Determination of Nanoparticle Sizes by Turbidity-Debye Method

Waters

THE SCIENCE OF WHAT'S POSSIBLE.®

Bei Niu, Xiangjin Song, Beatrice Muriithi, and Yuehong Xu*
Waters Corporation, 34 Maple Street, Milford MA 01757, USA

corresponding author: yuehong_xu@waters.com

ACS 2017: Poster ANYL 173—*2759475*

INTRODUCTION

Interest in nanoparticles has risen consistently and rapidly in recent years, and the determination of the sizes of these materials has become crucial. There are various techniques for nanoparticle size analyses, and different techniques provide different information and accuracy. We have developed an analytical method to determine nanoparticle sizes based on Debye theory using turbidity measurements, and compared with other techniques such as dynamic light scattering (DLS), field emission scanning electron microscope (FE-SEM) and calculation from specific surface area (SSA).

THEORY

Attenuance and Transmittance

$D = -\log_{10}(T)$ [1] Eq.1

$T = I/I_0 = \exp(-NC_{ext}L)$ [2] Eq.2

$D = 0.434 \times NC_{ext}L$ Eq.3

- D: attenuance, or absorbance for solution without scattering, measured by UV/Visible spectrophotometer
- T: transmittance
- I: transmitted intensity
- I_0: incident intensity
- N: number of the same kind of particles per unit volume
- C_{ext}: extinction cross section of a particle
- L: path length

Turbidity from Dielectric Rayleigh Scatters

For dielectric particles[2]

$C_{abs} = 0$ Eq.4

$C_{ext} = C_{sca} + C_{abs} = C_{sca}$ Eq.5

$\tau = NC_{sca} = D/0.434L$ Eq.6

- C_{abs}: absorption cross section
- C_{sca}: scattering cross section
- τ: turbidity

For Rayleigh Scatters[2]

$$\frac{\tau}{c} = \frac{D}{0.434Lc} = 4\pi^4\left(\frac{n^2-1}{n^2+1}\right)^2\left(\frac{d^3}{\lambda^4\rho_2}\right) \quad \text{Eq.7}$$

- n: relative refractive index = n_2/n_1
- n_1, n_2: refractive indexes of medium (1) and sphere (2)
- λ: wavelength in the medium = λ_0/n_1
- λ_0: wavelength in vacuum or air
- d: particle diameter
- c: mass of particles per unit volume
- ρ_2: density of sphere (2)

Debye Approach

Due to multiple scattering, τ/c (and thus D/c) decreases with concentration. Therefore, D/c should be measured at low concentrations and extrapolated to zero.
Debye Equation for the determination of the molecular weight of the solute in solution:

$$\frac{Hc}{\tau_E} = \frac{1}{M} + 2Bc \quad \text{where} \quad H = \frac{32\pi^3 n^2}{3\lambda_0^4 N_A}\left(\frac{\partial n}{\partial c}\right)^2_{T,P} \quad \text{Eq.8}$$

Debye approach: plot the linear curve of Hc/τ_E vs. c to obtain intercept (= 1/M) and slope (= 2B).

Application of the Debye approach to this work:

- Measure D at certain λ with various dilution factors (k_d).
- Plot the linear curve of $1/(Dk_d)$ vs. $1/(k_d)$ to determine the intercept and slope
- $1/(Dk_d)_{c=0}$ = intercept

$$c = \frac{\rho_{s,0} \times f_{w,0}}{k_d} \quad \text{Eq.9}$$

Replacement of c in Eq. 7 with Eq. 9

$$Dk_d = 0.434 \times 4\pi^4\left(\frac{n^2-1}{n^2+1}\right)^2\left(\frac{L\rho_{s,0}f_{w,0}}{\lambda^4\rho_2}\right)d^3 \quad \text{Eq.10}$$

- $\rho_{s,0}$: density of un-diluted suspension
- $f_{w,0}$: weight fraction of particles over un-diluted suspension
- k_d: dilution factor

EXPERIMENTAL

Samples were diluted in appropriate dilution factors in order to achieve linear correlation of $1/Dk_d$ vs. $1/K_d$ as well as sufficient signals for accurate measurements. All suspensions had a final buffer concentration of ~10mM and a pH of ~8.5 to keep the silica nanoparticles stable for measurements. UV/Visible spectrum was acquired from each suspension from 700nm to 300nm. The wavelength of 300nm is chosen because scattering cross section increases with the decrease of wavelength, and the silica nanoparticles behave as dielectric Rayleigh scatters at this wavelength. The measurements at 700nm are for reference.

RESULTS AND DISCUSSION

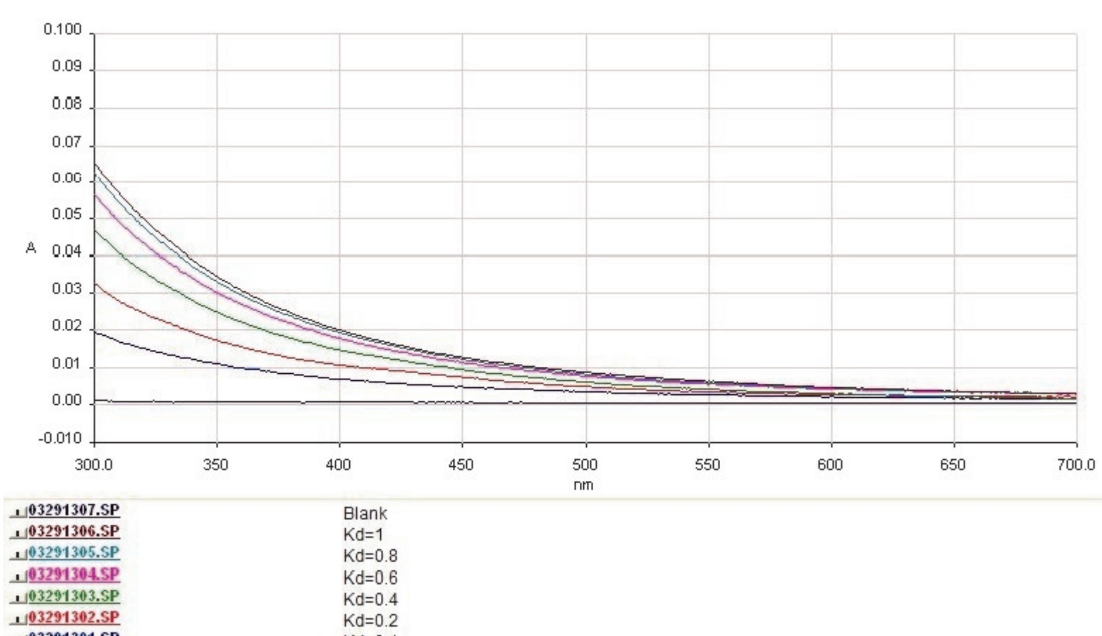
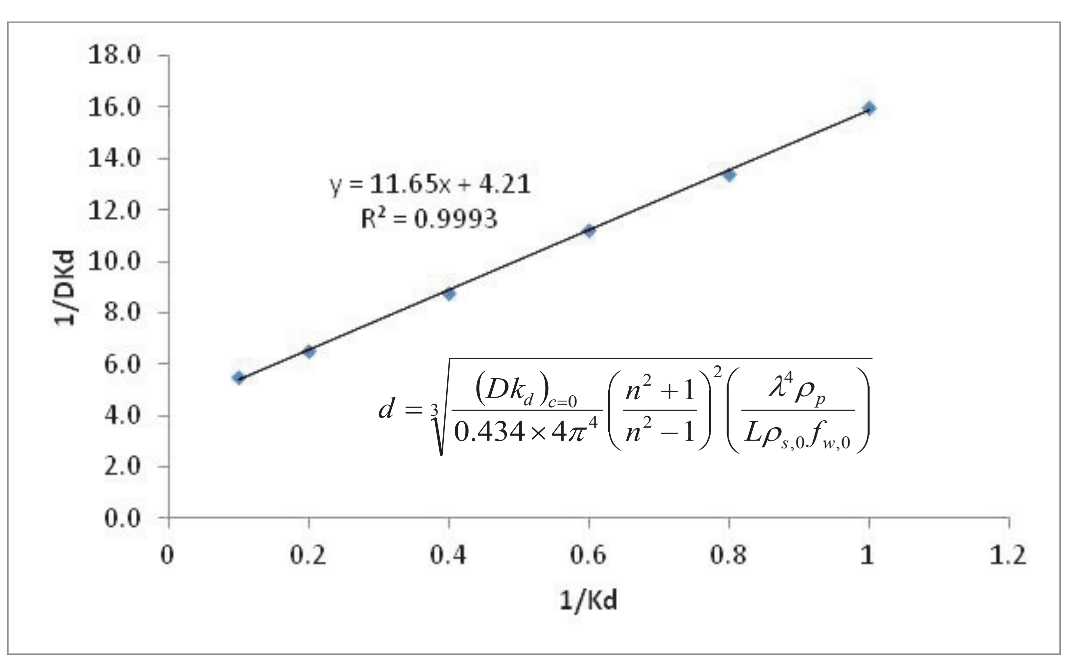


Figure 1. Example of UV/visible spectra of the diluted sample



$$d = \sqrt[3]{\frac{(Dk_d)_{c=0}}{0.434\times4\pi^4}\left(\frac{n^2+1}{n^2-1}\right)^2\left(\frac{\lambda^4\rho_p}{L\rho_{s,0}f_{w,0}}\right)}$$

Figure 2. Example Debye-like plot

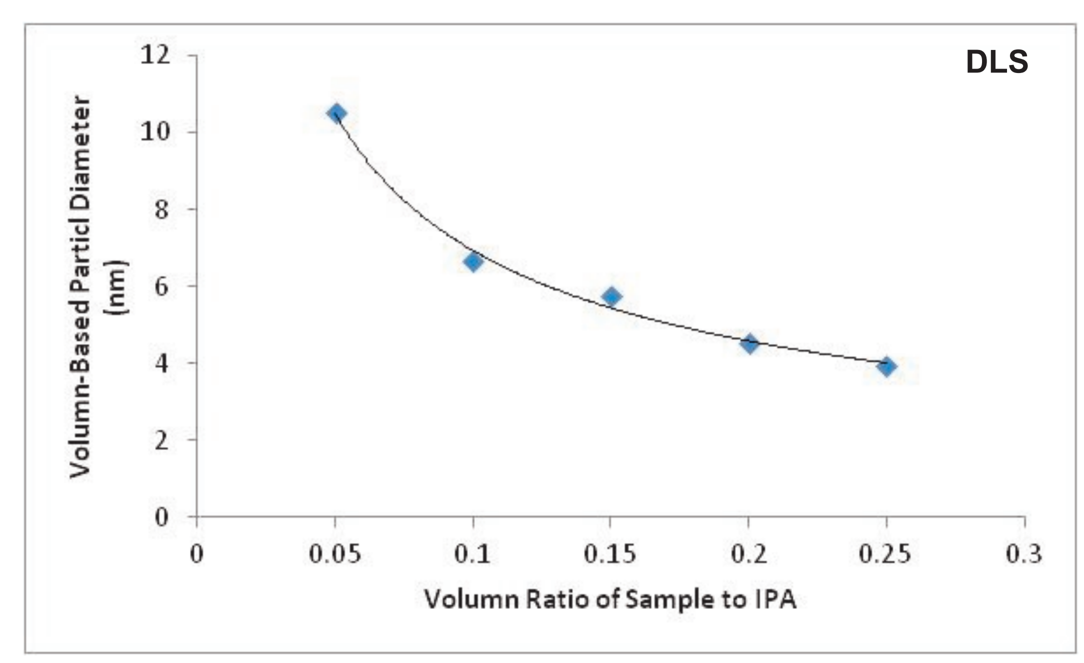


Figure 3. Impact of particle concentration on measured diameter

Comparison of Nanoparticle Diameters Determined by Different Techniques:

Table I. Reproducibility of Different Techniques

Technique	Measured Diameter	
	Average (nm)	%RSD
T-D	10.4	4.0
DLS	12.0	-
SSA	9.0	0.3
FE-SEM	8.4	18

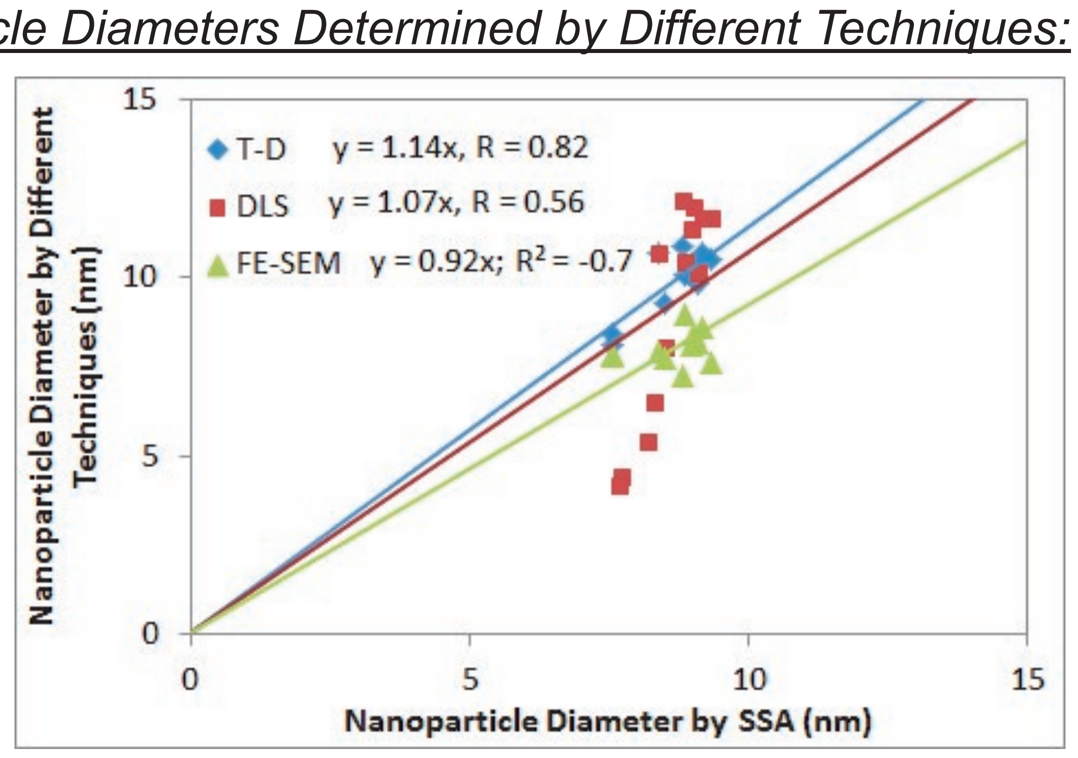


Figure 4. Correlation of particle diameters by different techniques

Advantages and Disadvantages:

- Both turbidity-Debye method (T-D) and dynamic light scattering (DLS) are the measurements of the light scattered by nanoparticles, and thus, are more sensitive to larger agglomerates, if present. As shown in Figure 3, the particle concentration has great impact on the particle diameter measurement. The diameter determination at zero concentration is achievable by the T-D method with excellent correlation coefficient in the Debye-like plot (refer to Figure 2).
- The specific surface area (SSA) method has excellent reproducibility (refer to Table I). However, nanoparticle diameters can be underestimated if they are fused.
- The T-D method had good correlation with the SSA method (refer to Figure 4). The diameters by T-D were 14% greater than those by SSA in this study.
- The DLS method has poor correlation with the SSA method when the intercept is set to zero. The accuracy of the DLS measurement is in question.
- FE-SEM provides the capability of viewing nanoparticle morphology, but the accuracy and reproducibility in the measurements of such small particles is very low.

SUMMARY

An analytical method for the determination of nanoparticle sizes based on Debye theory using turbidity measurements has been developed. The method uses intercept at zero concentration to eliminate the affects of particle-particle interactions, and thus, improves the accuracy of the particle size measurement. In this study, we have also compared the turbidity-Debye method to dynamic light scattering, field emission scanning electron microscopy, and nitrogen sorption. Accurate and reproducible results have been achieved using the turbidity-Debye method.

REFERENCES

[1] McNaught, A. D. and Wilkinson, A. (1997), “Compendium of Chemical Terminology – The Gold Book” (2nd Edition), Royal Society of Chemistry, Cambridge, UK.
[2] Kerker, M. (1969), *“The Scattering of Light and Other Electromagnetic radiation,”* Academic Press, New York.
[3] http://www.sciner.com/Opticsland/FS.htm
[4] Hale, G.M. and Querry, M.R. (1973), *APPLIED OPTICS*, **12**, 555.
[5] Heller, W. (1965), *J. Chem. Phys.*, **42**, 1609.

TO DOWNLOAD A COPY OF THIS POSTER, VISIT WWW.WATERS.COM/POSTERS