

Use of the Agilent 7020 ZetaProbe to control suspension stability

Application Note



Abstract

Some industrial processes require flocculated suspensions while others require the particles to be well dispersed. It can be a challenge to control these processes, because subtle changes in chemical composition can change the degree of aggregation. In this application note, we show how the fast and accurate zeta potential measurements from the Agilent 7020 ZetaProbe can be used for controlling the stability of a colloid.



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Properties of aggregated and dispersed suspensions are critical to performance

Colloidal particles are in a state of constant motion, and they collide with one another many millions of times per second. If there is no repulsion between them, the collisions will result in particles sticking together, forming doublets that quickly develop into triplets and larger groups. Soon, the entire suspension may become a single large aggregate. Alternately, the aggregates (or flocs as they are called) may settle rapidly to form a loose deposit, entrapping a large amount of the suspension medium.

When a suspension is highly dispersed, with strong repulsive forces preventing aggregation, it behaves in many ways like a simple liquid. For example:

1. It will usually have a low viscosity that is independent of shear rate, so it will flow easily and will not 'gel'.
2. It may be difficult to filter, either because the particles are so small that they pass straight through the filter, or because they enter the filter and clog the pores.
3. If the particles are not very dense, it may take a long time for them to settle. When they do settle, they will tend to form a dense deposit that may be very difficult to redisperse. (This is called 'caking').

The opposite is true of an unstable (aggregated) suspension. Such a suspension has the following properties:

1. It will almost always show unusual flow characteristics, with a much higher viscosity than the solvent. This viscosity will depend on how fast the suspension is sheared.
2. It will often behave like a solid if the shearing forces are too small to break down the structure.
3. The aggregates will settle rapidly, but they will form a very loose open network structure that will entrap a lot of water. This structure can be easily broken up by shaking the suspension.
4. The same sort of process may occur in filtration. The solid can easily be separated from the bulk of the suspension medium, but it may be difficult to dewater the remaining filter cake.

In most of the critical operations involved in handling colloidal suspensions, the state of aggregation or dispersion determines how the system will respond. For example, if the aim is to filter out the particles or to produce a slurry that is easily redispersed by shaking the container, an aggregated state is required. But if the aim is to produce a colloid that is easy to pump around, then a disperse state is needed. And a stable colloid is preferred in the colloidal processing of ceramics, for such a slurry produces a stronger ceramic [1].

Zeta potential often controls the state of aggregation

A suspension is stable if the repulsive force between the particles is strong enough to overcome the van der Waals attraction, so to control the aggregation, it is necessary to control the repulsive force.

There are a number of ways to increase this force. One can use a nonionic surfactant or a neutral polymer that adsorbs onto the particles to create a steric barrier to coagulation. Alternatively, one can use electric charge to provide the repulsive force. Aggregation in this case is usually controlled by:

1. Adjusting the solution pH
2. Adding an ionic surfactant
3. Adding a charged polymer, or
4. Adding a highly adsorbable ion, like polyphosphate.

Whenever a charge is present on the particle surfaces, it will contribute to repulsion, and may be the dominant cause of the repulsion. In all such cases, the zeta potential (the electrostatic potential near the surface of the particle) must be controlled in order to control the aggregation process.

Small changes in pH or in the concentration of highly adsorbable ions may influence the effective surface charge and, hence, the state of aggregation. Thus, a small change in the level of impurities in a batch component or a change in the composition of a recirculating water stream may cause a significant shift in zeta potential. In a poorly controlled situation, such changes can lead to different behavior on different days. In cases where a formulation must be made up fresh (as in the preparation of agricultural sprays), there may be problems with the formulation when using water supplies with varying salt composition.

Most process controllers are aware of the importance of maintaining control over the pH in oxide systems or systems involving proteins or weak organic acids, but *many do not realize that it is the zeta potential that must be controlled.*

pH can be used as a substitute control if nothing better is available, but it can sometimes be quite misleading, for the zeta usually depends on other parameters in addition to the pH. The pH is also a troublesome quantity to measure in a colloidal suspension, for the pH probes are rather delicate and are difficult to maintain.

Agilent 7020 ZetaProbe helps to pinpoint conditions for stable dispersions

In the case of electrostatically stabilized suspensions, the zeta potential provides a measure of the repulsive force between the particles. A zeta potential of at least 25 mV (positive or negative) is normally required to achieve a reasonably stable dispersion.

In Figure 1, we show Agilent 7020 ZetaProbe measurements of zeta as a function of pH for alumina, titania, and silica particles. The suspension of silica particles will be stable above pH 4, the alumina will be stable below pH 8, and the titania will be stable at about 2 pH units away from the isoelectric point of 6. From these titration curves, it is easy to determine the required pH range to make either stable or aggregated suspensions. Note that these curves depend on other factors, such as the concentration and type of the suspending electrolyte. Thus, there is no general rule for the pH range required for stability; the zeta curve for each suspension must be measured individually.

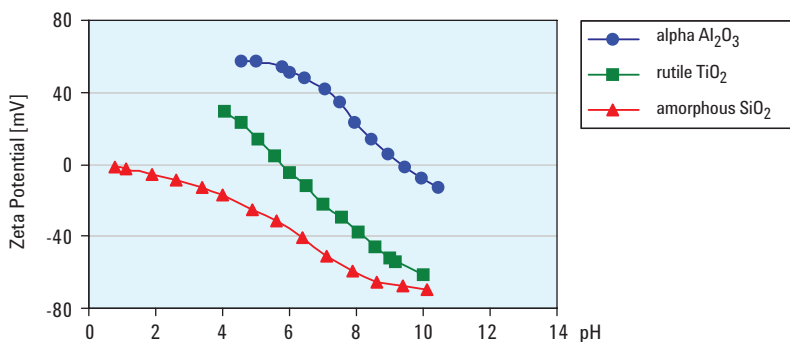


Figure 1. These titration curves show zeta potential versus pH for three metal oxides, and illustrate how the ZetaProbe can be used to determine the pH range where the zeta potential is large enough to produce stable suspensions.

Another use of zeta is in monitoring required levels of dispersant. Usually the dispersant is added until the particle surfaces are completely covered, and this occurs when the zeta potential levels off as a function of added dose. This is illustrated in Figure 2 for the case of a polyelectrolyte dispersant, Darvan C, added to an alumina suspension. In this example, the zeta potential has leveled off after about 2.5 mL of polyelectrolyte, so there would be no point in adding more Darvan C than this.

Even in the case when nonionic components are used for controlling dispersion, the zeta is usually reduced as these molecules adsorb, and so zeta measurements can be used to monitor the amount required for surface coverage. Reference [1] contains a number of excellent examples of the use of zeta for controlling levels of both ionic and nonionic dispersants.

ZetaProbe provides significant advantages over other methods

Since it is the zeta potential that actually determines the state of aggregation or dispersion in many systems, it is obvious that a direct and continuous measure of zeta potential would be the ideal way of controlling those industrial process streams. The problem in the past has been the difficulty of obtaining reliable measurements of the zeta potential of the particles in a suspension. Nearly all the other devices for measuring zeta rely on the traditional optical methods for observing the particle motion in an applied electric field. They can only be used effectively on very dilute suspensions. The dilution process takes time and it often changes the zeta potential.

This problem has been solved with the advent of the ZetaProbe. This device can be inserted into a colloidal suspension and within a few seconds can give a reading of the zeta potential that is both reproducible and reliable. No longer is it necessary to dilute the sample before measurement. The ZetaProbe can measure zeta in suspensions of almost any concentration greater than about 0.5% solids. Results are routinely obtained on emulsions up to 60% by volume.

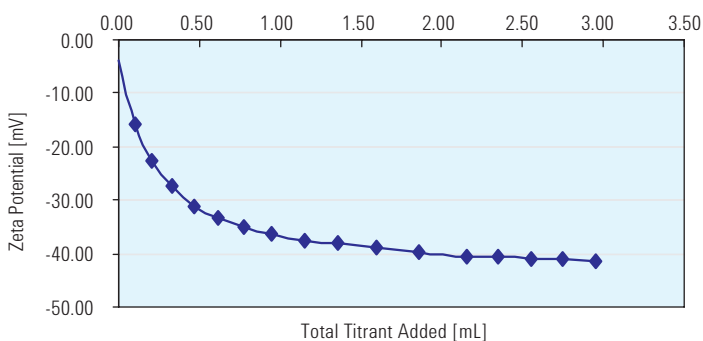


Figure 2. ZetaProbe measurement of zeta potential helps to determine the optimum dispersant dose.

Since the particles or droplets in a concentrated suspension have a large surface area, the relative effect of contamination is minimized, and the resulting ZetaProbe measurement is very robust. With other techniques that require sample dilution, contaminants are spread across a smaller particle surface area, which can lead to large errors in the measurement of zeta potential.

The ZetaProbe delivers consistent, dependable results that indicate true changes in colloids rather than instrument artifacts. With the optical procedures, one makes measurements on a small number of individual particles and seeks some sort of average value of zeta. Even with the light scattering methods, the number of particles that are sampled is relatively small. In the ZetaProbe, the measurement averages the effects of many billions of particles. Results on the same colloid are remarkably consistent from sample to sample, batch to batch, and day to day. Thus, any variations in the measured zeta indicate a real physical change in the colloid and not an instrument artifact.

Unlike other electroacoustic devices, with ZetaProbe there is no need to estimate the particle size by some additional measurement and hope you have the right particle size to make a sensible zeta calculation. The ZetaProbe is able to make an adequate estimate of the effective size and handles the entire calculation. This estimate is made using our patented multifrequency electroacoustic technique. The other electroacoustic devices cannot make such measurements because it would violate our patent and for this reason, they cannot estimate particle size.

With the ZetaProbe, the metal electrodes through which the field is applied are resistant to chemicals and abrasives, and the only other materials that come in contact with the suspension are highly chemically resistant polymers. Maintenance is minimal, the measurement time is around thirty seconds, and the results are extremely reliable.

Accessories help to customize the ZetaProbe for the application at hand. For example, the suspension can be stirred continuously and quite vigorously during the measurement, or it can be pumped in a flow loop to allow on-line simulation studies.

The ZetaProbe comes with computer-controlled syringes to allow titration with reagents like acids and bases, or with surfactant or dispersant solutions. This is one of the great strengths of the device. A reproducible and reliable plot of the zeta potential as a function of pH or additive dose can readily be obtained in a matter of minutes (limited essentially by the speed of equilibration of the particle surface with the bulk solution). This capability speeds process optimization.

Conclusion: a rapid, robust instrument to control particle aggregation

Many industrial processes require that colloidal particles be either aggregated or dispersed, but control of these processes is challenging because the degree of aggregation can be affected by small changes in chemistry of the dispersed system. Zeta potential can be used for controlling aggregation, for it provides a measure of the interparticle electrostatic repulsive force and the degree of adsorption of polymeric dispersant on the particle surface. The Agilent 7020 ZetaProbe provides reliable, reproducible measurements of zeta potential in undiluted colloidal suspensions. Because it requires no sample dilution and delivers repeatable readings in seconds, it is the ideal instrument for direct and continuous measurement of zeta potential in industrial process streams.

Reference

1. Greenwood, R. (2003) "Review of the measurement of zeta potentials in concentrated aqueous suspensions using electroacoustics," *Advances in Colloid and Interface Science* **106**, 55-81.

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