Multiangle DLS Measurements

Nicomp® DLS system

Most dynamic light scattering (DLS) systems have been designed to work at a fixed angle, either 90° or backscatter. No single measurement angle is ideal for every possible sample. For very small particles the scattering is equal at all angles, so any angle is acceptable. But for particles that are greater around 20 nm the scattering angle can affect results. This technical note explains how scattering angle influences results generated.

THEORY

For uniform diffusing particles the correlation function can be written as:

$$C(\Delta t) = \langle I_s(t) \times I_s(t-\Delta t) \rangle$$
$$= A \exp(-2DK^2 \Delta t) + B \quad (1)$$

Where C(Δt) is the autocorrelation function.
$I_s(t)$ is the instantaneous scattering intensity at time t.
$I_s(t-\Delta t)$ is the intensity at the previous time, t-Δt.
A is a normalization factor.
B is an instrumental factor.
D is the diffusion coefficient of the particles.

$$K = (4\pi n/\lambda) \sin(\theta/2) \quad (2)$$

The scattering wave vector.
Where n is the refractive index of the fluid surrounding the particles.
λ is the wavelength of the laser light.

The particle size is then calculated using the Stokes-Einstein equation:

$$D = kT/6\pi\eta R \quad (3)$$

Where k is the Boltzmann's constant.
T is the temperature in °K.
η is the viscosity of the liquid.
R is the radius of the particles.

In the normal case of a mixture of particles of different size, the autocorrelation function C(Δt) is no longer a single time-decaying exponential function, as shown in equation (1). Instead, it is a non-linear combination of decaying exponential functions of different decay times, each inversely proportional to the diffusivity, D_i, for particles of a given radius, R_i. Each of the decaying exponentials will potentially carry a different weighting, indicated here by F_i, where F_i represents the relative scattering intensity of particles of that size. The resulting weighted sum of decaying exponential functions will finally be squared (and added to a long-time baseline, B, proportional to the square of the average scattering intensity) to produce the autocorrelation function for the mixture of particles of different concentrations and sizes.

$$C(\Delta t) = A\{f_1 \exp(-D_1K^2\Delta t) + f_2 \exp(-D_2K^2\Delta t) + f_3 \exp(-D_3K^2\Delta t) + \ldots\}^2 + B \quad (4)$$

In the case of very small particles, where the characteristic particle dimension is much smaller than the laser wavelength l (i.e., d <λ/20, or d <30 nm), the particles behave nearly like "point" scatterers, in which all of the polarizable electrons in a given particle are exposed to essentially the same incident light wave (i.e., oscillating electric field) – i.e., where the phase is the same at each point. Hence, these electrons oscillate in unison, so that the individual radiated light waves are also in phase with each other. Therefore, the amplitude of the resulting scattered electric field, E_s , will be proportional to the number of oscillating electrons, which in turn is proportional to the volume, V, of the particle (or, equivalently, its molecular weight).

The quantity that is ultimately detected, I_s, is proportional to the square of E_s, and therefore it is proportional to the square of the particle volume.

$$I_s \propto N \times V^2 \quad (5)$$

(∝ = proportionality constant.)

In the case of spherical particles, of diameter d, this becomes:

$$I_s \propto N \times d^6 \quad (6)$$

which is the well-known Rayleigh 6^{th}-power law of intensity vs. particle size.

Importantly, in the case of such very small particles, there is no angular dependence of the scattering intensity, I_s.

Note: this assumes that the electric field of the incident light beam is linearly polarized and normal to the plane in which the scattering detector is located.

The scattering is "isotropic".

In the case of larger particles, no longer much smaller than the wavelength, λ, of the incident laser beam, the simple relationship between the scattered intensity and the particle size shown in equation (6) must be modified.

$I \propto N \times d^6 \times G^2$.....(7)

G^2 is often referred to as the "intensity form factor". It accounts for the fact that the individual scattered light waves originating from each of the oscillating electrons in a given particle are no longer in phase, because those electrons are no longer exposed to an incident light wave of the same phase, owing to the spatial extent of the particle relative to λ. The individual waves "interfere" with each other, giving rise to intra-particle Mie scattering. The net effect is that the intensity of light scattered by a particle of a given size is diminished relative to what it would have been if all of the scattering electrons had been in a sphere of smaller size, as described by equation (5) - i.e., where $G^2 = 1$ in equation (7). Instead, $G^2 < 1$ for particles no longer in the rayleigh range.

Moreover, G depends not only on particle size, but also on the refractive index of the particle and the scattering angle, and it varies non-linearly (i.e., with "reversals" in dependence) with each of these variables.

In the most general case of DLS analysis, involving a significant ("wide") distribution of particle sizes and concentrations, the measured autocorrelation function, C(Δt), consists of the non-linear, weighted combination of decaying exponential functions shown in equation (4). The unknown quantities that must be determined are the set of weighting coefficients, F_i, which depend not only on the concentration of particles of each diameter (the desired "answer"), but also on the scattering angle, often in a complex way, because of the complexity of G^2 as a function of these unknown quantities. Successful "inversion" of the autocorrelation function, C(Δt), consists of obtaining the most reliable (accurate) estimate of the set of coefficients F_i, which define the intensity-weighted particle size distribution (PSD). This is the "answer" which emerges from the Nicomp® system analysis:

$F_i \propto N_i \times d_i^6 \times G_i^2$.....(8)

From this "answer", the volume-weighted PSD can be obtained by dividing the set of coefficients f_i by G_i^2, one by one for each size (channel), and also by one power of volume, or d_i^3 , resulting in the set of values, $N_i \times d_i^3$, i.e., the volume-weighted PSD.

EXPERIMENTAL

Two polystyrene latex standards (PSL) were used in a study to investigate the effect of scattering angle on the accuracy of the calculated particle size distributions using the Nicomp dynamic light scattering (DLS) system. Figure 1 shows the intensity weighted Gaussian result for the 90 nm (nominal) PSL used in this study and Figure 2 shows the intensity weighted Gaussian result for the 300 nm (nominal) PSL used in this study, both measured at 90°.

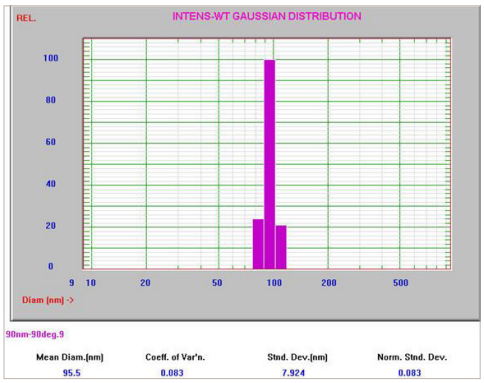

Figure 1. 90 nm PSL result measured at 90°

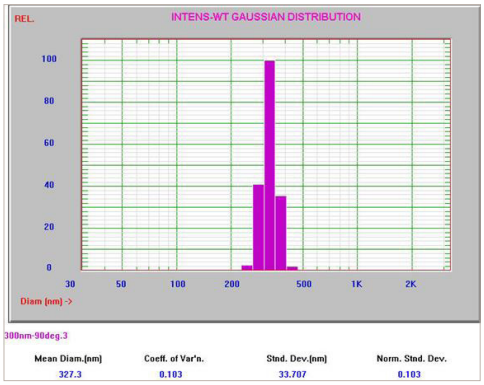

Figure 2. 300 nm PSL result measured at 90°

A bimodal mixture of 10% (wt) 90 nm + 1% (wt) 300 nm was prepared for all other measurements shown in this technical note. A perfect result should show approximately 90% of the distribution coming from the 90 nm peak and 9% coming from the 300 nm peak when viewed as the volume based distribution (not intensity). For samples with more than one peak, the Nicomp analysis model is the most accurate algorithm available, so this algorithm was used for all results. The bimodal sample was analyzed at varying scattering angles using the multi-angle goniometer option in a standard Nicomp DLS system.

Figure 3 shows the bimodal sample measured at 90°. The intensity form factor, G^2, is overlaid on the PSD plot, showing that the 300 nm particles lie close to the first minimum in G^2. The percentage ratio is less accurate than desired due to the proximity of the first G^2 minimum to the 300 nm peak.

Figure 4 shows the bimodal sample measured at 29°. This pushes the minimum in G^2 much further away from the 300 nm peak, which greatly improves the volume ratios in the results.

Figure 5 shows the bimodal sample measured in backscatter at angle 158°. At this angle the minimum in G^2 sits very close to the 300 nm peak. This creates the least accurate volume ratios of the two peaks and represents the worst approach to measuring this sample.

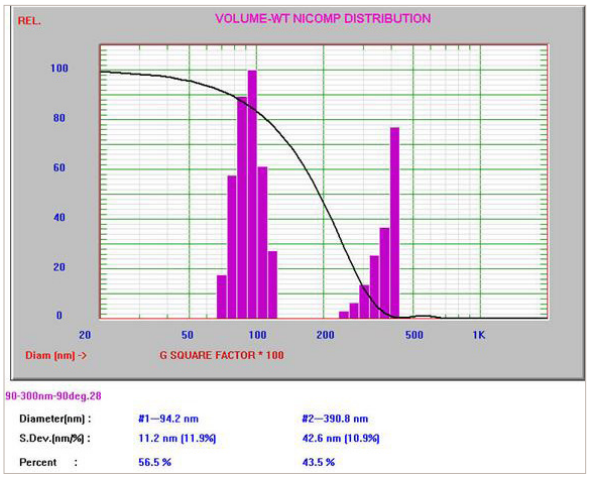

Figure 3. The bimodal sample measured at 90°

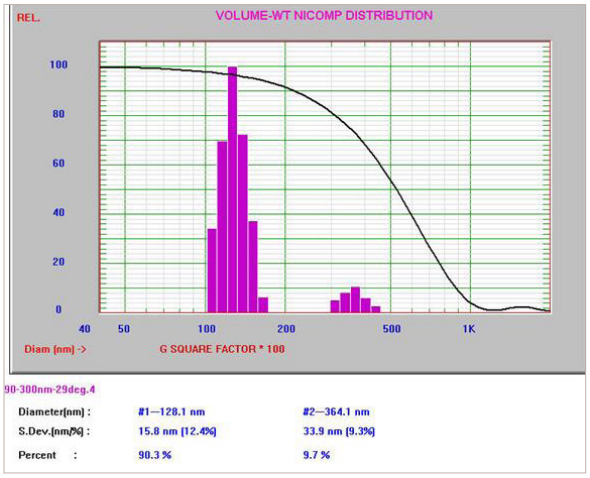

Figure 4. The bimodal sample measured at 29°

CONCLUSIONS

Results from DLS are sometimes dependent on the scattering angle at which the measurement is made. The variation in results changes as a function of size of the particles and the position of minima in the intensity form factor, G^2. For the bimodal mixture investigated in this study the forward angle (29°) provided the most accurate results, followed by the 90° result, with the backscatter result (158°) generating the least accurate depiction of the sample. It appears inappropriate to think that backscatter is always the best approach for any unknown sample.

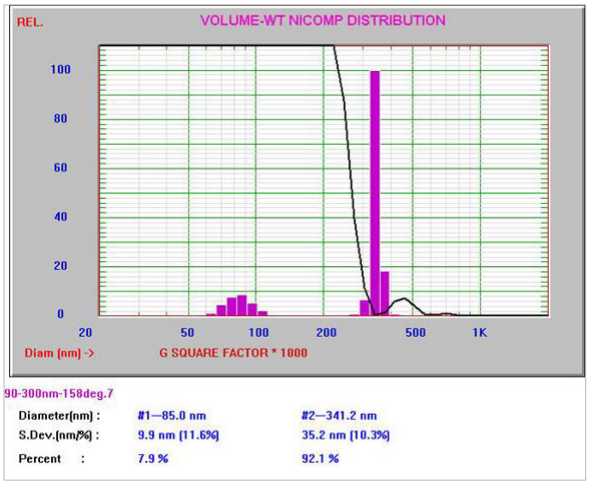

Figure 5. The bimodal sample measured at 158°

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