

Zeta Potential Analysis of Colloidal Systems by ELS, with Combined DLS Sizing Capability

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Introduction: The Significance of the Zeta Potential

There has been increasing interest recently in techniques which provide a quantitative measure of the charge on colloidal particles in liquid suspension. Electrophoretic light scattering (ELS), which can measure the "zeta potential" of these particles, is one such technique. It can be implemented immediately following production of colloidal particles, as a means of estimating their stability against subsequent aggregation. Zeta potential analysis by ELS requires no special expertise; it can be performed as effectively in demanding process environments as in traditional laboratory settings. Fortunately, zeta potential analysis by ELS dovetails nicely in a technological sense with that of particle size analysis by dynamic light scattering (DLS).

Given the ability of an ELS instrument to determine the zeta potential of colloidal particles in a simple and fast way, one is no longer limited to predicting the future stability of a colloidal system simply from its particle size distribution (PSD). The latter provides, at best, only a single "snapshot" of the present state of aggregation of the sys-

In other cases, the colloidal particles may already carry specific groups which are covalently bound to their surfaces and are ionizable. They carry a net positive or negative charge, or are neutral, depending on the pH of the surrounding aqueous solvent. Examples include many well-known oxides, such as silica, alumina, titanium dioxide, etc. For these materials the extent and sign of the surface charge depends on the pH of the solution, as well as the pKs of the ionizable groups bound to the particle surface. Hence, the pH of the suspension will strongly influence the net charge of the colloidal particles and therefore their stability against aggregation.

The well-known DLVO theory of colloidal stability provides a reliable analytical framework for estimating the extent of repulsion or attraction between two particles in suspension as a function of their separation. The repulsive contribution to the interparticle "pair potential" depends on the particle charge and size and the concentration of mobile ions. The attractive portion depends on the strength of the Van der Waals attractive forces, as characterized by the Hamaker coefficient.

shrinkage of the electrical double layers, so that they no longer overlap, then the value of ξ will be important in establishing whether the repulsive electrostatic potential barrier between neighbouring particles is high enough to preclude their agglomeration due to short-range attractive Van der Waals forces.

Review of ELS: Mobility, Doppler Shift and Zeta Potential

As its name implies, the ELS technique is based on the scattering of light from particles which move in liquid under the influence of an applied electric field. The charged particles quickly reach a constant "terminal" velocity v , proportional to the magnitude of the field, E . The proportionality constant, μ , defines the electrophoretic mobility,

$$v = \mu E \quad (1)$$

The units of electric field are V/cm, and therefore the units of μ are cm/s/V/cm. Because typical velocities are so small, it is useful to express μ in terms of the "mobility unit", M.U., $\mu\text{m/s/V/cm}$, which equals 10^{-4} cm/s/V/cm.

its particle size distribution (PSD). The latter provides, at best, only a single "snapshot" of the present state of aggregation of the system. Such an isolated measurement of the PSD is unable to reliably predict the future rate of aggregation of the particles. For this purpose, a measurement of the zeta potential is invaluable.

Electrostatic Repulsions and Colloidal Stability

The physical mechanism which is used to stabilize most aqueous colloidal systems is electrostatic repulsion. The colloidal particles of interest are charged, resulting in their mutual repulsion at extended distances. Ideally, the repulsive forces are sufficiently strong to prevent the particles from diffusing close to each other, where short-range Van der Waals attractive forces dominate and lead to aggregation.

There are several means by which a net electrical charge can be attached to the surface of a colloidal particle. For particles which are normally uncharged, such as oil droplets in a homogenized aqueous suspension, charged molecules can usually be adsorbed onto the particle surface. This is most commonly accomplished using an ionic surfactant, consisting of a polar head group attached to a hydrocarbon "tail". The latter, being hydrophobic, associates with the interior of the uncharged particle, while the polar head group resides at the surface, in contact with the surrounding water, and dissociates, thereby imparting a net charge to the oil droplet, polystyrene bead, etc.

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depends on the strength of the Van der Waals attractive forces, as characterized by the Hamaker coefficient.

The charged mobile ions in solution distribute themselves between the large particles according to the laws of electrostatics and thermodynamics. The ions which carry a charge opposite to that of the colloidal particle surface are attracted preferentially to it. Consequently, the electrical potential in the solution, Ψ , produced by the charged particle decreases with increasing distance from its surface, due to the "screening" of its electric field by the mobile ions. The maximum value of the potential, Ψ_0 , occurs at the surface of the particle. The higher the overall salt concentration, the steeper the "decay" in Ψ with distance from the surface. The charged particle surface and the diffuse layer of mostly oppositely-charged ions surrounding it comprise the electrical "double layer". Its thickness is defined as the distance from the particle surface at which the electrical potential Ψ falls to $1/e$ of Ψ_0 and is commonly referred to as the Debye-Hückel screening length, κ^{-1} . For a monovalent salt concentration of 1M, length κ^{-1} is only 3nm, while for 0.01M this length increases to 30nm.

The zeta potential, ξ , also called the electrokinetic potential, is defined as the value of the electrical potential at the "shear plane" of the particle. For typical colloids this point is close to the actual surface of the particle. For relatively low concentrations of added salt, the zeta potential as measured by ELS should provide a good representation of Ψ_0 at the surface of the particles.

In summary, if the electrical double layers of a colloidal system overlap, ie, if κ^{-1} exceeds the average interparticle separation, then the system will usually be stable, given a moderate amount of charge on the particles. However, if the concentration of salt ions is high enough to lead to significant

useful to express μ in terms of the mobility unit", M.U., $\mu\text{m/s/V/cm}$, which equals 10^4 cm/s/V/cm.

The moving particles scatter the incident light at a frequency ν_s , which is Doppler shifted with respect to the incident frequency ν_0 . The extent (and sign) of the Doppler shift in frequency, $\Delta\nu$, depends on the velocity of the particle, the wavelength of the incident light beam (in the liquid medium) and the angle of scattering. The relationship between these quantities is given simply by

$$2\pi \Delta\nu = \vec{k} \cdot \vec{v} \quad (2)$$

where \vec{k} is the scattering wave vector, familiar from the theory of DLS. The magnitude of K is given by

$$K = (4\pi n/\lambda_0) \sin \theta/2 \quad (3)$$

where λ_0 is the wavelength of the incident light beam (in vacuum), n the refractive index of the solvent, and θ the angle at which the scattered light is detected. The relationship between the electric field and particle velocity vectors, the incident wavevector \vec{k}_0 and the scattered wavevector \vec{k}_s is summarized in Figure 1.

The Doppler shift, $\Delta\nu$, in the frequency of the scattered light is easily computed from Figure 1 and Equations 2 and 3,

$$\begin{aligned} \Delta\nu &= (K v/2\pi) \cos \theta/2 \\ &= (2nv/\lambda_0) \sin \theta/2 \cos \theta/2 \end{aligned} \quad (4a)$$

Use of a common trigonometric identity reduces this to,

$$\Delta\nu = (nv/\lambda_0) \sin \theta \quad (4b)$$

Finally, substitution of Equation 1 into the above equation allows the electrophoretic mobility μ to be computed from the measured Doppler shift $\Delta\nu$, for a given applied electric field strength E ,

$$\mu = (\lambda_0/n \sin \theta) (1/E) \Delta\nu \quad (5)$$

It is useful to attach some typical numbers to the above formula. For the instrument recently developed by the authors, the NICOMP™ 370 ZLS Particle Size/Zeta Poten-

tial Analyzer, the relevant parameters for Equation 5 are: $\lambda_0 = 0.6328\mu\text{m}$ (HeNe laser), $n = 1.33$ (water) and $\theta = 14.8$ degrees. In this case, Equation 5 reduces to μ (M.U.) = 1.867 (1/E) Δv .

Finally, the value of the mean zeta potential ξ is obtained from the electrophoretic mobility μ . If the concentration of mobile ions in solution is sufficiently high that the thickness of the electrical double layer, κ^{-1} , is small compared to the mean diameter of the particles, a (ie, $\kappa a \gg 1$), then the Smoluchowski approximation applies. In this case, ξ is related in a simple, linear way to μ ,

$$\xi = \eta \mu / \epsilon \quad (6)$$

where η is the viscosity and ϵ the dielectric constant of the solvent.

In the opposite limit of ion screening, known as the Hückel limit, where $\kappa a \ll 1$, the electrical double layers of neighbouring particles overlap significantly. In this case the right-hand side of Equation 6 is multiplied by 3/2. For intermediate values of κa , an analytical approximation is needed in order to estimate the value of ξ from μ .

As expected (Equation 4b), the magnitude of the Doppler shift is proportional to the

component of the velocity vector lying along the direction of detected scattered light, k_s , proportional to $\sin \theta$. Hence, it would appear that the measured Doppler shift Δv can be increased simply by increasing the angle θ of detection of the scattered light. However, in practice, this is the opposite of what is required to optimize an ELS measurement, for reasons which are both practical and theoretical.

The practical requirement for small angles is related to the geometrical constraints imposed by the electrodes immersed in the sample solution. The parallel electrodes must be relatively closely spaced (typically 2-4mm), in order to achieve a uniform electric field where the scattered light is collected and also to reduce the applied voltage needed to achieve significant values of field strength. (The lower voltage reduces the amount of Joule heating and resulting convection which can occur at moderately high salt concentrations.) Hence, there is only a relatively small range of angles at which the scattered light can be collected (ie, not blocked by the electrodes).

However, there is a much more important, theoretical consideration which dictates the use of a small scattering angle. In addition to being subjected to a constant drift velocity due to imposition of an electric field, the particles always experience random-walk, Brownian motion, or diffusion, due to random collisions of the surrounding solvent molecules. Indeed, this is the ever-present phenomenon which gives rise to fluctuations in the scattered light intensity which are analyzed by the DLS technique. The autocorrelation function of these fluctuations yield the diffusion coefficient of the particles, from which the particle diameter can be derived.

The random motions of the particles due to diffusion also give rise to fluctuating Dop-

26.9Hz at $\theta = 90^\circ$ but only 0.89Hz at $\theta = 14.8^\circ$. For $a = 100\text{nm}$, the respective values are 269Hz and 8.9Hz, while for $a = 10\text{nm}$, the corresponding values are 2,690Hz and 89.3Hz.

Instrument Design: Capability for both ELS and DLS

A simplified block diagram of our combined particle size and zeta potential analyzer, the NICOMP 370 ZLS, is shown in Figure 2. The instrument employs a novel design, which permits both multi-angle particle size analysis by DLS and low-angle zeta potential analysis by ELS, using a minimum number of optical components. A single, precision optical fibre/collimator, together with a high-resolution stepper motor ($0.9^\circ/\text{step}$), is used to implement both the ELS and DLS measurements. This design offers scientific flexibility, without sacrificing ease of use and reliability.

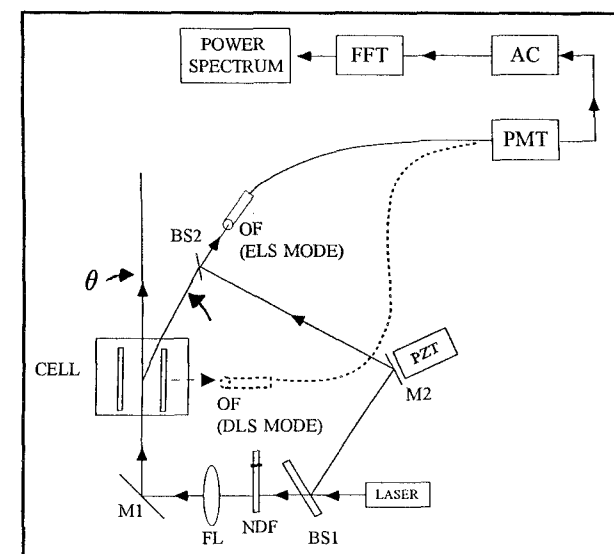
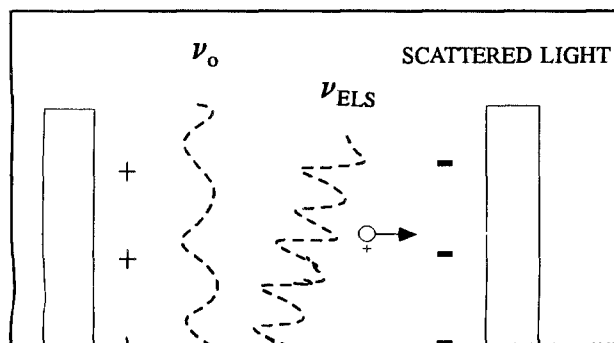


Figure 2. Simplified schematic diagram of the NICOMP 370 ZLS Zeta Potential and Particle Size Analyzer.



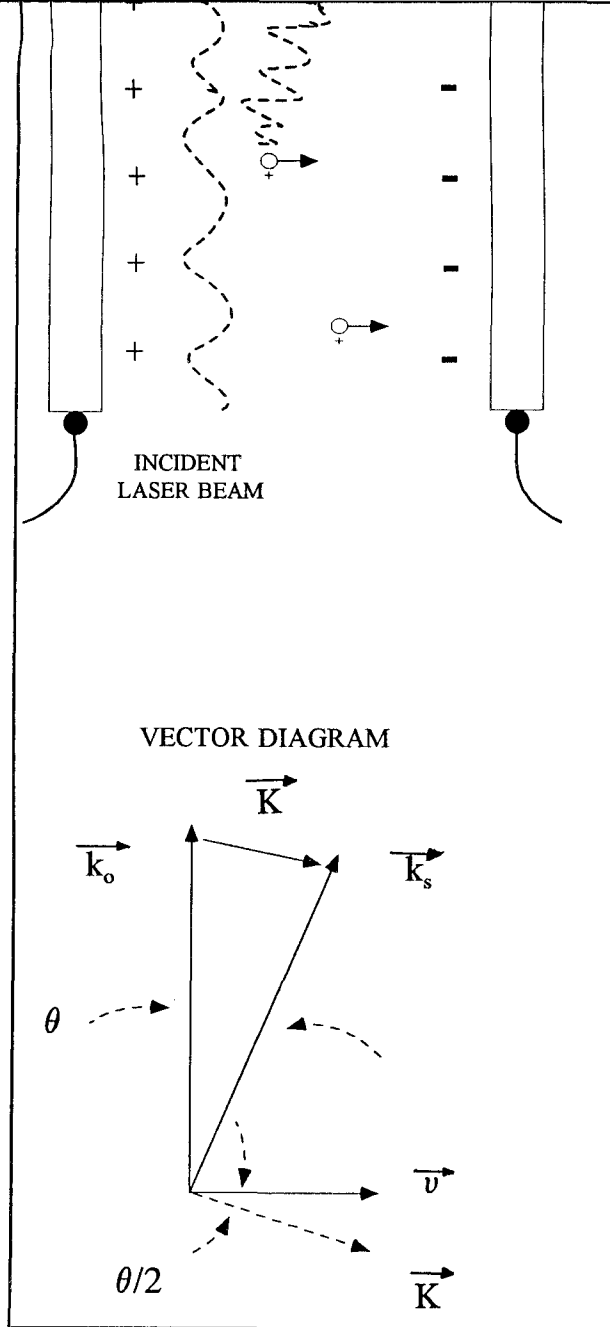


Figure 1. Relationship between the incident laser beam and scattered light wave for ELS; vector diagram relating these to the scattering wavevector K and particle velocity v .

cle diameter can be derived.

The random motions of the particles due to diffusion also give rise to fluctuating Doppler shifts in the frequency of the light waves scattered by each particle. These random shifts are *superimposed* on the constant shift $\Delta\nu$ associated with the drift velocity v caused by the applied electric field.

In the "heterodyne" light scattering technique which we use for the ELS measurement (described below), the half width Γ of frequency broadening of the detected scattered light due to Doppler shifting by the diffusing particles is given by

$$\Gamma = D K^2 \quad (7)$$

where K is the same scattering wave vector used above (Equation 3) and D is the diffusion coefficient of the particles, given by the Stokes-Einstein relation,

$$D = kT/3\pi\eta a \quad (8)$$

where k is Boltzmann's constant and a is the particle diameter. The Doppler shift due to electrophoretic mobility decreases with decreasing scattering angle, approximately as $\sin \theta/2$ (Equation 4a), while the frequency broadening due to diffusion also decreases with angle, but as the *square* of $\sin \theta/2$. Hence, the ability of the ELS technique to measure small frequency shifts associated with low electrophoretic mobilities dictates operation at a relatively small angle.

It is instructive to compare the extent of frequency broadening, Γ , of the scattered light due to random diffusion with the typical range of Doppler shifts $\Delta\nu$ encountered from electrophoretic mobility, typically 1-100Hz. We compute the value of Γ for two different scattering angles: 90° , used typically for DLS particle size analysis; and 14.8° , which we use for our zeta potential measurements. We assume HeNe laser light, water and a temperature of 23°C .

The value of Γ is inversely proportional to the particle diameter. For $a = 1,000\text{nm}$, $\Gamma =$

Figure 2. Simplified schematic diagram of the NICOMP 370 ZLS Zeta Potential and Particle Size Analyzer, based on ELS and DLS.

In the ELS mode, the optical fibre (OF) is rotated to an external angle of 19.8° , which translates (for water) into a scattering angle of 14.8° . Scattered light (ELS) at this angle is collected by OF and transmitted to the PMT detector. However, in addition a small fraction (approximately 4%) of the original laser light beam, referred to as the "local oscillator" (LO), is split off by beam splitter BS1, reflected by mirror M2 and directed at a second beam splitter, BS2. A small fraction of the LO light wave is reflected by BS2 into the OF pickup, where it *mixes coherently* with the LS wave. The resulting coherent superposition of light signals is transmitted to the PMT detector by the optical fibre. By analogy to a radio receiver, this scheme is referred to as a "heterodyne" light scattering system. Accurate heterodyne detection requires that the intensity of the LO wave greatly exceed (ie, 20:1 to 30:1) that of the LS wave with which it is mixed. A variable neutral-density filter (NDF) is used to automatically adjust the intensity of the detected ELS wave relative to the intensity of the LO wave. Typical intensities (expressed as photopulse rates) for the two waves are 2,000-4,000kHz and 100-200kHz, respectively.

The frequency of the LO wave, ν_0 , is enormous (eg, $5 \times 10^{14}\text{Hz}$ for red HeNe light) compared to the small Doppler shift, $\Delta\nu$, expected in the frequency of the ELS wave. Hence, it is not feasible to measure directly this miniscule relative change in frequency. However, the coherent mixing of the two waves at the detector provides the desired result. The electronic (photopulse) signal produced by the PMT detector contains a component which effectively oscillates at the "beat note", or difference, frequency between the two individual optical frequencies.

All that is required to determine $\Delta\nu$ is to measure the frequency power spectrum of the PMT output signal. In practice, however, the overall accuracy, or signal-noise ratio, of the measurement can be greatly improved by "shifting" the frequency range of interest from zero Hz ("DC") to some convenient frequency, away from the influence of common sources of electronic noise, and drift, which are especially prevalent at very-low frequencies. Hence, it is useful to "add" an arbitrary, fixed frequency to the existing frequency of the LO wave.

This added shift is conveniently accomplished by using the Doppler effect once again. A piezoelectric translator, PZT, attached to mirror M2, is driven at some arbitrary frequency, $\nu_{\text{PZT}} = 260\text{Hz}$ in our case. The frequency of the LO wave is shifted upward to $\nu_0 + \Delta\nu_{\text{PZT}}$. The "beat note" which therefore appears on the output of the PMT detector, representing the difference in frequencies of the ELS and LO waves, is similarly translated upward, to $\nu_{\text{PZT}} + \Delta\nu$. The electrophoretic mobility will therefore be manifested as a frequency shift $\Delta\nu$ with respect to ν_{PZT} . Proper design and synchronization of the electronic waveforms which drive the cell electrode voltage and PZT device allow the sign, as well as the magnitude, of the frequency shift to be determined.

The PMT photocurrent signal, consisting of individual photopulses of average frequency 2,000-4,000kHz, is passed to a multi-channel digital autocorrelator (AC). In the case of our NICOMP 370 ZLS instrument, the AC uses four fast digital signal processors (DSPs) with 32-bit architecture, operating with an adjustable number of channels and channel width. Typical ELS measurements are made using either 256 or 512 channels, with 500 μs /channel. The desired frequency shift of the ELS wave relative to the LO wave is obtained by Fourier analysis of the autocorrelation function (ACF) of the PMT photopulse signal. This is accomplished using a fast Fourier transform (FFT) algorithm, which yields the

ing of the spheres. The peak at the centre is the "reference" PS, with zero applied E field; the left-most (ELS) peak was obtained with an applied field of 10V/cm. The frequency scale has been offset by the modulation frequency of the LO wave, $\nu_{\text{PZT}} = 260\text{Hz}$, which shifts the reference peak to zero Hz. The centre of the ELS peak is shifted by -19.3Hz with respect to the reference peak, corresponding to an electrophoretic mobility μ of -3.61 M.U. , or a zeta potential ζ of

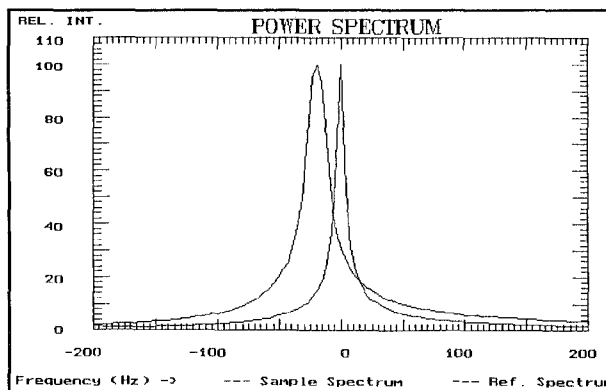


Figure 3. ELS power spectrum obtained for 262nm polystyrene latex spheres (5,000:1 aqueous dilution of 10% conc) with 0.2% added SDS surfactant, $e = 10\text{V/cm}$.

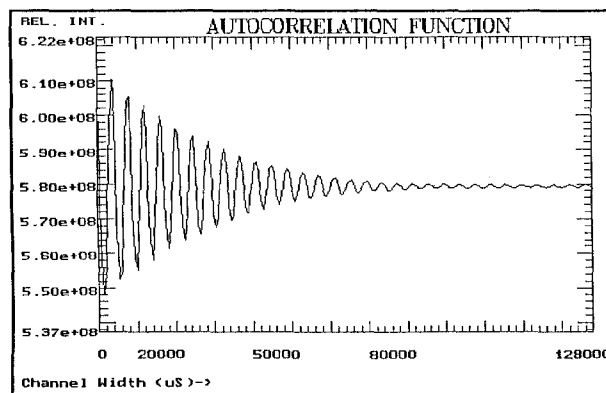


Figure 4. Heterodyne autocorrelation function (256

-48.8mV , assuming the Smoluchowski limit. The ELS peak is broadened significantly, indicating a range of mobilities, or zeta potentials, rather than a single value.

Figure 4 shows the ACF from which the shifted ELS peak in Figure 3 was obtained by FFT. This measurement was made using 256 channels and a channel width of 500 μs . As expected, the ACF resembles a smoothly decaying oscillating function, with a frequency corresponding to the mean frequency shift of the ELS wave relative to the LO wave — in this case, $260 - 19.3 = 240.7\text{Hz}$. The characteristic decay time of the "envelope" of the oscillatory function is inversely proportional to the width of the ELS peak. This width depends on the range of ζ values, as well as normal diffusion broadening (Equation 7), inversely related to the mean particle diameter (Equation 8). The broadening due to diffusion alone can be inferred from the width of the unshifted reference peak.

Interestingly, the zeta potential for these latex particles is observed to decrease when the amount of added SDS surfactant is reduced. The latex beads are stabilized during production with a substantial negative charge imparted by an adsorbed layer of anionic surfactant. However, if this concentrated dispersion is highly diluted, some of the surfactant must leave the particle surfaces in order to maintain the low concentration of free surfactant monomers and micelles in the aqueous phase. Hence, additional anionic surfactant must be added to keep the particles sufficiently charged to avoid aggregation.

This behaviour is illustrated by repeating the measurement above, by using decreasing concentrations of added SDS: 0.1%, 0.02%, 0.005% and 0.0025%. The resulting values for ζ were found to decrease monotonically with decreasing (SDS): -44.7 , -34.8 , -31.7 and -18.7mV , respectively. In principle, such values of ζ can be used to estimate the height of the repulsive potential barrier between two neighbouring particles. The

desired frequency shift of the ELS wave relative to the LO wave is obtained by Fourier analysis of the autocorrelation function (ACF) of the PMT photopulse signal. This is accomplished using a fast Fourier transform (FFT) algorithm, which yields the power spectrum (PS) of the heterodyne signal, ELS + LO.

Finally, the electrode assembly can be removed from the disposable sample cuvet, and the system used to determine the particle size distribution (PSD) by dynamic light scattering (DLS). It is possible to use a modified version of the heterodyne scheme discussed above for zeta potential analysis. In this case, the PZT modulator must be turned off, so that the LO wave is no longer Doppler shifted in frequency. However, for technical reasons it is preferable to make the DLS measurement using the more conventional homodyne scattering approach, in which the LO wave is turned off and only the light scattered from the diffusing particles is detected.

In the ideal case of uniform-size particles, the ACF is a simple decaying exponential function with decay time τ , where $1/\tau = 2\Gamma$, and Γ is given by Equation 7. The particle diameter, a , is then obtained from Equation 8. For non-trivial distributions, including simple log-normals and more complex bimodals or skewed unimodals, the PSD can be estimated from the ACF using either cumulants analysis or a more sophisticated Laplace transform algorithm. The multi-angle capability shown in Figure 2 is invaluable for broad PSDs at larger diameters ($a > 200\text{nm}$), when there is significant angular dependence of the scattering intensity due to intraparticle Mie scattering.

Representative ELS Results

Figure 3 shows the ELS power spectrum (PS) obtained for a dilute aqueous suspension (5,000:1 of 10% stock) of polystyrene latex spheres of diameter 262nm, with 0.2% added surfactant (SDS) to ensure full charg-

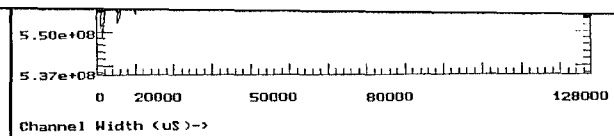


Figure 4. Heterodyne autocorrelation function (256 channels, 50 $\mu\text{s}/\text{ch}$) from which the ELS power spectrum (Figure 3) was obtained by FFT.

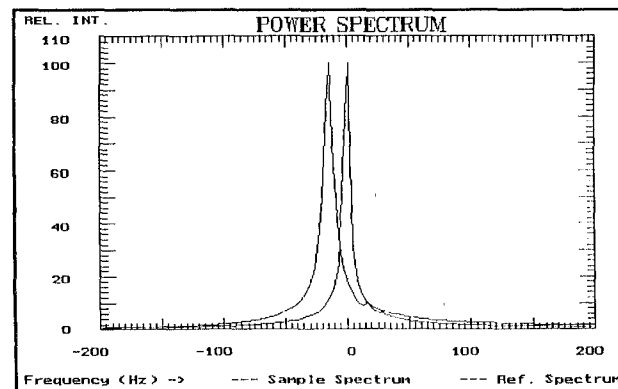


Figure 5. ELS power spectrum obtained for a 350nm injectable oil-in-water emulsion (1,000:1 aqueous dilution of 10% conc), $E = 10\text{V}/\text{cm}$.

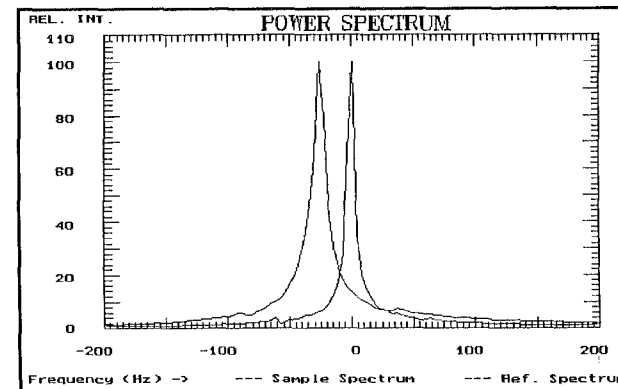


Figure 6. ELS power spectrum obtained for the same oil-in-water emulsion, but diluted 10,000:1, with 0.2% added SDS surfactant.

decreasing (SDS): -44.7 , -34.8 , -31.7 and -18.7mV , respectively. In principle, such values of ξ can be used to estimate the height of the repulsive potential barrier between two neighbouring particles. The barrier height can then be used to estimate the rate of aggregation of the colloidal suspension.

Finally, it is instructive to perform a similar experiment on an oil-in-water emulsion made by homogenization, used for intravenous drug delivery. Figure 5 shows the PS for a typical injectable emulsion, consisting of droplets of fatty oil surrounded by a layer of an appropriate anionic surfactant, with a mean diameter of approximately 350nm. The sample in Figure 5 was diluted 1,000:1 in water (starting conc 10%), and the mobility measured with $E = 10\text{V}/\text{cm}$. The resulting values of $\Delta\nu$, μ and ξ were -14.3Hz , -2.67M.U. and -36.1mV .

Next, we further diluted this sample in serial fashion: 2,000:1, 4,000:1 and 8,000:1. The zeta potential decreased monotonically to -25.6 , -22.9 and -15.1mV . This behaviour should not be surprising. Some of the surfactant adsorbed onto the oil droplets is caused to leave the oil droplets and enter the aqueous phase, for the same reason discussed above for the latex beads. Finally, it is instructive to add some anionic SDS surfactant to a 10,000:1 dilution of this same emulsion, in order to "recharge" the oil droplets. Figure 6 shows the PS resulting from this experiment. There is a dramatic increase in the value of ξ , to -67.9mV , corresponding to $\Delta\nu = -26.9\text{Hz}$ and $\mu = -5.02\text{M.U.}$

In summary, it is evident that the technique of ELS constitutes a powerful tool for the measurement of electrophoretic mobilities and zeta potentials of charged colloidal systems. It is especially useful when combined with DLS technology for multi-angle, high-resolution particle size analysis in the same instrument package.