Measuring zeta potential using phase analysis light scattering (PALS)

Introduction

The measurement of zeta potential in the Zetasizer range of instruments is made using the technique of laser Doppler electrophoresis. This technique is discussed at length in another technical note available from the Malvern Instruments website (www.malvern.co.uk). In brief, laser Doppler electrophoresis measures small frequency shifts in the scattered light that arise due to the movement of particles in an applied electric field.

The frequency shift Δf is equal to:

$$\Delta f = 2v\sin(\frac{\theta}{2})/\lambda$$

where
v is the particle velocity,
λ the laser wavelength and
θ the scattering angle.

In microelectrophoresis, the particle velocities that are measured are very small, typically around 10's of microns/second, and hence the frequency shifts are ~ 10Hz. In the Zetasizer Nano, measurement of the Malvern zeta potential standard DTS0050 in an applied field of 150V across the roughly 50mm length of the folded capillary cell have a frequency shift of around 50Hz.

The velocity of the particles undergoing electrophoresis is determined by comparing the beat frequency detected with that of a reference frequency. This reference frequency is produced by modulating one of the laser beams with an oscillating mirror. The mobility of the particles in an applied field will therefore produce a frequency shift away from that of the modulator frequency.

In previous instruments, Doppler shift analysis was performed by Fourier transformation. Analysis of the Doppler shift in the Zetasizer Nano series is done by using phase analysis light scattering (PALS). This technical note attempts to explain what PALS is.

Phase Analysis Light Scattering (PALS)

PALS is a technique that uses the same optical setup as conventional laser Doppler electrophoresis. However, a different signal processing method is employed. Instead of the frequency shift being measured, the phase shift is determined instead. The measured phase change is proportional to the change in the position of the particles. Phase, by definition, is frequency x time.

PALS can give an increase in performance of greater than 100 times than that associated with standard measurement techniques. This allows the measurement of high conductivity samples where low applied voltages need to be used to avoid any risk of sample effects due to Joule heating. In addition, PALS gives the ability to accurately measure other samples that have low particle mobilities, for example high viscosity or non-aqueous applications.

The electrophoretic contribution to the motion can only be detected by sampling many oscillations of the frequency-shifted signal. This is fine for high mobility particles since they pick up a lot of energy from the electric field that moves them quickly through the beam, producing many oscillations in a short space of time (figure 1).

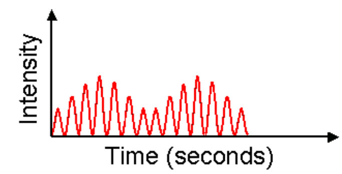

Figure 1: For high mobility particles, enough data is collected within the measurement time to produce an accurate determination of the particle motion.

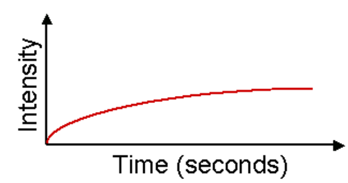

Figure 2: For low mobility particles, only a fraction of an oscillation may have been completed within the measurement time. In this case, determination of the particle's mobility would not be possible using Fourier transformation.

The effect of the field on low mobility particles is much weaker and consequently, to compensate, the electric field needs to be increased. However, increasing the electric field for high conductivity samples results in significant Joule heating which destroys any random motion and can denature the sample.

For low mobility particles only a fraction of an oscillation may have been completed within the measurement time (figure 2).

In this case it would be impossible to determine the particle's motion using standard Fourier transform analysis. However, if we consider phase, a particle moving just half a wavelength represents a large measurable shift in phase terms.

By measuring the phase difference between the beat frequency and a reference frequency, the changes in position of the particle can be determined more accurately when the particle displacements are small.

The reference frequency used in the Zetasizer Nano is that of the optical modulator. The mean phase shift with time gives us information on the electrophoretic motion of the particle. PALS measures the rate of change of the phase difference between the two signals.

As an example, imagine two frequencies that are both 50Hz (figure 3). If the phase difference (in radians) between these two signals is plotted over time, a flat line is obtained. Now consider two signals that have different frequencies (in this example, they are 50 and 51Hz respectively). A plot of the phase difference between the two signals shows a gradient (figure 4). The rate of change in the phase difference is related to the velocity at which the particles are moving. Therefore the mean zeta potential value can be determined. Figure 5 shows a typical phase plot obtained from a zeta potential measurement performed on the Zetasizer Nano. During the measurement sequence, the applied voltage is rapidly reversed a number of times. This plot shows well defined, alternating slopes of the phase difference with time that result from the rapid reversal of the applied field. These slopes are averaged to determine the mean phase difference and hence mean zeta potential.

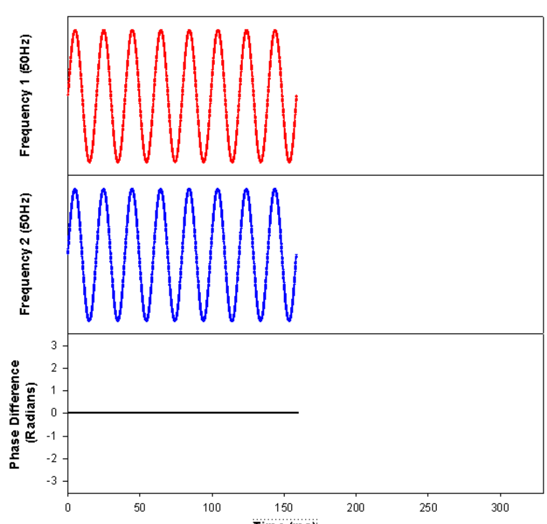

Figure 3: Schematic diagram showing the phase difference between two signals with the same frequency (50Hz)

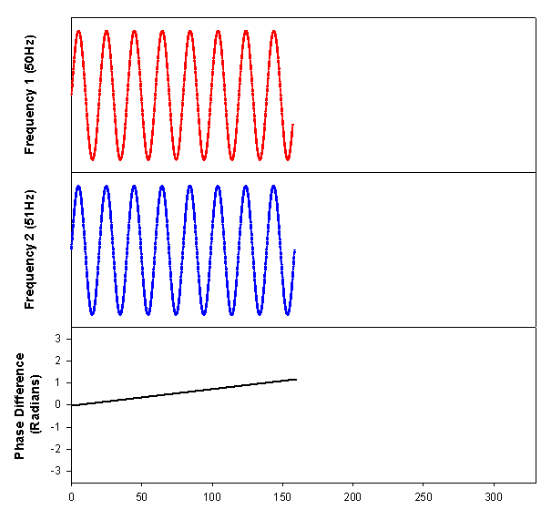

Figure 4: Schematic diagram showing the phase difference between two signals of different frequencies (50 and 51Hz**)**

MALVERN
INSTRUMENTS

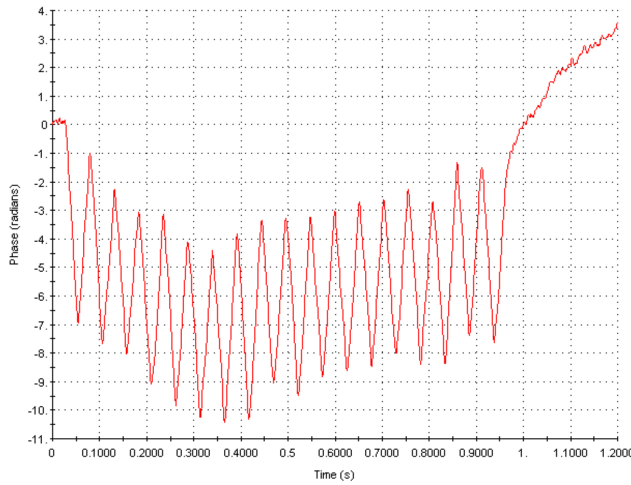

Figure 5: Typical phase plot from a zeta potential measurement performed on a Zetasizer Nano instrument

Malvern Instruments Ltd

Enigma Business Park • Grovewood Road • Malvern • Worcestershire • UK • WR14 1XZ
Tel: +44 (0)1684 892456 • Fax: +44 (0)1684 892789

Malvern Instruments Worldwide

Sales and service centers in over 50 countries for details visit www.malvern.co.uk/contact