

Measurement of the 100 nm NIST SRM 1963 by Differential Mobility Analysis

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ABSTRACT. The number mean diameter of 100 nm NIST Standard Reference Material (SRM) 1963 was measured to be 100.7 nm with an expanded uncertainty at the 95% confidence level of 1.0 nm by measurement with the differential mobility analyzer (DMA). The low level of uncertainty resulted from the use of the 1.0 μm SRM 1690 for calibrating the DMA. The largest single component of the Type B (systematic) uncertainty was a 0.29 nm uncertainty in the calibration diameter. Measurements of the 0.3 μm SRM with the calibrated DMA give results within 0.001 μm of the certified diameter. Results obtained by other investigators using transmission electron microscopy (TEM), angle dependent light scattering, electro-gravitational aerosol balance, and atomic force microscopy are consistent with this DMA value. The 100 nm NIST SRM 1963 and the Japanese 100 nm Calibration Standard are shown to differ by 10% based on TEM analysis and DMA measurements. This size difference has a significant effect on the calibration of scanning surface inspection systems and optical particle counters.

INTRODUCTION

The National Institute of Standards and Technology issues (NIST) Standard Reference Materials (SRM) for a wide range of particle sizes including 100 nm¹ (SRM 1963), 0.3 μm (SRM 1691), 1 μm (SRM 1690), 3 μm (SRM 1692), 10 μm (1960), and 30 μm (1961). These standards are monosize polystyrene spheres suspended in water at a concentration in the range of 0.5–1 % by mass.

The most recent SRM issued was the 100 nm size, whose calibration was based on measurements with a differential mobility analyzer (DMA), also called an electrostatic classifier. A comprehensive assessment of this method for accurately sizing 100 nm diameter spheres was made by Kinney et al. (1991), and it was found feasible for making particle size measurements with a relative expanded uncertainty (95% confidence level) of about 3%. Subsequently, monosize particles with a mean size close to 100 nm were purchased and several hundred 5 ml samples with a mass fraction of 0.5% were prepared. Measurements similar

¹The 100 nm size was referred to as 0.1 μm in the SRM Certification.

to those described by Kinney et al. (1991) were carried out to determine the particle size of a statistically meaningful number of samples. One major change in the methodology was to use the 1.0 μm SRM to calibrate the DMA. The 1 μm refers to the nominal diameter and the actual size is 0.895 μm . This technique enabled the reduction of the overall measurement uncertainty for the 100 nm SRM from about 3 nm to about 2 nm. The mean size and its uncertainty based on these measurements are included in the SRM 1963 certificate; however, the procedures used in making the measurements and performing the uncertainty analysis have not previously been published. This paper consists of the technical support for these measurements, including a description of this new method for calibrating the DMA. The new methodology used at NIST for reporting uncertainty is applied in computing the uncertainty of the 100 nm SRM.

Several other measurements of the 100 nm SRM 1963 particles were made by others using independent methods. These include transmission electron microscopy (TEM), light scattering measurements, electro-gravitational aerosol balance measurements, and atomic force microscopy. These results will be compared with the certified value.

JSR Company,² which synthesized the particles for SRM 1963, also provides a 100 nm calibration standard. However, the particles sold by JSR Company as 100 nm come from a different batch than those used in the NIST SRM. These particles are

used for calibrating optical particle counters and scanning surface inspection systems so it is important to know whether the two sizes are the same. We have made relative size measurements of these two standards by both TEM and by DMA measurements. The results of the comparison will be described and the implication of the results will be discussed.

METHOD AND MATERIALS

The 100 nm spheres were synthesized by JSR Company using emulsion polymerization with styrene monomer. In this case the surfactant is synthesized into the polymer itself as carboxyl groups so that no additional surfactant is added. The bulk suspension was diluted and bottled by Duke Scientific Company at a mass fraction of 0.5%. To prepare samples for analysis by the DMA, one drop of the suspension was diluted with 100 cm^3 of deionized water filtered with a 0.2 μm pore size filter. The suspensions of the 1 μm particle standard (SRM 1690) were prepared with 50 drops of the particle suspension and 100 cm^3 of clean water. The high concentration was necessary to produce an adequate number concentration for measurement by the nucleus counter.

The particle measurement system consists of an aerosol generation system, a DMA for size selection, and a condensation nucleus counter for monitoring the aerosol concentration (see Figure 1). A brief description of the instrumentation and methodology is given below; a detailed description is given by Kinney et al. (1991). The particle suspension is dispersed by placing the container in an ultrasonic bath for about 1 min. The suspension is then nebulized at a pressure of 103 kPa gauge (15 psig) to form an aerosol with droplets containing the polystyrene (PS) spheres. The water evaporates as the aerosol flows

²Certain commercial equipment, instruments, or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

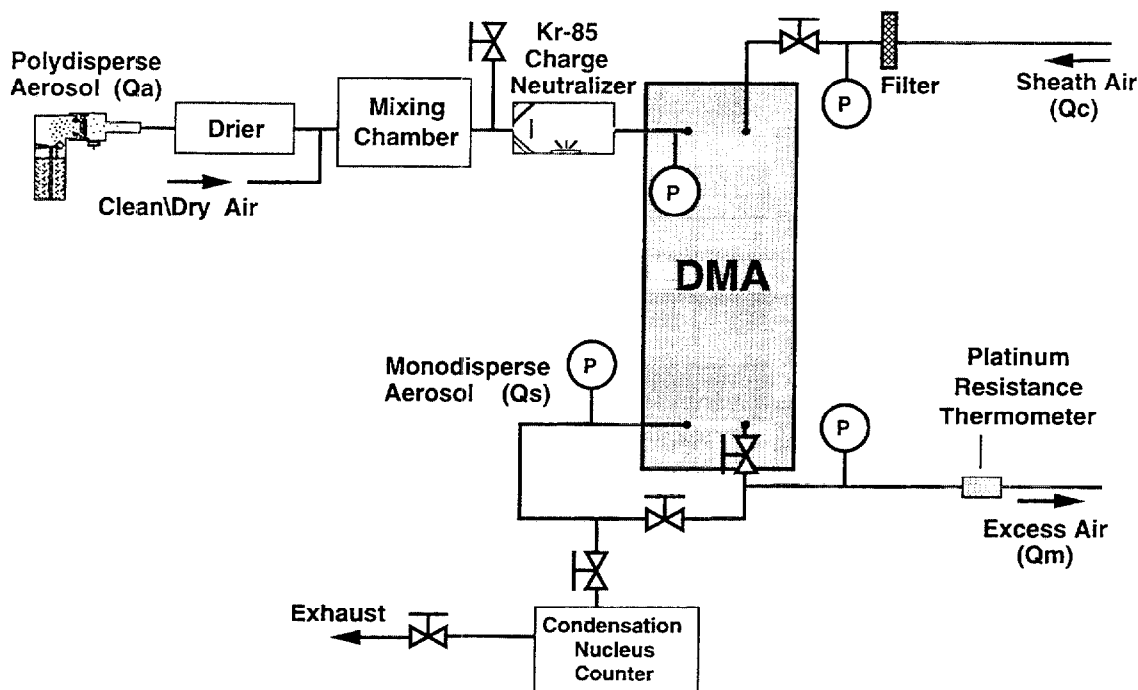


FIGURE 1. Schematic of the particle generation and measurement system.

at $83 \text{ cm}^3/\text{s}$ ($5 \text{ L}/\text{min}$) through a diffusion drier and then mixes with a flow of $40 \text{ cm}^3/\text{s}$ of clean, dry air. The PS aerosol is initially highly charged from the nebulization process and is "neutralized" with a bipolar charger so that the largest fraction of the particles have no charge, 20% have $+1 e$ charge, and another 20% have $-1 e$ charge, and a much smaller fraction are multiply charged particles.

The DMA consists of an inner cylinder rod connected to a variable (0 V to $-11,000 \text{ V}$) DC power supply and an outer annular tube connected to ground. Clean sheath air flows through the axial region while the charged aerosol enters through an axisymmetric opening along the outer cylinder. The positively charged PSK spheres move radially towards the center rod under the influence of the electric field. Near the bottom of the classifying region, a fraction of the airflow consisting of near-monosize aerosol exits through a slit in the center rod

and flows to a condensation nucleus counter, where the number concentration of the particles is measured. A measurement sequence consists of measuring the number concentration as a function of the inner rod voltage.

The quantity measured by the DMA is the electrical mobility, Z_p , defined as the velocity a particle attains under a unit electric field. Knutson and Whitby (1975) derived an expression for the average value of Z_p for the particles entering the slit involving the electrode voltage, V , the sheath airflow rate, Q_c , the inner and outer radii of the cylinders, r_1 and r_2 , and the length of the central electrode down to the slit, L .

$$Z_p = \frac{Q_c}{2\pi VL} \ln(r_2/r_1). \quad (1)$$

This equation is valid provided the sheath airflow, Q_c , is equal to the excess flow, Q_m , leaving the classifier.

An expression for the electric mobility of a singly charged particle involving the particle diameter is obtained by equating the electric field force with the Stokes friction force:

$$Z_p = \frac{eC(D_p)}{3\pi\mu D_p}, \quad (2)$$

where μ is the dynamic viscosity of air and e is the electron charge. The Cunningham slip correction $C(D_p)$, which corrects for the noncontinuum gas behavior on the motion of small particles, is given by

$$C(D_p) = 1 + K_n[A_1 + A_2 \exp(-A_3/K_n)], \quad (3)$$

where the Knudsen number is twice the mean free path of air divided by the particle diameter ($K_n = 2\lambda/D_p$) and $A_1 = 1.142$, $A_2 = 0.558$, and $A_3 = 0.999$ (Allen and Raabe 1985). For a measured value of Z_p , the particle diameter, D_p , is obtained iteratively from Equations (2) and (3), which has an implicit dependence on D_p via the Knudsen number.

Pressure and temperature corrections were made to the mean free path and viscosity based on the following equations (Allen and Raabe 1982):

$$\lambda = \lambda_0 \left(\frac{T}{T_0} \right) \left(\frac{P_0}{P} \right) \left(\frac{1.0 + \frac{110.4}{T_0}}{1.0 + \frac{110.4}{T}} \right), \quad (4)$$

$$\mu = \mu_0 \left(\frac{T}{T_0} \right)^{1.5} \left(\frac{T_0 + 110.4}{T + 110.4} \right), \quad (5)$$

where λ_0 is 67.3 nm for air at T_0, P_0 ; μ_0 is 1.8324×10^{-5} Pa·s for air at T_0, P_0 ; T_0 is reference temperature, 296.15 K; P_0 is reference pressure, 1.0133×10^5 Pa (760 mm Hg).

The range of flows was constrained by the relatively low flows and high voltage required to measure the 1 μ m SRM, which

was used to calibrate the DMA. A sheath flow of 133.3 cm³/s and an aerosol flow of 13.3 cm³/s resulted in a peak in the mobility distribution of triply charged 1 μ m spheres of about 10,000 V and a peak for the singly charged 100 nm particles of about 1,400 V. These flow conditions are near the ideal values for the classifier and were made possible by analyzing the triply charged 1.0 μ m particles. If singly charged particles were measured for the 1 μ m particles, the sheath flow would have had to be reduced to 44.3 cm³/s. This is outside the normal range of the classifier and would provide a challenge in terms of maintaining an aerosol flow into and out of the DMA with a value of 4.43 cm³/s needed to provide the same sizing resolution as is obtained at the higher flow.

Two types of measurement sequences were carried out. The first was designed to measure the particle size for a single SRM sample accurately. The second was designed to assess the sample-to-sample variability as well as the within sample variability. In the first sequence, the number concentration versus voltage was measured for the 1 μ m spheres. Next a four-jet impactor with a 0.5 μ m cut size was inserted just downstream of the nebulizer. The non-volatile impurities in the water increase the apparent particle size of the PS sphere as the water droplet surrounding the PS sphere evaporates. The nebulizer produces droplets as large as 5 μ m and those larger than 0.5 μ m are removed by the impactor. This was used to reduce the effect of the nonvolatile impurities in the droplets increasing the diameter of the dried 100 nm PS. The number concentration was then measured versus voltage for these particles. This sequence was repeated one or more times on five separate days to reduce the uncertainty associated with any day-to-day variability.

The second set of data involved the preparation of diluted samples from 15 in-

dividual samples selected at random from a total of 300 samples of the 100 nm material. One sample was used as the "standard" and a measurement of the standard and four or five other samples were made. This process was repeated until each of the samples was measured twice. All of these measurements were performed on the same day.

The measurement process consisted of measuring the number concentration at five voltages with the voltages selected so that the lowest and highest voltages gave number concentrations equal to approximately 1/3 of the peak value. These voltages were determined from a preliminary measurement set. A repeat measurement was made at the end of the sequence to check for drift in the generator output. Data was collected over 1 min for each voltage, and the average was computed over the last 30 s. Typical data sets are plotted for both the 100 nm and 1 μm data in Figure 2.

DATA ANALYSIS

The major difference from the previous study by Kinney et al. (1991) is the use of the 1 μm SRMs in calibrating the classifier. As shown in this paper, the largest measurement uncertainties in the earlier measurements were associated with flow uncertainty, which accounted for over half of the 3% relative expanded uncertainty. By using the 1 μm SRM, the uncertainty associated with the flow calibration is removed along with uncertainties associated with the dimensions (length and radii of central rod and concentric tube) of the classifier. This trades the uncertainty in the direct measurement of the 100 nm particles for the uncertainty in the 1 μm particles plus the factors that don't cancel directly.

The procedure for calibrating the DMA involves first computing the number aver-

age voltage for the 1 μm SRM particles. The electrical mobility corresponding to the average voltage is determined by using Equation (1) and the measured values of the sheath flow Q_c , the length of the classifier tube L (44.44 cm), and the inner and outer radii r_1 and r_2 (0.937 cm and 1.958 cm). The electrical mobility is also computed for the 1 μm SRM particle from Equations 2 and 3 based on the actual 0.895 μm diameter. Ideally these two values should be the same. If the measured value differs from the computed value, the value of the sheath flow in Equation (1) is varied until the measured and computed mobilities are equal. The data for the 100 nm particle size is then reduced using the corrected flow rates. Typically the corrected flow rate was slightly more than 1% greater than the measured flow rate.

In Table 1 the measured and corrected results are given for two sets of measurements for the 1 μm particles. In Table 2 the number concentration and voltage are presented along with the particle diameters derived from Equations (1) and (2) for these voltages. The number concentration versus particle diameter is plotted in Figure 3 for the first data set in Table 2. The number mean diameter is obtained using the following equation:

$$\bar{D}_p = \frac{\sum_i N_i D_i}{\sum_i N_i} \quad (6)$$

A summary of all 16 determinations of the particle size \bar{D}_p over five days is included in Table 3.

As mentioned above, the repeatability measurements did not involve calibration with the 1 μm spheres. They consisted of measurements on two samples from each of 14 vials of 100 nm particles plus a number of measurements from the control sample. The order of sample measurement was determined by a random number generator. The volumetric flow was selected so that

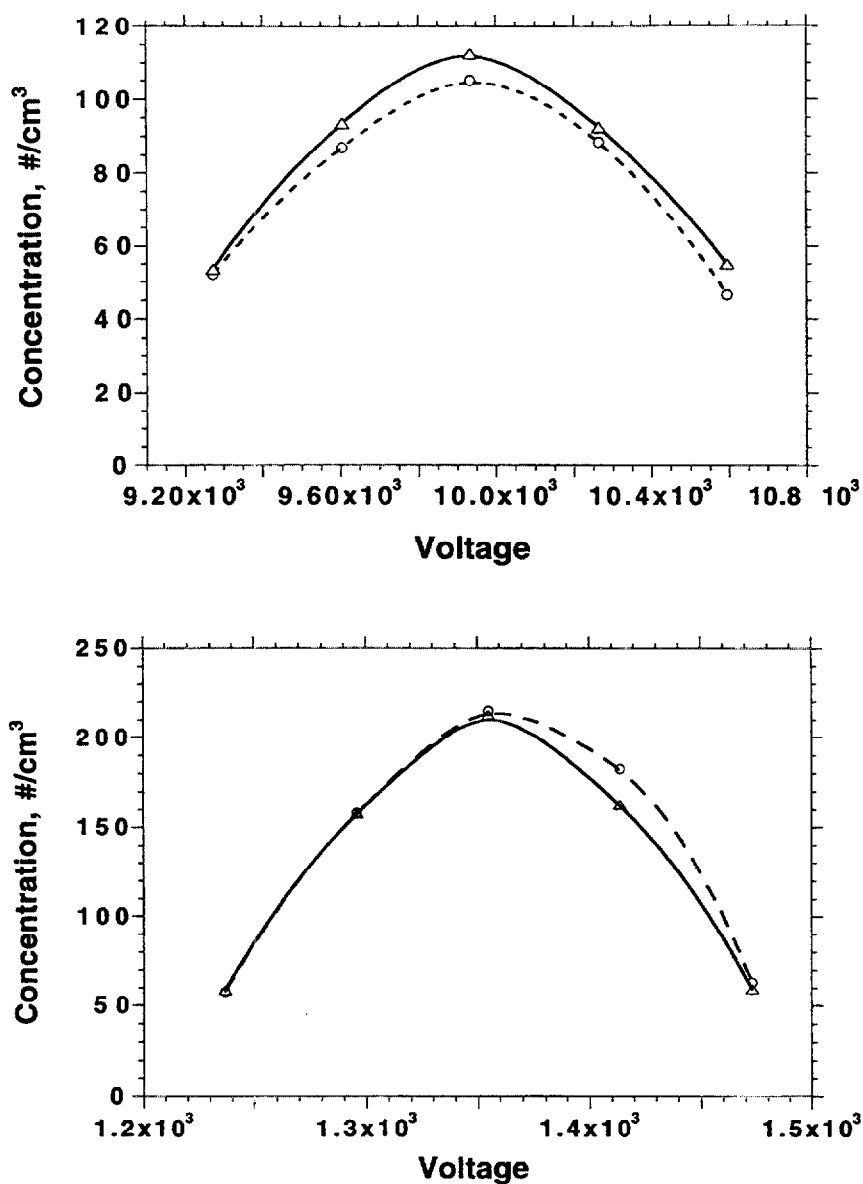


FIGURE 2. Number concentration versus voltage for 2 repeat runs for the 1 μm SRM spheres (upper) and for the 100 nm spheres (lower).

the particle size for the control of each of 15 data sets was equal to $0.1010 \mu\text{m}$. The first sample measured was from the control sample and the measurement of this sample was repeated after every four or five samples to check for drift. A summary of these results is given in Table 4. These measurements are the basis of determining

the repeatability and sample-to-sample variability of the measurement method.

MEASUREMENT OF 1 μm SRM PARTICLES WITH 4 CHARGES

The data analysis presented above is based on the measurement of the electrical mo-

TABLE 1. Results for 1 μm SRM (4/1/90)

Corrected Voltage ^a	F1 ^b , #/cm ³	G1, #/cm ³
9,273	52.0 ^c	53.5
9,603	87.0	93.5
9,934	105.0	112.5
10,264	88.5	92.5
10,595	46.5	55.0
Average	9926	9935
Voltage, V		
Sheath Flow, cm ³ /3	135.12	135.12
Z _p , cm ² /(Vs)	1.1977E-5	1.1966E-5
Z _p for 1 μm SRM	1.2122E-5	1.2122E-5
Corrected Sheath Flow	136.76	136.88
Pressure = 100.47 kPa (753.6 mm Hg), Temperature = 24.7°C		

^aThe indicated voltage by the classifier required a correction on the order of 350 V.

^bThe corrected sheath flow determined from the F1 calibration measurements is used in analyzing the data set F in Table 2.

^cThe average number concentration was determined to the nearest 0.5 particles/cm³.

bility of 1 μm spheres with three charges. In the process of going through the bipolar charger, a number of spheres acquire four

TABLE 2. Results for 100 nm SRM Particles (4/1/90)

Corrected Voltage ^a	Diameter ^b , nm	F ^c , #/cm ³	Diameter, nm	G, #/cm ³
1,237	95.78	57.5	95.72	58.5
1,296	98.36	158.0	98.30	157.5
1,355	100.89	215.0	100.83	212.5
1,414	103.38	182.5	103.32	162.5
1,473	105.84	63.0	105.78	59.0
Corrected		136.76		136.88
Sheath Flow, cm ³ /s				
\bar{D}_p , nm		101.00		100.83

^aThe indicated voltage by the DMA required a correction on the order of 15 V.

^bThe diameters corresponding to the corrected flow rate for data set F1 listed in Table 1.

^cData set F is analyzed based on the corrected flow computed in data set F1.

charges. A consistency check of the measurement procedure is made by comparing the particle's sizes inferred from the triply and quadruply charged spheres. This method cannot be extended to the singly and doubly charged spheres because the voltage range of the classifier is not high

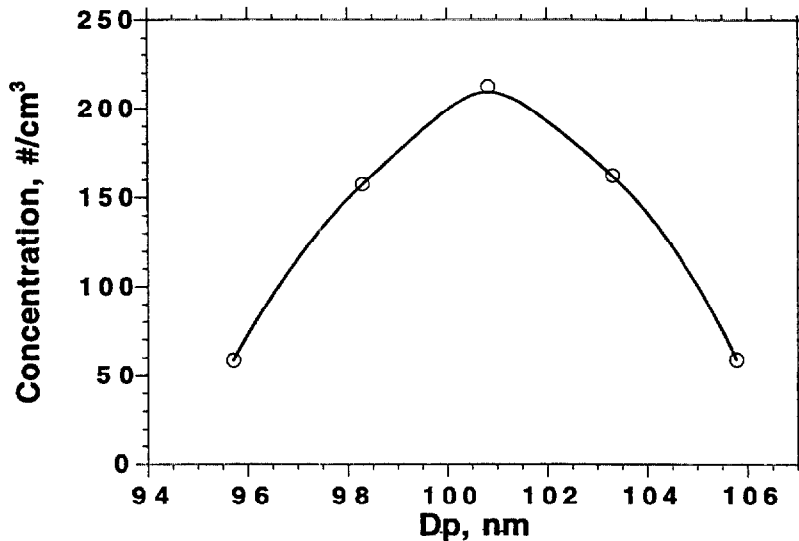


FIGURE 3. The size distribution for 1 measurement sequence for the 100 nm SRM 1963.

TABLE 3. Summary of 100 nm SRM Results

Date	\bar{D}_p , nm	Date	\bar{D}_p , nm
April 1, 1990	101.00	July 17, 1990	100.85
	100.83		100.87
	101.13	Average	100.86
	100.84	July 18, 1990	100.09
	100.86		100.02
Average / ± Sigma	100.93 ± 0.13	Average	100.06
April 3, 1990	101.23	July 19, 1990	100.44
	101.23		100.46
	101.25	Average	100.45
	101.27	Average of averages	100.71
	101.31	Standard deviation of averages	0.46
Average / ± Sigma	101.26 ± 0.03		

TABLE 4. Results from 15 Vials

Experi- ment #	4/2/90; 1:30 pm–4:00 pm		Experi- ment #	4/2/90; 8:00 pm–10:30 pm	
	N, #/ cm ³	\bar{D}_p^a , nm		N, #/ cm ³	\bar{D}_p , nm
Control 1 ^b	1,210	101.06	control 5	1,402	101.00
51-1	1,082	101.09	211-1	947	101.06
250-1	774	101.07	200-1	897	101.15
30-1	800	101.07	156-1	893	101.02
309-1	607	101.06	183-1	657	100.99
93-1	908	100.92	211-2	898	100.95
Control 2	1,122	101.00	Control 6	1,193	100.93
51-2	1,205	100.95	15-1	1,446	101.09
137-1	828	100.93	200-2	1,012	100.98
93-2	1,118	100.94	273-1	778	100.98
250-2	1,068	100.86	156-2	949	100.99
Control 3	1,280	100.94	Control 7	1,256	100.98
309-2	802	100.82	300-1	953	100.93
30-2	998	100.79	273-2	830	100.97
137-2	832	100.84	183-2	515	100.99
327-1	714	100.72	300-2	1,049	100.97
327-2	774	100.95	15-2	1,443	101.00
Control 4	1,168	100.93	Control 8	1,324	101.02

^aFlow rate adjusted in data analysis so that the size for Control 2 is 101.00 nm.

^bThe control samples were all obtained by diluting 1 sample vial. There was significant drift in the concentration during the measurement of Control 1, and for this reason the flow calibration was based on Control 2.

TABLE 5. Comparison of Sizing Results Based on 3 Charges and 4 Charges

Experiment #	# of Charges	Total Number Concentration,	
		# / cm ³	\bar{D}_p , μm
4	3	369	0.9233
5	3	380	0.9240
5 ^a	4	239	0.9276
6	4	240	0.9291

^aIn experiment 5, the mobility spectrum of the particles with 4 charges was taken immediately after completing the spectrum of the triply charged particles.

enough to collect these lower mobility particles. As is seen in Table 5, the difference in the measured size is about 0.005 μm . For experiment 5, where the three and four charge particles were measured in the same sequence, the difference is 0.0036 μm .

MEASUREMENT OF THE 0.3 μm SRM

As another consistency check, the average diameter of the 0.3 μm NIST SRM 1691 was measured using the same procedure as with the 100 nm spheres. First, the classifier was calibrated with the 1 μm spheres and then the average size of the 0.3 μm spheres was measured. In this case, the impactor was not inserted. The two measured values of 0.2690 μm and 0.2691 μm are in excellent agreement with the certified value of 0.269 μm . The 0.269 SRM was not used for calibrating the classifier because of the larger relative uncertainty for the 0.3 μm SRM ($\pm 2.6\%$) relative to 0.9% for the 1 μm SRM. A TEM photograph provided by Duke Scientific Corp. (Figure 4) shows a mixture of the 100 nm SRM spheres and the 0.3 μm spheres.

UNCERTAINTY ANALYSIS

A uniform methodology for reporting measurement uncertainty has been adopted at

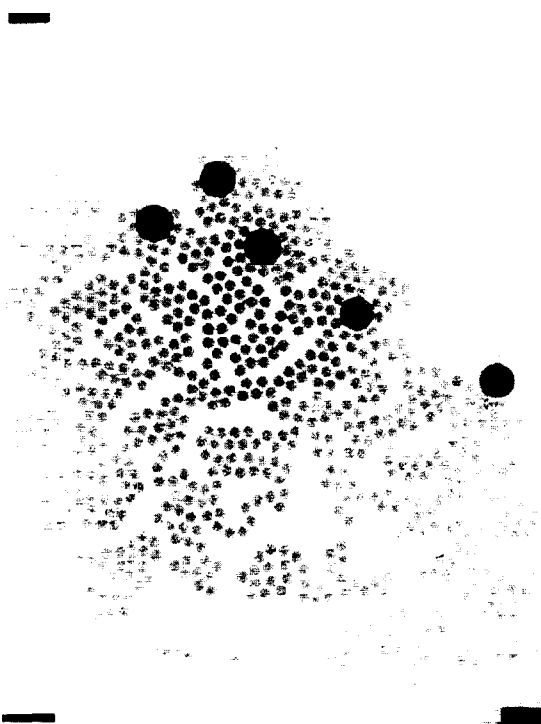


FIGURE 4. TEM of a mixture of 100 nm SRM 1963 spheres and 0.3 μm SRM 1691 spheres (provided by Duke Scientific Corp.).

NIST (Taylor and Kuyatt 1994), which is based on a much more extensive ISO document (1993). Our uncertainty analysis is based on this recommended method and differs somewhat from the method used in the earlier study (Kinney 1991). The components of uncertainty are divided into two categories: Type A are those evaluated by statistical methods and Type B are those evaluated by other means. Roughly speaking, these types correspond to the random and systematic components of the uncertainty. For the particle sizing measurements, the Type A uncertainty is evaluated by the measurement repeatability and sample variability while the Type B uncertainty is evaluated for the effects of the slip correction, voltage calibration, the uncertainty in the 1 μm calibration standard, pressure, temperature, viscosity, the data analysis

methodology, and the instrument resolution. These two types of uncertainty are treated separately below.

Type A Uncertainties

Two components contribute to the Type A uncertainty. One is the homogeneity of the sample; that is, vial-to-vial variability. The second is concerned with the measurement repeatability.

The homogeneity study consisted of eight measurements on a control vial and two measurements on each of 14 other vials (Table 4). The analysis of variance shows no significant difference between diameters of spheres from those vials; this finding translates into a between-vial standard deviation of zero. The repeatability standard deviation was estimated to be 0.090 nm. There are 7 degrees of freedom from the 8 measurements of the control vial and 1 degree of freedom from each of the 14 other vials. The degrees of freedom are pooled to be 21. Therefore, calibrated measurements on one vial, the control vial, are considered sufficient to certify a value for the entire batch.

The certification measurements consisted of repetitions over five days on samples drawn from the control vial with the number of repetitions equal to 5, 5, 2, 2, and 2 for the five days (Table 3). The notation for the measurements is $D_p(ij)$, where the index i ($i = 1, \dots, 5$) is over days and the index j ($j = 1, \dots, M_i$) is over repetitions within a day.

$$D_p(ij) = \mu + \delta_i + \epsilon_{ij}, \quad (7)$$

where μ is the true value, δ_i are random error terms attributable to between-day effects with standard deviation σ_δ ; and ϵ_{ij} are random errors under repeatability conditions with standard deviation σ_ϵ . The standard deviations, σ_δ and σ_ϵ , are esti-

mated to be

$\sigma_{\delta} = 0.447$ nm with ~ 4 degrees of freedom,
 $\sigma_{\epsilon} = 0.083$ nm with 11 degrees of freedom.

The repeatability standard deviation, σ_{ϵ} , agrees with the repeatability standard deviation from the homogeneity study. Thus, the components of Type A uncertainty are the between-day standard deviation and the repeatability standard deviation as listed above with the between-vial standard deviation being zero.

Because of the differences among the daily averages, the certified value is not weighted by the number of observations per day but is taken to be the unweighted average

$$\bar{D}_p = \frac{1}{5} \sum_i \bar{D}_p(i) = 100.71 \text{ nm}, \quad (8)$$

where $\bar{D}_p(i)$ are the daily averages

$$\bar{D}_p(i) = \frac{1}{M_i} \sum_{j=1}^{M_i} D_p(ij). \quad (9)$$

To calculate the uncertainty associated with \bar{D}_p , we need an expression for the variance of \bar{D}_p . If the design were balanced, i.e., with M repetitions per day, the variance would be

$$\frac{1}{5} \sigma_{\delta}^2 + \frac{1}{5M} \sigma_{\epsilon}^2. \quad (10)$$

In this case, M is not constant over days; however, the average, $\bar{M} = 3.2$, gives an estimate of

$$\frac{1}{5} \sigma_{\delta}^2 + \frac{1}{16} \sigma_{\epsilon}^2, \quad (11)$$

which is very close to the exact expression

$$V(\bar{D}_p) = \frac{1}{5} \sigma_{\delta}^2 + \frac{19}{250} \sigma_{\epsilon}^2. \quad (12)$$

Substituting the estimates for the individual variances in the formula above leads to the

estimated combined standard deviation

$$\delta(\bar{D}_p) = \sigma(D_A) = 0.20 \text{ nm}. \quad (13)$$

The subscript A refers to the total Type A uncertainty. Degrees of freedom cannot be computed exactly in this case, but because the term in Equation (12) involving the standard deviation for days, σ_{δ} , accounts for most of $\sigma(D_A)$, the effective degrees of freedom are taken to be four.

Type B Uncertainties

For five of the uncertainty components, voltage, the calibration particle size, pressure, temperature, and viscosity, the uncertainty analysis is straightforward. First an estimated standard uncertainty of the variable is obtained and then the resulting effect of this uncertainty on the particle diameter is obtained using Eqs. 1–5. Less direct analyses are required for slip correction, data analysis methodology, and instrument resolution.

Voltage. As discussed in Kinney et al. (1991), the voltmeter was calibrated using an accurate voltage divider allowing measurements up to 10,000 volts with a 1 volt full scale setting of an accurate digital voltmeter. The estimated standard uncertainty of the voltage calibration, $\sigma(V)$, is 0.2% of the reading.

Particle Standard. The 1 μm SRM has a 95% confidence interval of 0.008 μm (Mulholland et al. 1985) and we divide this by 2 to obtain a standard uncertainty, $\sigma(\text{CAL})$, equal to 0.004 μm . The 1 μm particles were used in calibrating the classifier.

Pressure, Temperature, and Viscosity. The estimated standard uncertainty for the pressure, 4.0×10^3 Pa (3 mm Hg) (Kinney et al. 1991), is due to uncertainty in the mercury barometer reading for ambient

pressure and the uncertainty in measuring the pressure difference between ambient air and the air within the DMA. The estimated standard uncertainty of temperature, which is measured with a platinum resistance thermometer, is 0.5°C (Kinney et al. 1991) and is a result of the slight drift in temperature during an experiment and the temperature difference between the sheath air and the air within the DMA. The estimated standard uncertainty in the viscosity for a fixed temperature and temperature is 7.3×10^{-9} Pa·s (0.04% of nominal value) (Birge 1945; Millikan 1947).

Uncertainty Propagation. The voltage and calibration particle size are changed by the amount of the corresponding standard uncertainty and the resulting change in the particle diameter is computed using Equations (1)–(3). There are two sets of voltage measurements. The first set is the voltage measurements associated with the calibration of the DMA with the 1 μm SRM. A change in the voltage affects the computed flow correction which in turn affects the measurement of the 100 nm spheres. Increasing the nominal voltage of 9926 V by 0.2% results in a decrease of the particle size by 0.11 nm, which is denoted $\sigma(D_{V1})$. The D refers to a component of the diameter uncertainty and the subscripted symbols refer to the variable affecting the uncertainty. The second set of voltage measurements is for determining the mobility of the 100 nm particles. In this case a 0.2% increase in the nominal 1,355 V results in an increase in the particle size by 0.11 nm, which is denoted $\sigma(D_{V0.1})$.

The value of the standard uncertainty associated with the 1 μm SRM, $\sigma(\text{CAL})$, is 0.004 μm . Increasing the 1 μm SRM size (actually 0.895 μm) by an amount equal to $\sigma(\text{CAL})$ results in an increase in the 100 nm particle size by 0.29 nm. This component of the standard uncertainty of the mean size is termed $\sigma(D_{\text{CAL}})$ and is the

largest component of the uncertainty for the mean particle size.

The uncertainty in the pressure and temperature affects the mean free path λ (Equation (4)), which in turn affects the slip correction C (Equation (3)), and the uncertainty in the temperature also affects the viscosity (Equation (5)). Increasing the pressure by 4.0×10^3 Pa decreases the particle size of a 100.7 nm particle by 0.17 nm ($\sigma(D_{Pr})$), while increasing the temperature by 0.5°C increases the particle diameter by 0.02 nm ($\sigma(D_T)$). Increasing the viscosity by 7.3×10^{-9} Pa·s results in an increase in the particle diameter by 0.03 nm ($\sigma(D_\mu)$). Table 6 summarizes all the uncertainty components for the Type B uncertainties.

Slip Correction. The slip correction for the 100 nm particles was computed based on the expression of Allen and Raabe (1985) given in Equation (3). This expression was determined using an improved Millikan apparatus and involved measurements of the settling velocity and the electric field force required to balance the gravitational force to keep the particle suspended. The standard uncertainty of the value of the slip correction C for 100.7 nm spheres was determined as 0.23% based on the uncertainties given by Allen and Raabe for the coefficients A_1 , A_2 , and A_3 . A new and independent measurement of the slip correction was made by Hutchins et al. (1995) based on modulated dynamic light scattering. The particle size is inferred from the Brownian motion of the particle, and, in this case, the slip correction appears in the Stokes–Einstein expression for the particle diffusion coefficient. The results for C for 100.7 nm spheres based on modulated dynamic light scattering was 0.89% larger than that obtained by Allen and Raabe with a standard uncertainty of 0.14%.

The effect of the uncertainty in the slip correction on the particle size is more subtle than for the other parameters. As seen

from Equations (2) and (3), the value of the slip correction affects the particle size, but the particle size also affects the slip correction. So one must find a consistent solution of these two equations. We have adjusted the coefficients in the slip correction by an amount consistent with the standard uncertainty of C for Allen and Raabe (1985) (from 1.142, 0.558, and 0.999 to 1.1436, 0.560, and 0.987). The diameter is first computed based on our nominal condition of $T = 24.7^\circ\text{C}$, 100.47 kPa (753.6 mm Hg), 1355 V, and a flow of 136.9 cm³/s. We obtain 100.887 nm. Then we repeat the calculation with the modified slip correction and obtain 100.968 nm or an increase of 0.081 nm. Our estimate of the standard uncertainty in the particle diameter associated with the uncertainty in the Allen and Raabe value of C is $\sigma(D_{S1}) = 0.08$ nm.

Since it is not evident which of the two slip correction studies is more accurate, we

have used the slip correction obtained by each study to analyze the first set of data in Tables 1 and 2. As indicated in Table 1, the corrected flow rate was 136.76 cm³/s based on the Allen and Raabe slip correction. The particle size corresponding to this flow and the peak voltage for the 100 nm particles, 1355 V, is 100.89 nm. For the case of the Hutchens et al. (1995) slip correction, the corrected flow is 138.33 cm³/s, and the particle size for the nominal 100 nm particles is 100.73 nm. This is only a 0.16% change in the particle diameter, while the difference in the slip correction evaluated for 100.7 nm particles is about 1%. The explanation for this seeming contradiction is that the Hutchens et al. (1995) slip correction is higher for both the 1 μm particle size and the 100 nm size, so the net effect of using the Hutchens et al. (1995) expression is a value almost identical to the Allen and Raabe value. The effective standard

TABLE 6. Summary of Measurement Uncertainties

Variable y , nominal value	$\sigma(y)^a$, $\sigma(y)/y$ in %	Component of $\sigma(D_p)$	Magnitude of component, nm
Voltage for 1 μm spheres, 9926	19.9 V, 0.2%	$\sigma(D_{V1})$	0.11
Voltage for 0.10089 μm spheres, 1355	2.7 V, 0.2%	$\sigma(D_{V0.1})$	0.11
Pressure, 1.0133×10^5 Pa	4.0×10^3 Pa, 0.4%	$\sigma(D_{Pr})$	0.17
Temperature, 23.0°C	0.5°C, 0.17%	$\sigma(D_T)$	0.02
Viscosity, 1.8324×10^{-5} Pa·s	7.3×10^3 Pa·s 0.04%	$\sigma(D_\mu)$	0.03
1 μm SRM, 0.895 μm	0.004 μm, 0.45%	$\sigma(D_{CAL})$	0.29
Slip correction, uncertainty in Allen-Raabe coefficients ^b		$\sigma(D_{S1})$	0.08
Difference in diameter from slip correction of Allen-Raabe (0.10089 μm) and of Hutchins et al. (0.10073 μm)		$\sigma(D_{S2})$	0.16
Determination of diameter from 5 point average		$\sigma(D_{Da})$	0.03
DMA resolution, flow ratio = 0.1		$\sigma(D_R)$	0.07
$\sigma(D_B)$, total class B uncertainty ^c			0.42
$\sigma(D_A)$, total class A uncertainty			0.20
$u(D)$, combined uncertainty			0.47
$U(D)$, expanded uncertainty (95%)			0.95

^a σ represents the standard uncertainty.

^bThe coefficients for the adjusted slip correction are $A_1 = 1.1436$, $A_2 = 0.558$, and $A_3 = 0.987$.

^cThe uncertainties are combined as a sum of squares.

uncertainty for the particle diameter associated with the different expressions for slip correction is estimated as this difference in particle size, $\sigma(D_{S2}) = 0.16$ nm.

Data Analysis. The determination of the number-averaged diameter \bar{D}_p is based on a relatively small number of points. An effort was made to select the five voltages so that the number distribution would be symmetric. The size distribution shown in Figure 3 is relatively symmetric. However, the ratio of the number concentration of the 2nd to 4th point varies over a range of values with an average of 1 and a standard uncertainty of 0.3. An estimate of the effect of an asymmetric distribution can be made by shifting the data points on the curve in Figure 3 by +0.4 nm. The concentration ratio for the 2nd to the 4th point increases from 1.0 to 1.3 and the mean particle diameter decreases by 0.03 nm. We approximate the standard uncertainty associated with the data analysis, $\sigma(D_{DA})$, as 0.03 nm.

DMA Resolution. The size distribution, such as that plotted in Figure 5, is an approxima-

tion of the true size distribution, $f(D_p)$. It is broadened relative to the true size distribution because of the instrument resolution. Below we estimate the effect of the DMA resolution on biasing the average particle size \bar{D}_p .

The relationship between the number concentration measured at voltage V and $f(D_p)$ is given by

$$N(V) = \int f(D_p)\Omega(VZ_p) dD_p, \quad (14)$$

where Ω is the transfer function of the DMA. The transfer function is implicitly a function of D_p via the relation between Z_p and D_p (Equations (2) and (3)). In the limit that the width of the transfer function is small compared to the width of the size distribution function, the transfer function approaches a delta function and the analysis we have used would provide an accurate measure of the size distribution function. However, for the 100 nm particles, the measured size distribution given in Figure 3, with a standard deviation of 3.4 nm, is broadened relative to the actual size distri-

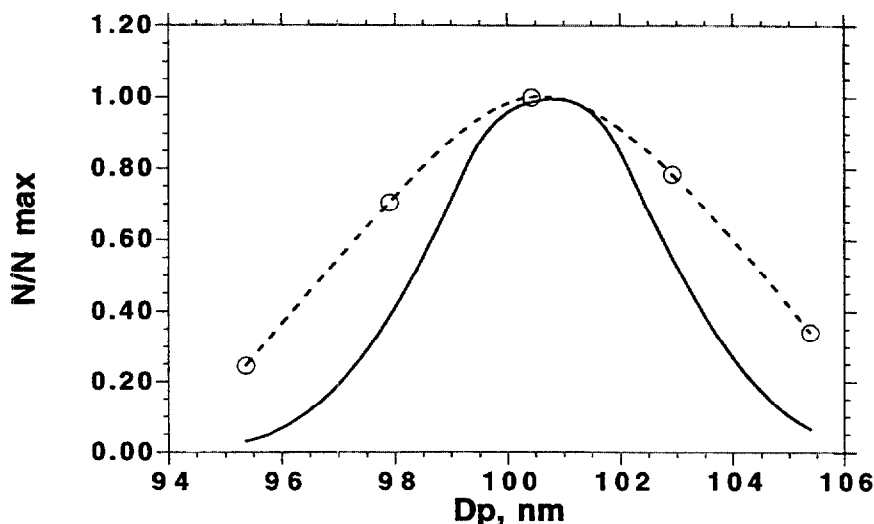


FIGURE 5. Comparison of an assumed normal distribution size distribution indicated by a solid line (number mean diameter of 100.7 nm and standard deviation of 2 nm) and the size distribution inferred from the model data analysis indicated by a dashed line (Equations (12) and (13)).

bution, which has a standard deviation of 2.2 nm as measured by electron microscopy. To estimate this broadening effect on the average particle diameter, the size distribution $f(D_p)$, is assumed to be Gaussian with a number average particle diameter of 100.7 nm and a standard deviation of 2.0 nm. The integration is performed for a fixed voltage with the transfer function expressed as (Knutson and Whitby 1975)

$$\Omega(Z_p V) = \frac{2\pi}{Q_a} \left[\left(\frac{Q_c + Q_a}{2\pi} + GZ_p V \right)^+ + \left(\frac{Q_c - Q_a}{2\pi} + GZ_p V \right)^+ - 2 \left(\frac{Q_c}{2\pi} + GZ_p V \right)^+ \right], \quad (15)$$

where Q_a is the aerosol flow rate, Q_c is the sheath flow, and G is a geometric factor given by

$$G = - \frac{L}{\ln(r_2/r_1)}. \quad (16)$$

The expression $(x)^+$ in Equation (15) is 0 if $x \leq 0$ and is x if $x > 0$. In this analysis, the sheath flow rate is $136.75 \text{ cm}^3/\text{s}$ at a temperature of 21°C and a pressure of 101.3 kPa (760 mm Hg). The number concentration is computed for the five experimental voltages. The number-average diameter is 100.63 , which is 0.07 nm less than the assumed diameter. This analysis assumes a Gaussian distribution, while the exact nature of the actual distribution is not known. The electron microscopy, based on sizing a few hundred particles, provides a good estimate of the standard deviation of the distribution, but is not adequate for providing information on the details of the distribution. In this first-order analysis, the standard uncertainty associated with the DMA resolution uncertainty, $\sigma(D_R)$, is estimated

as the difference in diameter described above, 0.07 nm .

Computation of Total Uncertainty

The total Type B uncertainty, σ_B , is obtained as the root-sum-of-squares of the individual standard uncertainties with the resulting $\sigma_B = 0.42 \text{ nm}$.

The total Type A and Type B standard uncertainties are combined as a root-sum-of-squares to obtain the combined standard uncertainty of the particle diameter, $u(D) = 0.47 \text{ nm}$. We wish to compute the expanded uncertainty, $U(D)$, defined such that there is an approximately 95% (95.45%) level of confidence that the true diameter is within $\pm U(D)$ of the measured diameter. For the case where there is a large number of degrees of freedom and a normal distribution applies, $U(D)$ is $2u(D)$. However, the Type A uncertainty for the measurement of particle diameter has 4 degrees of freedom. For the Type B uncertainty, we assign each component an infinite number of degrees of freedom. Because the estimate of the standard uncertainty for the Type B uncertainty is approximate to begin with, any estimate of the number of degrees of freedom would be fanciful.

To compute the expanded uncertainty, we first compute the effective degrees of freedom for the combined uncertainty and then determine the multiplicative factor based on the t-distribution. To compute the effective degrees of freedom, ν_{eff} , we use the Welch-Satterthwaite formula (Brownlee 1960):

$$\nu_{eff} = \frac{u^4(D)}{\sum_{i=1}^N \frac{\sigma_i^4(D)}{\nu_i}} = \frac{u^4(D)}{\sigma^4(D_A)/4}.$$

The expression on the right-hand side results from the infinite degrees of freedom from the Type B uncertainty. Substituting for $u(D)$ and $\sigma(D_A)$, we obtain $\nu_{eff} = 85$.

The corresponding multiplicative factor based on the *t*-distribution for 85 degrees of freedom is 2.03 for 95.45% confidence. The resulting expanded uncertainty *U* is 0.95 nm.

OTHER MEASUREMENTS OF THE 100 nm SRM

A variety of independent methods have been applied to the measurement of the 100 nm particles including TEM, field flow separation in combination with multiangle laser-light scattering (FFS-MALLS), and atomic force microscopy (AFM). There has not been a comprehensive uncertainty assessment on the FFS-MALLS or AFM for measurement of monosize spheres, but these methods are widely used for other metrology applications. Work is in progress at the National Research Laboratory of Metrology in Japan to accurately measure particle diameters using an electro-gravitational aerosol balance with a 30 cm diameter cell (Ehara and Koike 1997). Preliminary results with particles taken from the same batch as the 100 nm SRM give a diameter of 100.7 nm (Ehara 1998), which is identical to the number average diameter determined from our measurements.

The TEM analysis was carried out by Duke Scientific (1991) using the 0.3 μm NIST SRM 1691 to calibrate the TEM. The mean size obtained by TEM was 100.2 nm with an uncertainty of ± 2.6 nm.

The FFS-MALLS measurements were made at Wyatt Technology using the DAWN-DSP for multiangle detection at 18 angles (Thieking et al. 1995). The particle size is determined from the angle dependent scattering using Rayleigh-Debye scattering theory. The particle size is measured at least once a second as the liquid elutes from the field flow fractionation system with the smaller particles eluting first. The total elution time is about 20 min. The number-

average particle size determined by this method was 99.2 nm. One attractive feature of this instrument is that no size calibration is required. The particle size determination requires only the wavelength of the light, the refractive indices of the particles and of the suspending liquid, the scattering angles together with scattering volume, and the light intensity at these angles.

A monolayer of the 100 nm PS spheres were deposited as a hexagonally close packed array. Park Scientific measured the diameter of the spheres using AFM by dividing the array length by the number of spheres in the array. They obtained a value of 101.5 nm for the number-average diameter (Duke Scientific 1997).

COMPARISON WITH JSR COMPANY PARTICLES

As mentioned in the Introduction, there are 2 particle size standards very close to 100 nm. There are the NIST SRM 1963 with number mean diameter of 100.7 nm and the JSR Company Calibration Standard with number mean diameter of 100 nm. At NIST, a series of diagnostic measurements were made to see if there was a significant difference in the calibration standards. Both the DMA and a Philips CM 30 TEM were used to compare the size of these two sets of particles. The TEM was operated at 100 kV with an 800 k magnification with 15 NIST spheres analyzed and 19 JSR spheres. For both sets of measurements, it was found that the JSR standard particles were about 10% larger than the NIST particles; 11.2% in the case of DMA and 9.6% in the case of TEM analysis.

DISCUSSION

The calibration measurements with the DMA result in a number mean diameter of 100.7 nm with an expanded uncertainty for

a 95% confidence interval of ± 0.95 nm, which we round to ± 1.0 nm. This new value of the expanded uncertainty, ± 1.0 nm, is half the value of the previous value listed on the SRM 1963 Certificate. The two major reasons for the decrease in the value are the inclusion of recent results on slip correction measurements and the combination of the Type A and Type B uncertainties as root sum of squares as prescribed by NIST guidelines (Taylor and Kuyatt 1994) and the ISO guidelines (1993) rather than as a sum.

The consistency of the measurement is indicated by the measurements of the $0.3 \mu\text{m}$ calibration particle size being within $0.001 \mu\text{m}$ of the certified value. In addition, the particles' sizes measured by four independent methods, TEM, 100.2 nm, FFS/MALLS, 99.2 nm, electro-gravitational aerosol balance, 100.7 nm, and AFM of a hexagonal array, 101.5 nm, are further indications of the consistency of the measurement.

Accurate particle size standards are especially important for the semiconductor industry because the scanning surface inspection systems used for detecting particle contaminants on wafers are very sensitive to particle size for particles smaller than 200 nm (Mulholland et al. 1996). A 10% difference in particle size for 100 nm particles corresponds to about an 80% change in the output signal for scanning surface inspection systems. As pointed out above, a 10% difference was obtained between the number mean diameter for the NIST 100 nm SRM and the JSR Company Calibration Standard. So this 10% difference is significant for the calibration of the wafer scanners. It is also a significant difference for the calibration of optical particle counters used to measure the concentration and size of airborne particles in semiconductor fabrication facilities.

We believe the 100 nm particles SRM 1963 are accurately sized and have a narrow size distribution, and we recommend their use in the aerosol community. We urge further metrology be done with these particles by other labs to provide a broader consensus of the uncertainty in the these calibration particles.

The TEM was carried out by Eric Steel, Chemical Science and Technology Laboratory, NIST. The voltage calibration of the DMA was performed by Martin Misakian, Electronics and Electrical Engineering Laboratory, NIST.

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