Evaluation of Uncertainty in Nanoparticle Size Measurement by Differential Mobility Analysis

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ABSTRACT

This paper presents the measurement results and the uncertainty analysis for four batches of polystyrene latex (PSL) spheres with nominal sizes of 20 nm, 100 nm, 300 nm and 500 nm using the measurement system which differential mobility analysis (DMA) method is applied. The possible error sources are evaluated based on the DMA method and the measurement procedures. The resulting expanded uncertainties are 1.3 nm for the 20 nm particles and 13 nm for the 500 nm particles at 95% confidence interval.

Key words: nanoparticle size, measurement uncertainty, Differential Mobility Analysis.

1. INTRODUCTION

Nanoparticles have found their unique advantages and immediate applications in numerous industrial, commercial, and consumer products. The success of the nanoparticle applications rely first-hand on the advancements of nanometrology to support the increasing demands in measurement accuracy. One measurement parameters of great interests on nanoparticles is their sizes, or the more precisely defined term, diameters. However, existing techniques for nanoparticle size characterizations have resulted in performance inconsistency due to lack of standardization of nanoparticle measurements [1]. Therefore, it is crucial and necessary to establish measurement standards to accurately and consistently determine the sizes of the nanoparticles in nanometer range. A measurement system for particle size, based on the differential mobility analyzer (DMA), has been developed in Center for Measurement Standards of Industrial Technology Research Institute (CMS, ITRI) to obtain particle diameters with high accuracy and small uncertainty. The DMA is calibrated by the primary standard measurement system "electro- gravitational aerosol balance (EAB)", which was also developed in ITRI [2].

2. MEASUREMENT SYSTEM

The DMA, widely used in various applications, is capable of accurate size measurement with highly-resolved size-classification of aerosol particles. Basically, this equipment has two major applications: one is to measure the particle size distribution; the second is to sort out narrow-ranged particle size.

The approach used in this study is to sort aerosol particles according to their electrical mobility, Z, which is defined as the ratio of the velocity to the electric field. The electrical mobility is related to the particle diameter, D, and is given by

$$Z = \frac{v}{E} = \frac{q \cdot C}{3\pi \cdot \eta \cdot D} \quad (1)$$

Where v is the velocity of the particles in the electric field, E is the electric field applied to the particles, q is the charges carried by the particles, C is the slip correction factor determined by the properties or aerosol carrier gas, and η is the gas viscosity.

As shown in figure 1, differential mobility analyzer is an axially symmetric structure, which contains a cylindrical outer sheath of radius r_1 and a central cylindrical electrode of radius r_2. The central cylindrical electrode is connected to high voltage and the outer sheath is connected to ground to form a radiated high voltage electric field. When the particle is within this electric field, the electric field strength for any point of distance r to the center will have electric field strength of:

$$E = \frac{V}{r \cdot \ln(r_1/r_2)} \quad (2)$$

Where V is the voltage of the central cylindrical electrode.

From equation (1) and equation (2), we can obtain the radial velocity of particles in this system is v_E:

$$v_E = \frac{dr}{dt} = Z \cdot E = \frac{Z \cdot V}{r \cdot \ln(r_1/r_2)} \quad (3)$$

Where t is the time. And the axial velocity of this

particle is v_R:

$$v_R = \frac{dx}{dt} = u(r) \tag{4}$$

Where $u(r)$ is the radial velocity. From equation (3) and equation (4), we can obtain:

$$\begin{aligned} \int_0^L dx &= \int_{r_1}^{r_2} \frac{r \cdot \ln(r_1/r_2) \cdot u(r)}{Z \cdot V} dr \\ &= \frac{\ln(r_1/r_2)}{2\pi \cdot Z \cdot V} \int_{r_1}^{r_2} 2\pi \cdot r \cdot u(r) dr \end{aligned} \tag{5}$$

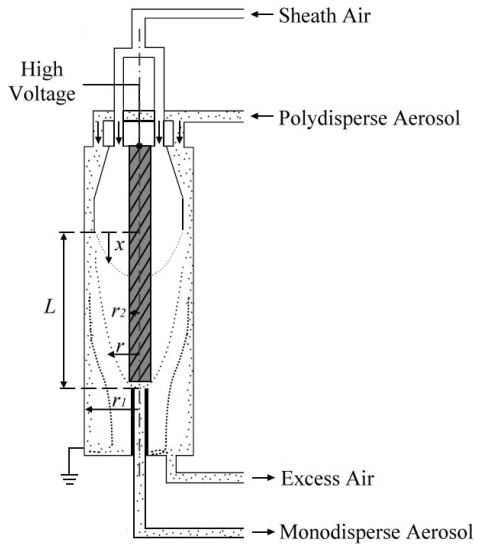

Figure 1: Differential mobility analyzer used in this work.

Equation (5) is used to describe the particle's behavior from the outer top of differential mobility analyzer ($r = r_1$ and $x = 0$) to the central bottom ($r = r_2$ and $x = L$) affected by electrostatic force and dragging force. When polydisperse aerosol flow rate (Q_a) is equal to monodisperse aerosol flow rate (Q_s), from equation (5), we can obtain:

$$Z = \frac{Q_c \cdot \ln(r_1/r_2)}{2\pi \cdot L \cdot V} \tag{6}$$

Where Q_c is sheath air flow rate. Therefore, from equation (1) and equation (6), we can obtain the particle size *D*:

$$D = \frac{2q \cdot L \cdot V \cdot C}{3\eta \cdot Q_c \cdot \ln(r_1/r_2)} \tag{7}$$

3. SYSTEM EVALUATION

Nanoparticle size measurement system using differential mobility analysis, through polystyrene particles, uses comparison method to be traced to EAB nanoparticle size calibration system. Meanwhile, based on ISO/IEC Guide 98-3:2008[3], each of the error source and standard uncertainty is analyzed. Finally, the expanded uncertainty is calculated. The polystyrene particles and flow rate setup of differential mobility analyzer for system evaluation are shown in table 1.

3.1. Mathematical model

We can obtain the calibration values of reference particles by EAB nanoparticle size calibration system. Meanwhile, when the geometrical parameters (r_1, r_2, L) and sheath air flow rate (Q_c) of differential mobility analyzer are all of constant values, the mobility of particle (Z) is only related to voltage (V) from equation (6). Therefore, under the same parameters setup, when nanoparticles size measurement system using differential mobility analysis is used respectively to perform the mobility measurement of reference particles and particles to be tested, the calibration equation of comparison method can be:

$$Z_t = \frac{\tilde{Z}_t}{\tilde{Z}_r} \times Z_r \tag{8}$$

Where Z_t is the mobility of particles to be tested, Z_r is the mobility corresponding to the traced particle size of reference particles (D_r). $\tilde{Z}_t$ and $\tilde{Z}_r$ is the mobility obtained by the measurement system for particles to be tested and reference particles, respectively. Meanwhile, from equation (1), we can obtain particle size measurement values of particles to be tested and reference particles of $\tilde{D}_t$ and $\tilde{D}_r$, respectively. Therefore, particle size calibration value (D_t) of particles to be tested can be obtained from equation (1) and equation (8):

$$D_t = (\frac{\tilde{D}_t}{\tilde{D}_r} \times D_r) \times (\frac{\tilde{C}_r}{\tilde{C}_t} \times \frac{C_t}{C_r}) \tag{9}$$

Where C_t, C_r, $\tilde{C}_t$ and $\tilde{C}_r$ are the slip correction factors corresponding to each particle size D_t, D_r, $\tilde{D}_t$ and $\tilde{D}_r$, respectively.

3.2. Uncertainty evaluation

Let the measured Y is the particle size calibration value D_t of particles to be tested, and we combine all the slip correction factors of equation (9) as C_C, then we can obtain the measuring equation:

$$Y = C_C(\frac{\tilde{D}_t}{\tilde{D}_r} \times D_r + e_r) + e_C \tag{10}$$

Where C_C and D_r are constant values, and their variances are e_C and e_r, respectively, and the estimated mean values of e_C and e_r are 0. Therefore, the sources of the measurement uncertainty include the uncertainty

source caused by the measurement process by particles to be tested and reference particles, and the combined standard uncertainty of the measuring system is:

$$u_c^2(Y) = C_C^2[(\frac{\partial D}{\partial \widetilde{D}_t})^2 \cdot u^2(\widetilde{D}_t) + (\frac{\partial D}{\partial \widetilde{D}_r})^2 \cdot u^2(\widetilde{D}_r) + u^2(e_r)] + u^2(e_C) = C_C^2 \cdot u^2(D) + u^2(e_C) \quad (11)$$

where $u(D)$ is the standard uncertainty generated during the measurement process. The sources of uncertainty are analyzed as following:

(a) Standard uncertainties caused by particles to be tested during the measurement process $u(\widetilde{D}_t)$:

The sources of uncertainty caused by particles to be tested during the measurement process include environmental parameters (temperature and atmospheric pressure), system setup (flow rate and voltage) and the stability of the particles to be tested, etc. The standard uncertainties are shown in table 2.

The uncertainty of five repeated measurements which are done on each particles to be tested are A type standard uncertainty. For B type standard uncertainty, the uncertainty might caused by the equipment resolution is considered, which includes the resolution of flow rate (0.1 L/min) and voltage (0.1 V). The uncertainty caused by the resolution of applied voltage can be neglected by the calculation.

(b) Standard uncertainty caused by reference particles during the measurement process $u(\widetilde{D}_r)$:

It is the same as the evaluation method for the uncertainty caused by particles to be tested during the measurement process. The standard uncertainties caused by reference particles during the measurement process are shown in table 3.

(c) Standard uncertainty of the particle size calibration value of reference particles $u(e_r)$:

The calibration values of reference particles by EAB nanoparticle size calibration system are used as constant value and each of the traced value is shown in table 1. Meanwhile, the relative uncertainty of each tracked value is supposed as 5 %, and we can obtain the standard uncertainty of 0.602 nm, sensitivity coefficient of 1, component of uncertainty of 0.602 nm, and degree of freedom of 200.

(d) Standard uncertainty caused by the measurement process $u(D)$:

The standard uncertainties caused during the measurement process include measurement uncertainty and traced uncertainty, etc., which are shown in equation (12). The calculation results of the standard uncertainty of each particles to be tested are summarized in table 4.

$$u^2(D) = (\frac{\partial D}{\partial \widetilde{D}_t})^2 u^2(\widetilde{D}_t) + (\frac{\partial D}{\partial \widetilde{D}_r})^2 u^2(\widetilde{D}_r) + u^2(e_r) \quad (12)$$

(e) Standard uncertainty generated by the variance of slip correction factor $u(e_C)$:

The slip correction factor representative equation will change the final measuring value of the particles to be tested and the value of slip correction factor. Therefore, seven kinds of slip correction factor representative equations as proposed in literature [4] are used to obtain respective slip correction factor and variance as corresponded to each particle size correction value. Meanwhile, B type evaluation method is used to obtain the standard uncertainty as shown in table 5.

From the above uncertainty source analysis and equation (11), we can obtain the $u_c(D_t)$ (the combined standard uncertainty) of each of the particles to be tested. The uncertainty evaluation result of this measurement system on each particles to be tested is shown in table 6. The U (the expanded uncertainty) is obtained from the multiplication of combined standard uncertainty by the coverage factor (k) at 95% confidence interval. The coverage factor can be obtained from effective degree of freedom (v_{eff}) [5].

4. CONCLUSION

From the uncertainty evaluation results of the measurement of particles to be tested by DMA method, the mean particle sizes of the measurement result of particles to be tested all fall within the calibration report values. Meanwhile, the expanded uncertainties for measurement range from 20 nm to 500nm are from 1.3 nm to 13 nm, respectively. Therefore, the measurement capability of this measurement system can be recognized. The completion of the setup of nanoparticle size measurement system using differential mobility analysis will provide the traceability system of domestic nanoparticle size standard.

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Table 1: Polystyrene particles and flow rate setup of differential mobility analyzer for system evaluation.

	Particles to be tested	Value of calibration report (nm)		Reference particles	Value of calibration report (nm)		Flow rate setup (L/min)	
		Average particle size	Uncertainty		Average particle size	Uncertainty	Q_c	Q_a
Number	DUKE-3020A	21	1.5	CMS-100	109.0	1.3	10.0	1.0
	JSR-SC-0100-D	100	3	CMS-100	109.0	1.3	10.0	1.0
	JSR-SC-032-S	309	9	CMS-300	284.9	1.3	6.0	6.0
	JSR-SC-051-S	506	12	CMS-500	532.4	1.3	3.0	3.0

Table 2: Standard uncertainty caused by the measurement process of the particles to be tested.

Number	Measured value of particle size	Repro-ducibility measure-ment	Error caused by flow rate resolution	Standard uncertainty	Sensitivity coefficient	Component of uncertainty	Degree of free-dom
DUKE-3020A	20.45 nm	0.15 nm	0.045 nm	0.157 nm	0.960	0.151 nm	4
JSR-SC-0100-D	101.21 nm	0.07 nm	0.222 nm	0.233 nm	0.960	0.223 nm	136
JSR-SC-032-S	306.39 nm	0.13 nm	1.213 nm	1.220 nm	0.999	1.219 nm	203
JSR-SC-051-S	504.38 nm	1.29 nm	4.307 nm	4.495 nm	0.997	4.478 nm	152

Table 3: Standard uncertainty caused by the measurement process of the reference particles.

Number	Measured value of particle size	Repro-ducibility measurement	Error caused by flow rate resolution	Standard uncertainty	Sensitivity coefficient	Component of uncertainty	Degree of freedom
CMS-100	113.51 nm	0.03 nm	0.249 nm	0.251 nm	0.173	0.043 nm	199
CMS-100	113.46 nm	0.03 nm	0.249 nm	0.255 nm	0.857	0.218 nm	191
CMS-300	284.69 nm	0.30 nm	1.127 nm	1.166 nm	1.075	1.254 nm	167
CMS-500	531.42 nm	1.23 nm	4.538 nm	4.700 nm	0.946	4.444 nm	168

Table 4: Standard uncertainty caused by the measurement process.

Number	D	$u(\tilde{D}_t)$	$u(\tilde{D}_r)$	$u(e_r)$	$u(D)$	Degree of freedom
DUKE-3020A	19.64 nm	0.151 nm	0.043 nm	0.602 nm	0.622 nm	199
JSR-SC-0100-D	97.23 nm	0.223 nm	0.218 nm	0.602 nm	0.678 nm	191
JSR-SC-032-S	306.08 nm	1.219 nm	1.254 nm	0.602 nm	1.849 nm	167
JSR-SC-051-S	502.46 nm	4.479 nm	4.444 nm	0.602 nm	6.338 nm	168

Table 5: Standard uncertainty caused by slip correction factor variance.

Number	D_t	C_C	D	ΔC_C	ΔY	$u(e_C)$	Degree of freedom
DUKE-3020A	19.74 nm	1.0052	19.64 nm	1.06E-03	0.0208 nm	0.006 nm	6
JSR-SC-0100-D	97.30 nm	1.0007	97.23 nm	2.96E-04	0.0288 nm	0.008 nm	6
JSR-SC-032-S	306.08 nm	1.0000	306.08 nm	1.70E-06	0.0005 nm	0.000 nm	6
JSR-SC-051-S	502.48 nm	1.0000	502.46 nm	2.37E-05	0.0119 nm	0.003 nm	6

Table 6: Expanded uncertainty of particles to be tested.

Number	D_t	$u(D)$	$u(e_C)$	$u_c(D_t)$	v_{eff}	U (k = 2.07)
DUKE-3020A	19.7 nm	0.626 nm	0.006 nm	0.630 nm	45	1.3 nm
JSR-SC-0100-D	97.3 nm	0.679 nm	0.008 nm	0.680 nm	221	1.4 nm
JSR-SC-032-S	306.1 nm	1.857 nm	0.000 nm	1.857 nm	60	3.9 nm
JSR-SC-051-S	502.5 nm	6.397 nm	0.003 nm	6.397 nm	23	13 nm