Evaluation of Uncertainty in Nanoparticle Size Measurement by Electro-gravitational Aerosol Balance

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ABSTRACT

This paper presents the measurement results and the uncertainty analysis for two batches of polystyrene latex (PSL) spheres with nominal sizes of 100 nm and 500 nm using the measurement system which electro-gravitational aerosol balance (EAB) method is applied. In the measurement system, charged particles are introduced into the space between horizontally placed planar electrodes. The evaluation of the number of survived particles after a short period of time can lead to determine the particle mass according to the balance between the electrostatic and gravitational forces exerted on the particles. Once the particle density is known, the particle size can be determined. The possible error sources are evaluated based on the EAB method and the measurement procedures. As a result, the measured mean diameters and expanded uncertainties for the two particles are 109.0 nm ± 1.2 nm and 529.4 nm ± 1.3 nm, respectively, for the EAB system.

Keywords: nanoparticle size, measurement uncertainty, electro-gravitational aerosol balance

1 INTRODUCTION

Nanotechnology is expected to play a major role in both traditional and emerging industry clusters. It brings new functions and properties to improve and develop new products, and to create new application possibilities. Particularly, nanoparticles are at the cutting edge of the rapidly developing area of nanotechnology, and the particle diameter is a key parameter to determine the behavior of the particle. Although there are many measurement techniques for particle size characterization, only a handful of them is capable of performing dimensional measurement in the nanometer scale range. However, inconsistence measurement was reported in the world-wide round robin test [1]. Therefore, it is necessary to develop appropriate particle size standards for instrument calibration.

A primary standard measurement system for particle size ranging from 100 nm to 500 nm, based on the electro-gravitational aerosol balance, has been developed in Center for Measurement Standards of Industrial Technology Research Institute to obtain particle diameters with high accuracy and low uncertainty. The system is primarily designed for measuring PSL spheres in water with a narrow size distribution. The calibrated particle diameters are used as size standards to calibrate nanoparticle size measurement instruments, such as dynamic light scattering, differential mobility analyzer, and electron microscope.

2 METHODOLOGY

The general approach to the measurement of particle size and measurement system in this study is similar to the ones described in the references [2,3]. A brief summary is listed below.

2.1 Theoretical Background

Two electrodes are placed parallel in a distance H to form a gap and to generate an electric field with a voltage V. At initial stage, assuming t = 0, particles with electric charge distribute uniformly inside of the two electrodes. As shown in Figure 1, a balance for the particle can be obtained between the static electric force F_E, assumed to be in the upward direction, and the gravity force F_G on a charged particle. After a relaxation time, τ, the particle will move at a constant terminal velocity, v. The terminal velocity, assumed to be in the upward direction, can be represented as:

$$v = \tau[\frac{qeV}{mH} - (1 - \frac{\rho_a}{\rho_p})g] \tag{1}$$

where e is elementary charge, q is the number of static charge on a particle, m is the mass of a single particle, and g is the gravitational acceleration. In addition, ρ_a and ρ_p are the densities of the air and the particle, respectively.

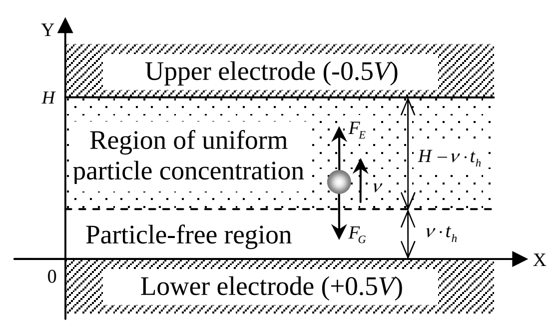

Figure 1: Schematic representation of the boundary between the uniform particle concentration region and the particle-free region.

Furthermore, the relaxation time, τ, is related to the size of the particle, d_p, the air density, ρ_a, and the gas viscosity, η, as shown in below:

$$\tau = \frac{d_p^2 \rho_p}{18\eta} C_c(d_p) \quad (2)$$

where $C_c(d_p)$ is the slip correction factor that corrects for the non-continuum gas behavior on the drag force for small particles. Due to the terminal velocity, the particles move in the upward direction. A portion of the charged particles will stop on the top electrode plate after a holding time, t_h, and a clear space without particles will be formed near the bottom of the electrode plate, as shown in Figure 1. A residual particle ratio, defined as the numbers of particles at $t = t_h$ to the numbers of particles at $t = 0$, can be specified by the survival function, $s(m, V)$, which is:

$$s(m,\ V) = \begin{cases} 1 - \nu \cdot t_h / H, & \text{If } t_h \le H/\nu \\ 0, & \text{Otherwise} \end{cases} \quad (3)$$

where the $s(m, V)$ is the survival function of the particle mass at the voltage, V. A slightly distorted isosceles triangle can be obtained if the survival function $s(m, V)$ is plotted according to the mass of the particles, as shown in Figure 2. Three measured m decided the 3 poles of the triangle for determination of the size of particles: the first two, $m_\pm$, are the triangle poles on the base line, and the third one is the top pole of the triangle at point m_0, The survival function $s(m, V)$ is equal to 1. The m_0 and $m_\pm$, can be determined by the following equations as:

$$m_0 = \frac{qeV}{(1 - \rho_a / \rho_p)Hg} \quad (4)$$

$$m_\pm = \frac{qeV}{[(1 - \rho_a / \rho_p)g \mp H / t_h \tau]H} \quad (5)$$

The m_0 represents the average mass of the particles. Accordingly, the sizes of the particles can be calculated with known average mass, m_0, as:

$$d_p = \left(\frac{6m_0}{\pi \cdot \rho_p}\right)^{1/3} \quad (6)$$

2.2 System Setup

The equipment consists of eight critical components as shown in the schematic diagram in Figure 3: an aerosol generator, a differential mobility analyzer, a pair of dc voltage sources, a digital multimeter, a thermometer, a condensation particle counter, a recirculation system, and homemade electrodes.

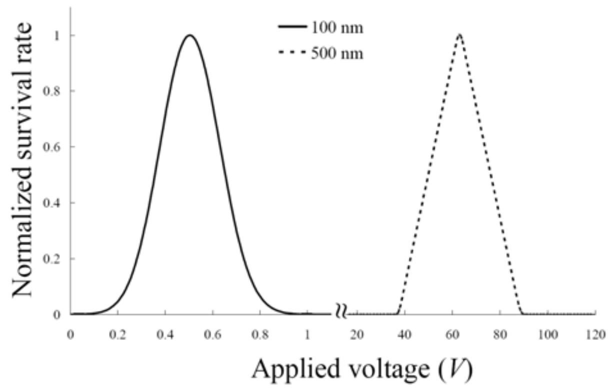

Figure 2: Survival functions for 100 nm (Brownian diffusion is considered, the holding time is 12 hours) and 500 nm (Brownian diffusion is neglected, the holding time is 75 minutes) in average diameters and the standard deviations are 2%.

The aerosol generator (Aeromaster-V, JSR Corp.) 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 particles as an aerosol. The flow then enters a diluter where it joins a clean air stream. The aerosol is initially highly charged from the nebulization process and is neutralized with an Am-241 bipolar charger. After passing through the bipolar charger, the aerosol flows to the differential mobility analyzer (Model 3080L, TSI Inc.). The differential mobility analyzer is installed on the top of the electrodes in order to filter out the multiple charged particles. As a result, all particles introduced into the space between the parallel plate electrodes are singly charged. The recirculation system pumps the sheath air through the differential mobility analyzer, draws out the excess air and then conditions it before it returns as the sheath air flow.

The two flat plate electrodes made of stainless steel, 280 mm in diameter and 10 mm in thickness, were separated by an alumina annulus. The nominal dimensions of the alumina annulus was 15 mm in height, 210 mm in internal diameter, and 250 mm in external diameter. The dimensions were determined by a coordinate measuring machine. The voltages of the electrodes are supplied by the pair of dc voltage sources (Model 2410, Keithley Instruments Inc.), and monitored by the digital multimeter (Model 2010, Keithley Instruments Inc.). The positively charged particles are the target of measurement, where the voltage of the upper electrode relative to the lower one is chosen to be negative,

After a proper holding time, particles are stable due to the balance of electrostatic force and the gravitational force. Consequently, a certain fraction of the particles are deposited onto the electrode surfaces from the space between the electrodes. The number of survival particles is determined using the condensation particle counter (Model 3775, TSI Inc.). The condensation particle counter detects

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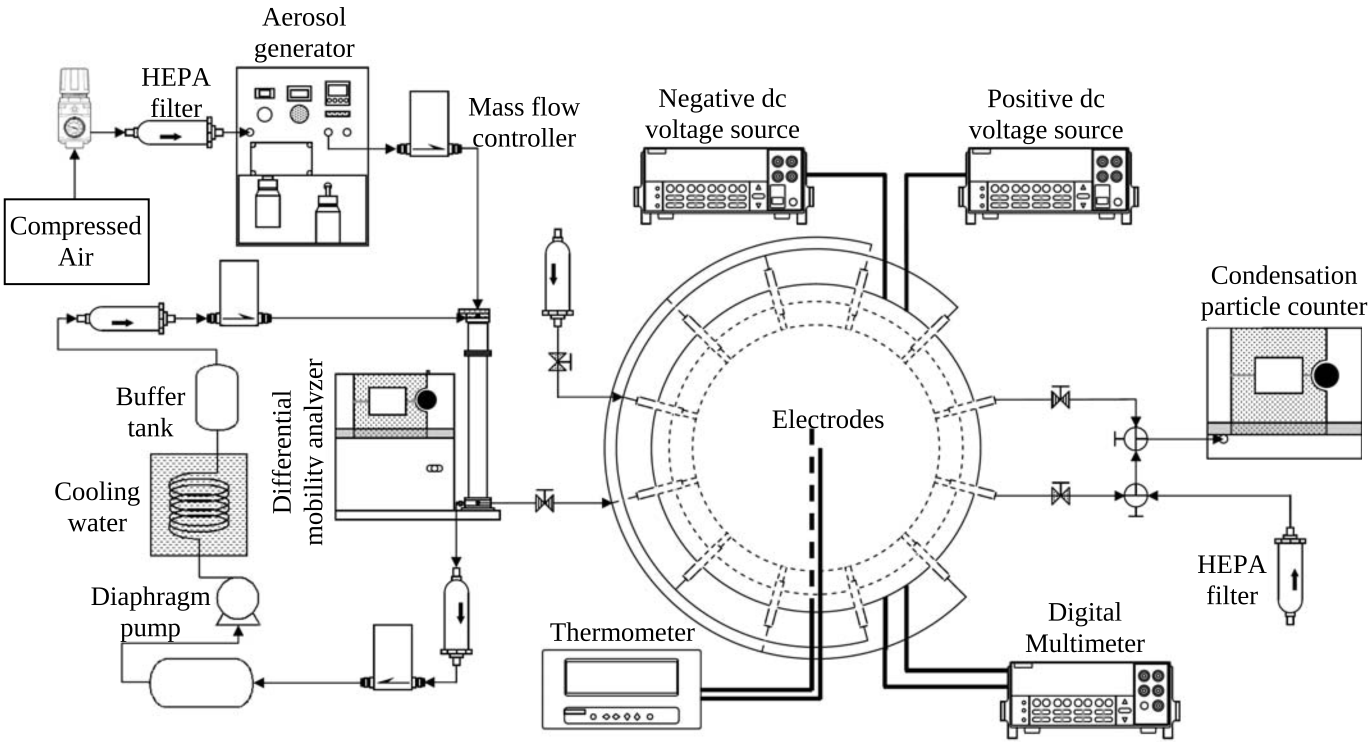

Figure 3: Diagrammatic sketch of the measurement system.

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. In addition, the electrodes are held in an adiabatic vessel to obtain a uniformly temperature over the two electrode surfaces, in order to suppress thermophoresis of particles. The difference in temperatures between the electrodes is measured by the thermometer.

3 SYSTEM EVALUATION

In order to decide the precision of the observed value, the uncertainty of the measurements must be evaluated according to ISO GUM (Guide to the Expression of Uncertainty in Measurement) [4]. Scanning electron microscope images of the PSL particles used the uncertainty evaluation of the system are shown in Figure 4.

3.1 Mathematical Model

The physical properties used to measure the particle size including elementary charge, e, voltage, V, particle density, ρ_p, air density, ρ_a, electrode gap, H, gravity, g. From equations (4) and (6), the derivation of the number average particle diameter, d_p, can be written as:

$$d_p = [\frac{6eV}{\pi(\rho_p - \rho_a)Hg}]^{1/3} \tag{7}$$

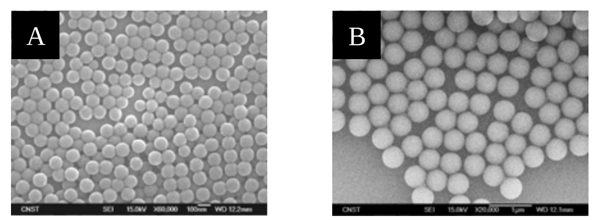

Figure 4: Scanning electron micrographs. (A) 100 nm PSL particles, and (B) 500 nm PSL particles.

3.2 Uncertainty Evaluation

Two components contribute to the uncertainty, besides the six parameters shown in equation (7). One is the residual fitting error of the survival rate, $u_r(m_0)$. The second is the measurement reproducibility, $u(R)$. Subsequently, the contributed variances can be represented by the combined standard uncertainty, u_c, as follows:

$$\begin{aligned} u_c(d_p) = \Big\{ & (\frac{d_P}{3e})^2 u^2(e) + (\frac{d_P}{3V})^2 u^2(V) \\ & + (-\frac{d_P}{3\rho_p})^2 [1 + \frac{\rho_a^2}{(\rho_P - \rho_a)^2}] u^2(\rho_p) \\ & + [\frac{d_P}{3(\rho_P - \rho_a)}]^2 u^2(\rho_a) + (-\frac{d_P}{3H})^2 u^2(H) \\ & + (-\frac{d_P}{3g})^2 u^2(g) + (\frac{d_P}{3m_0})^2 u_r^2(m_0) + u^2(R) \Big\}^{\frac{1}{2}} \end{aligned} \tag{8}$$

The uncertainties of 100 nm and 500 nm particle size measurements are summarized in Table 1 and Table 2, and the combined standard uncertainty were calculated as 0.501 nm and 0.582 nm, respectively. The effective degree of freedom for the system was determined to be 11 for the 100 nm particles, and 13 for the 500 nm particles. The coverage factors based on the t-distribution were 2.20 for the 100 nm particles and 2.16 for the 500 nm particles at the 95 % confidence interval. The resulting expanded uncertainties were 1.2 nm for the 100 nm particles and 1.3 nm for the 500 nm particles.

4 CONCLUSION

In order to achieve higher accuracy and lower uncertainty for nanoparticle size measurement in Center for Measurement Standards, the electro-gravitational aerosol balance method has been used to develop the primary nanoparticle size standard system, because of the simplicity of its principle. The average diameters and the corresponding uncertainties of polystyrene latex particles with nominal sizes 100 nm and 500 nm were determined. With the mathematical model built with survival function, each of the contributed variances to the measurement uncertainty of the system was analyzed. The measurement uncertainties for the 100 nm and 500 nm PSL spheres were found to be 1.2 nm and 1.3 nm, respectively. The evaluated uncertainties were closely related to the properties of particles under investigation.

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Error Quantity	Standard Uncertainty	Sensitivity Coefficient	Uncertainty Contribution
Elementary Charge	4.00×10^{-27} C	2.27×10^{20} nm/C	9.08×10^{-7} nm
Voltage	2.05×10^{-5} V	5.50×10^{1} nm/V	1.13×10^{-3} nm
Particle Density	1.16×10^{-3} g/cm^3	3.47×10^{1} nm·cm^3/g	4.03×10^{-2} nm
Air Density	3.00×10^{-5} g/cm^3	3.48×10^{1} nm·cm^3/g	1.04×10^{-3} nm
Electrode Gap	2.36×10^{-3} mm	2.43×10^{0} nm/mm	5.73×10^{-3} nm
Gravitational acceleration	4.24×10^{-5} m/s^2	3.71×10^{0} nm·s^2/m	1.57×10^{-4} nm
Survival Rate	9.31×10^{-6}	5.13×10^{4} nm	4.78×10^{-1} nm
Reproducibility	1.46×10^{-1} nm	1	1.46×10^{-1} nm
Combined Standard Uncertainty		5.01×10^{-1} nm	
Effective Degrees of Freedom		11	
Coverage Factor		2.20	
Expanded Uncertainty		1.2 nm	

Table 1: Uncertainty budget for 100 nm PSL particles.

Error Quantity	Standard Uncertainty	Sensitivity Coefficient	Uncertainty Contribution
Elementary Charge	4.00×10^{-27} C	1.10×10^{21} nm/C	4.40×10^{-6} nm
Voltage	5.31×10^{-3} V	2.34×10^{0} nm/V	1.24×10^{-2} nm
Particle Density	1.16×10^{-3} g/cm^3	1.68×10^{2} nm·cm^3/g	1.95×10^{-1} nm
Air Density	3.00×10^{-5} g/cm^3	1.69×10^{2} nm·cm^3/g	5.07×10^{-3} nm
Electrode Gap	2.36×10^{-3} mm	1.18×10^{1} nm/mm	2.78×10^{-2} nm
Gravitational acceleration	4.24×10^{-5} m/s^2	1.80×10^{1} nm·s^2/m	7.63×10^{-4} nm
Survival Rate	2.43×10^{-4}	2.17×10^{3} nm	5.27×10^{-1} nm
Reproducibility	1.46×10^{-1} nm	1	1.46×10^{-1} nm
Combined Standard Uncertainty		5.82×10^{-1} nm	
Effective Degrees of Freedom		13	
Coverage Factor		2.16	
Expanded Uncertainty		1.3 nm	

Table 2: Uncertainty budget for 500 nm PSL particles.

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