Particle Size Measurements for Spheres With Diameters of 50 nm to 400 nm

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NIST

National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

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ABSTRACT

This paper describes a calibration service NIST is offering that measures the effective diameter of particles suspended in liquids using electrical differential mobility analysis. Measurements are for particles with diameters in the range of 50 nm to 400 nm. Electrical differential mobility analysis separates aerosol particles based on the particle size dependence of their electrical mobility. This measurement method was chosen because it offers lower uncertainty for particles smaller than 400 nm compared to other methods. Detailed descriptions of the calibration system, operating procedures, and analysis method are included. Customer information regarding test sample requirements, measurement uncertainty analysis, and quality control procedures is also included in the paper.

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1. Description of Service

NIST is offering a calibration service to measure the effective diameter of particles suspended in liquids. The measurement method consists of nebulizing the particle suspension and measuring the size distribution of the particles in aerosol form by electrical differential mobility analysis. The service is primarily designed for measuring polystyrene latex (PSL) spheres in water with a narrow size distribution. Customers targeted are those who need to demonstrate NIST Traceability[1] or who cannot use other techniques to measure the particles. Particles of mean diameter size in the range of 50 nm to 400 nm are measured with an expanded uncertainty (95 % confidence interval) of 1.5 % of the peak size. Plans are to expand the measurement ability to range from 20 nm to 800 nm. The calibration facility will be able to provide a certified peak particle diameter and size distribution results (not certified). In the future we plan to provide certified information regarding the standard deviation of the size distribution.

Customers are asked to provide samples in aqueous suspensions in quantities of 5 mL to 50 mL of concentrated solutions (0.5 % volume fraction or higher). Dilute solutions will require at least 200 mL. The container should be insulated and shipped by next day mail to avoid extended exposure to high or low temperatures.

2. Design Philosophy and Theory

This particle size calibration method uses the physical principle of electrical differential mobility analysis, which separates aerosol particles based on the particle size dependence of their electrical mobility. The particle's electrical mobility Z is equal to the velocity U of a charged particle divided by the electrical field strength E.

$$Z = \frac{U}{E} \tag{1}$$

The electric mobility is computed from a balance of the electrical force due to the charge on the particle and the drag force given by Stoke's law:

$$neE = \frac{3\pi\mu U D_p}{C(D_p)} \tag{2}$$

where n is the number of charges, e is the charge of an electron, μ is the gas viscosity, D_p is the particle diameter, and $C(D_p)$ is the Cunningham slip correction. The factor $C(D_p)$ approaches one for a particle that is large compared to the mean free path of the gas, and increases as the particle size decreases. From equations (1) and (2), the following expression is obtained for the electrical mobility for the case of singly charged particles (n=1):

$$Z = \frac{eC(D_p)}{3\pi\mu D_p} \tag{3}$$

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[1] NIST has developed an organizational policy on traceability. Official statements regarding this policy and further information can be found at the website: http://www.nist.gov/traceability

The electrical mobility for our measurements is obtained by introducing a small flow of charged aerosol particles into a stream of clean air. The combination flows between two co-axial cylinders with a radial electrical field. A small flow through a narrow slit in the center electrode enables high resolution electrical mobility measurements. By scanning the voltage on the center electrode thereby scanning the electrical field strength, and measuring the number concentration of the aerosol exiting the slit, the electrical mobility distribution of the aerosol is determined.

Special considerations were given to the measurement system in order to obtain accurate measurements using the differential mobility analysis method. Most importantly, particle measurements are made relative to NIST Standard Reference Material 1963 (SRM® 1963). SRM® 1963 is a 100.7 nm PSL sphere solution traceable to the wavelength standard. The system also uses a steady aerosol generator to provide a constant concentration of particles. A carefully constructed recirculation system keeps the sheath flow rate balanced with the excess flow rate, and maintains a flow temperature near room temperature. An electronic barometric pressure gage and thermistors provide accurate temperature and pressure measurements for computing the viscosity and the Cunningham slip correction.

The differential mobility analysis method was chosen to measure the size of particles because it offers lower uncertainty for particles smaller than 400 nm compared to other methods. The relative expanded uncertainty for particles in the 50 nm to 400 nm size range is ± 1.5 % of the peak size. This method offers good statistics since each test measures thousands of particles. In addition, the transfer function for the NIST differential mobility analyzer has been determined and is used to help assess the measurement uncertainty.

Differential mobility analysis has crucial advantages compared to other measurement methods, such as electron microscopy and light scattering. Differential mobility analysis has lower uncertainties than electron microscopy for the measurement of PSL spheres. The dominant uncertainties for microscopy are magnification uncertainty, determination of the edge of the particle, and electron beam damage to the PSL sphere. Additional issues with electron microscopy are the relatively small number of particles sized and the collection of a representative sample.

While elastic light scattering methods have been shown to provide low uncertainty measurements for particle sizes greater than 500 nm, their uncertainty increases with decreasing particle size because of the lack of structure in the scattering pattern. Quasi-elastic light scattering is sensitive to particle sizes as small as 10 nm to 30 nm; however, this method provides a particle size weighted by the scattering efficiency of the particle. While there are methods for determining the number average diameter, there can be large uncertainties if there is a small population of off-size particles. All the particles contribute to the mean size and it is difficult to remove the effect of the off-size particles on the results.

While the differential mobility analysis method provides the lowest uncertainty, the other methods provide complementary information. For example, electron microcopy provides particle shape information that cannot be obtained by the differential mobility analysis method.

3. Description of System

The equipment comprising the calibration facility consists of five critical components as shown in the block diagram in Figure 1: the aerosol generator, the electrostatic classifier, the condensation particle counter, the recirculation system, and the data acquisition system. All of the components, excluding the recirculation system are commercially available equipment.
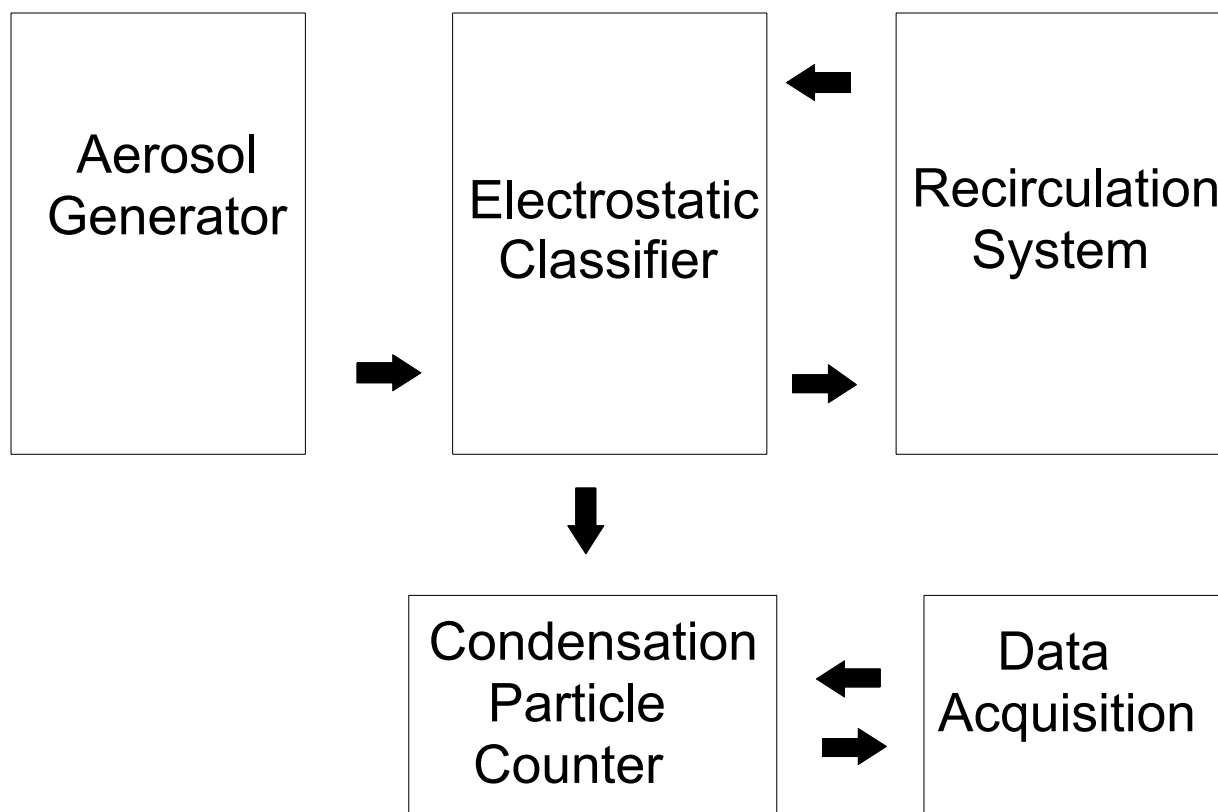
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┌─────────────┐      ┌─────────────┐  ◄──  ┌─────────────┐
│             │      │             │       │             │
│  Aerosol    │      │Electrostatic│       │Recirculation│
│  Generator  │  ──► │ Classifier  │  ──►  │   System    │
│             │      │             │       │             │
└─────────────┘      └─────────────┘       └─────────────┘
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                     ┌─────────────┐       ┌─────────────┐
                     │Condensation │  ◄──  │    Data     │
                     │  Particle   │       │ Acquisition │
                     │  Counter    │  ──►  │             │
                     └─────────────┘       └─────────────┘
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Figure 1. Equipment for particle measurements.

The PSL aerosol is created using an Aeromaster Constant Number PSL Standard Particle Generator manufactured by JSR Corporation[2]. The generator is a pneumatic atomizer that operates by using a clean air stream to nebulize the liquid solution containing the PSL particles. The liquid aerosol passes through a heated tube where the liquid evaporates leaving only the solid PSL particles as an aerosol. The flow then enters a diluter where it joins a clean air stream. The flow passes through a bipolar charger to reduce the droplet charge. This generator is very stable and maintains a steady particle concentration during testing. The generator is equipped with an air filtration system to ensure that the pressurized input air is free of moisture and particles. Inside the generator, the air passes through a mist trap, a dryer, a coarse filter, and finally a High Efficiency Particulate Air (HEPA) filter before reaching the atomizer or the diluter.

The flow leaving the aerosol generator enters an integrating chamber. The chamber has a volume of approximately 14 L and serves to dampen any short-term fluctuation in the flow. The flow leaves the chamber and reaches the classifier via a path containing regulating vents. The vents are adjusted so only the desired flow rate enters the classifier and the remaining flow is

sent to the exhaust. This is necessary since the aerosol generator supplies a flow of approximately 16 L/min (267 cm³/s) while the typical flow into the classifier is less than 2 L/min (33 cm³/s).

The electrostatic classifier used in these experiments is a model 3071A Electrostatic Classifier manufactured by TSI Incorporated. The classifier separates aerosol particles based on their electrical mobility, which is dependent on their charge state and particle size. This allows for a flow of monosize particles to exit the classifier. The classifier contains a bipolar charger (TSI Model 3077 Aerosol Neutralizer) consisting of 2 mCi (7.4 x 10⁷ Bq) of Kr-85 radioactive gas contained in a capillary tube. Here the particles collide with bipolar ions resulting in an equilibrium charge distribution that is a function of the particle size. For example, 100 nm particles would emerge from the bipolar charger with 42.6 % of the particles uncharged, 24.1 % with a +1 charge, 24.1 % with a −1 charge, and smaller percentages with multiply charged particles.

After passing through the bipolar charger, the aerosol flows to the differential mobility analyzer (DMA), also located inside the classifier. The DMA is a long cylindrical chamber with a radius of 1.958 cm. Inside the chamber is a 0.937 cm radius rod, concentric to the walls of the chamber so that an annulus is formed between the rod and the chamber walls. The rod voltage can be adjusted from 0 V to -10,000 V. The outer cylindrical chamber is kept at ground potential, allowing for an electrical field to develop within the annulus. The aerosol flow enters the top of the chamber and is joined by a sheath flow of clean air. Both flows travel through the annulus to the bottom of the chamber. Along the way, charged particles move towards the center rod due to the voltage potential. A small slit in the rod allows for the passage of particles with electrical mobility, Z, as computed by the following equation:

$$ Z = \frac{q_{sheath}}{2\pi VL} ln\left(\frac{r_2}{r_1}\right) \tag{4} $$

where q_{sheath} is the sheath flow, V is the rod voltage, L is the length from the aerosol entrance to the slit, and r_1 and r_2 are the inner and outer radii of the annulus, respectively. By adjusting the voltage, particles of a narrow mobility range are selected. A nearly monosize particle output is achieved by selecting particles based on mobility results. The flow comprised of monosize particles passes through the rod opening and exits the classifier, then flows into the CPC where the number of particles is counted. The rest of the flow leaves the classifier through an excess flow outlet and enters the recirculation system.

A recirculation system pumps the sheath air through the classifier, draws out the excess air and then conditions it before returning it as the sheath air flow. Recirculating the excess air into the sheath inlet ensures that the excess and sheath flow rates are equal. This significantly reduces uncertainties in the size calculations that would be present if these flows were not matched and needed to be measured independently. The recirculation system was not supplied with the TSI model 3071A Electrostatic Classifier. It was built separately at NIST for use with the electrostatic classifier.

A schematic diagram of the recirculation system is shown in Figure 2. Excess air leaves the classifier, passes through an adjustable needle valve and is then filtered through an ultra high efficiency pleated membrane cartridge filter to remove any particles. From the filter, the flow enters a buffer tank. The tank is a brass cylinder 40 cm long with a volume of 6 L. The buffer tank serves to dampen the pulsations caused by the pump. After the buffer tank are two
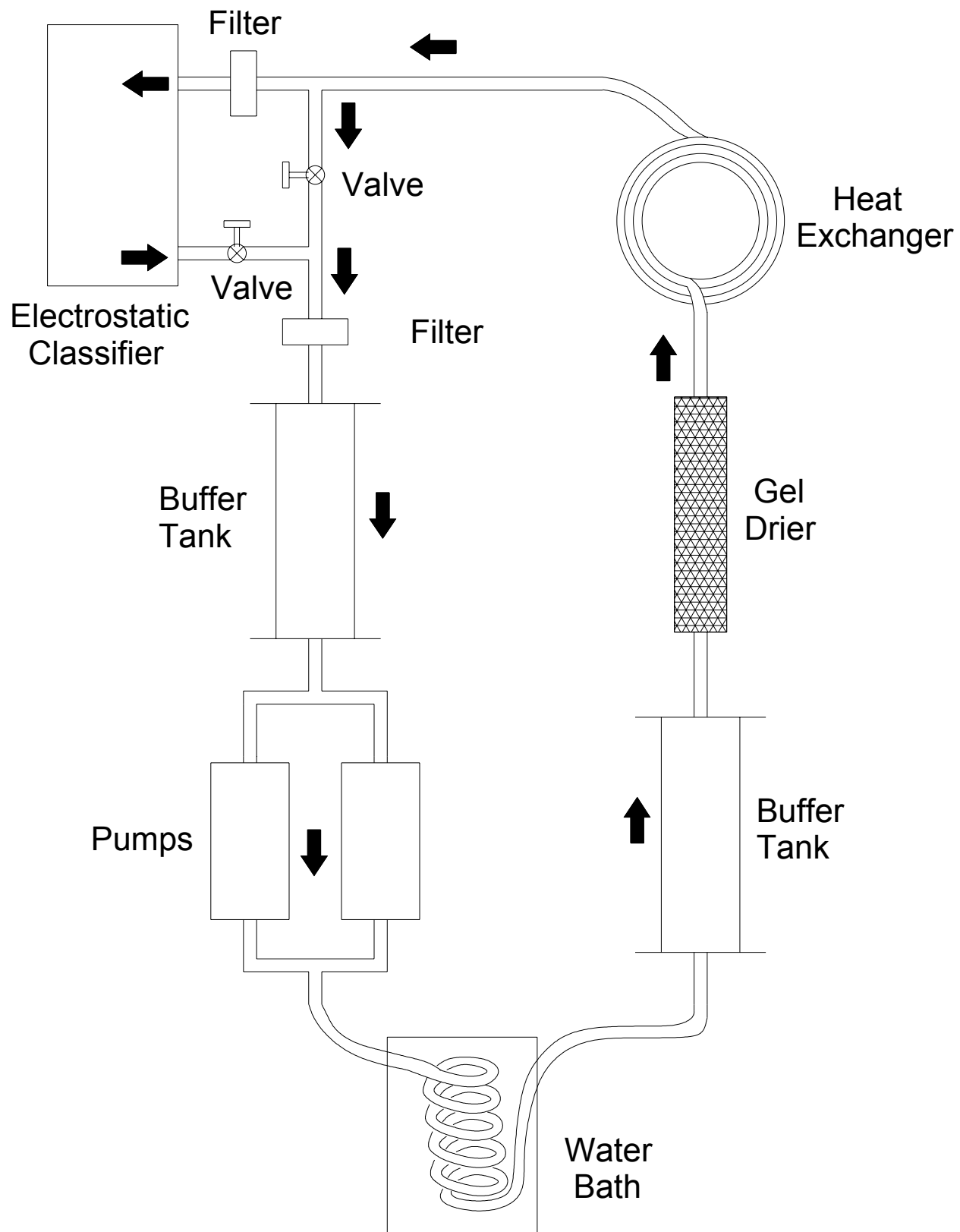
Figure 2. Recirculation system.

diaphragm pumps connected in parallel. The operator can choose to have only one pump operate for low flow rates, or have two pumps operate for higher flow rates. After the pumps, the flow travels through coils submerged in a water bath. Since moving through the pumps heats the flow, the water bath is needed to reduce the temperature of the flow. The bath itself is cooled by a second set of coils carrying chilled water. After leaving the bath, the flow enters another buffer tank, the same size as the first one, to further dampen the effects of the pump. From there the flow travels through a drier packed with silica gel to remove moisture from the flow. It then travels through a coiled section that acts as a heat exchanger to allow the flow to reach room temperature. The conditioned flow reaches a final needle valve where it is split into two flows. Part of the flow is sent through another pleated membrane cartridge filter, to remove any residual particles, and then into the top of the classifier as the sheath flow. The rest of the flow is diverted back into the recirculation system, joining the excess air as it leaves the classifier. Adjusting the needle valve regulates the sheath flow by adjusting how much of the recirculated air enters the classifier.

In addition to the recirculation system, equipment was added to the electrostatic classifier to obtain accurate pressure and temperature measurements. The barometric pressure is measured using a Mensor Corporation Model 4011 digital pressure transducer. The pressure transducer has an accuracy of 0.010 % over the range of 70 kPa to 140 kPa. The transducer provides a digital output to the computer at a rate of 1 Hz. Two ultra-stable thermistors provide temperature measurements of the sheath flow, accurate to $\pm$ 0.01 °C. The thermistors are type CSP Thermoprobes manufactured by Thermometrics, Incorporated with NIST traceable calibrations. One thermistor is located in the upper sheath flow just before it enters the DMA and the other is located after the DMA exit, where the sheath flow becomes the excess flow. The DMA rod was calibrated by using a Spellman HUD-100-1 precision resistor ladder to step down the voltage, which was then measured using a Fluke Corporation 8060A digital multimeter. The DMA output signal was then adjusted so that it matched the actual voltage as measured by the multimeter.

The particle concentration is determined using a model 302201 Condensation Particle Counter (CPC) manufactured by TSI Incorporated. The CPC detects particles by condensing supersaturated butanol vapor onto the particles to make them appear larger before they enter the optical sensing zone where they are counted. The CPC is capable of detecting particles of size 7 nm and larger.

The data acquisition system consists of a desktop computer equipped with data acquisition boards and software for communication with the instruments. Communication with the CPC and the electrostatic classifier is accomplished via an RS-232 serial communications port. Information from the digital pressure transducer is collected using a National Instruments PCI-6503 digital input/output board. Thermistors are connected to a National Instruments TBX-68T Isothermal Terminal Block, which relays the temperature information to a National Instruments 4351 PCI board. A customized data acquisition software program is used to control the instruments and collect the data. Another custom program performs data analysis and computations. Both programs are written using National Instruments LabVIEW software. Detailed descriptions of the programs are included in section 4.

An important element of this measurement process is the NIST SRM® 1963 used to calibrate the system. By using the SRM®, we are able to accurately determine the flow rates and establish consistent diameter measurements even if environmental conditions change during testing. The SRM® 1963 is sized at 100.7 nm, which is in the midrange of the particle sizes

measured. The SRM® 1963 has been sized relative to the NIST one micrometer standard, which is sized relative to the wavelength standard. Use of the SRM® allows us to obtain accurate particle measurements and to identify possible problems or inconsistencies in the equipment. One potential source of concern using SRM® 1963 is the agglomeration of the particles in the suspension so that the SRM® cannot be used for calibrating the system. It is also crucial that the dilution of the SRM® particles be made with water containing very small amounts of non-volatile impurities, less than 1 µg impurities per g of water, to minimize the size of the residue layer surrounding the PSL spheres as the water in the droplets evaporates.

4. Operating Procedures and Assessment of Uncertainty

Detailed Operating Procedure
The following is a complete description of the procedures for actual measurements to calibrate a customer's particle sample.
System start-up:

      Turn on CPC and let it warm up. Display will indicate when it is ready.

      Turn on electrostatic classifier and make sure rod voltage is set to zero.

      Turn on aerosol particle generator.

      Supply inlet air to particle generator at a pressure between 240 kPa and 275 kPa.

      Set the aerosol particle generator pressure to 177 kPa (1.8 kg/cm^2) and flow rate to 16.0 L/min (267 cm^3/s).

      Turn on recirculation pump (or pumps) and turn on cooling water for water bath.

      Set the electrostatic classifier flows to desired rates. Typically, the aerosol flow into the classifier is set between 0.5 L/min (8.3 cm^3/s) and 2.0 L/min (33.3 cm^3/s) and the sheath flow is set to either 10 L/min (167 cm^3/s) or 20 L/min (333 cm^3/s). The aerosol flow into the classifier is controlled by adjusting the vents in-line before the classifier so that the correct amount of flow is vented, leaving the desired flow for the classifier. The sheath flow is controlled by adjusting the two valves in the recirculation system. For higher sheath flows, both recirculation pumps will need to be used. The two flow settings will impact one another, so rechecking and readjusting is necessary until both are at their desired flow rates.

      Rinse a clean testing bottle 6 times with filtered, deionized water.

      Fill the test bottle with at least 45 mL of filtered, deionized water and place test bottle in the particle generator sample compartment. Lock the test bottle in place, making sure the connection between the test bottle and the generator is sealed by the o-ring.

      Allow system to run for at least 30 min with filtered, deionized water before the first calibration to warm up the equipment, prime the system, and stabilize flows and temperatures.

Prepare an SRM® 1963 particle suspension:

      Rinse a 250 mL polyethylene container 6 times with filtered, deionized water.

      Add 200 mL of filtered, deionized water to the container.

      Add 4 drops of SRM® 1963 to container, and then shake to mix.

      Place the container in ultrasonic bath for 2 min to further mix contents.

      SRM® concentration will be approximately 5 x 10^9 particles/mL.

First calibration run using SRM$^{\circledR}$ 1963 sample:

Place the SRM$^{\circledR}$ 1963 container in ultrasonic bath for 60 s.

Rinse a clean testing bottle 6 times with filtered, deionized water.

Pour at least 45 mL of SRM$^{\circledR}$ solution into test bottle and place bottle in particle generator sample compartment. Lock the test bottle in place, and check that the connection is sealed by the o-ring.

Check particle generator pressure and flow and adjust if necessary.

Adjust aerosol flow regulating vents, and recirculation system flow controls so that the electrostatic classifier aerosol inlet flow and sheath flow are at desired settings. Rechecking and readjusting may be necessary until both are at their desired flow rates.

Open the data collection program on the computer.

Input a list of classifier voltage settings for the SRM$^{\circledR}$ sample into the computer.

Select data filename for SRM$^{\circledR}$ 1963 calibration file and input into the computer.

Record the filename, aerosol flow setting, sheath flow setting, and SRM$^{\circledR}$ 1963 mixture information in the laboratory notebook.

Start data collection program.

> Program will record the voltage, particle concentration, barometric pressure, and both temperature measurements at a frequency of 1 Hz.
> All data are written to specified data file.
> Readings are collected at each voltage setting for 45 s before changing to the next voltage setting.
> Voltage is reset to zero at end of test.

Sample measurement test:

Sample to be tested should contain at least 5 x 10^9 particles/mL.

Remove particle generator test bottle containing SRM$^{\circledR}$ 1963.

Place the container of test sample in ultrasonic bath for 60 s.

Rinse a clean testing bottle 6 times with filtered, deionized water.

Pour at least 45 mL of test sample solution into clean, rinsed test bottle and secure bottle in generator sample compartment, making sure the connection is sealed by the o-ring.

Do NOT make any adjustments to any flow or pressure settings on either the particle generator or the classifier.

Input list of desired classifier voltage settings for the sample into the computer.

Select filename for data collection file and input into the computer.

Record the filename, aerosol flow setting, sheath flow setting, and test sample identifying information in the laboratory notebook.

Start data collection program, it will scan the voltages and collect data as before.

Repeat sample measurement test for up to three samples.

After measuring the test samples, do another SRM$^{\circledR}$ 1963 calibration run, but do NOT adjust any of the flows:

Remove particle generator test bottle containing sample.

Place the SRM$^{\circledR}$ 1963 container in ultrasonic bath for 60 s.

Rinse a clean testing bottle 6 times with filtered, deionized water.

Pour at least 45 mL of SRM® solution into clean, rinsed test bottle and place the bottle in the particle generator sample compartment. Lock the bottle in place, and check that the connection is sealed by the o-ring.

Do NOT adjust any flow or pressure settings on either the particle generator or the classifier.

Input a list of classifier SRM® voltage settings to the computer.

Select data filename for SRM® calibration file and input into the computer.

Record the filename, aerosol flow setting, sheath flow setting, and SRM® mixture information in the laboratory notebook.

Start data collection program, it will scan the voltages and collect data as before.

Explanation of Computer Programs for Data Collection and Analysis

A customized data acquisition software program written using National Instruments LabVIEW software is used for data collection. The program allows the user to input a sequence of voltage settings for the electrostatic classifier. The user can also select a unique data file name for each test. The software program sets the DMA rod to the desired voltage and then collects readings of the temperatures, barometric pressure, and CPC particle concentration at a frequency of 1 Hz. Measurements are collected for a total of 45 s at each voltage setting. A real-time display of the readings, including the CPC particle concentration allows inspection of the data during testing so the experimenter can easily identify if the system is working properly. All of the measurements are recorded in the specified data file in spreadsheet format for easy processing or plotting.

After measurement data are collected, the files are analyzed using a program also written using National Instruments LabVIEW software. Calculations for the diameter size are made using a software program written to automatically perform the computations based on the theoretical equations outlined in the previous section. All of the calculations are made using the best available constants for values such as viscosity, mean free path, the charge of an electron, and the Cunningham slip correction.

First, an accurate sheath flow rate is computed using the SRM® 1963 calibration runs collected before and after each set of sample tests. The sheath flow is calculated from the ratio of the theoretical mobility and the experimental mobility. Using the measured barometric pressure and temperature, and setting the diameter to 100.7 nm for the SRM® particles, the theoretical mobility is calculated by equation (3). Next, from the experimental data for the SRM® 1963 runs, the voltage corresponding to the peak particle concentration is determined by fitting a third order polynomial to and solving for the voltage setting at the peak. From this voltage, and using the nominal value for the sheath flow rate, the experimental mobility is computed using equation (4). Multiplying the nominal sheath flow by the ratio of the theoretical mobility to the experimental mobility gives the corrected sheath flow measurement. An average of the corrected sheath flows for the two SRM® runs is used as the sheath flow rate in the test sample calculations. A detailed description of the sheath flow calculations, including constants and intermediate values is given in the appendix.

The test sample data files are reduced to eliminate the transient data collected after a voltage change. The particle concentration generally reaches a stable reading 30 s after a new voltage is set; therefore, the final 15 s of data for each voltage setting are used in the calculations. Mean values are then computed for the temperature, pressure and particle concentration at each

voltage setting. Using the temperature and pressure, the viscosity and mean free path are calculated. Next, the mobility is computed from equation (4) for each voltage setting, using the sheath flow as calculated from the SRM® files. Finally, the particle diameter is calculated using the terms computed as given in equation (3) of the previous section. Because the slip correction, C, is a function of the diameter, an iterative process is used to solve for the particle diameter. A detailed description of the diameter calculations, including the iterative process, is given in the appendix. Once the particle diameter for each voltage setting is calculated, a graph of the particle number concentration verses the corresponding particle diameter is then plotted. The peak diameter size is determined by fitting a third order polynomial to the graph and calculating the diameter at the peak of the curve fit. In cases where samples have a broad size distribution, a correction factor is used that is based on the instrument convolution integral and involves the product of the transfer function times, the charging probability, and the size distribution.

Uncertainty Analysis

      The uncertainty analysis presented below is based on a paper by Mulholland and Fernandez[3]. 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. These types roughly 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 SRM® 1963 and the uncertainty in the various physical quantities appearing in equations (1-3). The Type A and Type B uncertainty are combined by a root-sum-of-squares to determine the combined uncertainty. Taking twice the combined uncertainty gives the expanded uncertainty, which is the total uncertainty statement for the calibration.

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 shown in Figure 3. 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, $D_{peak}(avg)$, 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.

[3] Mulholland, G.W. and Fernandez, M., "Accurate Size Measurement of Monosize Calibration Spheres by Differential Mobility Analysis," American Institute of Physics Conference Proceedings 449, *Characterization and Metrology for ULSI Technology: 1998 International Conference*, edited by D.G. Seiler, A.C. Diebold, W.M. Bullis, T.J. Shaffner, R. McDonald, and E.J. Walters, pp. 819-823, Gaithersburg, Maryland, March 1998.
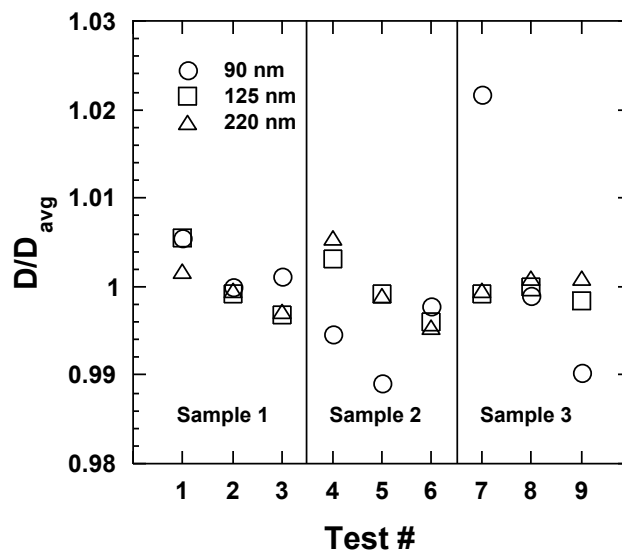
Figure 3. The ratio of the measured peaks in the size distribution to the average for each particle size are plotted to show the repeatability and sample to sample variability.

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 equations (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 a paper describing the measurement of SRM® 1963 by differential mobility analysis.[4]

Voltage Calibration

Because errors in the DMA voltage readings were observed in the range of 1 % to 3 % in a previous study, 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 to 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 Corporation, 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. (1999), the voltage

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[4] Mulholland, G.W., Bryner, N.P., and Croarkin, C., "Measurement of the 100 nm NIST SRM 1963 by Differential Mobility Analysis," *Aerosol Science and Technology*, Vol. 31, pp. 39-55, 1999.

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 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 λ, which affects the slip correction. The 4×10^3 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 equations (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. For the 200 nm particle, the effect of the slip correction uncertainty (0.5 %) is as large as the effect of the 100.7 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. Second, 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 and assuming Gaussian size distributions for the three 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 $2u(\ D_{peak})$.

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[5] Allen, M.D. and Raabe, O.G., "Slip Correction Measurements of Spherical Solid Aerosol Particles in an Improved Millikan Apparatus," *Aerosol Science and Technology*, Vol. 4, pp. 269-286, 1985.

Summary of Uncertainty Analysis

The values of the average peak diameters D_{peak} (avg) and the associated expanded uncertainty $U(D_{peak})$ are the following: 92.4 nm ± 1.1 nm, 126.9 nm ± 1.4 nm, and 217.7 nm ± 3.4 nm. We believe that these three sizes together with the 100.7 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 accuracy of calibration and measurement equipment.

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

Variable y, nominal value	σ(y)	σ(90), nm	σ(125), nm	σ(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				
101 kPa	4 kPa	0.16	0.21	0.29
Temperature				
22.0 °C	0.5 °C	0.02	0.01	0.04
Viscosity				
1.8277×10^{-5} Pa · s	7.3×10^{-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
σ(B), total class B uncertainty		0.47	0.71	1.71
σ(A), total class A uncertainty		0.30	0.12	0.21
$u(D_{peak})$, combined uncertainty		0.56	0.72	1.72
$U(D_{peak})$, expanded uncertainty		1.12	1.44	3.44

5. Quality Control Procedures

In order to ensure that the calibrations are performed correctly, only qualified personnel will be authorized to perform the calibration measurements. They are trained to monitor the performance of the system and to recognize any malfunctions with the equipment that may cause inaccurate results. The report of calibration will also be reviewed by certified personnel to ensure that it is accurate in every respect.

Because the customer will be supplying a test sample that will be consumed during the measurement process, there will be no device or sample to be retuned to the customer. The customer will receive a report detailing the size measurement results.

The checking mechanism for determining if the equipment is operating properly during the measurement is the calibration of the equipment using the SRM® 1963. Calibrations with the SRM® are performed before, after, and between regular measurements. Inconsistencies in the

results of SRM® calibration tests performed over several months indicate system troubles including calibration of equipment or leaks in the flow. A recalibration of the DMA voltage using the resistor ladder is performed periodically to maintain accurate voltage measurements. Recalibration of the thermistors and digital pressure transducer are completed periodically using resources available at NIST. Calibration documentation will be update as necessary to include any changes to the equipment or procedure.

6. Safety Considerations

The calibration process involves possible safety hazards, therefore, precautions must be taken when performing these measurements. The electrostatic classifier contains a high voltage DC source with a maximum voltage of 10000 V. This voltage is contained within the inner column with the outer column grounded so the user is not exposed to the high voltage. The current associated with the high voltage is relatively small (maximum of 100 µA). Caution must be exercised when calibrating the voltage using a voltage divider and a precision voltmeter since a connection will be made from the high voltage power supply and the divider circuit.

The electrostatic classifier contains a Kr-85 radioactive source, which emits β radiation. The source strength is 2 mCi (7.4×10^7 Bq). It is contained within a capillary tube and there is no external exposure. Still, proper handling, inventorying, and shipping procedures need to be followed.

The condensing liquid for the condensation particle counter is n-butanol. The Materials Safety Data Sheet advises that n-butanol is a severe irritant, that can cause damage through inhalation, ingestion or skin absorption. Inhalation or ingestion of n-butanol can result in severe internal injuries and possible death. Contact should be avoided since it can cause damage to eyes or skin. During normal system operations, the n-butanol is fully contained within sealed lines and containers. The experimenter has potential contact with the n-butanol only when filling or draining the containers, and safety gloves, safety glasses, and a laboratory coat are worn at these times. Additionally, the containers will be filled or drained only under a well-ventilated hood. The condensation particle counter exhaust that contains n-butanol vapor is vented from the lab to avoid exposure by the experimenter.

The excess flow from the aerosol generator and the electrostatic classifier is also vented from the laboratory, since the flows contain a large fraction of aerosol particles in the size range that may be respired deep into the lungs if inhaled.

7. Education and Training Considerations

There are no plans for providing training material at this time. If there is a need for more detailed information by other laboratories providing size calibration, training material will be provided in the future.

APPENDIX

Sheath Flow Calculations

T = Temperature from data file [K]
P = Pressure from data file [mm Hg], (barometric pressure + pressure drop in DMA)
$e = 1.60219 \times 10^{-19}$, charge of one electron [C]

Theoretical Mobility
Set Diameter to 100.7 nm: $D = 100.7 \times 10^{-9}$ [m]

Compute Viscosity : $\mu = \dfrac{1.4618 \times 10^{-6} \left(T^{1.5}\right)}{T + 110.4}$ [kg / m·s]

Compute Mean Free Path: $MFP = \dfrac{\left(2.3709 \times 10^{-7}\right)(T)}{P\left(1 + \dfrac{110.4}{T}\right)}$ [m]

Compute Knudsen number: $Kn = \dfrac{2MFP}{D}$

Compute Cunningham Slip Correction: $C = 1 + Kn\left(1.142 + 0.558 \exp(\dfrac{-0.999}{Kn})\right)$

Compute Theoretical Mobility: $Z_{theory} = \dfrac{eC}{(3\pi\mu)D}$ [C·s/kg]

Experimental Mobility

$L = 0.4444$ [m], length from aerosol entrance to slit in DMA
$r_1 = 0.009370$ [m], inner radius of DMA annulus
$r_2 = 0.019580$ [m], outer radius of DMA annulus
$q_{nominal}$ = nominal sheath flow [m³/s]
V_{peak} = voltage corresponding to the peak particle concentration from SRM® test

Compute Experimental Mobility: $Z_{experimental} = \dfrac{q_{nominal}}{2\pi V_{peak} L} \ln\left(\dfrac{r_2}{r_1}\right)$ [C·s/kg]

Corrected Sheath Flow

$q_{sheath} = \dfrac{Z_{theory}}{Z_{experimental}} \left(q_{nominal}\right)$ [m³/s]

Diameter Calculations

q_{sheath} = corrected sheath flow as computed from above [m³/s]
V = Voltage from data file [V]
T = Temperature from data file [K]
P = Pressure from data file [mm Hg], (barometric pressure + pressure drop in DMA)
$e = 1.60219 \times 10^{-19}$, charge of one electron [C]
$L = 0.4444$ [m], length from aerosol entrance to slit in DMA
$r_1 = 0.009370$ [m], inner radius of DMA annulus
$r_2 = 0.019580$ [m], outer radius of DMA annulus

Compute Viscosity : $\mu = \dfrac{1.4618 \times 10^{-6}\left(T^{1.5}\right)}{T + 110.4}$ [kg / m·s]

Compute Mean Free Path : $MFP = \dfrac{\left(2.3709 \times 10^{-7}\right)(T)}{P\left(1 + \dfrac{110.4}{T}\right)}$ [m]

Compute Mobility: $Z = \dfrac{q_{sheath}}{2\pi V L}\ln(\dfrac{r_2}{r_1})$ [C·s/kg]

Compute intermediate term PAR (solve for D without Slip Correction): $PAR = \dfrac{e}{3\pi\mu Z}$ [m]

Calculate Initial Guess for Diameter: $D_{initial} = \dfrac{PAR + \sqrt{PAR(PAR + (8 \times MFP \times 1.142))}}{2}$ [m]

Start Iterative Process to Determine Particle Diameter

Compute Knudsen number: $Kn = \dfrac{2MFP}{D_{initial}}$

Compute Cunningham Slip Correction: $C = 1 + Kn\left(1.142 + 0.558\exp(\dfrac{-0.999}{Kn})\right)$

Compute Diameter with Slip Correction: $D_{slip} = C(PAR)$ [m]

Compare Diameter with Slip Correction to Initial Guess: $Comparison = \left|\dfrac{D_{initial} - D_{slip}}{D_{slip}}\right|$

If *Comparison* is not less than 1 x 10^{-14} [m] then Calculate D_i as: $\quad D_i = \dfrac{D_{initial} + D_{slip}}{2}$ [m]

Using D_i Repeat the Iterative Process as follows until the *Comparison* between D_i and D_{slip} is less than 1 x 10^{-14} [m].

Repeat Iterative Process

Compute Knudsen number: $\quad Kn = \dfrac{2MFP}{D_i}$

Compute Cunningham Slip Correction: $\quad C = 1 + Kn\left(1.142 + 0.558\exp(\dfrac{-0.999}{Kn})\right)$

Compute Diameter with Slip Correction: $\quad D_{slip} = C(PAR)$ [m]

Compare Diameter with Slip Correction to Initial Guess: $\quad Comparison = \left|\dfrac{D_i - D_{slip}}{D_{slip}}\right|$

Compute a new value for D_i by: $\quad D_i = \dfrac{D_i + D_{slip}}{2}$ [m]

If *Comparison* is not less than 1 x 10^{-14} [m] then go back and repeat the iterative process again, using the new value for D_i, and starting with computing a new Knudsen Number.

If *Comparison* is less than 1 x 10^{-14} [m] then you have solved for the particle diameter: $D_{particle} = D_i$.