

# Accurate Size Measurement of Monosize Calibration Spheres by Differential Mobility Analysis

George W. Mulholland and Marco Fernandez

*Fire Science Division  
National Institute of Standards and Technology  
Gaithersburg, MD 20899-0001*

A differential mobility analyzer was used to measure the mean particle size of three monosize suspensions of polystyrene spheres in water. Key features of the experiment to minimize the uncertainty in the results include developing a recirculating flow to ensure equal flows into and out of the classifier, an accurate divider circuit for calibrating the electrode voltage, and use of the 100.7 nm NIST SRM<sup>TM</sup> for calibrating the flow of the classifier. The measured average sizes and expanded uncertainties with a coverage factor of 2 are 92.4 nm  $\pm$  1.1 nm, 126.9 nm  $\pm$  1.4 nm, and 217.7 nm  $\pm$  3.4 nm. These calibration sizes were characterized by NIST to improve the calibration of scanning surface inspection systems.

## INTRODUCTION

The 1997 National Technology Roadmap for Semiconductors (NTRS) discusses particles as small as 65 nm in diameter being a concern by year 2003. Polystyrene spheres have been widely used by the wafer scanner manufacturers for calibrating their instruments. There are three impediments to achieving accurate detection and measurement of the Roadmap targeted particle diameters. First, the scanner and test equipment manufacturers have made extensive use of non-certified, non-traceable particles as calibration standards. Second, some of the particles used were incorrectly sized by the particle suppliers (1). Third, improved methods of synthesizing monosize particles smaller than 100 nm are needed.

A joint project of National Institute of Standards and Technology (NIST), SEMATECH, and VLSI Standards, Inc., along with the collaboration of Duke Scientific Corp., has made strides toward developing accurate monosize standards covering the diameter range from 70 nm to 900 nm. In the first phase of this project, the following nominal sizes of polystyrene spheres have been targeted: 72 nm, 87 nm, 125 nm, 180 nm, and 216 nm. Five suppliers provided samples for each of these particle sizes. A differential mobility analyzer (DMA) and a scanning electron microscope (SEM) were used at NIST to select the best sample for each targeted size in terms of mean particle size and width of the size distribution. This study (1) showed that at least half of the size measurements by the suppliers differed by more than 5 % from the DMA size, with two differing by 20 % or more. This demonstrates that accurate measurement of particle size is an issue for particle sizes less than 250 nm.

As a first step it was decided to perform accurate sizing measurements on three of these five particle sizes. The preliminary particle size characterization based on the screening measurements for the peak in the size distribution and the half-width at half-height were as follows: 93 nm, 4.2 nm; 130 nm, 2.5 nm; and 224 nm, 4.0 nm. All three materials

were made by Duke Scientific Corporation<sup>1</sup>, which specified diameters of 89 nm  $\pm$  3 nm, 126 nm  $\pm$  3 nm, and 220 nm  $\pm$  6 nm, using transmission electron microscopy with NIST Standard Reference Materials as internal standards (2).

These measurements were performed using a high ratio of the sheath flow to aerosol flow (40 to 1) in the DMA to enable the measurement of the width of the size distribution. In the present study we focus on accurate measurement of the mean particle size. While the high flow ratio is best for high resolution, the accuracy is lower because of flow recirculation and electric field penetration near the inlet. Lower uncertainty in the mean particle size is obtained at lower flow ratios and a 10 to 1 flow ratio is used in this study.

This paper describes the experimental method used for accurately determining the mean particle size with the DMA and provides an uncertainty assessment for the peak particle size for each of the three sizes. Key features of the measurement are the calibration of the DMA using NIST SRM<sup>TM</sup> 1963 100.7 nm particle standard, the development of an accurate voltage calibration facility, and the experimental design for determining the contributions of repeatability and sample to sample variability on the uncertainty in the peak particle size.

## EXPERIMENTAL PROCEDURE

The particle measurement system consists of an aerosol generation system, a differential mobility analyzer (DMA) for size selection, and a condensation nucleus counter for

---

CONTRIBUTION OF THE NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY. NOT SUBJECT TO COPYRIGHT.

<sup>1</sup> Certain commercial equipment 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.

Characterization and Metrology for ULSI Technology. International Conference, 1998. CP449. Proceedings. March 1998, Gaithersburg, MD, American Institute of Physics, Seiler, D. G.; Diebold, A. C.; Bullis, W. M.; Shaffner, T. J., Editors, 819-823 pp, 1998.

monitoring the aerosol concentration (see Fig. 1). A brief description of the instrumentation and methodology is given below; a detailed description is given by Kinney *et al.* (3). Several drops (1 drop per 200 cm<sup>3</sup> for 90 nm spheres, 2 drops per 200 cm<sup>3</sup> for 125 nm spheres, and six drops per 250 cm<sup>3</sup> for 220 nm spheres) of the 1 % by mass polystyrene spheres are diluted with de-ionized/filtered (0.2 μm pore size) water. The resulting suspensions are mixed by shaking and by placing the container in an ultrasonic bath for about 60 s. The suspension is nebulized at 107 kPa at gauge (15 psig) to form an aerosol with droplets containing the polystyrene spheres. The water evaporates as the aerosol flows at 83 cm<sup>3</sup>/s (5 L/min) through a diffusion drier and then mixes with 40 cm<sup>3</sup>/s of clean, dry air. The polystyrene 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, about 20 % have a +1 *e* and another 20 % have a -1 *e* charge, and much smaller fractions of multiply charged particles. It is the +1 *e* polystyrene spheres that are measured by the DMA.

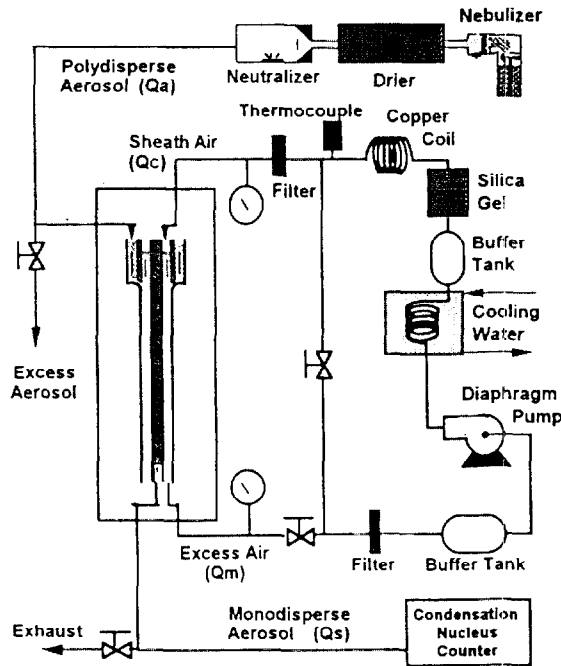


FIGURE 1. The particle measuring system includes an aerosol generation system (nebulizer), the DMA, and the condensation nucleus counter. The excess air is recirculated to match the sheath flow in this closed loop operation of the DMA.

The DMA consists of an inner cylinder rod connected to a variable (0 V to -11000 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 axially symmetric opening along the outer cylinder. The positively charged polystyrene 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 flow consisting of near-monosize aerosol flows out of the

DMA via a slit in the center rod. The particles next flow to a condensation nucleus counter, where the number concentration is measured. A typical measurement sequence is to measure the number concentration as a function of the 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 (4) derived an expression for the average value of  $Z_p$  for the particles entering the slit involving the electrode voltage,  $V$ , the sheath air flow,  $Q_c$ , the inner and outer radii of the cylinders,  $r_1$  and  $r_2$ , and the length of the electrode down to the slit,  $L$ :

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

This equation is valid provided the sheath air flow,  $Q_c$ , 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 Drag force,

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

where  $\mu$  is the air viscosity and  $e$  is the electron charge. The Cunningham slip correction  $C(D_p)$ , which corrects for the non-continuum 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 in air divided by the particle diameter ( $K_n = 2\lambda / D_p$ ) with  $A_1 = 1.142$ ,  $A_2 = 0.558$ , and  $A_3 = 0.999$  (5). For a measured value of  $D_p$ , the particle diameter,  $D_p$ , is obtained iteratively from Eqs. (2) and (3).

In this study we operated the DMA with a flow ratio of 10 with a sheath air flow,  $Q_c$ , of 167 cm<sup>3</sup>/s (10 L/min), and a aerosol inlet flow,  $Q_a$ , at a flow of 16.7 cm<sup>3</sup>/s. For Eq. (1) to be valid, the sheath air and excess air flows,  $Q_c$  and  $Q_m$ , must be equal. As illustrated in Fig. 1, the excess air was recirculated back into the inlet for the sheath air, assuring, in principle, that the flows were matched. The recirculating system includes the following components: two small pumps and buffer tanks before and after the pumps to minimize pulsation, cooling water and an ambient heat exchanger to cool the recirculated air, a filter to remove the particles, silica gel to remove water vapor, and a thermocouple. The measured leak rate was less than 0.017 cm<sup>3</sup>/s or 0.01 % of the sheath air flow at a sheath air flow of 167 cm<sup>3</sup>/s. This is to be compared with about a 1 % to 2 % difference in  $Q_c$  and  $Q_m$  using high resolution flow meters without flow recirculation. The nominal 167 cm<sup>3</sup>/s flow of the sheath and excess air is set by adjusting the two valves indicated in Fig. 1 external to the classifier so that the classifier flow meter reads 167 cm<sup>3</sup>/s. An automated soap-film flowmeter (Gilibrator-2) was plumbed into the system

before the first valve to more accurately determine the flow. The temperature of the sheath air was monitored with a thermocouple to 0.1 °C, the ambient pressure to 13 Pa (0.1 mm Hg) using a Hg column barometer, and the pressure difference between ambient and the pressure in the classifier to the nearest 10 Pa (0.1 cm H<sub>2</sub>O). The pressure and temperature in the classifier are needed for computing the air viscosity and the slip correction.

A typical experiment consists of starting the nebulizer, setting the voltage, collecting number concentration data for 45 seconds, then repeating the same process for a total of seven increasing voltages. Then the same sequence is repeated in reverse going from the highest to the lowest voltage. From a preliminary experiment, the voltage for the peak number concentration would be determined along with the voltages corresponding to about 80 %, 50 %, and 30 % of the peak concentration. For each voltage setting the concentration reading is obtained from the last 20 s of the interval to ensure particles classified at the previous voltage have exited the nucleus counter. The number concentration data is recorded with a PC.

A measurement sequence consists of measuring the voltage versus number concentration for all four particle sets at one time. A total of about 1.5 hour is required for this. This procedure is important, because the SRM particle is used to calibrate the other measurements as described below. Typical data sets for each of the four particle sizes are shown in Fig. 2. As the particle size increases from 90 nm to 220 nm, the peak voltage increases from about 1400 V to about 5900 V.

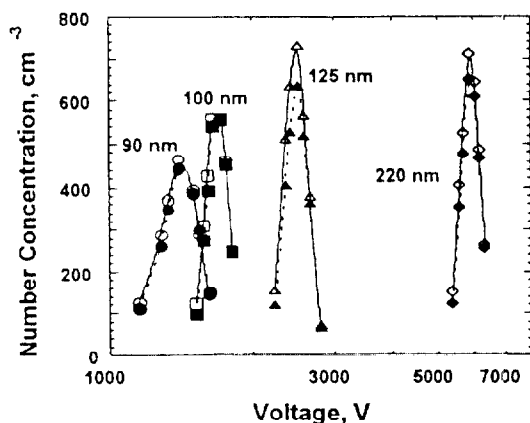


FIGURE 2. Plot of the number versus the voltage setting of the DMA for the three calibration particles and the 100 nm SRM.

A total of nine sets of data were collected for each particle size. For each particle size, the vendor supplied 3 samples from the batch of particles that were synthesized. In turn, for each of these three samples, three sets of measurements were made. By using this experimental design, both the sample to sample variability and the repeatability of the measurements could be assessed.

## DATA ANALYSIS

The 100 nm NIST SRM1963 particles (actual size, 100.7 nm) are used to calibrate the DMA (6). First, the electrical mobility corresponding to the average voltage for the 100 nm SRM spheres is determined using Eq.(1) and the measured values for the sheath flow  $Q_c$ , the length of the classifier  $L$ , and the inner and outer radii  $r_1$  and  $r_2$ . The electrical mobility is also computed for 100 nm SRM using Eqs. (2) and (3) based on the actual 100.7 nm 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 Eq. (1) is varied until the measured and computed mobilities are equal.

In some cases the average voltage is slightly different between the up-scan and the down-scan due to a slight drift in the aerosol generator. The particle concentration drifts downward on the order of 10 % over a 20 minute period. The difference in the peak voltage is typically 0.1 % or less with the largest difference being 0.3 %. In our analyses we use the average of the up-scan and down-scan results.

As described above, a corrected flow velocity is computed for each of the nine sets of experiments with each set consisting of the three unknown particle sizes and the 100 nm SRM. For each particle size, Eqs. (1) and (2) are used to compute the particle diameter corresponding to each of the seven voltages. Typical size distributions are plotted in Fig. 3 for the two smaller particle sizes.

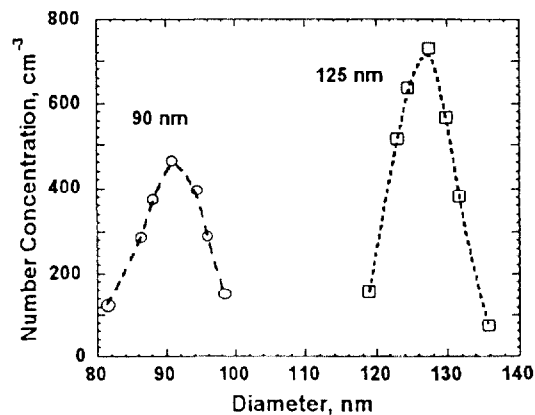


FIGURE 3. The number concentration versus voltage plots of Fig. 2 are expressed in terms of particle diameter for two smallest calibration particle sizes.

The peak diameter for the particle size distribution is computed for each distribution. The first three points and the last three points are fitted with cubic polynomials with the requirement that the 1st and 2nd derivatives be continuous at the middle point where the two polynomials meet. We have also computed the number average diameter and obtained results in close agreement to the value given by the peak diameter.

## UNCERTAINTY ANALYSIS

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 (7,8). These types correspond to random and systematic effects. For the particle sizing measurements, the Type A uncertainty is determined from the measurement repeatability and sample variability. The Type B uncertainty includes the uncertainty in the 100 nm SRM and the uncertainty in the various physical quantities appearing in Eqs. (1-3).

### Type A Uncertainty

Two components contribute to the Type A uncertainty. One is the homogeneity of the sample: that is, sample-to-sample variability. The second is concerned with the measurement repeatability. Both of these components were obtained by making three repeat measurements on each of three different samples. The results are displayed in Fig. 4. It is seen that all the results are within about 1 % of the average of the peak diameters with the exception of one apparent outlier for the nominal 90 nm particle size. It is evident that the spread in the results are somewhat greater for the 90 nm particles relative to the larger sizes.

The analysis of variance shows no significant difference among diameters from the three different samples from each particle size. This finding translates into a between-sample deviation of zero.

The mean of the nine values of peak diameter,  $D_{\text{peak}}(\text{avg})$ , and the standard deviation of the mean,  $\sigma(A)$ , are computed for each of the three particle sizes with the following results. 92.4 nm, 0.30 nm; 126.9 nm, 0.12 nm; 217.7 nm, 0.21 nm. The standard deviation  $\sigma(A)$  is the total type A uncertainty.

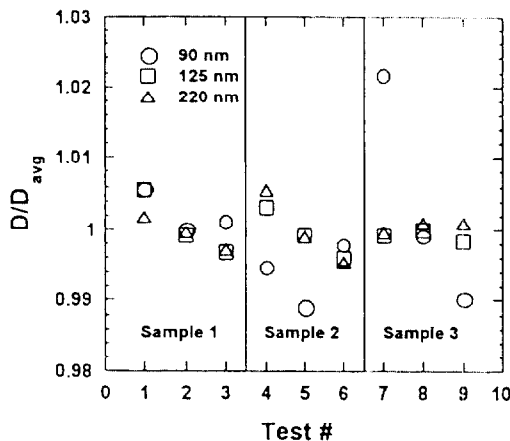


FIGURE 4. The ratio of the measured peaks in the size distribution to the average for each particle size are plotted to show the repeatability and sample to sample variability.

## Type B Uncertainty

For five of the uncertainty components - voltage, the calibration particle size, pressure, temperature, and viscosity - the uncertainty analysis is straightforward. First an estimated standard deviation of the variable is obtained and then the resulting effect of changing the variable by one standard deviation on the particle diameter is obtained using Eqs. (1-3). Less direct analysis is required for slip correction, DMA resolution, and data analysis methodology. Here a brief account of the analysis is presented and the unique features of the study described. A more detailed description of the uncertainty analysis is contained in the paper on the 100 nm SRM (6).

### Voltage Calibration

Because errors in the DMA voltage readings were observed in the range of 1 % to 3 % in a previous study (3), a high voltage (1000 V to 10000 V) calibration facility was set up. The facility consists of a high voltage divider and a digital voltmeter. The high voltage divider (Spellman High Voltage Electronics Corp., Model HVD-100-1) has a standard deviation equal 0.05 % of the nominal reading. The 10000 to 1 divider output was used resulting in output voltages to the digital voltmeter in the range of 0.1 V to 1.0 V. The digital voltmeter (Fluke, 8060A) also has a standard deviation of 0.05 % of the nominal reading over this range. Combining in quadrature the two standard deviations leads to a total uncertainty for the voltage calibration of 0.071 % of the reading. In computing the total uncertainty associated with the voltage measurement, the 1.0 V resolution of the DMA voltmeter is also included.

The effect of the change of voltage on particle size is determined via the particle mobility equations. As explained in more detail by Mulholland *et al.* (6), the voltage uncertainty affects the measurement of the unknown particle size directly but also indirectly through the calibration measurement of the 100 nm SRM. A change in the voltage for the calibration measurement will affect the corrected flow which will, in turn, affect the measured particle size. Table 1 contains the estimated voltage uncertainty and the resulting uncertainty in the particle size measurement.

### Particle Standard

The 100 nm SRM has a combined uncertainty of 0.47 nm (6) and this uncertainty has the largest effect on the overall uncertainty in the calibration particles. Changing the diameter of the 100 nm calibration particle changes the corrected flow, which, in turn, affects all of the derived particle sizes. As seen in Table 1, the effect is about 0.5 % for each of the three sizes.

### Pressure, Temperature, and Viscosity

The uncertainty in the pressure affects the mean free path  $\lambda$ , which in turn affects the slip correction. The  $4 \times 10^3$  Pa

uncertainty in the pressure results in changes of 0.13 % to 0.17 % in the three particle diameters. The temperature and viscosity uncertainties, listed for completeness, have a negligible effect on the overall uncertainty.

#### Slip Correction

The effect of the uncertainty in the slip correction on the particle size is subtle. As seen from Eqs. (2) and (3), the value of the slip correction affects the particle size, but the particle size also affects the slip correction. Two separate effects of uncertainty associated with the slip correction have been analyzed. The first, listed as Slip Correction A, is a result of the uncertainty in the constants  $A_1$ ,  $A_2$ , and  $A_3$  as determined by Allen and Raabe (5). The second, Slip Correction B, is the larger of the two and results from assessing the effect of using two different expressions for the slip correction (5,9). For the 200 nm particle size, the effect of the slip correction uncertainty (0.5 %) is as large as the effect of the 100 nm SRM.

#### DMA Resolution/Data Analysis

There are two issues regarding the data analysis that are discussed here even though their impact on the uncertainty analysis is negligible. First, the size distribution output of the DMA is broadened relative to the true size distribution. Secondly, there is a possibility that the peak size would be shifted by a change in the voltages selected for the analysis. Both of these effects were estimated using the DMA transfer function (4,6) and assuming Gaussian size distributions for the 3 calibration particles. In one set of calculations the voltages were also adjusted by 20 V to 50 V. As shown in Table 1, the largest effect was only 0.06 % of the particle size.

#### Computation of Total Uncertainty

The total Type B uncertainty,  $\sigma(B)$ , is obtained as the root-sum-of-squares of the individual standard deviations. The total Type A and Type B uncertainty are also combined as a root-sum-of-squares to obtain the combined uncertainty,  $u(D_{peak})$ . The expanded uncertainty  $U(D_{peak})$ , defined such that there is an approximately 95 % level of confidence that the true average peak diameter is within  $\pm U(D_{peak})$  of the measured average, is calculated as  $2u(D_{peak})$ .

### CONCLUSION

The values of the average peak diameters  $D_{peak}(avg)$  and the associated expanded uncertainty  $U(D_{peak})$  are the following: 92.4 nm  $\pm$  1.1 nm, 126.9 nm  $\pm$  1.4 nm, and 217.7 nm  $\pm$  3.4 nm. We believe that these three sizes together with the 100 nm SRM are the most accurately characterized particles in the size range less than 250 nm. The use of these materials together with other commercially available size standards based on these materials is expected to greatly improve the reliability of scanner calibrations.

Table 1. Uncertainties of Nominal 90 nm, 125 nm, and 220 nm Calibration Particles

Variable y, nominal value	$\sigma(y)$	$\sigma(90)$ , nm	$\sigma(125)$ , nm	$\sigma(220)$ , nm
Voltage				
1400 V	1.4 V	0.05		
2520 V	2.0 V		0.06	
5900 V	4.3 V			0.11
1650 V	1.5 V	0.05	0.06	0.11
Pressure				
$1.0053 \times 10^5$ Pa	4000 Pa	0.16	0.21	0.29
Temperature				
22.0 °C	0.5 °C	0.02	0.01	0.04
Viscosity				
$1.8277 \times 10^{-5}$ Pa • s	$7.3 \times 10^{-9}$ Pa • s	0.02	0.03	0.06
100.7 nm SRM	0.47 nm	0.43	0.63	1.20
Slip Correction A		0.07	0.11	0.17
Slip Correction B		0.05	0.20	1.16
DMA Resolution		0.06	0.04	0.09
Spline Fit		0.01	0.06	0.05
$\sigma(B)$ , total class		0.47	0.71	1.71
B uncertainty				
$\sigma(A)$ , total class		0.30	0.12	0.21
A uncertainty				
$u(D_{peak})$ , com- bined uncertainty		0.56	0.72	1.72
$U(D_{peak})$ , expan- ded uncertainty		1.12	1.44	3.44

### ACKNOWLEDGEMENTS

The authors thank SEMATECH for its financial support and for its technical support from Howard Huff and Randal Goodall.

### REFERENCES

- Mulholland, G.W., Bryner, N.P., Liggett, W., Scheer, B.W., Goodall, R.K., *Proceedings of the Society of Photo-Optical Instrumentation Engineers* 2862, 104-118 (1996).
- Duke, S.D. and Layendecker, E.B., "Internal Standard Method for Size Calibration of Sub-Micron Spherical Particles by Electron Microscopy," presented at Fine Particle Society (1988). Available from Duke Scientific Corp.
- Kinney, P.D., Pui, D.Y.H., Mulholland, G.W., and Bryner, N.P., *J. Res. Natl. Inst. Stand. Technol* 96, 147-176 (1991).
- Knutson, E.O. and Whitby, K.T., *J. Aer. Sci.* 6, 443-451 (1975).
- Allen, M.D. and Raabe, O.G., *Aerosol Sci. Tech.* 4, 269-286 (1985).
- Mulholland, G.W., Bryner, N.P., and Croarkin, C., submitted to *Aerosol Sci. Tech.*
- Taylor, B.N. and Kuyatt, C.E., "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results," NIST Technote 1297 (1994).
- International Organization for Standardization, "Guide to the Expression of Uncertainty in Measurement," Geneva Switzerland (Corrected and reprinted 1995).
- Hutchins, D.K., Harper, M.H., and Felder, R.L., *Aerosol Sci. Technol.* 22, 202-218 (1995).