A comparison study on the measurement of nanoparticles

Chen-Yu Wang*[a], Shan-Peng Pan [a], Gwo-Sheng Peng [a], Jen-Hui Tsai [b]
[a]Center for Measurement Standards (CMS) / Industrial Technology Research Institute (ITRI)
No. 321, Sec. 2, Kuang Fu Rd., Hsinchu, Taiwan 300, R.O.C.
[b]NanoTechnology Research Center (NTRC) / Industrial Technology Research Institute (ITRI)
No. 195, Sec. 4, Chung Hsing Rd., Chutung, Hsinchu, Taiwan 310, R.O.C.

ABSTRACT

Despite the fact that there exists several techniques capable of characterizing the nanoparticle sizes, their measurement results from the same sample often deviate from each other at an amount that is considered significant in the nanometer scale. The principles of measurements these techniques or instruments based upon might contribute a notable portion to the disagreement of the measurement results. The sample preparation itself could only further add to the complexity of the problem. In the absence of international standards, or world-wide recognized protocols dealing with nanoparticle characterization, a comparison study was carried out to investigate the systematic deviations in measuring nanoparticle diameters. Three types of commonly used nanoparticle sizing instruments, Photon Correlation Spectroscopy (PCS), Atomic Force Microscopy (AFM), and Transmission Electron Microscopy (TEM) were utilized to take measurements on traceable polystyrene latex samples at 100 nm, 50 nm, and 20 nm in diameter. The final analysis showed a fairly satisfactory agreement of the measured data from the samples' certified values, with the exception of the result from the Field-Emission TEM (FE-TEM). It was later determined that the major source of the deviation was attributed to the instrument rather than to the sample. Instrument calibration was the course of action taken to bring the outlier to the desired accuracy. Additionally, discussions were also made with regards to the need of standardization in nanoparticle measurements.

Keywords: Nanoparticle, size characterization, measurement comparison

1. INTRODUCTION

Nanoparticles have found their unique advantages and immediate applications in numerous industrial, commercial, and consumer products. The strengths stem from the profound changes in their physical and/or chemical properties as particle sizes are reduced to the vicinity of 100 nm or smaller. Without a doubt, accurate determination of the particle diameters in the nanometer range has become one of the most important issues in the development of nanoparticle applications. Although there long exits several measurement techniques for particle size characterization, only a handful is capable of dimensional measurement in the nanometer scale range. Measurement techniques such as PCS, TEM, and AFM are often used to measure nanoparticle sizes. However, due to different principles these techniques base on, measurement results sometimes do not agree with each other to a certain degree. In some cases, the deviation on the measurement of the same sample is rather significant that would easily lead to the questions of which instrument could be trusted when it comes to determining the sizes of certain particle compositions and how to translate the difference in measurements among these instruments. Surely, there are a number of reasons that would attribute to the disagreement in measurements. Sample homogeneity, sample preparations, instrument operating procedures, and statistical practices, just to name a few, are likely to add to the complexity of the problem. It would certainly improve the situation a lot if there exists international or industrial standards that would sufficiently comprehend details of the measurements or if these nanoscale instruments sitting in the laboratories are properly evaluated with uncertainty budget and validated with recognized protocols. Unfortunately, these are all the challenges that would have to be overcome under the current situation. A measurement comparison could serve as the intermediate study in establishing the effectiveness and comparability of measurement methods. This paper will present a comparison study on the measurement of nanoparticles that was carried out at the end of 2004. Methodology of the comparison, measurement data, and the final results will be discussed throughout the paper.

2. METHODOLOGY

2.1 Measurement instruments

Particle measuring techniques can be broadly divided into two categories, direct observation and behavioral techniques[1]. Microscopy-based techniques for particle size characterization provide a powerful tool for characterization of particle size, size distribution, and morphology. They involve direct observation of particles and the consequent determination of size based on a defined measure of diameter. Typically, the calculated sizes are expressed as the diameter of a sphere that has the same projected area as the projected image of the particle[2].

As shown in Figure 1, four different instruments capable of dimensional measurement in nanometer scale range were used in this comparison study. TEM, Field-Emission TEM (FE-TEM), and AFM are of microscopy-based techniques. Another instrument is PCS, which determines the particle size by analyzing the behavior of the particles under investigation. PCS is also known as Quasi-Elastic Light Scattering (QELS) or more commonly Dynamic Light Scattering (DLS). PCS takes advantage of the high spatial coherence of monochromatic light sources to analyze the intensity fluctuation of scattered light from particulate samples dispersed in solutions. By employing the Stokes-Einstein equation applicable to spheres in Brownian motion, the diffusion coefficient of the particulate samples are computed and derived to average particle diameters. It is a non-evasive method and measurement time is usually in the order of minutes. Commercially available PCS can easily achieve the measurement range from 5 nm to 5000 nm in particle sizes. As a variation to the typical PCS, a special type Photon Cross-Correlation Spectroscopy (PCCS) instrument is used in this comparison. As opposed to the single optical path PCS that employs the auto-correlation function to determine the particle size, dual laser beams cross over in the sample container and generate two similar signal patterns in a PCCS system. When cross-correlated, multiple scattering is thereafter minimized especially for the analysis of high concentration samples.

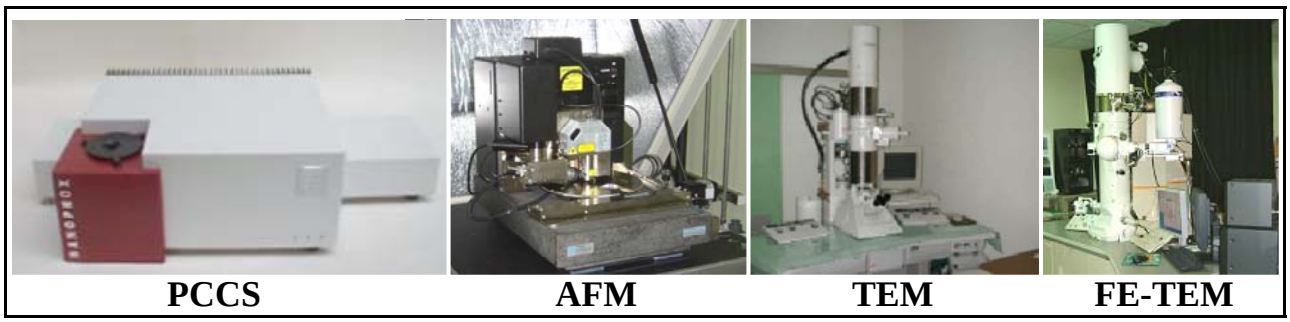

Figure 1: Instruments used for comparison

2.2 Description of the samples

For this measurement comparison, four samples from two different manufacturers were used, one from the National Institute of Standards and Technology, NIST (http://www.nist.gov/) and three others from Duke Scientific Corporation (http://www.dukescientific.com/). These particulate materials are nearly mono-dispersed polystyrene spheres and classified as the Certified Reference Materials (CRM). That is, their sizes are to be served as particle standards with certified analytical values traceable to a national standards organization or a metrological laboratory. The NIST sample Standard Reference Material® (SRM) 1963 consists of carboxylated polystyrene spheres with nominal size of 0.1µm in diameter suspended in deionized filtered water and is intended for the calibration of electron microscopes and of surface scanning inspection systems. Its certified average particle size diameter of 100.7 ± 1.0 nm is determined in air as aerosol by electrical mobility measurements[1]. The Duke Scientific sample Nanosphere™ size standards consists of polymer microspheres suspected in water. The choices of samples come in three different nominal sizes of 20 nm, 50 nm, and 100 nm with certified mean diameters of 21.0 nm ± 1.5 nm, 50.0 nm ± 2.0 nm, and 102 nm ± 3 nm, respectively. Their traceability claims were transferred by TEM or PCS from NIST SRM® 1963, 1691 or 1690[4, 5, 6]. Detail sample information is summarized in Table 1.

The selection of the samples was based on several criteria. First, in a measurement comparison it is critical that the properties of the chosen artifacts for the samples exhibit long term stability in terms of their certified sizes and chemical

composition of the dispersion medium so that deviation factor on the artifacts are minimized. The NIST and Duke Scientific's particle standards meet such prerequisite and they are commercially available as CRM. In addition, polystyrene materials are considered harmless to human bodies although extra care still must be taken in the handling, distribution, and use due to their nanometer scale sizes. Secondly, the choice of particulate material of 100 nm nominal size is mostly attributed to the general perception that nanotechnology developments nowadays deal with physical dimensions equal to or less than 100 nm. Duke Scientific 3100A and NIST SRM® 1963 samples represent the 100 nm "barrier" while NIST's offers narrower size distribution and better uncertainty values. On the other hand, the 20 nm Duke Scientific 3020A sample is by far the smallest CRM-class particle standards of polystyrene materials on the market. It is under the presumption that instruments capable of dimensional measurements in the nanometer scale should be sufficient in determining the chosen sample sizes with reasonable accuracy.

Table 1: List of measurement samples

Sample Code	Materials	Certified Diameter	Manufacturer Product No.
NIST100	Polystyrene	100.7 nm ± 1.0 nm	NIST SRM® 1963
DUKE100	Polystyrene	102 nm ± 3 nm	Duke Scientific 3100A
DUKE50	Polystyrene	50.0 nm ± 2.0 nm	Duke Scientific 3050A
DUKE20	Polystyrene	21.0 nm ± 1.5 nm	Duke Scientific 3020A

2.3 Comparison scheme and sample preparation

Due to the nature of the selected artifacts, a distributed scheme was chosen for the measurement comparison[7, 8]. Particulate samples were taken from the bulk sample and allocated into separate vials to serve as test samples. The sample vials contain particulate materials suspended in distill water with identical quantities and concentrations. All the test samples were distributed to various instrument operators at the same time and a period of two weeks were given for each to complete the measurements. Special attention was also paid to the transportation of the samples to make sure that no extreme temperature fluctuation through different laboratory facilities. Once the samples are taken out from the original bulk storage, the stability of the test samples becomes an issue. As a general rule of thumb, the stability of the test samples should hold for about a month under regular laboratory condition. The two-week grace period given for the measurement includes the time needed for sample preparation such as the dry-out treatment for measurements by TEM and AFM.

3. MEASUREMENT DATA AND COMPARISON RESULTS

A total number of six measurements were requested for each sample. An average diameter and standard deviation were computed for each instrument. Table 2, Table 3, Table 4, and Table 5 shown are the measurement data for NIST100, DUKE100, DUKE50, and DUKE20 test samples, respectively. All instruments returned their measurement values of the test samples except for the DUKE20. FE-TEM and AFM did not provide measurement results. Their operators claimed that the concentration for the 20 nm test sample was too low that the instruments were not able to allocate enough number of particles to determine their values after several unsuccessful trials despite the fact that the instruments capability should be able to accommodate dimensional measurements at this range. Although all instruments provided measurement values with significant digits down to two decimal points, they were the result from the software calculation. The number of significant digits was rounded off to agree with that of the samples' certified values when taking the average values and standard deviations.

Table 2: NIST100 measurement data

Unit: nm

Instruments	Measurements						Average Diameter	Standard Deviation
	1	2	3	4	5	6		
PCCS	99.13	93.61	95.40	96.70	95.33	103.27	97.2	3.5
TEM	90.63	91.27	92.91	96.15	95.32	88.31	92.4	2.4
FE-TEM	81.53	83.91	83.29	73.82	72.58	73.25	78.1	5.4
AFM	98.63	103.52	97.67	96.68	101.56	100.52	99.8	3.5
NIST Certified Value	100.7 ± 1.0							

Table 3: DUKE100 measurement data

Unit: nm

Instruments	Measurements						Average Diameter	Standard Deviation
	1	2	3	4	5	6		
PCCS	98.60	99.73	102.27	95.97	99.17	110.14	101	5
TEM	86.83	90.44	88.16	91.01	87.02	89.71	89	2
FE-TEM	87.51	91.51	89.89	79.65	78.42	78.51	84	6
AFM	112.58	111.77	116.52	104.52	106.42	101.02	109	6
Duke Certified Value	102 ± 3							

Table 4: DUKE50 measurement data

Unit: nm

Instruments	Measurements						Average Diameter	Standard Deviation
	1	2	3	4	5	6		
PCCS	52.97	53.61	52.69	53.30	54.19	50.08	52.8	1.4
TEM	53.96	46.73	40.12	47.96	51.68	53.21	48.9	5.3
FE-TEM	44.10	45.78	47.60	39.23	38.99	35.89	41.9	4.6
AFM	52.73	54.69	50.78	54.69	50.78	52.73	52.7	1.8
Duke Certified Value	50.0 ± 2.0							

Table 5: DUKE20 measurement data

Unit: nm

Instruments	Measurements						Average Diameter	Standard Deviation
	1	2	3	4	5	6		
PCCS	22.72	21.29	21.30	22.54	22.34	23.42	22.3	0.8
TEM	29.01	34.08	27.20	32.37	29.39	26.46	29.8	2.8
FE-TEM	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
AFM	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Duke Certified Value	21.0 ± 1.5							

The measurement data for each test sample were plotted with certified values serving as reference values and two times the standard deviations as the upper and lower control limits. For each measurement, two times the standard deviation represents the error bar. The comparison results for NIST100, DUKE100, DUKE50, and DUKE20 test samples are shown in Figure 2, Figure 3, Figure 4, and Figure 5, respectively.

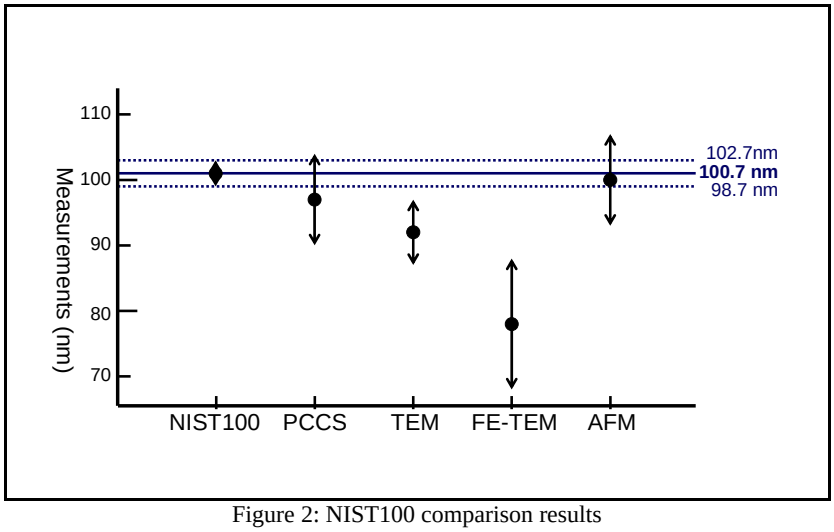

Figure 2: NIST100 comparison results

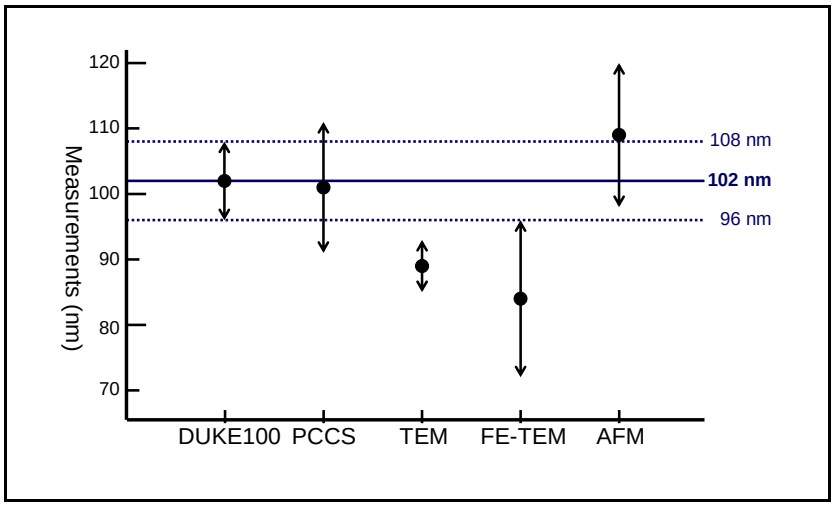

Figure 3: DUKE100 comparison results

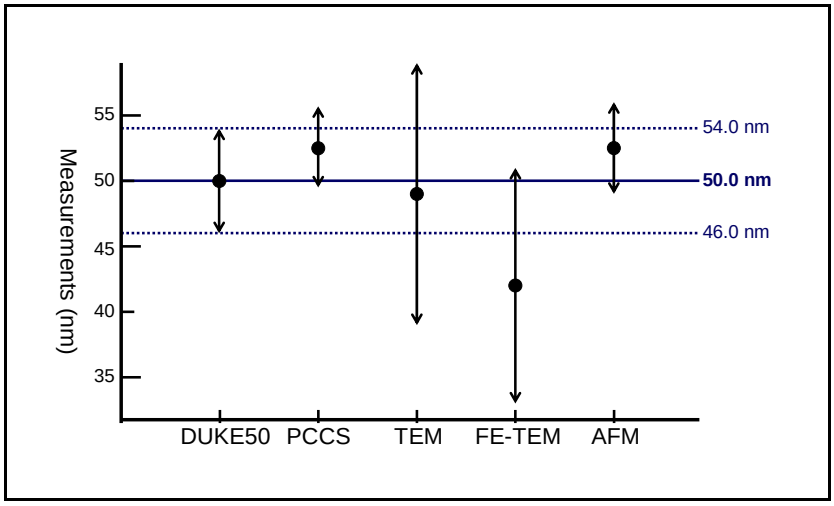

Figure 4: DUKE50 comparison results

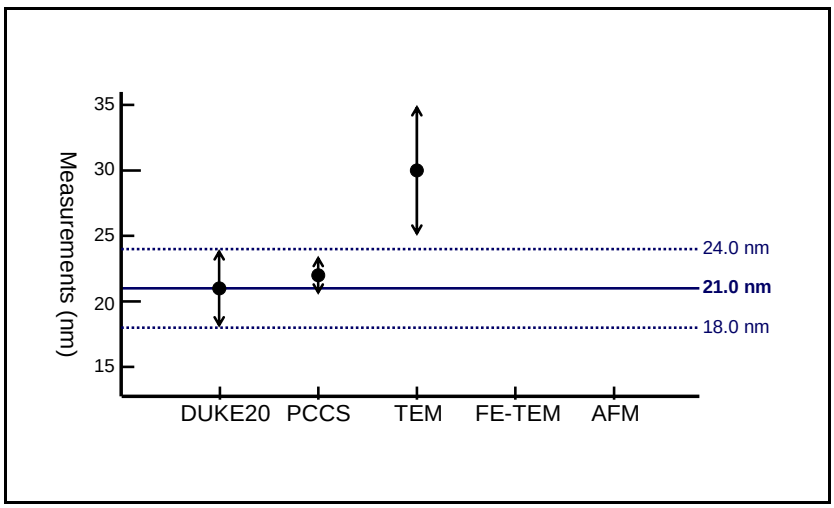

Figure 5: DUKE20 comparison results

4. DISCUSSIONS

A quick look through the comparison results reveals the outliers from the FE-TEM instrument. All its measurement values are outside the control limits of the certified values. It is later determined that instrument calibration is needed on the FE-TEM since its values are way off from the certified values and other instruments'. On the contrary, the AFM produced relatively well measurement results as compared to the samples' certified values except for the unsuccessful determination on the 20 nm test sample. The overall performance from the PCCS seems fairly well in all four test samples despite the earlier anticipation that measurement values from PCCS tend to be larger than the ones from microscopy-based techniques. PCCS is the only technique in this comparison that conducts particle measurement directly in suspension. What it measures is in fact the hydrodynamic diameter of the particles. As for the TEM, the measurement results are far from satisfactory. Although its result on the 50 nm test sample is the only measurement that lies within the control limits, its large error bar indicates the repeatability on the six measurements is relatively low as compared to other instruments. The primary cause for the deviation of the measurement values from TEM is not clear. It is suspected that sample preparation could be the major contribution to the error.

It is apparent that there are other possibilities that these measurement results could be further interpreted. It is also true that the overall comparison scheme could be more thoroughly designed so that specific instrument factors could be taken into consideration in terms of comparability. As mentioned in the introduction, the lack of well recognized standards in this area is an ongoing issue. Of the four measurement instruments used in this comparison, there is only the ISO 13321 standards available for particle size analysis by PCS. Written standards are necessary to ensure consistent sample preparation and measurement procedures. In all, this comparison serves as a preliminary study. A more comprehensive interlaboratory comparison to involve more participating laboratories and robust statistical analysis is in the plan.

ACKNOWLEDGMENTS

This comparison study was part of the APEC ISTWG sponsored project "Technological Cooperative Framework on Nanoscale Analytical and Measurement Methods". Special thanks were given to many researchers at NanoTechnology Research Center, Center for Measurement Standards, Materials Research Laboratories, and Union Chemical Laboratories, of Industrial Technology Research Institute for their support in providing these measurements for the comparison study.

REFERENCES

1. B. Scarlett, *Standardization of nanoparticle measurements*, Journal of Nanoparticle Research 2: 1-2, Kluwer Academic Publishers, Netherland, 2000.
2. A. Jillavenkatesa, S. J. Dapkunas, and L. H. Lum, *Particle Size Characterization*, NIST Special Publication 960-1, US Government Printing Office, Washington, 2001.
3. W. L. Grosshandler and J. Rumble, *Certificate of Analysis – Standard Reference Materials® 1963*, NIST, Gaithersburg, 2003.
4. C. Tuttle, *Certificate of Calibration and Traceability – Catalog Number 3020 and 3020A, Nanosphere™ Size Standards*, Duke Scientific Corporation, Palo Alto, 2004.
5. E. B. Layendecker, *Certificate of Calibration and Traceability – Catalog Number 3050 and 3050A, Nanosphere™ Size Standards*, Duke Scientific Corporation, Palo Alto, 2004.
6. E. B. Layendecker, *Certificate of Calibration and Traceability – Catalog Number 3100 and 3100A, Nanosphere™ Size Standards*, Duke Scientific Corporation, Palo Alto, 2004.
7. ISO/IEC Guide 43-1, *Proficiency testing by interlaboratory comparisons – Part 1: Development and operation of proficiency testing schemes*, ISO, 19997.
8. ISO/IEC Guide 43-2, *Proficiency testing by interlaboratory comparisons – Part 2: Selection and use of proficiency testing schemes by laboratory accreditation bodies*, ISO, 1997.

*chez@itri.org.tw; phone +886 3 5743717; fax +886 3 5726445; www.itri.org.tw