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Uncertainty Analysis on Precision Measurement for Polystyrene Nanospheres Using Dynamic Light Scattering

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Dynamic light scattering (DLS) is the most commonly used technique for measuring nanosphere sizes. In order to establish the traceability of the DLS method to SI units, relevant parameters have been measured in this study. Several studies have been reported on error sources in DLS. However, these studies lacked a systematic method of analyzing the uncertainty of DLS. In this paper we describe the DLS method and present a measurement uncertainty budget. Monodispersed polystyrene latex (PSL) spheres are selected as reference materials in the uncertainty evaluation. The measured nanosphere sizes are 20, 50, 100, 300, 500, and 1000 nm, among which the measurement results of 100, 300, and 500 nm nanospheres obtained using DLS are compared with those for an electrogravitational aerosol balance (EAB) method. The uncertainties for both methods are calculated, and the results of repeated measurements are presented with confidence levels of 95%.

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1. Introduction

The development of nanotechnology, particularly of nanometer-scale particulate materials or nanoparticles, is having a revolutionary effect in science and technology. The particle diameter is a key property in differentiating behaviors among nanoparticles, and the measurement of nanoparticle diameter is becoming increasingly challenging as the particle diameter decreases. Dynamic light scattering (DLS) is the most commonly used technique for measuring nanosphere sizes. An interlaboratory comparison of measured nanosphese sizes was carried out involving 10 participants (laboratories) from six countries in the Asia-Pacific Economic Cooperation (APEC) zone, and the results obtained using different instruments were published.[1)] However, different instruments used in the comparison gave different values. In order to establish the traceability of the DLS method to SI units, relevant parameters have been measured in this study. Several papers[2–5)] have been reported on error sources in DLS. However, these studies lacked a systematic method of analyzing the uncertainty of DLS. In accordance with ISO/IEC Guide 98-3: 2008,[6)] in this paper we describe the DLS method and present an uncertainty analysis of measured nanosphere sizes. Monodispersed polystyrene latex (PSL) spheres are selected as reference materials. The measured nanosphere sizes range from 20 to 1000 nm, among which the measurement results of 100, 300, and 500 nm nanospheres obtained using DLS are compared with those for an electrogravitational aerosol balance (EAB) method. The uncertainties for both methods are determined, and the results of repeated measurements are presented with confidence levels of 95%.

2. Measurement Principles and Instruments

DLS is the most commonly used technique for measuring nanosphere sizes. In order to validate the accuracy of this method, a custom-built height-resolution EAB system was used to measure nanospheres with sizes of 100, 300, and 500 nm. Both methods are described as follows.

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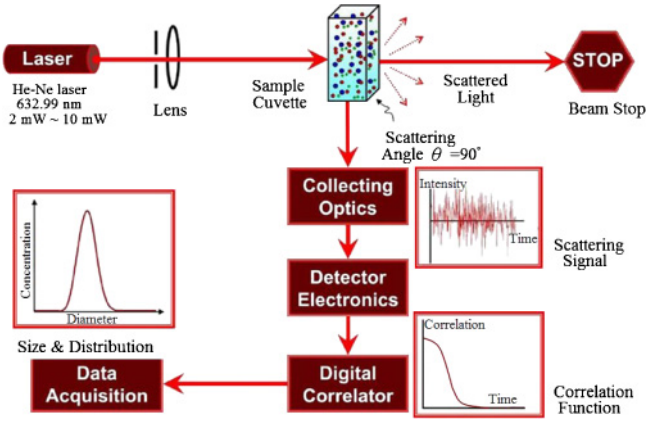

Fig. 1. (Color online) Schematic of DLS method.

2.1 DLS method

DLS, also known as photon correlation spectroscopy (PCS) or quasi-elastic light scattering (QELS), takes advantage of the high spatial coherence of monochromatic light sources to analyze the intensity fluctuation of scattering light for particulate samples that are dispersed in solutions. DLS determines nanosphere sizes by observing nanosphere behavior when undergoing Brownian motion.[7)] Figure 1 shows the basic principle of the DLS technique.

As depicted in Fig. 1, a laser light passes through a sample cuvette with nanospheres suspended in a solution. The incident light is then scattered by these nanospheres. Since the nanospheres have a nonzero absolute temperature, their relative positions are constantly changing and, thus, the observed scattering intensity varies with the scattering angles θ. Hence, the information obtained from the motion of dispersed nanospheres can be analyzed. In a DLS experiment, time analysis is carried out by using a correlator, constructed from the time autocorrelation function $G_2(\tau)$ of the scattering intensity:[8)]

$$G_2(\tau) = \langle I(t) \cdot I(t+\tau) \rangle, \quad (1)$$

where $G_2(\tau)$ is the product of the scattering intensities I at a specific time t and after a time lag τ. For a large number of monodispersed nanospheres undergoing Brownian motion,

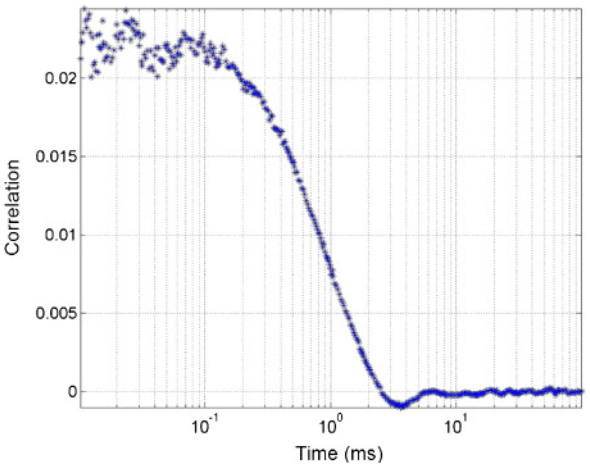

Fig. 2. (Color online) Decay rate, given by the slope of the correlation curve.

$G_2(\tau)$ is an exponentialy decaying function of time lag τ written as

$$G_2(\tau) = A[1 + Be^{-2\Gamma\tau}], \tag{2}$$

where A is a time-independent constant proportional to the square of the time-averaged scattering intensity $\langle I \rangle$ and B is the intercept of the autocorrelation function.[9] The inverse of the correlation time is the decay rate Γ, which is related to the diffusion rate. An example of the decay rate obtained from the autocorrelation function is shown in Fig. 2, where the slope of the linear past of the correlation curve represents the decay rate. Data analysis is carried out using eq. (1) to compute scattering signals and autocorrelation functions for different nanosphere sizes.

2.2 EAB method

In this study we employ a custom-built height-resolution EAB system to measure the nanosphere size. This approach to measuring the nanosphere size and the measurement system are similar to those of Ehara *et al.*[10,11] The experimental setup of the EAB method is shown in Fig. 3, which includes an aerosol generator, a differential mobility analyzer, dc voltage sources, a digital multimeter, a thermometer, a condensation particle counter, a recirculation system, and electrodes. The aerosol generator, produced by JSR Aeromaster-V, is a pneumatic atomizer that operates by using a clean air stream to nebulize the liquid solution containing PSL nanospheres. First, the liquid aerosol passes through a heated tube where the liquid evaporates, leaving only the solid nanospheres as an aerosol. The aerosol is initially highly charged from the nebulization process and is neutralized with an Am-241 bipolar charger using an aerosol generator. Both the aerosol and the clean air simultaneously flow into a differential mobility analyzer (DMA; TSI 3080L). The DMA system allows only nanospheres with particular diameter to enter the EAB system. After a certain time, the nanospheres become stable owing to the balance between the electrostatic and gravitational forces. The number of remaining nanospheres is determined by using a condensation particle counter. Once the nanosphere density is known, the nanosphere size can be deduced.

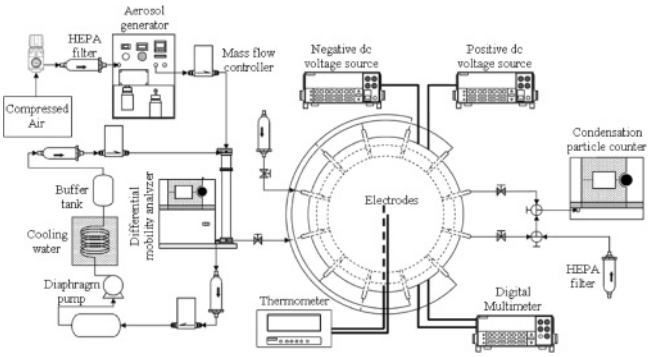

Fig. 3. Experimental setup of EAB method.

3. Sources of Uncertainty

Referring to ISO 13321[8] (particle size analysis–photon correlation spectroscopy), the decay rate Γ is linked to the translational diffusion coefficient D of isotropic spherical particles undergoing Brownian motion. Their relationship can be written as

$$\Gamma = Dq^2, \tag{3}$$

where q is the modulus of the scattering vector, defined as the vector difference between the incident and scattering wave vectors. The modulus can be expressed as[8]

$$q = \frac{4\pi n}{\lambda_0} \cdot \sin\left(\frac{\theta}{2}\right), \tag{4}$$

where n is the refractive index of the dispersion medium and θ is the scattering angle with respect to incident light of wavelength λ_0. By applying the Stokes–Einstein relation,[12] the diffusion coefficient D can be expressed as

$$D = \frac{k_B T}{3\pi\eta x}, \tag{5}$$

where k_B denotes the Boltzmann constant, T is the absolute temperature, η is the dynamic viscosity of the dispersion medium, and x is the nanosphere diameter expressed by[8]

$$x = \frac{k_B T\left[4\pi n \cdot \sin\left(\frac{\theta}{2}\right)\right]^2}{3\pi\Gamma\eta\lambda_0^2}, \tag{6}$$

It follows that the nanosphere diameter x can be expressed as

$$\begin{aligned} x &= f(\lambda_0, T, k_B, n, \theta, \Gamma, \eta) \\ &= f(c_1, c_2, c_3, c_4, c_5, c_6, c_7), \end{aligned} \tag{7}$$

According to ISO/IEC Guide 98-3:2008,[6] to measure the nanosphere size, the contributory variances can be represented by the combined standard uncertainty u_c, i.e.,

$$\begin{aligned} u_c{}^2(x) &= \sum_i c_i{}^2 u^2(x_i) \\ &= \left(\frac{\partial f}{\partial k_B}\right)^2 u^2(k_B) + \left(\frac{\partial f}{\partial T}\right)^2 u^2(T) + \left(\frac{\partial f}{\partial n}\right)^2 u^2(n) \\ &\quad + \left(\frac{\partial f}{\partial \theta}\right)^2 u^2(\theta) + \left(\frac{\partial f}{\partial \Gamma}\right)^2 u^2(\Gamma) \\ &\quad + \left(\frac{\partial f}{\partial \eta}\right)^2 u^2(\eta) + \left(\frac{\partial f}{\partial \lambda_0}\right)^2 u^2(\lambda_0), \end{aligned} \tag{8}$$

with

Table I. List of decay rates for different nanosphere diameters.

Decay rate (s^{-1})	Diameter (nm)					
	20	50	100	300	500	1000
Γ_1	8244.7021	3065.7501	1516.536	289.8322	281.4724	147.0413
Γ_2	7276.8632	2898.6031	1441.053	306.9719	276.8562	149.9654
Γ_3	8057.9289	2941.4058	1499.488	287.6003	274.3326	148.4971
Γ_4	7030.3059	3149.7787	1457.787	291.0915	268.8879	143.466
Γ_5	7165.1799	2908.1955	1437.448	289.658	285.2239	151.486
Γ_6	6598.675	2861.4059	1426.468	303.3689	277.2168	145.0991
Γ_7	8016.1331	3102.6792	1455.656	303.3689	278.5438	144.484
Γ_8	6842.9957	2870.7533	1497.609	303.3689	271.3374	150.8842
Γ_9	6863.4303	2849.3992	1452.119	303.3689	269.4887	143.3361
Average	7344.0238	2960.8856	1464.907	297.6255	275.9289	147.1399
SD	606.74042	114.16361	31.68441	7.799946	5.490510	3.200176

*SD: standard deviation

$$c_i = \partial f/\partial x_i, \text{ and } i = 1, 2, 3, \ldots, 7. \tag{9}$$

The partial derivatives c_i in eq. (8) are interpreted as sensitivity coefficients associated with the input quantities x_i.[13] As a consequence, the sensitivity coefficients for the parameters in eqs. (6) and (7) can be derived as

$$\begin{aligned}
\frac{\partial f}{\partial k_B} &= \frac{T[4\pi n \cdot \sin(\theta/2)]^2}{3\pi\Gamma\eta\lambda_0^2} \\
\frac{\partial f}{\partial T} &= \frac{k_B[4\pi n \cdot \sin(\theta/2)]^2}{3\pi\Gamma\eta\lambda_0^2} \\
\frac{\partial f}{\partial n} &= \frac{2Tk_B[4\pi n \cdot \sin(\theta/2)][4\pi \cdot \sin(\theta/2)]}{3\pi\Gamma\eta\lambda_0^2} \\
\frac{\partial f}{\partial \theta} &= \frac{Tk_B[4\pi n \cdot \cos(\theta/2)][4\pi n \cdot \sin(\theta/2)]}{3\pi\Gamma\eta\lambda_0^2} \\
\frac{\partial f}{\partial \eta} &= -\frac{Tk_B[4\pi n \cdot \sin(\theta/2)]^2}{3\pi\Gamma\eta^2\lambda_0^2} \\
\frac{\partial f}{\partial \Gamma} &= -\frac{Tk_B[4\pi n \cdot \sin(\theta/2)]^2}{3\pi\Gamma^2\eta\lambda_0^2} \\
\frac{\partial f}{\partial \lambda_0} &= -\frac{2Tk_B[4\pi n \cdot \sin(\theta/2)]^2}{3\pi\Gamma\eta\lambda_0^3}
\end{aligned} \tag{10}$$

The uncertainty evaluation for the parameters in eq. (6) used to calculate nanosphere sizes is described as follows. A He–Ne laser was utilized as the light source. By tracing to a calibrated laser wavelength meter, its wavelength λ_0 was measured as 632.9907 nm with a standard uncertainty of 7.2×10^{-11} m. The system measurement environment was 20 °C in a laboratory with an isolated thermocontrolled sample holder capable of maintaining the temperature T at 20.0 ± 0.2 °C, i.e., 293.15 ± 0.20 K. If the uncertainty of the temperature is assumed to be rectangularly distributed, its standard uncertainty is $0.20/\sqrt{3} = 0.115$ K.[14] In addition, according to the database of fundamental physics constants published by the Committee on Data for Science and Technology, the recommended value for k_B[15] is $1.3806504 \times 10^{-23}$ J·K^{-1} with a standard uncertainty of 2.4×10^{-29} J·K^{-1}. The standard dispersion medium for the DLS method is pure water, whose refractive index n is 1.331 at 20 °C. By considering the effect of the refractive index of pure water on the measurement result, the refractive index of pure water is set as 1.331 for $\lambda = 633$ nm at 20 °C, and the standard uncertainty of the refractive index n[16] is set as 0.001. In the DLS method, the scattering signal is collected by a detector with a fiber diameter of 40 μm, and the scattering angle is 90°. The linear distance between sample and fiber is 110 mm. The scattering angle θ is determined to contribute a variance is ±0.01042°. If the uncertainty of the scattering angle has a of rectangular distribution, its standard uncertainty is $(0.01042 \times \pi/180)/\sqrt{3} = 1.05 \times 10^{-4}$ rad. In addition, the decay rate is computed from the time correlation of nanospheres undergoing Brownian motion and is used to determine the nanosphere size as well as the uncertainty. Table I lists the average decay rate Γ from nine repeated measurements for 20, 50, 100, 300, 500, and 1000 nm nanospheres sizes. With regard to a liquid of viscosity η, according to ISO/TR 3666 — viscosity of water,[17] the dynamic viscosity of water at 20 °C is 1.002×10^{-3} Pa·s and the standard uncertainty of viscosity is 2.51×10^{-6} Pa·s. The values of k_B, T, n, θ, η, Γ, and λ_0 are prescribed for calculating the nanosphere sizes using eq. (6).

4. Results and Discussion

Using the DLS method, we carried out the uncertainty evaluation of measurement for PSL nanospheres with sizes of 20, 50, 100, 300, 500, and 1000 nm. The nanospheres were synthesized by emulsion polymerization of the styrene monomer. In order to prevent the aggregation of PSL nanospheres in water, the particulate samples were inspected for any coagulation or condensation. If any coagulation or condensation exists, appropriate methods should be applied such as filtration and/or ultrasonication to disperse the samples properly.[8] According to eqs. (6) and (7), there are seven input parameters whose uncertainty budgets must be evaluated. Table II summarizes the significant contributors to uncertainty for 100 nm nanospheres in the DLS method. Furthermore, in Table II the sensitivity coefficients are calculated using eq. (10). The standard uncertainties multiplied by the sensitivity coefficients give the uncertainty contributions. In accordance with ISO GUM, the combined standard uncertainties u_c for PSL are calculated by using eq. (8). Finally, the expanded uncertainty $U = k \times u_c$[14] using DLS, is shown in Table III with a confidence level of 95% and coverage factor $k = 2$.

Table II. Uncertainty budget for 100 nm polystyrene spheres.

Input quantity	Symbol coefficient	Standard uncertainty contribution	Sensitivity	Uncertainty (nm)
Laser wavelength	λ_0	7.2×10^{-11} m	-0.334	2.41×10^{-2}
Boltzmann constant	k_B	2.4×10^{-29} J·K^{-1}	7.66×10^{15} J^{-1}·K·m	1.84×10^{-4}
Temperature	T	0.115 K	3.61×10^{-10} K^{-1}·m	4.15×10^{-2}
Refractive index	N	0.001	1.59×10^{-7} m	1.59×10^{-1}
Scattering angle	θ	1.05×10^{-4} rad	-1.06×10^{-7} m	1.11×10^{-2}
Decay rate	Γ	31.684 s^{-1}	-7.50×10^{-11} m·s	2.38
Viscosity	H	2.51×10^{-3} Pa·s	1.06×10^{-10} m·Pa^{-1}·s^{-1}	2.65×10^{-4}

Table III. Expanded uncertainty using DLS method.

PSL	Diameter (nm)					
	20	50	100	300	500	1000
Measurement results (nm)	20.5	50.5	107.8	294.3	541.6	1015.8
Uncertainty ($k = 2$)	3.5 nm	4.3 nm	5.8 nm	15.0 nm	30.0	52.8 nm

Table V. Expanded uncertainty of EAB system.

PSL	Diameter (nm)		
	100	300	500
Measurement results (nm)	109.0	284.7	529.4
Uncertainty ($k = 2$)	1.2 nm	1.3 nm	1.3 nm

Table IV. Uncertainty budget for 100 nm PSL nanospheres using EAB method.

Input quantity	Symbol coefficient	Standard uncertainty contribution	Sensitivity	Uncertainty (nm)
Elementary charge	e	4.00×10^{-27} C	2.27×10^{20} nm/C	9.08×10^{-7}
Voltage	V	2.05×10^{-5} V	5.50×10^{1} nm/V	1.13×10^{-3}
Nanosphere density	ρ_p	1.16×10^{-3} g/cm^3	3.47×10^{1} nm·cm^3/g	4.03×10^{-2}
Air density	ρ_a	3.00×10^{-5} g/cm^3	3.48×10^{1} nm·cm^3/g	1.04×10^{-3}
Electrode gap	H	2.36×10^{-3} mm	2.43 nm/mm	5.73×10^{-3}
Gravitational acceleration	g	4.00×10^{-5} m/s^2	3.71 nm·s^2/m	1.57×10^{-4}
Survival rate	m_0	9.31×10^{-6}	5.13×10^{4} nm	4.78×10^{-1}
Reproducibility	R	1.46×10^{-1} nm	1	1.46×10^{-1}

Furthermore, the measurement range for the EAB method is from 100 to 500 nm in this study. The uncertainty evaluation of EAB was carried out for PSL nanospheres of 100, 300, and 500 nm, whose measurement results were 109.0, 284.7, and 529.4 nm, respectively. In order to ensure system accuracy, we measured parameters including elementary charge e, voltage V, nanosphere density ρ_p, air density ρ_a, electrode gap H, gravity g, survival rate m_0, and reproducibility R. Table IV summarizes the uncertainties of the significant contributors for 100 nm nanosphere for the EAB method. The expanded uncertainty and the measurement results for the EAB method[18] are summarized in Table V.

The EAB method can accurately measure the size of PSL nanospheres. In this paper we have presented both the DLS and EAB methods for measuring the sizes of polystyrene nanospheres. Polystyrene nanospheres of sizes 20 to 1000 nm were measured by using the DLS method, and the results for 100 and 300 nm nanospheres were confirmed by using the EAB method. The measurement results and uncertainty are also plotted in Fig. 4, the DLS measurement results are in agreement with the EAB measurement results.

Finally, in order to establish the traceability of the DLS method to SI units, we carried out measurements to obtain parameters including the Boltzmann constant, laser wavelength, scattering angle, the refractive index and dynamic viscosity of the solvent, sample temperature, and the decay rate of the correlation function. Figure 5 depicts the standard uncertainty contributions of the parameters obtained from Table II. According to Fig. 5, the decay rate is the main source of the measurement uncertainty, whereas the Boltzmann constant and viscosity have the smallest contributions. The error source of the decay rate Γ consists of measurement repeatability, the quality of the particle dispersion, fluctuations in laser intensity, unwanted laser light interference with scattering light, and the possibility of

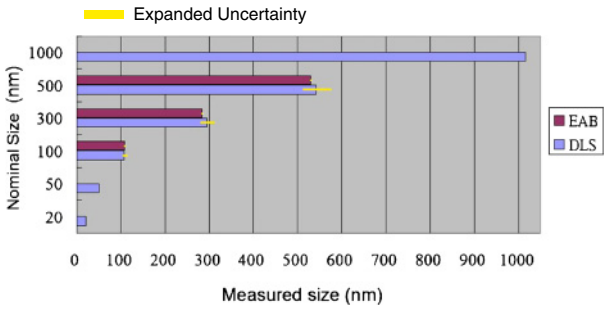

Fig. 4. (Color online) Comparison between DLS and EAB methods for measuring PLS nanosphere size.

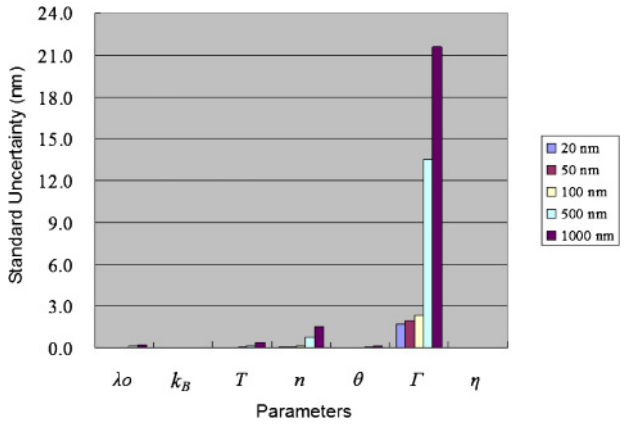

Fig. 5. (Color online) Contributions to standard uncertainty of DLS method.

sedimentation or agglomeration, all of which contribute to the uncertainty. Therefore, the measurement uncertainty of the DLS method can be reduced by using a stabilized laser source or by measuring high-quality monodispersion particles.

5. Conclusions

In this study, the uncertainties in measuring polystyrene nanospheres by using DLS have been evaluated. In order to establish the traceability of the DLS method to SI units, relevant parameters have been considered. Monodispersed polystyrene latex (PSL) spheres were selected as reference materials. The measurement results of nanospheres obtained using DLS were compared with those for the EAB method. The uncertainties for both methods were determined. In addition, the decay rate was found to dominate measurement uncertainty for each nanosphere size.

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