

focus on Microscopy & Microtechnology

New ISO Standards for Zeta Potential Analysis

Mark Bumiller, Horiba Scientific

Zeta potential is a measure of the charge on a particle surface in a specific liquid medium. With growing interest in nanotechnology and protein research, zeta potential analysis has become an increasingly important analytical technique. Since few chemists possess an extensive background in zeta potential theory or practice, an ISO working group was formed to create new several new standards on this subject. These new ISO standards [1, 2] provide excellent background material and advice to chemists new to the analysis of zeta potential.

What is zeta potential?

Particle surfaces pick up an electric charge due to several phenomenon including ionisation, ion adsorption, and ion dissolution. The charge on the surface of a particle influences the ionic environment in the region close to the particle surface. This ionic environment is typically described using a double layer model – the Stern layer of ions firmly attached adjacent to the particle surface, and the diffuse layer further away from the particle surface, but still attracted to the particle such that these ions will move with the particle. Beyond the double layer the ions are in equilibrium with the solution. The boundary between the electric double layer and the ions in equilibrium in the solution is called the slipping plane, as shown in *Figure 1*. Zeta potential is defined as the potential measured in mV at the slipping plane distance from the particle surface.

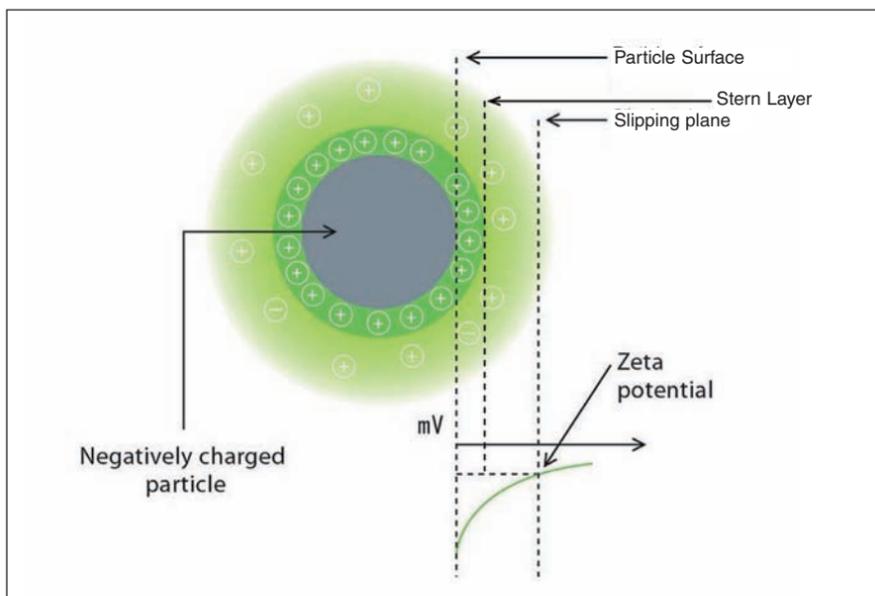


Figure 1. Zeta potential definition

How is it measured?

There are microscopic, optical and acoustic techniques for measuring the zeta potential of charged particles. Optical techniques are typically based on electrophoretic light scattering and acoustic techniques are based on either electrokinetic sonic amplitude (ESA) or colloid vibration current (CVI). This article will focus on the more popular electrophoretic light scattering technique.

Most zeta potential measurements are fairly easy in practice. A small quantity of sample is injected into a cell containing two electrodes that are used to create an induced electric field. Once the electric field is applied the particles move toward either the anode or cathode depending on whether the surfaces are positively or negatively charged. The direction of the motion indicates positive vs. negative charge. The speed of the particle motion is used to calculate the magnitude of the charge. Factors influencing the particle motion include the temperature, viscosity, and dielectric constant of the dispersing medium, the electric field strength, and the zeta potential of the particles. The particle motion is measured using laser Doppler electrophoresis, basically detecting the Doppler shift from the particle motion as they pass through a laser beam within the applied electric field.

Equation 1 is used to calculate the electrophoretic mobility (μ) using the measured frequency shift (ω) and the applied electric field strength (E). The other variables include the refractive index of the medium (n) the laser wavelength λ , and the angular light scattering information contained in θ' .

$$\mu = \frac{\Delta\omega\lambda_0}{4\pi n E \sin(\frac{\theta'}{2})} \quad (1)$$

After the electrophoretic mobility is determined using equation 1, the zeta potential (ζ) is calculated using equation 2 where the other variables include the dielectric permittivity (ϵ) of the medium, the viscosity (η_0), and a function $f(\kappa r)$ that describes the relationship between the ratio of particle radius and the distance from the particle surface to the slipping plane.

$$\mu = \frac{2\zeta\epsilon}{3\eta_0} f(\kappa r) \quad (2)$$

Applications

There are many applications for the information derived from zeta potential measurements, the most common ones being related to predicting dispersion stability and determining the surface chemistry conditions that create a state of zero zeta potential – the iso-electric point (IEP).

Dispersion Stability

Solid in liquid suspensions and oil in water emulsions can be stabilised by increasing the charge on the particle surfaces, increasing the repulsion forces that inhibit aggregation. Many chemists working in new product formulation use zeta potential as a predictive value, altering surface chemistry conditions to maximise zeta potential. Chemistry conditions that can be altered to manipulate the zeta potential for a formulation include pH, salt concentration, type of surfactant and surfactant concentration. Higher zeta potential magnitudes (independent of whether the sign is positive or negative) typically indicate that a given chemical formulation will be more stable over time.

Conversely, in other applications the goal is to find the conditions that lead to near zero zeta potential. This is where the system will likely destabilise and aggregate, making it easier to separate the particles through processes such as filtration. A typical example of this approach is water treatment where coagulant concentration as a function of zeta potential is studied to find the optimum conditions to promote aggregation prior to filtration.

Figure 2 shows a plot of zeta potential as a function of coagulant (alum and gypsum) concentration from a study looking for ideal conditions to filter clay from a wastewater stream.

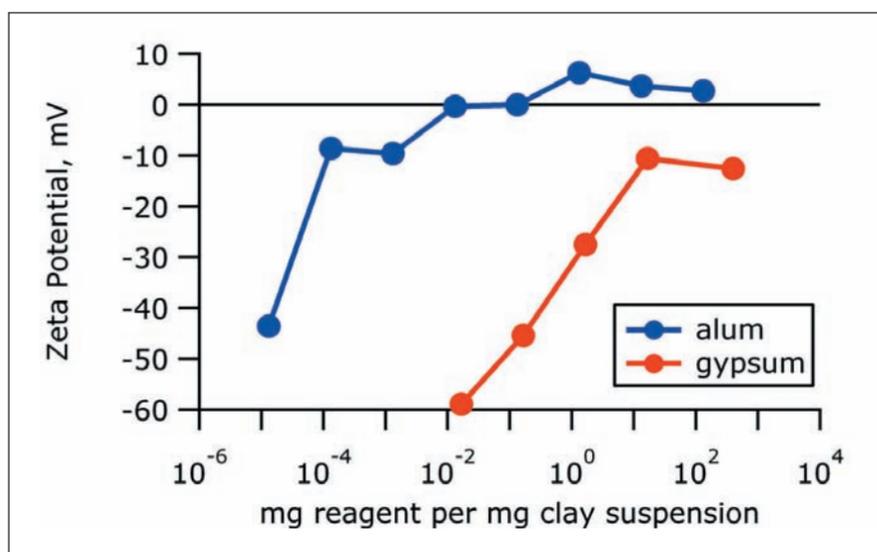


Figure 2. Coagulant concentration vs. zeta potential

IEP Determination

Most IEP studies investigate the change in zeta potential as a function of pH, but other chemistry changes such as surfactant concentration are also examined. Figure 3 shows an IEP study for the protein lysozyme, particle size approximately 3.5nm. The pH was altered using NaOH as the base and HCl as the acid. As the sample passed through the IEP the physical aggregation of the protein was visible to the eye as the aggregate size increased.

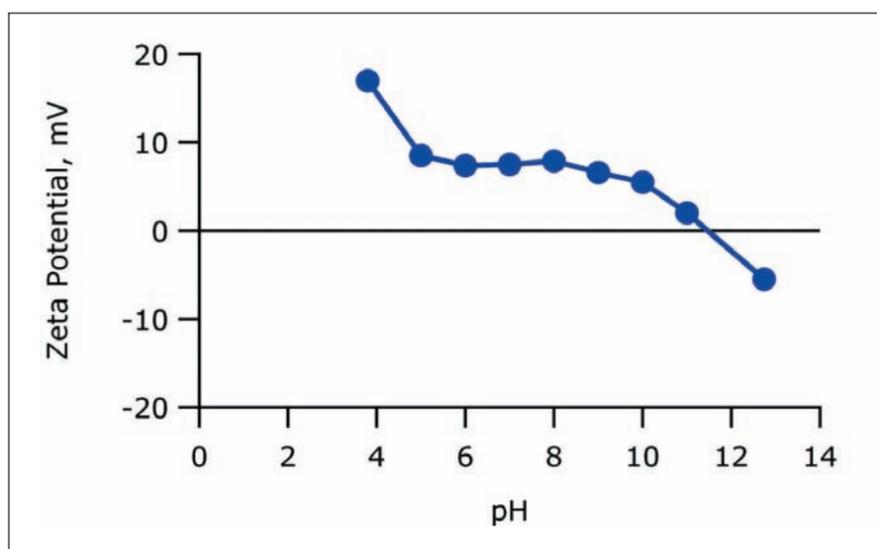


Figure 3. Iso-electric point (IEP) determination of lysozyme

Older zeta potential cells using gold coated electrodes suffered damage when measuring proteins like lysozyme due to Joule heating at the electrode surface. This made IEP measurements as shown in Figure 1 almost impossible because the operator was not sure when the cell became too damaged for accurate measurements.

The newest generation of zeta potential cells such as those supplied with the HORIBA SZ-100 system includes electrodes coated with a porous carbon layer that minimises damage by protein 'baking' on the surface, greatly extending the lifetime of the cell. Carbon coated electrodes improve data quality and drastically reduce the cost of ownership since the cells can now last for hundreds of measurements, depending on the sample.

Figure 4 shows over 800 zeta potential measurements of an emulsion using a single cell. Note that the change seen around measurement number 100 is due to the preparation of a new sample once it was realised how long this experiment would take.

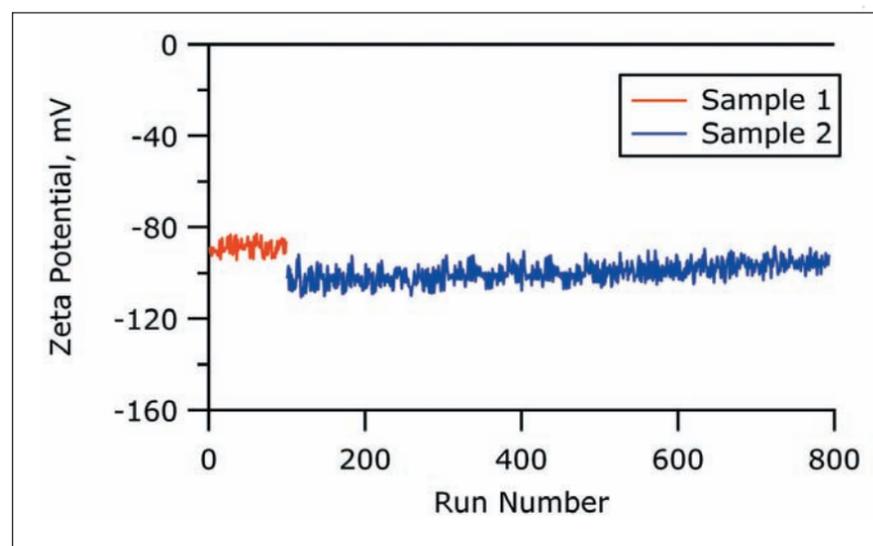


Figure 4. Zeta potential of an emulsion sample; 800 analyses with one cell

Guidance from ISO Standards

International Organization for Standardization (ISO) standards are useful for chemists new to an analytical technique because they provide information on the theory, use, and verification process for a given technique. Working group 17 within ISO TC24/SC 4, particle characterisation, recently completed the first 2 of three documents on methods for zeta potential determination; Part 1: Introduction, and Part 2: Optical Methods. Part 1 provides excellent background and theoretical reviews. Part 2 provides expert information on how the measurements are made, suggests best practices when using optical techniques, and discusses potential sources of error. A summary of useful guidance procedures are described below.

Dilution: Measurements without dilution are preferred whenever possible. Dilution for zeta potential measurements can be troublesome because zeta potential is not a property of the particles alone but also on the chemical equilibrium between particle surface and dispersing medium. Any alteration of the surface chemistry therefore affects the zeta potential. The worst possible approach is to dilute with DI water, which is almost certain to alter the surface chemistry. The ISO standard suggests diluting the sample using the so-called equilibrium dilution procedure, which uses the same liquid as in the original system as a diluent. This is typically performed by extracting the supernatant from the sample after either sedimentation or centrifugation.

Verification: All analytical instruments should undergo a verification process on a regular basis, and at least one a year. There is only one standard reference material for zeta potential available at this time, the NIST SRM 1980. This is a powder hematite sample that is not easily dispersed and is not very popular. The ISO standard acknowledges this, so users typically test their system with the sample supplied by the vendor. The system meets the requirements defined by the ISO standard if the following criteria are met after making three measurements of the reference material.

Repeatability (coefficient of variation) must be less than 10%
Accuracy of the mean value must be within 10% of the published value

Reproducibility can also be tested and the system meets the ISO standard requirements if three separate aliquots are analysed and the coefficient of variation for the mean value is less than 15%. Note that in the standard the reference values are stated in units of electrophoretic mobility, but most customers typically use the calculated zeta potential values.

Conclusions

Zeta potential is a growing analytical technique used in many industries for dispersion stability studies and IEP determination. The new ISO 13099 standards are helpful documents for chemists new to the technique or experienced users looking for best practice and verification procedure recommendations.

Note: All data presented in this article were analyzed on the HORIBA SZ-100 system.

References

- [1]. ISO 13099-1 Methods for Zeta Potential Determination - Part 1: Introduction.
- [2]. ISO 13099-1 Methods for Zeta Potential Determination - Part 2: Optical Methods




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