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Nanoparticle Sizing: Dynamic Light Scattering Analysis in the Frequency Spectrum Mode

Instruments: Nanotrac series

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SL-AN-14 Rev. F

Abstract

Dynamic Light Scattering analysis is the basis of a common particle sizing measurement covering the range of nanometers to microns. At the nanometer end of the range, measurement becomes progressively more difficult as the particle optical scattering coefficients drop sharply, reducing the scattered light intensity. Two modes of optical measurement are commonly used, self-beating detection and controlled reference or heterodyne detection. With those two detection modes dynamic light scattering signals can be analyzed as either the autocorrelation function or the frequency shift power spectrum. This paper will discuss recent advances in signal processing in the controlled reference mode using the analysis of the frequency power spectrum. Issues of detectability, signal to noise, and size accuracy will be discussed with measurement examples in the size range down to nanometers.

Introduction

Particles in suspension are in constant random motion (Brownian motion) as the result of the interaction with the molecules of the suspending fluid. In the Stokes-Einstein (Furth 1956) theory of Brownian motion, particle motion is determined by the suspending fluid viscosity, the temperature and the size of the particle. From a measurement of the particle motion in a fluid of known temperature and viscosity, the particle size can be determined. The Dynamic Light Scattering (DLS) technique (Pecora 1967 and Dubin 1967) measures the motion optically. The suspended particles are illuminated with a coherent light source. The light scattered from the suspended particles has frequency shifts imparted to it from the time dependent position or velocity of the suspended particles. Measured over time, random particle motion forms a distribution of optical frequency shifts.

DLS Optical Detection

The use of a coherent optical reference allows, through optical wave interference, the conversion from optical frequencies to the difference between optical frequencies, the shift frequencies. For DLS the shift frequencies are on the scale of 1 Hz to 100KHz, readily detected by modest frequency electronics. Two methods of referencing are commonly used and are illustrated in Figure 1.
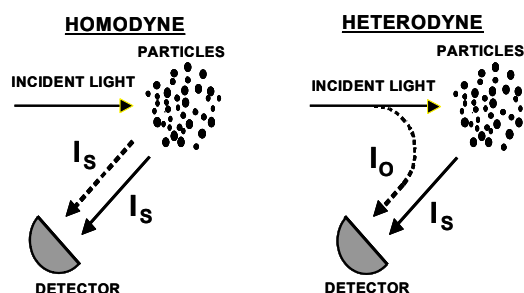
Fig. 1: DLS detection modes

Self-referencing, self-beating, or homodyne detection all refer to the left side of Figure 1. The mixing at the optical detector of all the collected scattered light provides the reference for difference frequency measurement. Controlled reference or heterodyne detection, shown on the right side of Figure 1, mixes the scattered light with a portion of the incident light. The un-shifted incident light provides the reference for the difference frequency measurement. The resulting detector output from either mode contains a distribution of frequencies representative of the particle size of the suspended particles.

The measured signal is generally processed by one of two modes, time-based autocorrelation or frequency-based power spectrum. One is the Fourier transform of the other. This paper deals with the frequency power spectrum mode and shows that through this mode a better-conditioned form of the particle size response matrix can be established. The forms of the power spectrum for heterodyne and homodyne detection are shown as equations (1) and (2).

Homodyne - Self -Beating

$$P(\omega) = \langle i_s \rangle^2 \frac{2\omega_o}{\omega^2 + (2\omega_o)^2} \quad (1)$$

Heterodyne – Reference-Beating (Microtrac)

$$P(\omega) = i_o \langle i_s \rangle \frac{2\omega_o}{\omega^2 + (\omega_o)^2} \quad (2)$$

Characteristic Frequency

$$\omega_o = \frac{1}{r} \frac{8\pi kT}{3\lambda^2 \eta} \sin^2(\theta/2) \quad (3)$$

The parameters determining the power spectrum, P(ω), include:
Λ= wavelength in suspending medium, **ω** = frequency,
ω$_o$ = frequency from particle at the half-height, **η** = viscosity, **θ**= scatter angle,
i$_s$ = scattered optical intensity, **i$_o$** = reference optical intensity, **r** = particle radius,
k = Boltzmann constant, **T**=temperature.

Of the two power spectrum modes, the controlled reference, heterodyne mode offers many advantages over self-referencing, homodyne mode. The major one is the measured signal level. Signal level in the self-referencing, homodyne mode is proportional to i_s^2, the average scatter intensity squared. In contrast the signal level in the controlled reference mode is proportional to i_s x i_o, the product of the scatter intensity times the reference intensity. The signal level for the controlled reference mode can be made to be orders of magnitude larger than the homodyne mode by providing a high level of reference intensity. The high signal level allows the use of laser diode optical source and silicon photodiode optical detector. The enhanced signal level facilitates the measurement down to the nanometer range where low particle optical scattering efficiencies reduce the available signal.

Controlled Reference

Controlled reference mode is implemented by means of an optical probe. The probe delivers laser light to a particle suspension, collects the light backscattered from the particle suspension and generates the controlled reference at the interface between the suspension and probe tip. The backscattered light collected by the probe is directed back through an optical splitter in the opposite direction from the delivered laser light. Light, reflected from the tip-suspension interface, is also directed back through the splitter. This component, un-shifted by the reflection from the stationary interface, combines with the back-scattered light and acts as the reference to the shifted scattered light. The two components mix and interfere at the photodetector producing a fluctuating electrical signal containing the distribution of shift frequencies. The detector signal is digitized and the frequency power spectrum of the signal is determined using fast Fourier transform digital signal processing.

Power Spectrum

The power spectrum has the Lorentzian function form shown in equations (1) and (2). The characteristic frequency, ω_o, (Eq. 3) is inversely proportional to the particle size and represents the half power point of the spectrum. Figure 2 plots the power spectrum for different particle sizes. The inverse relationship of the characteristic frequency with particle size is evident.
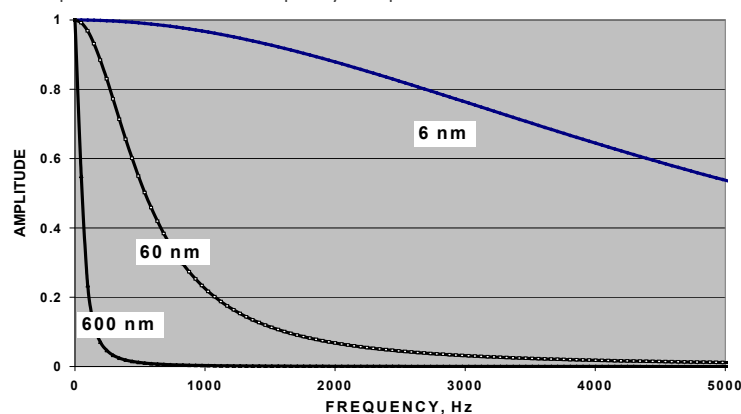

Fig. 2: *Linear Power Spectrum*

The measured response to a distribution of particle sizes is a weighted sum of individual particle size responses as shown in the matrix equation (4) below.

Measured response(vector) = Lorentzian (matrix) x volume Particle Size Distribution(vector)

$$r = L \bullet v \qquad (4)$$

Inversion of equation 4 to determine the volume particle size distribution, **v**, is difficult due to the ill conditioned Lorentzian form of the power spectrum. Transforming the frequency coordinates from a linear to a logarithmic basis (Equation 6 and Figure 3) can relieve this difficulty.

$$P(\omega)d\omega = i_o \langle i_s \rangle \frac{2\omega_o}{\omega^2 + \omega_o^2} d\omega \qquad (5)$$

LOGARITHMIC TRANSFORM

$$\text{Where, } x = \ln(\omega) \qquad (6)$$
$$x_o = \ln(\omega_o) \qquad (7)$$

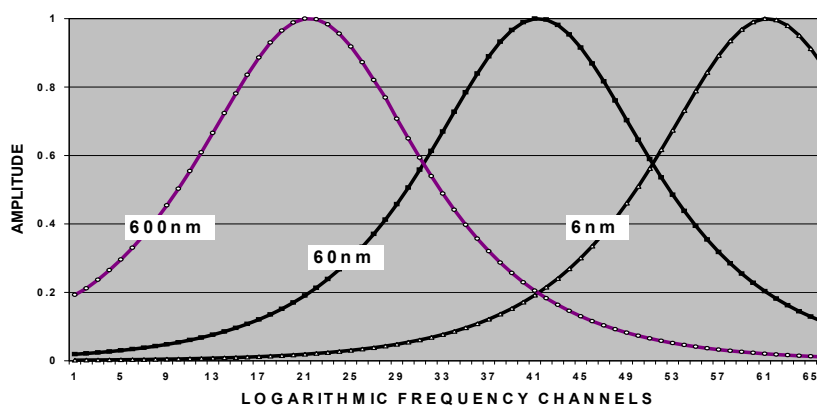$$P(x)dx = i_o \langle i_s \rangle \frac{1}{e^{(x-x_o)} + e^{-(x-x_o)}} dx \qquad (8)$$

Fig. 3: *Power Spectrum Logarithmic Coordinates*

In logarithmic coordinates the response matrix is shift invariant. The single particle responses are equivalent and only shift along the log frequency axis. Figure 3 shows the response functions for three particle sizes. The functions peak at the log of the characteristic frequency, ω_o. The matrix equation (4) becomes a convolution with R, the response function as in equation (8).

$$r_n = \sum R(x_m - x_n)v(x_n) \qquad (9)$$

The inversion of the logarithmic coordinate frequency power spectrum (equation 9) is greatly simplified over the inversion of (4) and can be accomplished with linear iteration techniques (Trainer July 92).

Nanosize

At particle sizes below 100 nanometers the optical scattering efficiency drops rapidly with particle size. In this size region the scattering is described by Rayleigh scattering where the scattering efficiency per unit volume of particles is proportional to the particle diameter cubed, D^3. The amplitude of the power spectrum is determined by the average scattered light intensity, i_s as shown in equations (2) and (5) for the controlled reference mode. This in turn is proportional to the volume concentration of the scattering particles times the scattering efficiency. Therefore, in the Rayleigh size region, the amplitude of the measured power spectrum will be proportional to both the concentration and to the diameter cubed. In the nanosize range (1-100nm) the detectability limit will be determined by the uncertainty in the amplitude of the measured power spectrum, a signal to noise determination.

The content of the power spectrum is determined mainly by the scattering from the particle suspension as described by equation 2. There is also a contribution from the background noise of the laser, detector and electronic processing system. The background noise contribution is measured as the power spectrum with only pure suspending medium present and is subtracted from the power spectrum with suspended particles. As the particle size is reduced, decreasing the amplitude of the power spectrum by D^3, the background contribution to the power spectrum becomes a larger fraction of the total power spectrum. At the smallest sizes measured the main source of uncertainty in the power spectrum is the stability of the background power spectrum.

A determination of the detection limits is established through a measurement of the background stability of the system and a comparison with the power spectrum amplitudes for particles of various sizes in the nanometer range. If noise is equated with stability of the background then a criterion of signal to noise can be established. A simple criterion is to require a 5:1 signal peak to noise ratio as the detection limit. The power spectrums for four particle materials and 8 sizes at known concentrations were made with the Microtrac® Inc. DLS Nanotrac® instrument. From these measurements the power spectrum amplitude peak per unit volume concentration were calculated for each sample. In order to compare particles of different materials the index of refraction dependent part of the scattering coefficient is utilized. The back-scattering coefficient is given by equations (10) and (11) (van de Hulst 1957) in terms of:

m = relative index, λ = wavelength, n_m = index of medium, V = particle volume

$$\text{Polarizability} = \alpha = \frac{3(m^2-1)}{(m^2+2)} \frac{V_{part}}{4} \quad (10)$$

$$\text{Scattering Coefficient} = \alpha^2 \left(\frac{2\pi}{\lambda/n_m}\right)^4 \quad (11)$$

Material	Refractive Index	Scattering coefficient. Relative to silica
SILICA	1.49	1
POLYSTYRENE	1.59	2
GOLD (Shenhar 2003)	N/A	13
LYSOZYME	1.55	1.5

The power spectrum peak amplitudes per unit volume concentration normalized to the relative scattering coefficients are compared in Figure 4. It is seen that the diameter cubed relationship is maintained consistent with Rayleigh scattering. Also plotted is the background uncertainty for the peak channel. For a signal to noise of 5 the power spectrum peak must be greater than 5 times the background uncertainty appropriate to that size. This criterion determines the minimum concentration required. As an example, polystyrene at 10 nm would have a peak of 6×10^{-2} and a background uncertainty of 1×10^{-6}. 10 nm polystyrene is detectable at a peak amplitude of 5×10^{-6}, equivalent to a concentration of 0.01vol%. Similarly, 3.5 nm Lysozyme is detectable at concentrations greater than 0.3 vol%. The graph shows agreement with expected relative size values.
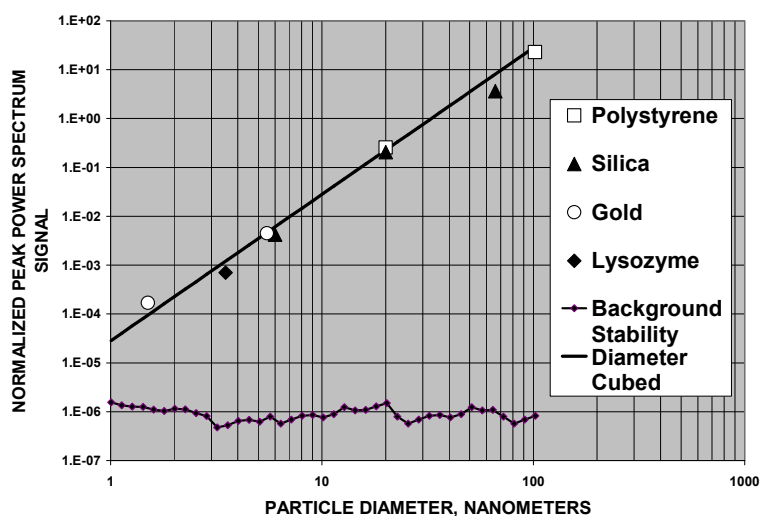

Fig. 4: *Normalized Power Spectrum Peak versus Particle Diameter*

Conclusion

The challenge of measuring the size distribution of nanoparticles can be met with controlled reference dynamic light scattering. Data collection in the controlled reference mode provides inherently higher signal level to overcome the low optical scattering intensity of nanoparticles. The logarithmic power spectrum of a particle suspension is corrected for background noise by simple background subtraction and the resulting power spectrum is deconvolved by linear iterative techniques. The limitations of particle size measurement are determined by the uncertainty in the system noise. Particle size measurement down to 1nm is performed for a wide range of materials with controlled reference dynamic light scattering.

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