTAINTY REVISIONS FOR DLS AND AFM

Suggestions were made at the International Workshop on Nanoparticle Size Measurement in June, 2013, Taipei, to consider some obvious uncertainties identified in recent publications for AFM and DLS. For example, when the AFM is used to measure particle sizes, the effect of particle deformation should be taken into account. These suggestions for AFM and DLS were taken from workshops taking place after the conclusion of the comparison, and were included here for improving the measurements in next comparisons in the future. The recommended procedures for deformation uncertainty evaluation in the AFM measurement are enclosed as D1 below:

In the case of the DLS measurements, the possible sources of uncertainty are: (1) the effect of the finite width of particle size distributions, (2) the effects of the scattering angle dependence and the particle concentration dependence of DLS measurements, and (3) the thickness of the water-molecule layer adsorbed on particle surfaces. The recommended procedures for uncertainty evaluations of (1) to (3) in the DLS measurement are enclosed as D2 below.

The participants can also use their own evaluation procedures that reasonably account for these uncertainty factors (on their own responsibility).

D1. *A RECOMMENDED PROCEDURE TO ESTIMATE PARTICLE DEFORMATION CAUSED BY AFM*

At the Taipei Workshop on June 18, 2013, it was resolved that in particle height measurements by the AFM, the effect of particle deformation should be taken into account, unless it had already been considered. The purpose of this section is to provide a recommended procedure to estimate the amount of particle deformation at the bottom part of the particles based on a plastic deformation model (Maugis-Pollock model) and possible material property values that can be used in the model, and to evaluate the uncertainty associated with this estimate. However, the participant labs are free to choose any model, material property values, and a policy for uncertainty evaluation on their own responsibility.

D1.1. Particle deformation model

Maugis-Pollock model (MP model) [D1~D3] is expressed as

$$a = \sqrt{\frac{2w_a R}{3Y}} \qquad \text{D1}$$

where a is the radius of the contact area, w_a is the work caused by an adhesion between the particle and the substrate, R is the radius of the particle, and Y is the yield point of the particle. The work w_a is given by

$$w_a = \gamma_p + \gamma_s - \gamma_{ps} = \gamma_p + \gamma_s - \left(\gamma_p + \gamma_s - 2\sqrt{\gamma_p \cdot \gamma_s}\right) = 2\sqrt{\gamma_p \cdot \gamma_s} \quad \text{D2}$$

where γ_p and γ_s are the surface energies of the particle and the substrate, respectively, and γ_{ps} is the interfacial energy between the particle and the substrate, which can be calculated from $\gamma_{ps} = \gamma_p + \gamma_s - 2\sqrt{\gamma_p \cdot \gamma_s}$ [D4]. From Equations (D1) and (D2), the particle deformation Δd can be expressed as

$$\Delta d = R - \sqrt{R^2 - a^2} = R - \sqrt{R^2 - \frac{4\sqrt{\gamma_p \cdot \gamma_s} R}{3Y}} \quad \text{D3}$$

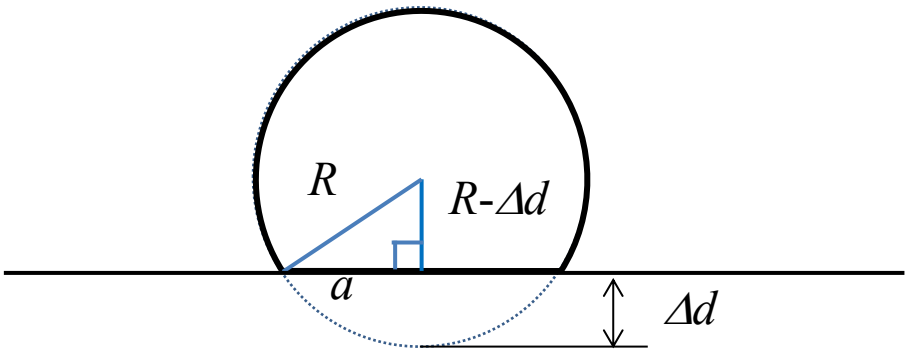

Figure D1**.** Particle deformation model

D1.2. Material properties

Table D1 shows possible values of the relevant material properties. These values were picked up from existing literature, but we do not know whether these values are the most reliable ones. Unfortunately, we could not find appropriate values of the properties of silver and SiO_2. In the absence of these values, the values for gold and mica might be substituted for the values for silver and SiO_2, respectively, with due consideration at uncertainty evaluation.

Table D1**.** Material properties

	Surface energy	Yield point
PSL	45 mN · m^{-1} [D2]	9 MPa [D2, D3]
Gold	580 mN · m^{-1} [D1]	167 MPa [D1]
Silver	? (unknown for now)[a)]	? (unknown for now)[a)]
Mica	47.7 mN · m^{-1} [D5]	
SiO2	? (unknown for now)[b)]	

[a)] Use of the values for Gold is suggested.

[b)] Use of the value for Mica is suggested.

D1.3. Uncertainty evaluation

At this moment, the reliability of the material property values given above is not well-known. This implies that an uncertainty evaluation based on the law of propagation of uncertainty is difficult. Under this situation, it would not be unreasonable to assume that the uncertainty in Δd is represented by a uniform distribution whose half width is given by $\Delta d/2$ as a rough and possibly conservative estimate. The standard uncertainty of Δd is then given by

$$u(\Delta d) = \frac{\Delta d}{2} \cdot \frac{1}{\sqrt{3}} \qquad \text{D4}$$

D1.4. Example of calculation

As an example, calculation of the deformation of a PSL 100 nm particle (P4) on a mica substrate is presented. If we use the values in Table D1, the particle deformation is obtained from Equation (D3) as Δd = 3.56 nm. The standard uncertainty associated with this value is obtained from Equation (D4) as $u(\Delta d)$ = 1.03 nm.

D1.5. Remarks

A more detailed update-to-date discussion can be found by the recently published article for the particle deformation modelling [D6]. Elastic models of particle deformation are also proposed [D7~D9]. There are some recent reports stating that the pressure caused by the adhesion force is larger than the hardness of PSL and metal particles [D2~D4], suggesting that a plastic model such as the MP model is more reasonable. It is very much desired to fill the empty cells of Table D1. If you have any information on the material properties of silver or SiO_2, please let the pilot lab know it as early as possible.

D2. *A RECOMMENDED PROCEDURE IN EVALUATING UNCERTAINTY OF DLS MEASUREMENT*

At the Taipei Workshop on 18 June, 2013, it was resolved that in uncertainty evaluation of DLS measurements, the following factors should be taken into account: 1) the effect of the finite width of particle size distributions, 2) the effects of the scattering angle dependence and the particle concentration dependence of DLS measurements, and 3) the thickness of the water-molecule layer adsorbed on particle surfaces. The present document provides a recommended procedure to account for these factors. The basic idea in this procedure is to estimate the biases due to these factors (please see sections D2.1. ~ D2.3.), and to include the sum of them in the uncertainty evaluation; please see sections D2.4.). However, the participant labs are free to adopt other procedures that can reasonably account for these factors on their own responsibility.

D2.1. The effect of the finite width of particle size distributions

At the Taipei Workshop, it was agreed that the number-average particle diameter is tentatively regarded as the unified measurand for all the measurement methods used in the present supplementary comparison. The number-average diameter is given by

$$D_N = \frac{\int Dn(D)dD}{\int n(D)dD} \quad \text{D5}$$

where D is the particle diameter, and $n(D)$ is the number-based size distribution function. On the other hand, the average diameter obtained by the DLS is the 5th power weighted diameter [D10]:

$$D_{DLS} = \frac{\int D^6 n(D)dD}{\int D^5 n(D)dD} \quad \text{D6}$$

The difference between D_{DLS} and D_N is regarded as a bias in a DLS measurement:

$$\delta D_1 = D_{DLS} - D_N \quad \text{D7}$$

The values of δD_1 estimated for the five sample particles using available information on $n(D)$ are given in Table D2 (see D2.6.). The values in Table D2 may be used in the uncertainty evaluation in DLS measurements. If a lab obtains $n(D)$ by themselves, and estimates δD_1 using this $n(D)$, the measurement result may be corrected for δD_1. Otherwise, δD_1 should not be corrected for in the measurement result, but should be included in the uncertainty (see D2.4.).

Table D2. Estimates of δD_1 for the five types of particles

Particle type	δD_1 (nm)	Source of $n(D)$ in calculating δD_1
G1	0.3	TEM by NMIA
S2	1.1	TSEM by PTB
P3	3.0	TSEM by PTB
P4	0.4	TSEM by PTB
P5	0.1	AFM by NMIA

D2.2. The effects of the scattering angle dependence and the particle concentration dependence

The apparent particle size obtained by the DLS, D_{app}, often depends on the light scattering angle and the particle concentration of the sample suspension [D11]. The dependence can be

approximately represented by

$$D_{app}(q, C) = a_{00} + a_{10}C + a_{01}q^2 + a_{11}Cq^2 \qquad \text{D8}$$

where C is the particle number concentration of the suspension (number of particles/mL), and q is the magnitude of the scattering vector

$$q = \frac{4\pi n}{\lambda} sin\left(\frac{\theta}{2}\right) \qquad \text{D9}$$

with n being the refractive index of the suspension medium, and λ being the wavelength of the incident laser light in vacuum. The constants of a_{00}, a_{10}, a_{01}, and a_{11} can be determined by fitting Equation (D8) to experimental data obtained with a DLS instrument for which the scattering angle can be varied, such as shown in Figure D2. The values of a_{00}, a_{10}, a_{01}, and a_{11} for the five sample particles determined in this way at NMIJ are given in Table D3. Because the "true" particle diameter is theoretically given by $D_{app}(q = 0, C = 0)$, an estimate of the bias included in D_{app} is given by

$$\delta D_2 = D_{app}(q, C) - D_{app}(0,0) = a_{10}C + a_{01}q^2 + a_{11}Cq^2 \qquad \text{D10}$$

Each lab can estimate δD_2 by substituting the values of q and C in their experiment into Equation (D10) and using Table D3 (see D2.5.). If a lab obtains $D_{app}(q, C)$ by themselves, and estimates δD_2 using this $D_{app}(q, C)$, the measurement result may be corrected for δD_2. Otherwise, δD_2should not be corrected for, but should be included in the measurement uncertainty.

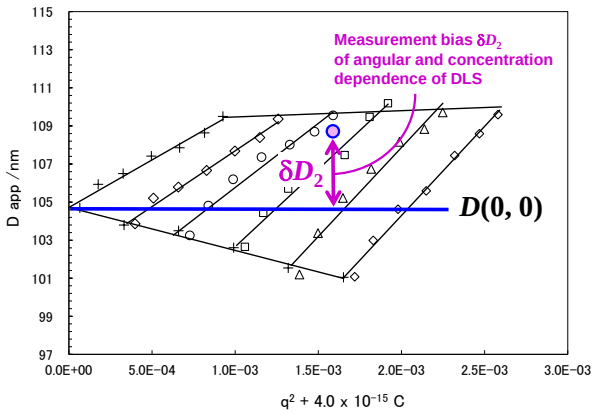

Figure D2. Zimm plot representing the scattering angle dependence and the concentration dependence of the DLS measurement for the P4 particles. The data were obtained at NMIJ for the combinations of seven angles and five concentrations.

Table D3. The values of a_{00}, a_{10}, a_{01}, and a_{11} estimated at NMIJ.

Sample	a_{00} (nm)	a_{10} (nm·mL)	a_{01} (nm^3)	a_{11} (nm^3·mL)
G1	10.3	-3.73×10^{-13}	-1.64×10^{2}	4.01×10^{-12}
S2	25.0	-4.84×10^{-12}	6.55×10^{2}	-4.64×10^{-10}
P3	33.2	-2.38×10^{-14}	7.49×10^{3}	-8.50×10^{-12}
P4	104.7	-9.03×10^{-12}	5.00×10^{3}	1.17×10^{-8}
P5	288.2	1.58×10^{-9}	1.38×10^{5}	1.13×10^{-5}

D2.3. The effect of the water molecule layer adsorbed on particle surfaces

There is a study indicating that a layer of water molecules of approximately 1 nm thickness is adsorbed on surfaces of polystyrene latex particles of approximately 30 nm in diameter [D12, D13] (see D2.7.). Because no experimental data on the layer thickness are available for the particles used in the present supplementary comparison, it would not be unreasonable to assume that the thickness is approximately 1.3 nm irrespective of the particle types. The bias δD_3 in the apparent particle diameter obtained by the DLS can then be estimated as

$$\delta D_3 = 2.6\ nm \qquad \text{D11}$$

Because this value of δD_3 is only a rough estimate, it is reasonable not to correct the measurement results for δD_3, but to include it in the measurement uncertainty.

D2.4. Uncertainty evaluation

The total bias in the DLS measurement is estimated as

$$\delta D = \delta D_1 + \delta D_2 + \delta D_3 \qquad \text{D12}$$

Note that δD_2 can be either positive or negative, and if it is negative, it partly cancels the other terms which are positive. When the bias δD is not corrected for in the measurement result, the standard uncertainty associated with δD is evaluated as [D14]

$$u_{bias}(D) = |\delta D| \qquad \text{D13}$$

The standard uncertainty $u_{bias}(D)$ should be included in the uncertainty budget of the DLS measurement.

D2.5. Example of uncertainty evaluation

An example of evaluating $u_{bias}(D)$ for the P4 particles is provided in this section.

δD_1:

From Table D2, δD_1 for the P4 particles is given by

$\delta D_1 = 0.4\ nm$

δD_2:

The particle number concentration of the original suspension of the P4 particles is 1.8×10^{13} particles/mL according to the measurement protocol of the present comparison. Let us assume that a lab diluted the original suspension by a factor of $3/100$. The concentration of the diluted suspension is then

$C = \frac{(1.8\times10^{13})\times3}{(100+3)} = 5.4 \times 10^{11}$ particles/mL.

If the lab used a DLS instrument with $\theta = 173$ degree and $\lambda = 633\ nm$, then

$$q = \frac{4\pi n}{\lambda} sin\left(\frac{\theta}{2}\right) = 2.63 \times 10^{-2}\ nm^{-1}$$

where $n = 1.33$ (the refractive index of water) is used. From Equation (D10) and Table D3, δD_2 for the P4 particles is

$\delta D_2 = 2.9\ nm$

δD_3:

Using Equation (D11), we have

$\delta D_3 = 2.6\ nm$

$u_{bias}(D)$:

From Equations. (D12) and (D13), the standard uncertainty associated with the biases in the DLS measurement is given by

$u_{bias}(D) = |0.4 + 2.9 + 2.6| \approx 5.9\ nm$

D2.6. Estimate of the bias due to the finite width of particle size distributions, δD_1

In this section, how the values of δD_1 in Table D2 are evaluated is described, taking the P4 particles as an example. The solid circles in Figure A1 show the size distribution $n(D)$ obtained experimentally by the TSEM at PTB. The experimental data can be fitted by a Gaussian distribution[a]:

$$G(D) = \frac{N}{\sqrt{2\pi}\sigma} exp\left[-\frac{(D-\mu)^2}{2\sigma^2}\right] \quad \text{D14}$$

The parameters N, σ, and μ can be determined by the least squares fitting as

$$N = 6702 \quad \text{D15}$$

$$\sigma = 2.68\ nm \quad \text{D16}$$

$$\mu = 101.6\ nm \quad \text{D17}$$

Substituting Equation (D14) in Equations (D5) and (D6), we obtain $D_N = 101.6\ nm$ and $D_{DLS} = 102.0\ nm$, respectively, which leads to

$$\delta D_1 = 0.4\ nm \quad \text{D18}$$

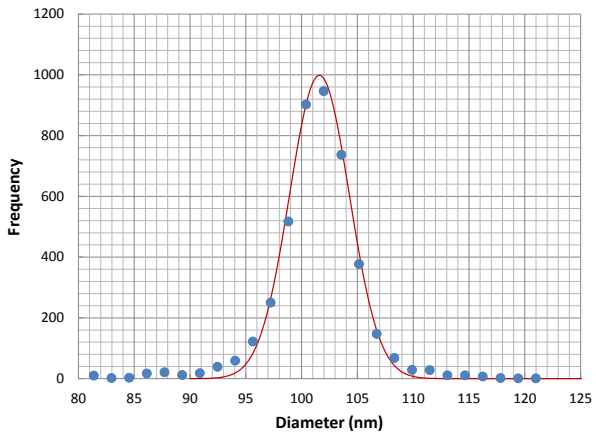

Figure D3**.** Size distribution of the P4 particles obtained by the TSEM at PTB (solid circles), and the Gaussian distribution fitted to the experimental data (solid curve).

[a] Considering the slight asymmetry in the size distribution, we might use an asymmetric Gaussian in the fitting. It was found, however, that the use of the asymmetric Gaussian introduces a difference in δD_1 of only 0.1 nm at the maximum for the five sample particles. Therefore, the Gaussian distribution is used in this document.

D2.7. Estimate of the bias associated with the layer of water molecules adsorbed on particles surfaces

It is reported in [D12] that the ratio of the number of water molecules adsorbed on particle surfaces to the number of bulk water molecules, I/I_0, in a suspension of polystyrene latex particles of 30 nm in diameter, measured by the pulsed field gradient nuclear magnetic resonance (PFG-NMR) method, is expressed as:

$$ln(I/I_0) = -5.9 \text{ or } I/I_0 \approx 0.0027 \qquad \text{D18}$$

This means that the number fraction of water molecules adsorbed on the polystyrene latex particles is about 0.27 % of all water molecules in aqueous PS latex suspension. If we assume that the density of the absorbed water layer is the same as that of bulk water, the thickness of the water molecule layer can be approximately estimated as 1.3 nm by using the particle size (32.2 nm [D12]) and the number concentration of particles (7.0×10^{14} particles/mL [D13]). The bias in the DLS measurement associated with the thickness of the water molecule layer is estimated as

$$\delta D_3 = 1.3 \times 2 = 2.6\, nm \qquad \text{D19}$$

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