Jar testing, commonly used to calculate the amount of coagulant needed for suspended particles to settle in water, has its drawbacks. Incorporating zeta potential provides numerous advantages.

There are two bench-test methods that use zeta potential measurements; different situations determine the suitability of each method.

Measuring zeta potential has advanced as an effective testing method with expanded applications.

*Photo by Vincent Hart*
One of the main goals of surface water treatment is to remove suspended particles. Large particles in source waters typically settle easily, but colloidal particles (a few microns in size and smaller) are more affected by their negative charges, so when they collide, they don’t stick together or coagulate to a size at which gravity can take over.

Zeta potential provides a measure of the charge of particles in water, and its value indicates the ability of particles to “stick” when they collide. Zero or near-zero zeta potential values mean that the conditions are right for a “sticky” particle that can grow and ultimately settle.

In water treatment, coagulants are typically used to provide a positive charge that neutralizes negatively charged raw water particles. The following are examples of coagulants:

- Aluminum sulfate
- Aluminum chlorohydrate
- Polyaluminum chloride
- Ferric chloride
- Ferric sulfate
- Low-molecular-weight organic cationic polymers (i.e., polydiallyldimethylammonium chloride, commonly referred to as PolyDADMAC)

In addition to these conventional coagulants, acids can also act as coagulants through the addition of positively charged hydrogen ions.

Zeta potential is the electric potential difference between the water and the layer around a particle. It is measured in terms of millivolts (mV). An illustration of charge neutralization is shown in Figure 1.

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Challenges of Jar Testing
Historically, jar tests have been used by operators to determine the coagulant dose needed to neutralize the charge of raw water particles so that they settle. However, certain challenges are associated with jar testing:

- Jar tests take a long time to perform (batchwise, 30–45 minutes of flocculation time and five to 30 minutes of settling plus collection and analysis).
- There is no single accepted jar test protocol, and different approaches are common but make comparisons between sites difficult.
- Settled turbidity is not always a good indicator of filterability, especially for raw water with low turbidity.

Unless jar tests are performed frequently and proficiently, operators may not have strong faith in the test results.

Regarding the third point, the relative insignificance of settled water turbidity as an indicator of filterability was demonstrated through full-scale testing in Texas by the City of Odessa. As shown in Figure 2, the city’s water treatment plant (WTP) was below the combined filtered water turbidity standard, represented by the green line in the figure, at a level of 0.30 ntu; however, Odessa’s desired level (<0.10 ntu) was not often met. The initial zeta potential was measured at –11 mV in mid-October, so the coagulant dose was increased until a zeta potential of –4 mV was achieved. The increased coagulant dose resulted in a more charge-neutral zeta potential measurement, and the filtered water turbidity dropped below the city’s 0.10 ntu goal. Throughout this process, the settled water turbidity was not a good surrogate measure for the optimal coagulant dose.

Zeta Titration
Regarding the amount of time jar testing takes, operators often comment that by the time they are done with a jar test, the water quality has changed and the new dose is then incorrect. Also, unless jar tests are performed frequently and proficiently, operators may not have strong faith in the test results.

In a pinch, a simple but fast jar test method that incorporates zeta potential, referred to here as method 1, proceeds as follows:

- Start the jar test apparatus at high speed (rapid mix)
- Add coagulant
- Wait 30 seconds and sample
- Run zeta measurement
- Dump the water and start this procedure over (with a higher or lower dose, depending on the zeta measurement)
Although this method is faster than a conventional jar test, it is still slow when operators need to make quick decisions—e.g., with flashy water. A new method for bench testing called zeta titration, referred to here as method 2, consists of the following steps:
- Start the jar test apparatus at high speed (rapid mix)
- Add coagulant
- Wait 30 seconds and sample
- Measure zeta potential
- Continue to run the jar test apparatus at high speed
- If not at target zeta potential, add more coagulant
- Wait 30 seconds and sample
- Check new zeta measurement

This procedure continues until the operator reaches the desired zeta potential. Once the appropriate dose is determined, a confirmation jar test with the entire coagulant dose can be added to make sure the zeta titration matches.

It should be noted that the zeta titration method does not work well for every water. There are some waters with high levels of very reactive organics (high specific ultraviolet absorbance) for which zeta titration will not provide applicable values because the zeta potential changes rapidly after coagulant addition. In these situations, an online zeta meter, or method 1, is more appropriate. This scenario is easy to detect by comparing the zeta titration determined dose with the confirmation jar test (jar test with the entire coagulant dose added all at once). If they are different, the organics should be considered very reactive, and zeta titration should not be used.

It should also be noted that high-intensity mixing during method 2 is required to keep particles from agglomerating.

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**Illustration of Charge Neutralization**

Coagulant/Polymer/Acid

Collisions result in particles “bouncing off” each other

A zeta meter measures the magnitude of the repulsive forces

Collisions result in particles sticking to each other and surfaces (like filter media)

**Figure 1**

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**Odessa, Texas: Relative Insignificance of Settled Water Turbidity**

- Alum dose
- Settled water turbidity
- Finished water turbidity

**Figure 2**
Agglomeration reduces the number of neutralized particles and affects the zeta measurement because zeta potential measures the average charge of the particles in the water. The zeta potential is not affected if the particle is small or large; it is measured the same. Agglomeration can produce artificially negative zeta potential measurements. For example, a zeta titration (method 2) is shown in Figure 3 in which aluminum sulfate doses in 10-mg/L increments were added to the jar until a target of -2 mV was achieved. After a drought/fire/flood event in 2017, zeta titration results on February 14 at the Fairbairn WTP in Sacramento, Calif., showed that the coagulant demand was five times higher than the historical coagulant dose.

**Resolving Backwash Recycle**

The possible benefits of measuring zeta potential extend beyond coagulant addition, as it can sometimes help explain and address water quality events. The operations staff at Parker Water and Sanitation District in Parker, Colo., recognized that returning clarified filter backwash to the front of the plant affected the overall treatment process. Using zeta titration, the coagulant demand of the highly charged backwash recycle stream was quantified at ~60 mg/L. Operations staff were then able to adjust the total coagulant dose to compensate for the contribution from the recycle stream, as shown in Figure 4, which resulted in reduced membrane fouling.

**Organic Materials**

Technological improvements in measuring zeta potential have expanded its efficacy to include water with high-molecular-weight organic material. Historically, predictions based on zeta potential for these waters have underpredicted coagulant demand. The recent shift in the market from a microscope-based to a laser-based approach has improved reliability and repeatability and has allowed for smaller-sized particles to be analyzed. These improvements have allowed the target of zeta potential to include high-molecular-weight organics as well as particles. On a mass basis, the charge
of organic material found in water can be up to 15 times higher than the charge of silt/sand particles—this means that organics can exert high coagulant demands and also that raw water turbidity is not always a reliable indicator of coagulant demand.

For utilities targeting removal of organic matter that is amenable to coagulation, using zeta potential can optimize the process. Although it may be a treatment goal, organics removal must be balanced with producing filterable particles. An example of this is shown in Figure 5, in which removal of total organic carbon (TOC) reached a point of diminishing returns when the zeta potential was close to neutral.

Recognizing that the charge on organic matter plays a role in coagulant demand can be critical to a utility’s success in addressing multiple treatment goals. Organics solubility changes with pH, potentially resulting in more organics removal at lower pH during coagulation. Colorado Springs Utilities (Colorado Springs, Colo.) had historically determined that coagulation with polyaluminum chloride was not effective at removing organic matter in its source water, making it difficult to meet the regulatory TOC removal requirements. On the basis of jar tests of the raw water, the utility determined that ferric sulfate provided much better organic carbon removal, so it constructed a ferric sulfate feed system that was used in combination with a polyaluminum chloride feed system to “dial in” the right organics removal while balancing chemical costs (settled water pH adjustment) and solids production. The utility was concerned about maintaining coagulant control for good particle removal, so zeta potential testing was included in the test protocol.

Zeta titrations were completed separately for polyaluminum chloride (results shown in Figure 6) and ferric sulfate (Figure 7). These titrations show that as ferric sulfate was added, the characteristics of the organics changed, resulting in much higher charge demand and
subsequently much higher organics removal. It appears that as the coagulation pH dropped, the organics became insoluble, resulting in a charge demand. The results of the jar testing based on zeta potential showed a polyaluminum chloride demand of 15.8 mg/L (as product), with a coagulation pH of 7.65 and a corresponding TOC removal of 5%. At the same zeta potential, the ferric sulfate test showed a ferric sulfate demand of 107 mg/L (as ferric sulfate), with a coagulation pH of 5.83 and a corresponding TOC removal of 67%. Tracking zeta potential allowed the utility to achieve the goals of organics and turbidity removal while balancing chemical costs and solids production (the ferric sulfate, because of the high doses, costs more, and the higher doses produce more solids). Colorado Springs currently adds both polyaluminum chloride and ferric sulfate in different ratios to maintain this balance.

**Cationic Polymers**

One of the challenges with cationic polymers and their procurement is that, from a charge perspective, all cationic polymers are not created equal. From zeta potential testing around the United States, and as shown at the Binney WTP in Aurora, Colo., where zeta potential titrations were used to establish the effective charge neutralization for different polymers (Figure 8), we have found that cationic polymers have a range of charge equivalents, and for 1 mg/L of cationic polymer, this can be from 1 mg/L of aluminum sulfate up to 26 mg/L of ferric sulfate (all determined by comparing zeta titrations—ferric sulfate is typically 50%–75% of the required dose of aluminum sulfate). This broad range of charges makes polymer comparisons and bidding difficult. One proposed solution is to perform zeta potential titrations on the different polymers with the actual source water, thereby providing a bidding factor that levels the playing field. For example, in Figure 8, the Polymer 6 would have a bidding factor of 0.5, while...
Polymer 4 would have a bidding factor of 1.0. This compensates for the fact that Polymer 4 requires a dose that is twice as high as the Polymer 6 to achieve the same charge neutralization.

**What Is the Right Zeta Potential Target?**

After conducting tests on a wide range of utility source waters, it was noticed that the zeta potential target also varied, ranging from +3 to –11.5 mV, as shown in Figure 9. As data were gathered, we recognized two trends:

- Utilities that used iron-based coagulants had lower zeta targets than utilities that used aluminum-based coagulants.
- The stronger the preoxidant, the lower the zeta target.

From previous research—i.e., The Water Research Foundation’s 2004 study, *Using Oxidants to Enhance Filter Performance*, it is understood that metal hydroxide (aluminum or iron-based coagulants) with absorbed natural organic matter results in reduced attachment efficiency to filter media. From this research, it was also found that oxidation reduces particle stability as a result of interactions with and changes to the natural organic matter coating on particles. These phenomena likely influence the zeta potential that corresponds with good filtered-water quality, although more research is needed to identify the influence of coagulant type and preoxidation on zeta potential and filterability.

**Benefits of Measuring Zeta Potential**

Incorporating measurement of zeta potential at a WTP provides the following advantages:

- It is quick measure of particle charge and destabilization conditions.
- It is faster and more reliable than jar testing to predict filtered water quality; it doesn’t rely on settled water turbidity.
- It helps with chemical procurement and testing.
- Within coagulation and filtration optimization, it can account for preoxidation.
- It can help when balancing organics and turbidity removal.

**Variations in Zeta Potential Targets**

![Variations in Zeta Potential Targets](image)

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