

# Zeta potential and particle size analysis of colloids using ELS and DLS

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THE PHYSICAL effect responsible for stabilizing most colloidal particle suspensions in water against aggregation due to Van der Waals attraction is electrostatic repulsion. Colloidal particles that are normally uncharged, such as oil droplets in an oil-in-water emulsion, can be stabilized by adsorbing ionic surfactant molecules onto their surfaces. Conversely, there are colloidal particles that are charged due to ionizable groups covalently bound to their surfaces, such as the oxides silica, alumina, and titanium dioxide.

Consequently, there is increasing interest in techniques that can easily and reliably quantify the "repulsiveness" of charged particles in liquid suspension. One such technique is electrophoretic light scattering (ELS), which measures the zeta potential,  $\zeta$ , of charged particles in suspension. The latter is defined as the value of the electrical potential,  $\Psi$ , at the shear plane of the particle—typically, close to its surface, where  $\Psi$  equals  $\Psi_0$ . The value of  $\Psi$  in solution decreases with increasing distance from the surface due to the screening of the electric field by mobile counterions, as described by the DLVO theory. The higher the ion concentration, the faster  $\Psi$  falls with increasing distance from the particle surface, characterized by the Debye-Hückel screening length,  $\kappa^{-1}$ . For relatively low concentrations of added salt (e.g.,  $\leq 0.01 M$ ),  $\zeta$  provides a good approximation to  $\Psi_0$ .

An instrument that performs both zeta potential analysis by ELS and multiangle particle size analysis by DLS (dynamic light scattering) using a single optical fiber/collimator and high-resolution stepper motor ( $0.9^\circ/\text{step}$ ) has been developed. A simplified block diagram of the Nicomp™ 380 ZLS system (Particle Sizing Systems, Santa Barbara, CA) is shown in Figure 1. This design offers the flexibility desired in research laboratories without sacrificing the reliability and ease of use demanded in QC settings.

In the zeta potential mode of operation, the optical fiber (OF) is positioned automatically at a preset small angle, allowing it to collect scattered light from a particle suspension located between parallel electrodes (spacing =  $h$ ) immersed in a disposable cuvette. Application of an alternating voltage,  $\pm V$ , across the electrodes results in an electric field,  $E = \pm V/h$ . The charged particles move back and forth, quickly reaching a terminal velocity,  $v$ , proportional to  $E$ , thus defining the electrophoretic mobility,  $\mu$ ,

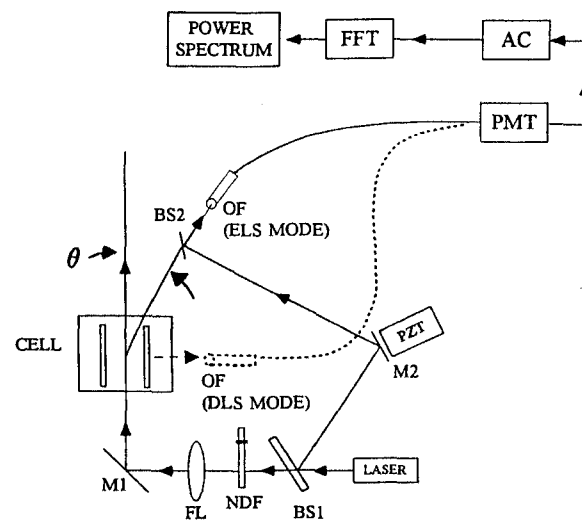


Figure 1 Simplified block diagram of Nicomp 380/ZLS, combining zeta potential analysis by ELS and submicron particle size analysis by DLS.

layers, and the above value of  $\zeta$  must be multiplied by  $3/2$ . For intermediate values of  $ka$ , Henry's equation must be used to estimate  $\zeta$  from  $\mu$ .

The magnitude of the frequency shift  $\Delta\nu$ —typically only a few Hz to 100 Hz, at most—is insignificant compared to  $\nu_0$  (approx.  $5 \times 10^{14}$  Hz for red light). Hence, it is not possible to measure directly this miniscule relative change in light frequency. A simple, well-known solution is to apply the heterodyne technique, analogous to the approach used in a radio receiver.

A small fraction (typically 4%) of the laser beam is diverted by a beam splitter (BS1 in Figure 1), to create a local oscillator (LO). This is steered by mirror M2 toward a second beam splitter, BS2, which allows a small fraction of the LO light wave to mix coherently with scattered light LS from the colloidal suspension. The resulting coherent superposition of light signals is carried by OF to a photomultiplier tube (PMT) detector. A variable ND (neutral density) filter automatically adjusts the intensity of the LS wave so that it is much weaker ( $\leq 1:20$ ) than the LO wave,

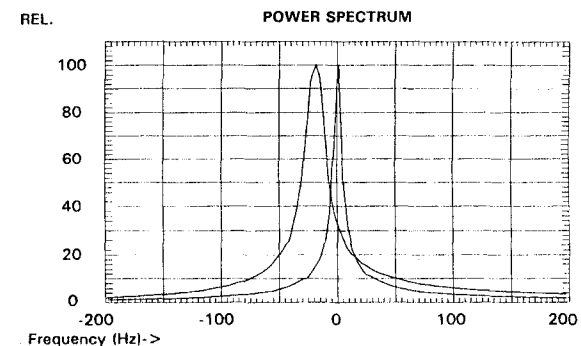


Figure 2 ELS power spectrum obtained for a dilute suspension of polystyrene latex spheres (diam 262 nm) with 0.2% SDS surfactant—with and without applied electric field,  $E = 10 \text{ V/cm}$ .

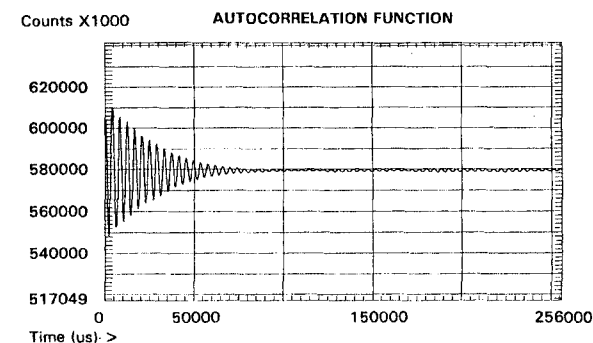


Figure 3 Auto correlation function (256 channels,  $500 \mu\text{s}/\text{channel}$ ) from which the ELS power spectrum in Figure 2 was obtained by FFT—mean frequency =  $260 - 19.3 = 240.7 \text{ Hz}$ .

where  $k$  is Boltzmann's constant and  $T$  the absolute temperature.

Of course, "real" samples usually contain particles over a broad size range. For particle size distributions (PSDs), which are roughly log-normal in shape, simple cumulants analysis can be used to invert the AC function. In the case of skewed unimodal or multimodal PSDs, a more sophisticated Laplace transform algorithm is

mersed in a disposable cuvette. Application of an alternating voltage,  $\pm V$ , across the electrodes results in an electric field,  $E = \pm V/h$ . The charged particles move back and forth, quickly reaching a terminal velocity,  $v$ , proportional to  $E$ , thus defining the electrophoretic mobility,  $\mu$ ,

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

The induced particle velocity causes the frequency of the scattered light,  $\nu_s$ , to be Doppler shifted with respect to that of the incident laser light,  $\nu_0$ , by an amount  $\Delta\nu$ , given by

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

where  $\vec{K}$  is the scattering wavevector, familiar from DLS theory. The mobility,  $\mu$ , can be easily calculated from the measured Doppler shift,  $\Delta\nu$ , for a given applied electric field strength,  $E$ ,

$$\mu = (\lambda_0/n \sin \theta) (1/E) \Delta\nu \quad (3)$$

For a HeNe laser ( $\lambda_0 = 633$  nm), water ( $n = 1.33$ ) and  $\theta = 14^\circ$ , this reduces to  $\mu = 1.967 (1/E) \Delta\nu$ .

Finally, the zeta potential,  $\zeta$ , must be calculated from  $\mu$ . If the concentration of mobile ions is sufficiently high that  $\kappa^{-1}$  is small compared to the mean particle diameter,  $a$  (i.e.,  $\kappa a \gg 1$ ), then Smoluchowski's approximation applies, and  $\zeta = \eta\mu/\epsilon$ , where  $\eta$  is the viscosity, and  $\epsilon$  the dielectric constant of the solvent. In the opposite limit of screening ( $\kappa a \ll 1$ ), there is significant overlap of the electrical double

of the LO light wave to mix coherently with scattered light LS from the colloidal suspension. The resulting coherent superposition of light signals is carried by OF to a photomultiplier tube (PMT) detector. A variable ND (neutral density) filter automatically adjusts the intensity of the LS wave so that it is much weaker ( $\leq 1:20$ ) than the LO wave, required by the heterodyne technique.

The photopulse signal from the PMT now contains a beat note signal, with a characteristic frequency equal to the difference in frequencies of the LS and LO light signals, or  $\Delta\nu$ . The signal/noise ratio is greatly improved by raising the frequency range away from dc. This is easily accomplished by vibrating mirror M2 at a low frequency,  $\nu_{PZT}$ , using a piezoelectric translator. The frequency of the LO wave is thus Doppler shifted upward to  $\nu_0 + \nu_{PZT}$ . The electrophoretic mobility  $\mu$  will now be manifested as a frequency shift  $\Delta\nu$  with respect to  $\nu_{PZT}$  in the power spectrum (PS) of the heterodyne signal, LS + LO. In the Nicomp 380 ZLS system, the PMT photopulse signal is processed by a DSP-based digital autocorrelator (ac), typically using 256 or 512 channels and 500  $\mu\text{sec}/\text{channel}$ . The AC function is analyzed using a fast Fourier transform (FFT) algorithm, resulting in real-time display of the heterodyne PS.

The system can also be automatically converted to a particle size analyzer, based on the homodyne DLS technique, by removing the electrode assembly from the sample cuvette, turning off the LO wave, and directing the optical fiber to the desired scattering angle (typically  $90^\circ$ ). The intensity of the LS signal fluctuates in time due to random changes in the phases of the constituent scattered wavelets, caused by random Brownian motion, or diffusion, of the particles. In the trivial case of uniform-size particles, the AC function is a simple decaying exponential, with decay time  $\tau$  given by  $\tau = 1/2DK^2$ , where the diffusivity,  $D$ , is related to the particle diameter,  $a$ , by the Stokes-Einstein relation,

$$D = kT/3\pi\eta a \quad (4)$$

Of course, "real" samples usually contain particles over a broad size range. For particle size distributions (PSDs), which are roughly log-normal in shape, simple cumulants analysis can be used to invert the AC function. In the case of skewed unimodal or multimodal PSDs, a more sophisticated Laplace transform algorithm is needed. The multiangle capability of the new instrument is useful for analyzing broad PSDs containing larger particles where the scattering intensity varies with angle due to intraparticle Mie scattering.

Figure 2 shows the ELS PS obtained for dilute aqueous suspension (5000:1 of 10% stock) of polystyrene latex spheres, 262 nm diam, with 0.2% surfactant (SDS) added to ensure full charging of the spheres. The peak at the center is the reference, obtained with  $E = 0$ ; the left-most (ELS) peak was obtained with an applied field,  $E = 10$  V/cm. (The frequency scale has been offset by the modulation frequency of the LO wave,  $\nu_{PZT} = 260$  Hz.) The ELS peak has been shifted by  $-19.3$  Hz, which corresponds to  $\mu = -3.61$   $\mu\text{m/s/V/cm}$  and  $\zeta = -48.8$  mV, assuming the Smoluchowski limit. The ELS spectrum is broadened significantly relative to the reference PS, indicating a range of mobilities, or zeta potentials, rather than a single value.

Figure 3 shows the AC function from which the ELS power spectrum in Figure 2 was obtained by FFT. As expected, it resembles a smoothly decaying oscillating function, with a frequency equal to the mean shift of the LS wave relative to the LO wave,  $260 - 19.3 = 240.7$  Hz. The characteristic decay time of the envelope of the oscillatory function is inversely related to the width of the ELS peak in Figure 2.

In summary, 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 in the same instrument package with DLS technology for multiangle, multicomponent particle size analysis.

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