Colloidal Dynamics
leaders in colloid measurement

HOW DO THE ZETAPROBE AND ACOUSTOSIZER II MEASURE ZETA POTENTIAL AND PARTICLE SIZE?

The ZetaProbe and the AcoustoSizer II measure the particle size and zeta potential in concentrated colloids. Most of the other commercial devices need to dilute the colloid to make these measurements. The dilution takes time, and it often alters the very things you are trying to measure. In this article we will describe how our products actually determine size and zeta in concentrates, and we will present some applications.

Introduction

The ZetaProbe and AcoustoSizer II have become routine instruments for the measurement of particle size and zeta potential in colloidal systems. One of the great advantages of these devices is that they can measure size and zeta *without dilution.*

The traditional devices for measuring size and zeta use optical techniques such as light scattering. The samples need to be quite transparent to use these products, and this usually means they must be diluted down to concentrations of approximately 10 mg per litre. Even the more recent optical devices that claim to be able to measure zeta potential in 'concentrated' suspensions can only do so at concentrations of 0.5 % w/v under favourable conditions of low opacity. This is still one to two orders of magnitude more dilute than most colloids.

This dilution is time consuming, an important consideration in QC labs where sample throughput is vital. And the dilution can lead to large errors in the zeta potential if there is a change in the concentration of the background electrolyte. Furthermore, the diluted sample has such a small particle surface area that the zeta can be altered by trace amounts of surface-active impurities in the sample.

How can the ZetaProbe and AcoustoSizer II measure in concentrates? The reason is that they measure *sound* rather than

Background: What is the Zeta Potential?
Colloidal particles are usually electrically charged. They are surrounded, in suspension by a cloud of ions that carry an equal and opposite charge. The zeta potential is the voltage difference between the particle surface and the liquid beyond the charge cloud. In colloids that are electrostatically stabilized, zeta provides a measure of the electrical repulsive force between the particles. For other systems where the stability comes from steric components, the zeta potential can be used as a measure of the state of the surface. It can be used to monitor optimum levels of dispersant or other agents to be added to the particles.

Thus zeta potential can be used for monitoring and controlling colloid stability and as an indicator of the particle surface chemistry.

light, and so it is not necessary to see through the suspension to measure it.

Two measurement techniques are employed – *electroacoustics* and *ultrasonic attenuation.* The first technique is used in both products, while the attenuation method is only used in the AcoustoSizer II, for getting particle size.

We will begin our description with the electroacoustic method, since this is common to both products.

THE ESA MEASUREMENT

In this technique we measure ultrasound generated *by the particles*. A MHz voltage is applied across a pair of electrodes in contact with the suspension. Colloidal particles are electrically charged, so they move back and forth, first towards one electrode and then the other. It is this particle motion that generates the ultrasound, in the same way that the back and forth motion of a loudspeaker generates sound. The sound wave from each particle is very tiny, but the particles move in phase and this cooperative motion results in a measurable beam of ultrasound.

This effect, of sound waves generated by an applied electric field, is called the *Electrokinetic Sonic Amplitude Effect*, or *ESA* for short.
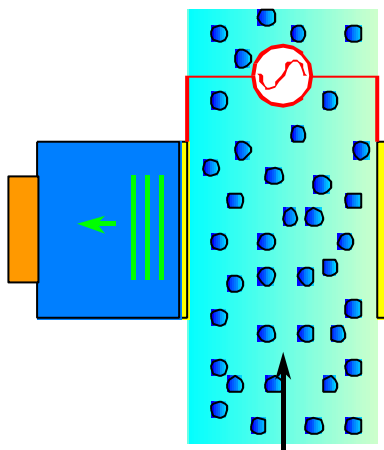

Figure 1 The AcoustoSizer II ESA measurement cell

In figure 1 we show a schematic diagram of the AcoustoSizer measurement cell. The colloid flows up between a pair of parallel plate electrodes that are connected to a MHz voltage source. The ESA sound wave passes out of the suspension and travels through a glass block where it is picked

up by a piezoelectric transducer shown on the left-hand side of the diagram.

The ESA depends on the particle velocity, which in turn depends on the particle charge. The ESA also depends on the particle size, for bigger particles have more inertia, and this causes them to lag behind the electric field. Thus there will be a time delay between the field changing direction and the particle velocity changing direction. Hence the particle size affects the *phase* of the ESA, and so by measuring the magnitude and phase of the ESA sound wave we can determine both particle charge (or zeta potential) and size.

The dynamic mobility

The ESA depends on particle size and zeta, but it also depends on the geometry of the measuring cell, the strength of the applied field, the material the cell is made of, the type of transducer used and so on. The first step in the process of getting size and zeta is to extract, from the measurement, a quantity that only depends on the colloid and not on the device used for making the measurement.

The colloidal property that we extract from the ESA measurement is called the **dynamic mobility**, denoted by the symbol m_D. This is like the normal electrophoretic mobility, but it is defined for a sinusoidal electric field instead of a steady field. In this section we will give a precise definition of this quantity.

A sinusoidal electric field of the form

$$E \cos \boldsymbol{w} t \qquad (1)$$

will cause the colloidal particles to move with a sinusoidal velocity

$$V \cos\left(\boldsymbol{w} t - \boldsymbol{q}\right) \qquad (2)$$

where t is time and $\boldsymbol{w}$ is the angular frequency. The phase angle $\boldsymbol{q}$ has been introduced to allow for the phase lag caused by particle inertia.

The particle velocity and the applied field are represented by the curves in figure 2, for the case of a 30^0 phase lag.

The standard electrophoretic mobility is defined by the single quantity *V/E*, but in the case of a sinusoidal field, *two* quantities are required to define the mobility, viz the ratio *V/E* and the phase angle *q*.
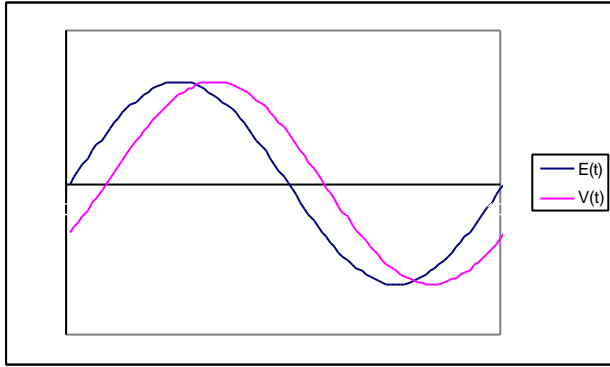

Figure 2 The sinusoidal particle velocity V and electric field E

These two parameters are combined in the definition of the dynamic mobility, which is a complex number with a magnitude and argument are given by

$$\text{Mag}\left(m_D\right) = \frac{V}{E}, \text{ and Arg}\left(m_D\right) = -q \qquad (3)$$

Readers who are not familiar with the terms Mag and Arg may recall that a complex number z can be represented as a point on the x-y plane, where the x coordinate is the real part and the y coordinate is the imaginary part of the complex number. The magnitude (or Mag) of z is the distance from the origin to the point (x,y), and the argument (Arg) is the angle that the line from the origin to the point makes with the x axis. Thus the magnitude of the dynamic mobility is defined in the same way as the electrophoretic mobility, and its argument is minus the phase lag.

At low frequencies, the inertia forces are very small and the particles will move in phase with the electric field. In this limit the dynamic mobility is the same as the electrophoretic mobility. But as the frequency increases, and the inertia becomes significant, a phase lag will develop and the dynamic mobility will have a negative argument. The inertia forces only usually become significant for colloidal particles at frequencies in the MHz range. It would be impossible to measure the dynamic mobility by optical techniques at such high frequencies, but the ESA effect provides a way of determining this quantity.

Before moving on to this next step of getting the mobility from the ESA, we note that if the sign of the zeta potential is reversed- something that can be done for oxide particles by altering the pH- the argument of the mobility will swing through 180 degrees. This is because the particle velocity will now be in the opposite direction. Hence there will be a minus sign out the front of the formula (2), which is the same as adding 180 degrees to the argument in that formula.

This is how we determine the **isolectric point** (iep) of a colloid- that is, the pH at which the particle has zero zeta potential. As we change the pH from one side of the iep to the other, the argument of the mobility swings through 180 degrees. This allows us to determine the iep very accurately.

Getting the dynamic mobility from the ESA

To find the mathematical relation between the measured ESA and the dynamic mobility, it is necessary to solve the equations of motion for a colloid subjected to an applied electric field. The mathematical details are set out in the Appendix of the 2003 paper by O'Brien, Jones and Rowlands (see the references for details), where it is shown that

$$ESA = A(w) \frac{z_s z_g}{z_s + z_g} f \frac{r_p - r}{r} m_D \qquad (4)$$

There are a number of new terms in this formula. The quantity f is the particle volume fraction, that is, the fraction of

the total suspension volume occupied by the particles. r_p is the density of the particles and r is the solvent density. *A* is an instrument factor; this depends on things like the transducer dimensions, the applied field, and the instrument geometry but it does *not* depend on the colloid.

Finally, the quantities z_s and z_g are the acoustic impedance of the suspension and the AZR2 glass block respectively. The acoustic impedance is a measure of how much force is required to generate an ultrasound beam in a material. It is defined as follows: suppose that a material- the suspension say- is bounded by a flat solid surface which is acted on by a sinusoidal pressure. This will cause the surface to move back and forward with a sinusoidal velocity of amplitude *V*. The pressure *P* on the material will be proportional to the velocity. The acoustic impedance z of the material is defined by as the constant of proportionality between the pressure and the velocity, that is

$$z = \frac{P}{V} \qquad (5)$$

In the case of a homogeneous material, such as the glass block, the acoustic impedance is equal to the speed of sound times the density of the material, but for a suspension, it depends on the properties of the particles and the solvent. We determine the acoustic impedance by measuring the reflection of various waves from the suspension interface.

When the ESA sound wave strikes the transducer at the far end of the glass block in figure 1, it generates a sinusoidal voltage signal. The quantity on the left hand side of (4) is a complex number with a magnitude equal to the amplitude of that sinusoidal voltage, and an argument equal to the phase difference between this voltage and the driving voltage that is applied to the colloid to generate the ESA signal. Thus the ESA in this formula is a complex number, like the dynamic mobility, with a magnitude and an argument.

Calibration

To determine the dynamic mobility from the ESA using the formula (4), it is necessary to know the instrument factor $A(w)$. We determine this by measuring the ESA from a solution with a known dynamic mobility factor.

This step, of determining the instrument factor by measuring the ESA from a reference solution is known as **calibration**.

In the other commercial electroacoustic devices, the calibration is carried out by making measurements on a colloid with a "known" zeta potential, that is, one for which zeta has been determined on one of the standard optical instruments. But there are problems with this approach: first, the colloid has to be diluted for measurement in the optical device and this can alter zeta, and secondly the zeta potential of a colloid often changes with time, so a colloid that has been left standing in a bottle will have a different zeta from a fresh sample.

At Colloidal Dynamics we have overcome these problems by using an electrolyte as a calibrant. The ESA in this case is generated by the ions, rather than colloidal sized particles, but the formula (4), still applies; the only difference is that the term

$$f \frac{r_p - r}{r} m_D \qquad (6)$$

is replaced by a sum over the individual ionic species. A solution of potassium silico tungstate (KSiW) ions has been chosen as the calibrant because it gives a large, stable ESA signal. In the 1995 paper by O'Brien, Cannon and Rowlands, it is shown that the quantity (6) for this electrolyte is equal to $-3.02 \times 10^{-9} K$, where K is the conductivity of the solution in SI units.

Thus the calibration involves the measurement of the ESA and the conductivity from a KSiW solution. The instrument factor is determined from the measured ESA using a formula obtained by solving equation (4) for $A(\mathbf{w})$.

Dynamic mobility measurements

In figure 3 we show AcoustoSizer II measurements of the dynamic mobility spectra of four silica samples:
  - A one micron spherical colloidal silica sol from Geltech,
  - An 0.3 micron diameter spherical colloidal silica from Nissan Chemical,
  - Klebesol, 30N50 colloidal silica with median diameter around 70nm, and
  - Cabot SCE fumed silica, with median diameter of about 50 nm.

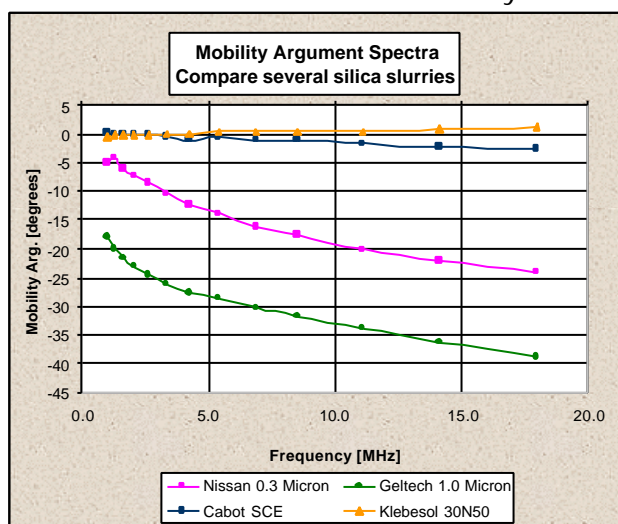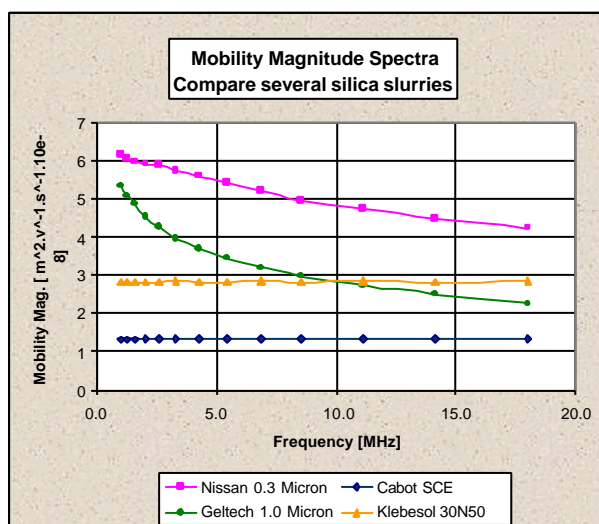The units for mobility magnitudes in the left hand graph are 10^{-8} SI units.

From these measurements it can be seen that the mobility magnitudes drop off more rapidly with frequency for larger particles, and the phase lags increase more rapidly as the particle size goes up. Thus the size can be determined from the shape of the dynamic mobility spectrum. And once the size has been calculated the zeta can be determined from the absolute mobility magnitudes.

From the data in Figure 3 it can be seen that the two nanoparticle suspensions have quite flat magnitude spectra, and small arguments. This is because the inertia forces are very small compared to the viscous forces for these particles. These particles are moving with almost the same mobility as for a steady field, even at our highest measurement frequency of 18 MHz. For the Klebersol, the inertia forces are so small that the particles cannot be sized by the ESA method over this frequency range. We can still determine its zeta potential of course, but to size these particles we need to use the ultrasonic attenuation method, which will be discussed shortly.

At very high frequencies, the inertia forces are so large that the particles barely move in the electric field, and the ESA is then too small to measure. This is what happens for particles larger than about 10 microns in the AcoustoSizer II. Even at our lowest measurement frequency of 1 MHz, the ESA signal is too small to allow particle size determination for particles much larger than 10-15 microns.

Thus, in the AcoustoSizer II, the ESA method can be used for getting particle size in the range of about 70 nm to 10 microns diameter. For smaller particles the ESA technique can give the zeta potential, but not the particle size.

Our **ZetaProbe** zeta potential analyzer also measures the Dynamic Mobility Spectrum but uses a different frequency range than the AcoustoSizer II. The ZetaProbe measures the Dynamic

Figure 3 The measured dynamic mobility magnitudes for four silica

Mobility at 7 different frequencies over a frequency range of 300 kHz to 3 MHz. By operating at lower frequencies, the ZetaProbe can accurately fit the Mobility Spectrum for average particle sizes up to about 30 microns for the particle d50 size. In this lower frequency range, the Mobility Spectrum will be flat for particle sizes less than about 0.5 microns. For this reason, the ZetaProbe is primarily a zeta potential analyzer, not a particle sizing device. The instrument automatically compensates for the effect of particle inertia for large particles and has no lower limit in particle size. Both the ZetaProbe and the AcoustoSizer II can measure the zeta potential of nanoparticles approaching the dimensions of macro ions.

Getting size and zeta from the dynamic mobility spectrum

To determine a particle size distribution and a zeta potential from the measured dynamic mobility spectrum, it is necessary to have a theoretical formula that relates dynamic mobility to particle size and zeta. Such a formula is now available for concentrated colloids (in O'Brien et al's 2003 paper), so the measured mobility spectra can now be used for obtaining the zeta and size distribution in colloids of *arbitrary* concentration. Our software routines do this by adjusting the size distribution and zeta potential to give the best fit between the measured and theoretical dynamic mobility spectra.

Note that we use the entire mobility spectrum in the determination of size and zeta from the ESA. This method of using the mobility measurements *over a range of frequencies* is part of our patented technology. The other commercial electroacoustic devices are limited, because of our patents, to measurements at a single frequency. As a result they cannot get size and zeta from their ESA measurements. The best they can do is to determine zeta for colloids with a known particle size.

This completes our introductory description of the ESA method for getting size and zeta. There is much more that can be said on this topic, but these details, will be deferred for other articles. The main aim of this document is to describe the measurement techniques used in the AcoustoSizer II and the ZetaProbe, so we will now leave the ESA method and turn to the second measurement technique, ultrasonic attenuation.

THE ULTRASONIC ATTENUATION METHOD

In the ESA method, the particles create the ultrasound, but in the ultrasonic attenuation measurements the ultrasound is generated by an external transducer. This beam of ultrasound is then measured on a second transducer after passing through the colloid. The colloid attenuates the ultrasound by an amount that depends on the particle size and concentration. By measuring the attenuation as a function of frequency we can therefore determine a particle size distribution.

The measurement is carried out in the AcoustoSizer cell shown in figure 4. This is the same cell used for the ESA measurement, but now we have included the extra glass block and transducer on the right hand side of the diagram. These were not shown in figure 1 because they are not used in the ESA measurement.

In the attenuation measurement a large sinusoidal voltage pulse is applied to the transducer on the right hand side of the cell in figure 4. This causes the transducer to expand and contract in a sinusoidal fashion, thereby generating a beam of ultrasound. This beam travels through the glass block on the right, through the suspension and then through the glass block on the left hand side, where it is picked up by the transducer attached to the back of that block.

As the sound wave passes through the suspension it moves the particles back and forth. If the density of the particles is different from the solvent, the different inertia forces will cause the

particles to move relative to the solvent. This relative motion generates a local flow around each particle. Energy is dissipated in this local flow by the frictional forces in the liquid. Hence some of the sound wave energy is converted into heat and thus the soundwave is attenuated as it passes through the colloid.
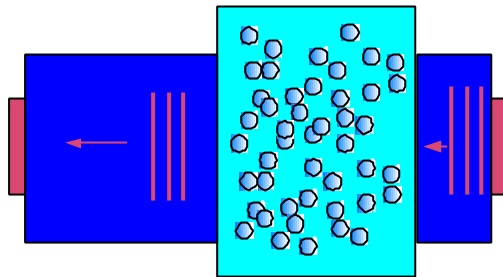
This dissipation mechanism, caused by

Figure 4 A sketch of the AZRII measurement cell

the relative motion between the particles and the liquid, is usually the dominant cause of attenuation in colloids. It is often referred to as **viscous attenuation** because it arises from the frictional forces in the liquid.

The attenuation coefficient

When a locally planar sound wave passes through a suspension, its amplitude drops off like $\exp(-\boldsymbol{a}x)$, where x is distance into the suspension.

The voltage signal in the receiving transducer of the AcoustoSizer II is obviously related to this attenuation factor $\boldsymbol{a}$, for as the attention increases the signal will decrease. The precise mathematical form of this relation can be shown to be

$$S = B(\boldsymbol{w}) \frac{z_s z_g}{\left(z_s + z_g\right)^2} \exp(-\boldsymbol{a}L) \qquad (7)$$

where B is an instrument factor and L is distance across the suspension.

The instrument factor B is determined by measuring the signal S with water in the cell, using the known attenuation factor for water.

The acoustic impedance of the suspension is measured by comparing the signal that has passed once through the suspension with the signal that has passed through the suspension three times, having been reflected internally at each of the glass/suspension interfaces.

With the instrument factor and z_s known, the formula (7) can be used for
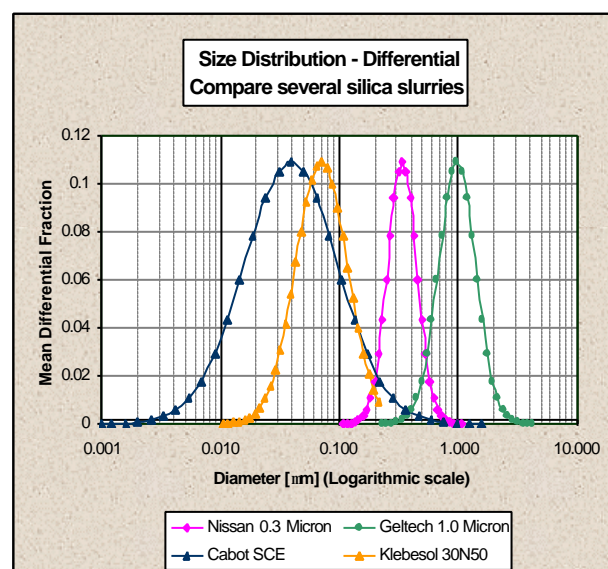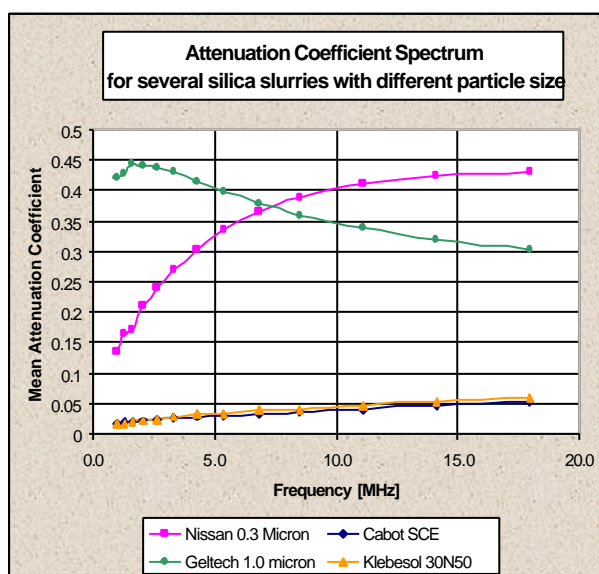

Figure 5 The measured attenuation coefficient spectra, and the size distributions obtained from those spectra for the four silica suspensions of table 1.

determining the attenuation factor a from the measured S value.

In the AcoustoSizer II the attenuation measurements are reported in terms of the non-dimensional **attenuation coefficient c**, where

$$c = \frac{al}{f} \qquad (8)$$

Here l is the wavelength of sound in the solvent, and as before f is the particle volume fraction.

In left hand graph in figure 5 we show the measured attenuation coefficient spectrum for the silica suspensions used in the dynamic mobility measurements of figure 3.

The trends in these graphs are not as clear as those in the dynamic mobility graphs of figure 3. For the very small Klebesol and Cabot particles, the attenuation coefficient is small and rises monotonically with frequency. For the 0.3 micron Nissan suspension the attenuation is still increasing monotonically with frequency, but it seems to be reaching a maximum at the highest frequency, and for the 1 micron Geltech silica is reaches a maximum and then decreases with increasing frequency.

The problem of determining the theoretical link between the attenuation coefficient and the particle size is very similar to the dynamic mobility problem, and the same methods can be used to obtain the theoretical formula.

We will not go into the theory here, but one useful feature of the theory that deserves mention is that the maximum in the attenuation coefficient as a function of frequency occurs at

$$w = O\left(n/a^2\right) \qquad (9)$$

where a is the particle radius and n is the kinematic viscosity of the liquid.

For the Klebersol and Cabot colloids, the particle radius is small and thus the maximum lies far to the right on the graph, outside the measurement range. And for the 0.3 micron Nissan the maximum occurs at a frequency that is about nine times higher than that for the 1 micron Geltech sample. With this rule of thumb you can get a rough idea of the particle size just by looking at the attenuation coefficient spectrum. Of course to get accurate size estimates it is necessary to use software to fit the theoretical and measured spectra. Again, the mathematical process is almost identical to that used with the dynamic mobility spectra.

In the right hand graph in figure 5 we show the size distributions obtained for these silica sols from the attenuation measurements.

These sizes for these suspensions are consistent with those from those obtained from electron micrographs.

Measurements on concentrated colloids

A number of independent studies have been undertaken to determine the accuracy of our ESA and attenuation size and zeta estimates in concentrated colloids. To carry out these tests it is necessary to compare the concentrated measurements with measurements on dilute samples. Since dilution can easily alter zeta, and sometimes alter size, the authors in these studies took great care to dilute the colloid using the same background electrolyte as that in the concentrated suspensions. For suspensions where the particles readily sediment, this involves decanting the supernatant after the particles have settled out and using it to dilute a small sample of the concentrated suspension. For smaller particles it is necessary to separate out the supernatant by filtration or centrifugation. Of course, this is only necessary for carrying out comparisons with dilute measurements. To make ZetaProbe and AcoustoSizer II measurements in practice there is no

need to obtain supernatant; you just measure the suspension as is.

In figure 6 we show ESA zeta potential measurements obtained by Johson at al (1998) on a series of alumina slurries. The first measurements were made on a sample with a particle volume fraction of 30%. This sample was then diluted with supernatant in a series of steps, down to 3% by volume. At each stage the suspension was titrated and the zeta determined by ESA measurements. From this figure it can be seen that the zeta potentials for each concentration are consistent, as is expected in systems with the same background electrolyte. The solid curve in the graph represents the zeta values obtained from electrophoresis studies on an extremely dilute sample. Thus the ESA zeta in this case is consistent with the electrophoretic mobility zeta. This is a good demonstration of the validity of the electrolyte calibration procedure used in our ESA measurements.
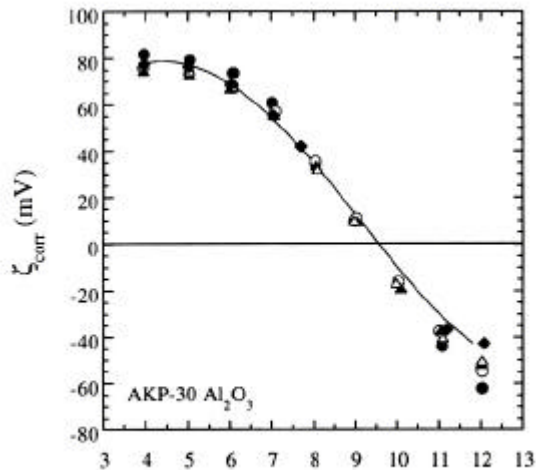

Figure 6 Zeta potential curves for an alumina concentration series.

In figure 7 we show results from another careful dilution sequence, this time from the 2001 paper by Kong et al. The graph represents the median diameter, in microns, of droplets in a sunflower-oil-in-water emulsion. The droplets were stabilised with SDS surfactant and then carefully diluted with a surfactant

solution of the same composition as the water phase.

From this figure it can be seen that the ESA yields a consistent size over this concentration range.
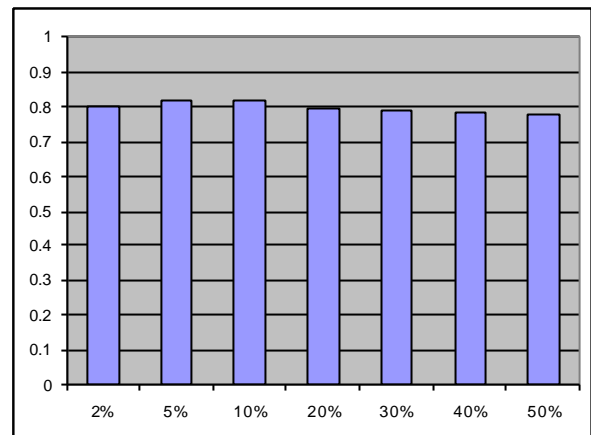

Figure 7 Median droplet diameter, in microns vs droplet volume fraction for an oil in water emulsion

Comparison with other sizing methods

Our products can only measure down to a minimum particle concentration of about 0.5 wt%, so to compare with other techniques, which require extremely dilute samples, it is necessary to dilute in a way that does not alter particle size. In figures 8 and 9 we show the comparison of the AcoustoSizer II size measurements with measurements on a Malvern PCS device and the Matec CHDF device; the former product uses light scattering and the latter uses the Capillary Hydrodynamic Fractionation method to get particle size.

The results are presented in terms of three diameters:

- ❑ D50-the median size (in microns)
- ❑ D15- the diameter that is smaller than 85% of the population, and
- ❑ D85 – the diameter that is larger than 85% of the population.

These three parameters give a measure of the spread of the particle size
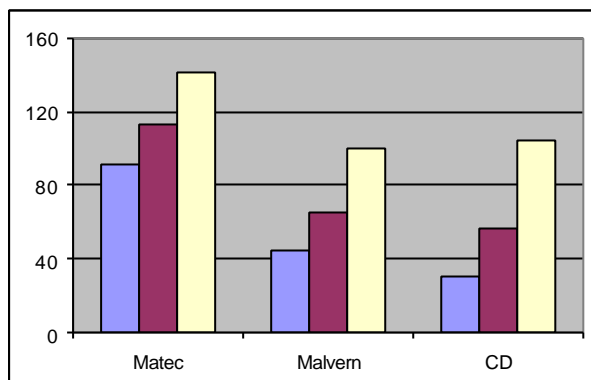

Figure 8 Comparing size distributions for DuPont DP106 Silica

distribution.

The vertical bars in figure 8 represent the three diameters. These measurements were carried out on a suspension of spheroidal silica particles manufactured by DuPont. The vertical axis gives the particle size in nm. From this graph it can be seen that the AcoustoSizer II size distribution is similar to that of the Malvern device in this case, while the Matec gives a bigger size.

The electron micrograph of this sample is shown in figure 9.

The "correct" size distribution for this colloid depends on how the particles are weighted; for example a size distribution based on particle number will be different to one that is based on the particle mass. And the reported distribution from the various instruments also depends on the degree of flocculation of the particles.

The different measuring techniques all give the same size when used on monodisperse spherical particles, but this is the ideal case. When the different techniques are applied to real suspensions as shown above, they can yield different sizes. For engineers who are controlling particle size and to give the suspension desired properties, such as colour and rheology, the important thing is not the absolute value of the

measurements, but the *variation* in these parameter from batch to batch. It is vital that changes in the reported particle size and zeta represent real changes in the suspension and not variability due to instrument artefacts. Thus measurement precision is a key property.

The ZetaProbe and AcoustoSizer II have been designed to give excellent measurement precision, and furthermore they can be used for on-line monitoring of the production stream, since they do not require sample dilution. Thus these products have found a place, not only in R&D and QC labs, but also on the factory floor where they are used to keep the colloidal product within specifications.
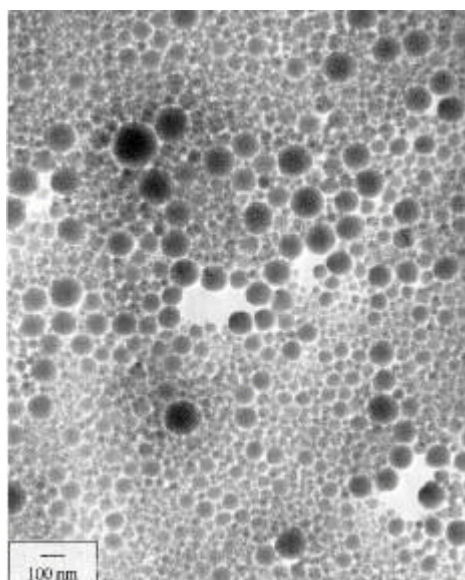

Figure 9 TEM of the DuPont silica

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