Comparing Nanorulers for Nanoparticles

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ABSTRACT

Different techniques can be used to determine the size of nanoparticles. There are two scattering techniques that are popular. They are dynamic light scattering (DLS) and laser diffraction (LD). While the latter is more traditionally associated with larger particles with sizes over one micron, laser diffraction has been extended down to particle sizes in the tens of nanometers. DLS, is used for particles with sizes from less than one nanometer to several microns. Since the useful size ranges of these techniques overlap significantly both can be used for nanoparticles. Results obtained by each technique are often different and understanding the reasons and the magnitude of the difference is important when interpreting data or selecting a technique. A series of nanoemulsion samples were studied with both techniques and the results are compared. Size results typically differed by about 10~20% but in one case the difference was much larger. This difference arises due to te different physical basis of each measurment.

Keywords: Particle Size, Laser Diffraction, Dynamic Light Scattering, Nanoemulsion

1 INTRODUCTION

Nanoparticle development and manufacturing require appropriate particle characterization techniques to determine if design and quality goals are being met. Scattering techniques, due to their relatively low cost and high speed, are the method of choice for analyzing average size and size distribution. There are two light scattering techniques that can be applied to the nanoscale: laser diffraction (LD) and dynamic light scattering (DLS). Even though both techniques are based on scattering phenomena, the measurement physics and therefore the measurement results differ. This effort directly compares the two methods.

Laser diffraction is the measurement of the intensity of light scattered from particles as a function of angle. A schematic of a typical measurement setup is shown in Figure 1 below. As the particle size changes, the intensity of light scattered as a function of angle varies in a predictable manner. In modern instruments, this situation is modeled by the Mie scattering equations which are an exact solution of Maxwell's equations for a uniform sphere. The scattering pattern from a collection of spheres is treated as the sum of scattering from individual spheres. Scattering data is then interpreted by fitting the measured scattering to an appropriately weighted sum of the scattering from model spheres [1,2]. In this way, the size of a sphere that scatters the same as the particle is reported as particle size.

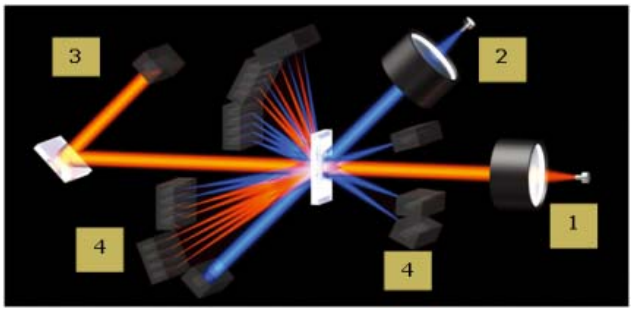

Figure 1: Schematic of Laser Diffraction Instrument

Dynamic light scattering is the measurement of variation in the scattering intensity at a single angle as a function of time on a short (microsecond) time scale. A schematic of a typical measurement setup is shown in Figure 2 below.

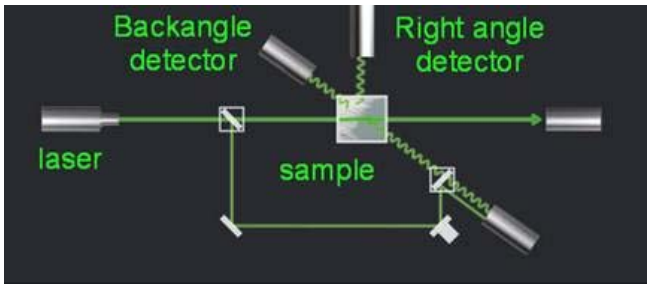

Figure 2: Schematic of dynamic light scattering measurement.

In contrast to laser diffraction, scattering data is collected at a single angle as a function of time. This is a less direct measurement inasmuch as the time-dependent scattering carries information about particle motion. This particle motion arises from random (Brownian) diffusion.

Typically, DLS data is interpreted using the method of cumulants to extract the so-called z-average particle size [3,4]. Since the diffusive motion is random in time, so is the scattered light intensity. The autocorrelation function is calculated in real time from the raw scattered light signal.

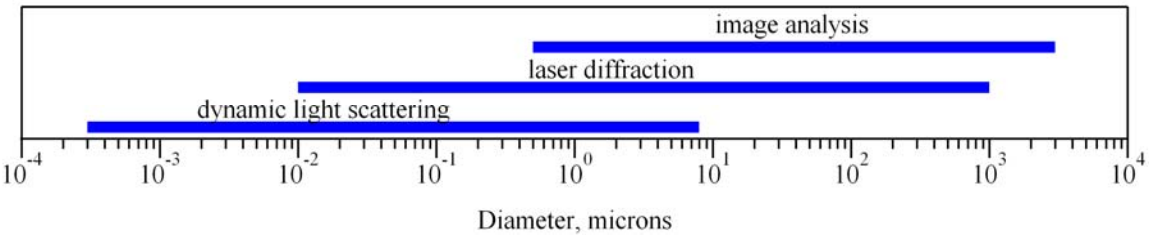

Figure 3: Applicable size range of dynamic light scattering and laser diffraction.

This data is then fit to a form corresponding to an exponential decay and this fit provides information about the average diffusion coefficient. Diffusion coefficients are converted to particle size using the Stokes-Einstein relation. In this way the size of a sphere that diffuses the same way as the particle is reported as particle size.

Both of these techniques can be used for nanoparticles. The applicable size ranges and their overlap are shown in Figure 3. However, since the techniques measure different physical phenomena, the measurement results differ. The work here is to directly compare results from the two techniques by moving a sample from one instrument to the other and therefore minimizing the usual confounding factors of preparation (batches) and time between measurements. The difference in obtained size is negligible for standard samples which are usually spherical and have extremely narrow size distributions. However, the magnitude of the difference for more common industrial samples is not usually reported.

2 METHODS

Initial measurements on narrowly distributed latex samples showed no significant difference in size results. Here, measurements were made on a nanoemulsion. This edible emulsion from a manufacturing result was concentrated and therefore had to be diluted to ensure that multiple scattering effects did not perturb the measurement. The manufacturing process for each emulsion was somewhat different and therefore similar behavior is not expected. After appropriate dilution of the concentrated emulsion, the sample was measured by laser diffraction with a HORIBA LA-950. Data was analyzed with the Twomey method [2] and the volume median size, D50, was obtained. A portion of the sample was then immediately transferred directly to a cuvette for dynamic light scattering. Dynamic light scattering measurements were performed with a HORIBA SZ-100. The DLS size results are reported after a cumulants calculation for Z-average. Laplace inversion was used to obtain the volume weighted value for D50. Results are reported as the average of 3 repeats.

3 RESULTS AND DISCUSSION

A comparison of obtained size results is shown in Figure 1 below. In all cases, the size determined by DLS increased along with the size determined by laser diffraction. That is, the results from both techniques will show the same trend. However, there are significant differences between the obtained sizes. This is likely due to the different way each technique responds to the width of the size distribution.

	D50 (vol. basis), nm LD	D50 (vol. basis), nm DLS	% diff in D50 (DLS/LD-1)	Z-avg. Diameter, nm DLS	% diff in size (DLS Z-avg./LD-1)
E-1	129.8	146.6	12.9	118.3	-8.9
E-2	149.8	170.5	13.8	138.7	-7.4
E-3	110.0	100.2	-8.9	112.7	2.5
E-4	49.4	45.5	-7.9	32.4	-34.4

Table 1: Size results from industrial nanoemulsions by two different techniques, laser diffraction and dynamic light scattering. D_{50} results along with the more reliable Z-average diameter are shown for the dynamic light scattering results.

In order to quantitatively show the differences, the data is given in Table 1 below along with the percent difference as one goes from LD to DLS results. For the first three samples, the difference is about 10~15%. For the fourth sample, E-4, the difference is larger, nearly 35%. It may be that sample E-4 has a particularly wide size distribution. As the distribution becomes wider, the effect of stronger scattering on the obtained size will tend to increase the Z-average size. The obtained results suggest that if there is no other available information, one can usually expect a 10~20% difference between the sizing techniques but not be surprised by a larger difference.

For a group of samples with similar properties (distribution shape, particle shape) a study similar to this can be used to generate a correlation between the techniques to allow regular comparison between the techniques. However, for such a correlation to be useful it should be supported by some understanding of the system under study.

Which answer is correct? In fact, all of the answers in Table 1 are correct to within experimental error. The differences arise due to the fact that different phenomena are being measured. Recall that the LD results correspond to a sphere that scatters the same way as the particle under study. In contrast, the DLS results correspond to a sphere that diffuses the same way as the particle under study. When particles have surface features that scatter weakly compared to the material in the bulk of the particle but still cause enhanced viscous drag, this difference between LD and DLS becomes quite noticeable.

4 CONCLUSIONS

In conclusion, both laser diffraction and dynamic light scattering can be used to characterize nanoparticles. The results differed by about 10~20% and sometimes much more between the techniques. This suggests that the results can be used for semiquantitative comparison. Detailed comparison will require that the particle system be systematically studied. Thus it is preferable to choose one technique when comparing results as a function of, for example, nanoparticle preparation conditions. Since the results from each technique differ, these differences need to be considered when comparing results from these techniques or choosing a technique for nanoparticle analysis.

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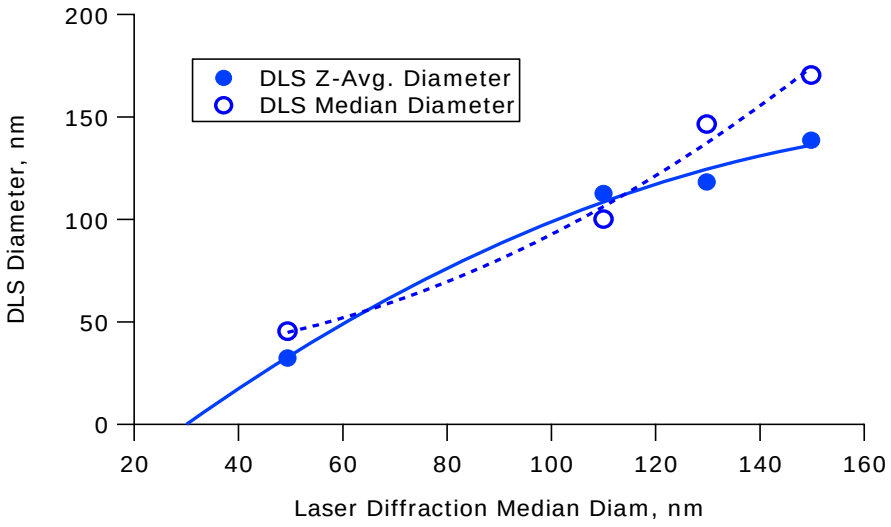

Figure 4: Comparison of size determined by dynamic light scattering as a function of median size determined by laser diffraction for a series of nanoemulsions. The lines are to guide the eye.