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Charge-Related Measurements – A Reappraisal.

Part 1. Streaming Current

A 1995 article in this magazine raised concerns about the use and interpretation of two kinds of measurements that are being carried out in paper mills to evaluate the electrical charges at surfaces in fibre slurries.

This article relates to the streaming current method, which is widely used for endpoint detection when testing the charge demand of whitewater or filtrate samples from fibre stock.

Although there is still some truth in the statement that the “streaming current detector has no established theoretical basis,” subsequent work has helped to define ranges of experimental conditions within which the test gives reliable results. Also, some specific sources of interference have become better understood.

In a 1995 article in this journal Jaycock⁽¹⁾ expressed concerns about the accuracy and interpretation of two types of charge-related measurements that have become increasingly common in papermaking applications, namely, the streaming current (SC) and the streaming potential (SP) methods.

In the intervening years there does not appear to have been any attempt either to support or to refute those cautionary statements. Rather, there has been increasing use in the paper industry of the test methods that Jaycock cautioned us about.⁽²⁻¹⁰⁾ The present article deals with SC measurements. A companion article will deal with a second type of measurement discussed in the same article.⁽¹¹⁾

It seems that there are two ways in which one could view the set of circumstances described in the first paragraph.

i) On the one hand, maybe the increased use of SC devices – even without considering other factors – is sufficient proof that the method must be providing practical value to the users. Otherwise, the thinking goes, cost conscious managers of paper companies and chemical supply companies would not continue to invest in that technology.

ii) Another way to view the situation is to assume that Jaycock’s worst fears were correct, and that much of the data obtained by SC measurements in paper mills over the intervening years have been either inaccurate or misleading.

Fortunately, due to some ongoing research during the period between 1995 and now, we are now in a better position to answer some of the concerns raised by in the 1995 article.⁽¹⁾ Some of that continued work was conducted by us North Carolina State University⁽¹²⁻¹⁴⁾ and some was done by others.⁽¹⁵⁻²⁰⁾

The purpose of this review article is to re-examine the main concerns raised by Jaycock and to give qualified support for continued efforts to implement SC measurements, both in the laboratory and online in paper machine systems. The reason that the support needs to be “qualified” is that

(a) various factors can interfere with the analyses, and

(b) one should not stray too far outside of the ranges of conditions under which the methods can be expected to give reliable answers.

(c) In addition to these two reasons, there are concerns about the interpretation of SC data obtained in paper mills.

To start, it is worth quoting Jaycock’s statements about the SC method in the Conclusions section of the article:⁽¹⁾

“The piston type streaming current detector has no established theoretical basis! It is assumed that the measured potential is related to the zeta potential, and that the adsorbed layers responsible for the generation of this potential are characteristic of the papermaking system as a whole, being in equilibrium with it. There are doubts about the validity of both of these assumptions.”

In addition, Jaycock advocated use of microelectrophoresis^(10,21) as the best way to obtain zeta potential data for a papermaking furnish.

To address Jaycock’s concerns, it is first necessary to describe the main equipment and a little bit about the procedure of analysis used in a typical papermaking application.

The streaming current (SC) method

Figure 1 (next page) is a schematic diagram of a typical SC device. It is worth bearing in mind that different brands of equipment can be quite different in appearance, despite their sharing the same basic operating principles. Suppliers of SC equipment, in different forms, include Rank Brothers, Müttek, Chemtrac, and Milton-Roy companies.

As noted by others,^(1,22-24) the main wetted parts of the SC device consist of a plastic piston that moves in a sinusoidal manner back and forth within a dead-ended plastic cylinder, usually at a frequency of about 4 Hz. Because the gap between the piston and cylinder is narrow (often less than 1 mm) compared to the diameter of the piston (often about 12 mm), the motion of the piston gives

rise to a more rapid movement of aqueous fluid back and forth within the annulus.

Also, there are two metal electrodes built into the cylinder wall at different axial positions. The probes are connected to an electronic system capable of rectifying and smoothing any electrical signal that results from the reciprocating motion.

Except in some unusual cases,⁽²⁵⁾ the origin of most of the electrical signal that is observed with SC devices arises due to the electrically charged nature of the plastic surfaces, with the understanding that the word "surface" includes anything that becomes adsorbed onto the plastic itself.

Many SC devices are made with poly-tetrafluoroethylene (PTFE), a contamination-resistant substance which, if absolutely pure, would have no surface charge of its own. Practical use of the SC method, especially in the case of paper machine applications, requires that the plastic becomes charged due to the adsorption of polyelectrolytes and colloidal materials from the sample.

The user makes an implicit assumption that any excess of charged materials existing in the sample will determine the sign of the electrical current signal that is generated.

Setting aside, for the moment, the question about whether the water-loving, charged materials present in paper mill water samples actually adsorb to a significant extent onto the low-energy plastic surfaces, the reciprocating flow of aqueous solution past a charged surface gives rise to an electrical signal due to the presence of counter-ions.⁽¹⁵⁻²⁰⁾

For example, if the net charge of the PTFE, with its covering of colloidal materials, is negative, then there needs to be an equal and opposite excess of positively charged ions in the solution phase adjacent to the surface.

These "extra" ionic charges will exist very near to the surface in a region that is often called the "double layer." The average distribution of counter-ion charges in the double layer depends on

- (a) attraction to the surface
- (b) random diffusion of the ions in all directions, and
- (c) screening of the electrostatic effects by salt ions.⁽²⁶⁻²⁸⁾

The movement of aqueous solution past the charged surface causes net movement of the counter-ions, especially in the "tail" of the counter-ion distribution lying farthest from the charged surface.

The most common use of SC devices in the paper mill has been to determine the cationic demand or anionic demand of samples of process water, usually in the absence of fibres.^(5-8,12,17) In other words, the device is used as the means of detecting the endpoint of a titration.

A solution of charged polymer is gradually added to a stirred aliquot of process water, and a "zero" reading on the SC device is taken as evidence that a sufficient amount of polymer solution has been added to the mixture to just neutralize any excess of electrical charge.

This excess is understood to exist at the surfaces of particles, very finely divided materials (i.e. "colloidal matter"), dissolved polyelectrolytes, and various surface-active molecules in the mixture, such as salts of resin acid molecules from the wood.⁽²⁹⁾

Theoretical limitations to the SC method

Before considering practical uses of SC tests, let's consider what Jaycock meant by saying that the SC method has "no theoretical basis".⁽¹⁾ To help justify these strong words, it is worth noting that typical raw output of an SC device does not have a simple, quantitative relationship to zeta potential. The inventor of the SC method used only a rudimentary theoretical approach to rationalize the observed output signals in terms of a zeta potential at the plastic surfaces of the piston and cylinder in the SC device.⁽²²⁾

Though there has been important progress more recently in quantifying the SC signal in ideal cases,⁽¹⁶⁻²⁰⁾ the calculation depends critically on the annular distance between the piston and cylinder. That distance is subject to change due to wear, a "ribbed" pattern of some SC pistons, and possible changes in alignment of the piston within the device.

Further support of the words "no theoretical basis" involves the fact that one is measuring an electronic quantity related to a coated PTFE surface, despite the fact that PTFE has a completely different surface character compared to that of the fibres, fine particles, or colloidal materials in a sample of process

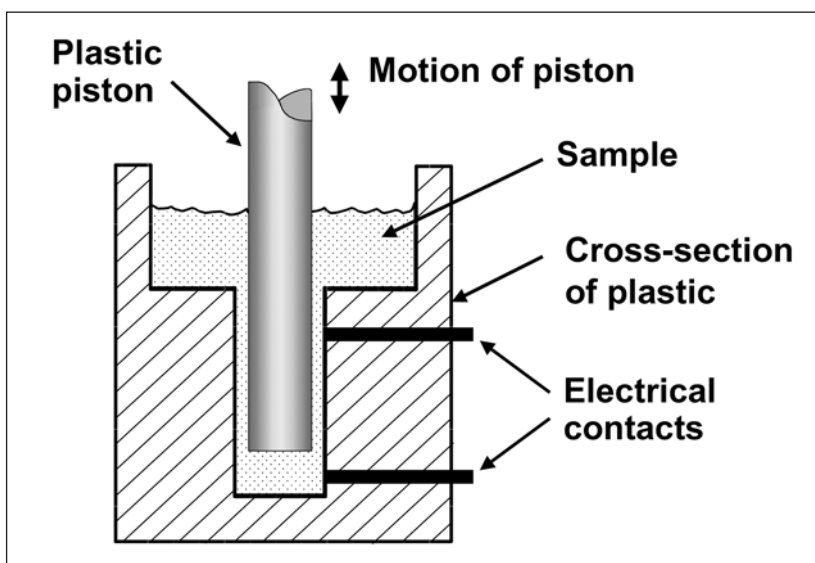


Figure 1 Schematic diagram of wetted parts of a common type of streaming current detector

water from a paper mill. After all, it takes a brave individual to place their trust in that the PTFE (i.e. Teflon®) surface becomes uniformly and consistently coated by the colloidal materials in the sample.

Ordinarily, if your goal is to evaluate zeta potential, then you ought to use some method other than SC. However, it is worth noting a few careful laboratory studies that show exceptions to this rule. By using relatively pure samples and repeated cleaning of the probe surfaces it is sometimes possible to achieve a high correlation between SC output vs. zeta potential values derived from microelectrophoresis.⁽¹⁵⁾

But don't try this in the paper mill! There is just too much variability in electrical conductivity, hardness, surfactant content, and other attributes of paper mill process water that are likely to throw off any correlation between SC measurements and zeta potential measurements.

In practice, some issues related to zeta potential often can be ignored, depending on how the SC equipment is used. The cited article⁽¹⁾ admits that SC measurements are mainly used for determining the endpoint of charge titrations – not for zeta potential. For instance, an article by Kaunonen and Springer⁽³⁰⁾ is cited, saying that “it is possible to use the SCD as a detector for cationic demand measurement.”

However, even those measurements involve an assumption that a SC value of zero corresponds to a condition of neutral zeta potential. Some important early work with the SC device, involving samples from papermaking fibre systems, showed cases where such an assumption can be quite inaccurate.⁽³¹⁾ Thus, there has been a need for follow-up tests to determine the range of validity of the SC method, even when it comes to charge titrations.

Streaming current – the range of reliability

For purposes of process control, it is often more important that a measurement be reproducible, regardless of whether the results can be described as quantitatively accurate. In the case of charge measurements, as long as the measured signal has a strong and reliable relationship to the added amount of a charged chemical, the signal can have value for controlling the flow of that chemical.

The usefulness of such a control strategy can be judged later, based on such factors as production efficiency, product quality measures, and opportunities to reduce chemical costs. The important question then becomes, “within what range of process conditions are SC titration results reproducible?”

To answer these concerns, starting in 1999 we set out to find out how SC titrations responded to increasing levels of salt. *Figure 2* shows some typical results, titrating a solution of a highly dilute polyvinylsulphate, potassium salt (PVSK) with poly-diallyldimethylammonium chloride (poly-DADMAC).⁽¹²⁾

Before describing the effect of salt, it is helpful first to consider what happens in the absence of salt, as represented by the lowest curve in the plot. As shown, the initial signal, before the addition of cationic titrant, was negative. The sign of charge is consistent with

(a) a low, but finite level of negatively charged sites on the plastic surface, due to impurities, and

(b) some adsorption of the PVSK. The fact that negatively charged PVSK adsorbs onto PVSK is readily apparent from other experiments showing an increase in the negative signal when the PVSK is first introduced.

The initial, horizontal portion of the titration curve in *Figure 2* usually is attributed to consumption of titrant molecules by an excess of anionic polymer in solution.

Since high-mass polyelectrolytes often exhibit “high affinity” adsorption behavior,⁽³²⁾ the fact that some polyelectrolyte complexes (PECs) are forming in the bulk phase does not necessarily imply a change in the amount of adsorbed anionic polymer. In other words, a reduction in the effective concentration of dissolved polymers in the bulk phase does not necessarily cause polymers at the plastic surface to come off.

The situation changes as the titration progresses far enough so that most of the polymer in the solution phase has been neutralized. Thereafter, the SC signal decreases more rapidly to zero. The decrease can be attributed to either

- (a) cationic titrant molecules adsorbing directly on the surface
- (b) cationic titrant molecules complexing with pre-adsorbed PVSK molecules, and
- (c) formation of PECs in the bulk phase, followed by their adsorption.

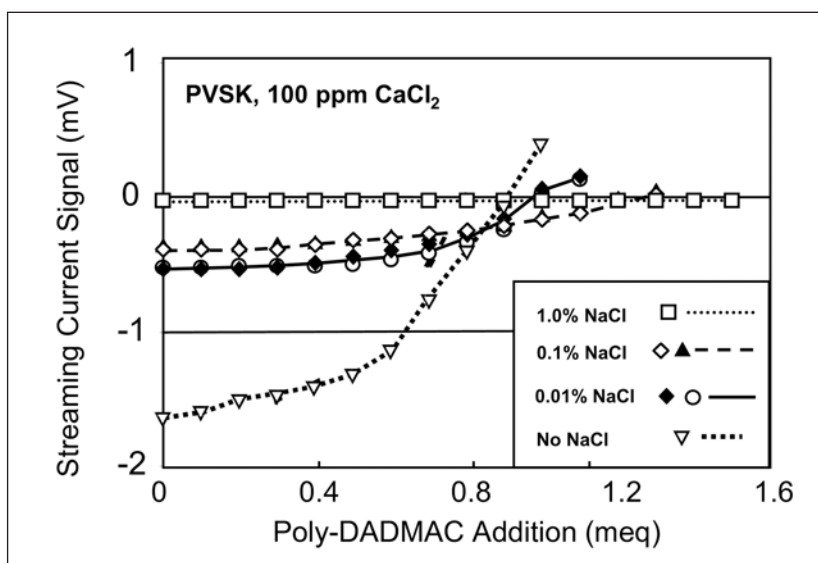


Figure 2 Effect of salt on results of titrating a solution of polyvinylsulphate potassium salt (PVSK) with poly-diallyldimethylammonium chloride (poly-DADMAC).

Surprisingly, there does not seem to have been any reported research as to which of these possible mechanisms tends to be most important. Partial support for mechanism (b), complexation of a cationic titrant with pre-adsorbed anionic polymer, comes from studies of PE multilayer adsorption.⁽³³⁻³⁵⁾ Either of the first two mechanisms (a or b) involving titrant molecules arriving individually at the surface can account for a reversal in the sign of charge, based on past work.^(32-33,36-37) In fact, it is reasonable to expect that more than both mechanisms occur simultaneously.

The addition of salt affects the SC signal in three ways, all of which can be observed in *Figure 2*, comparing the positions of the plotted lines. First, as shown by others,^(12,15,22,38) increased salt concentration depresses the initial signal. Second, salt causes a shift in the endpoint towards greater amounts of titrant. And third, at the highest level of salts considered, the device may be unable to detect any change in signal due to the addition of titrant.

Before attempting to explain any of these effects, it is worth considering the results of some similar experiments carried out with a different type of sample. *Figure 3* comes from an experiment in which the sample was a dilute solution of oxidized starch. In contrast to PVSK, for which every unit of the polymer has a negative charge, the oxidized starch sample had a charge content of only about 2%, based on repeat units of the polymer.

The most striking difference, when comparing these results to the case shown in *Figure 2*, is the different shape of the curves. The shape suggests that added titrant molecules are able to reach the probe surfaces even at the very beginning of the titration. Evidently, at least some of the poly-DADMAC molecules are able to adsorb onto the plastic surfaces of the device right from the start of the titration. Possibly the cationic polymer

adsorbs in the form of a polyelectrolyte complex, together with the oxidized starch.⁽³⁹⁻⁴⁰⁾

Another difference, when comparing *Figures 2 and 3*, is that the lower-charge polymer sample was even more susceptible to salt. *Figure 3* shows that a clear endpoint was not achieved in the case of oxidized starch if the salt content was 0.1% or higher, even if twice the stoichiometrically expected amount of titrant was added.⁽¹²⁾

Explaining the effects of salt on SC results

The effect of salt on the initial SC output, before addition of titrant, can be explained in terms of two effects. The first effect involves the thickness of the ionic double-layer at the plastic surface.

To explain this effect, it is worth noting that shear flow across a flat surface under predominantly laminar conditions within an SC device is expected to produce an approximately linear gradient of velocity with respect to distance from the surface.⁽²²⁾ That means that the flow velocity decreases as you move towards the surface. Meanwhile, the reciprocal of the Debye-Hückel parameter, representing an effective distance of counter-ions from the surface, decreases in proportion to the square-root of the ionic strength of the aqueous solution.⁽⁴¹⁾

In other words, the average distance of counter-ions from the surface decreases with increasing salt. Since the flows within an SC device are fixed by the dimensions of the device, the stroke length, and the frequency of piston motion, it follows that increasing salt ought to decrease the average velocity at which the counter-ions move relative to the plastic surface.

The second effect can be described as short-circuiting of the SC measurement system. This effect is related to the way in which conventional SC devices detect the electrical signal.⁽²²⁻²³⁾

At low levels of ionic strength, the current, which is induced by the ionic motions at the plastic surface, is allowed to complete a circuit between the two electrical probes, see *Figure 1*, by means of an external circuit. By designing the external circuit with a suitably low resistance, it is possible, in principle, to detect essentially all of the current that is produced by the motion of the piston.

However, as the electrical conductivity of the aqueous solution becomes higher and higher, with the addition of salt, a second route for current flow becomes increasingly important. Since the external device cannot detect the part of the current that flows through the liquid phase of the sample, the output signal is decreased.

The cause of the shift in titration endpoints, as illustrated by the results in *Figures 2 and 3*, was not known until recently.⁽¹³⁾ An

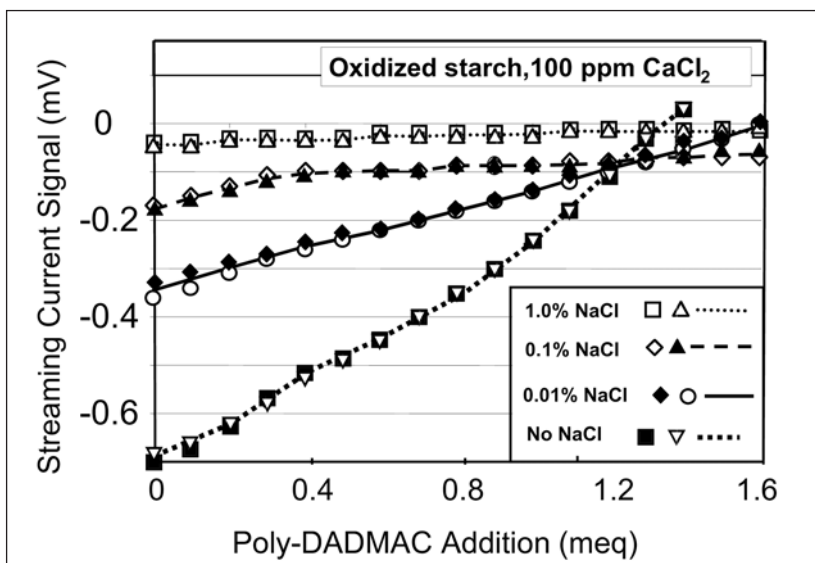


Figure 3 Effect of salt on results of SC titration of oxidised starch solution by poly-DADMAC

important clue as to the mechanism was the surprising finding that the titration results depended not only on salt concentration, but also on the direction in which the titration was carried out. Regardless of which charged polymer was used as the sample, and which was used as the titrant, the amount of titrant needed to reach the endpoint always increased with increasing concentration of salt.

A mechanism to explain such results is illustrated in *Figure 4*, in which the dark lines represent the polymer used as the “sample” and the light-shaded lines represent the titrant, which was added gradually as a solution to a solution of the sample. The idea is that, at the endpoint of a SC titration, the sample mixture contains charge-stabilized polyelectrolyte complexes. As shown in the figure, each such complex has an excess of titrant molecules on its outer surface.

Supporting evidence for this mechanism was obtained by microelectrophoresis and turbidity tests.⁽¹³⁾ The results are also consistent with some recent theoretical and experimental work by others.⁽³³⁻³⁵⁾ It is worth noting that such deviations from 1:1 stoichiometry, as well as problems related to indistinct titration endpoints, usually can be minimized by diluting all of the samples with a fixed ratio, e.g. 10:1, of distilled water so that the conductivities of the samples are well below 1000 $\mu\text{S}/\text{cm}$ during the titrations.⁽¹²⁻¹³⁾

How Al ions affect SC measurements

St. John and Gallagher⁽⁴²⁾ used the word “interference” to describe the effect of aluminum ions on the results of certain charge titrations. The word “interference” suggests unpredictability. Experiments were carried out to find out if the same word is justified

when aluminum ions are present during SC titrations.

Surprisingly, the experimental results showed that, under certain conditions of NaOH addition, there was a fixed ratio between the amount of soluble aluminum and the amount of PVSK titrant required to reach the SC endpoint.^(14,43) In other words, there was a stoichiometric relationship.

The observed stoichiometry was consistent with one-to-one interactions between the electrical charges of PVSK and the $[\text{AlO}_4\text{Al}_2(\text{OH})_4(\text{H}_2\text{O})_{12}]^{7+}$ ion, which in the scientific literature is sometimes called the Al_{13} ion.⁽⁴⁴⁻⁴⁵⁾ By contrast, the SC titration results showed no evidence of interaction of Al species with PVSK under conditions of pH where the Al_{13} ion is not expected to exist.

In principle, it may be possible to explain effects of aluminum ions in quantitative terms, by calculating the amount of different aluminum species likely to be present at different pH values and aluminum concentrations.⁽⁴⁶⁾ However, the practical reality is that aluminum chemistry is complicated, especially after aluminum compounds are added to papermaking furnish.

In that sense, interference is a good word to describe the practical effect of aluminum compounds on SC measurements in the paper mill. For example, results of SC tests carried out in papermaking systems to which alum has been added are likely to be affected greatly by the concentration of aluminum ions, as well as by the pH at which the set is conducted.

Effects of solid particles

Near the beginning of this article it was noted that double-layer effects at the plastic surfaces may not be the only significant contribution to observed SC signals in all cases. In fact, one can expect a second, little-known contribution to observed SC signals if the sample contains solids particles that differ greatly in density from the aqueous solution.^(25,47)

For example, a strong SC signal is observed if one places a suspension of filler particles in the device.^(15,48) Though the resulting “particle charge” signal is sometimes attributed to temporary or lasting attachment of particles to the plastic surfaces of the device,^(1,15,17,22-23,49-51) it is not necessary to assume that such attachment takes place.

Rather, a contribution to the SC signal also can be explained in terms of an inertial effect. The idea is that the momentum of dense particles, for instance, will cause them to lag behind the reciprocating motion of the surrounding fluid. Since each particle is surrounded by a loose atmosphere of counterions, the relative motion will produce a net current.

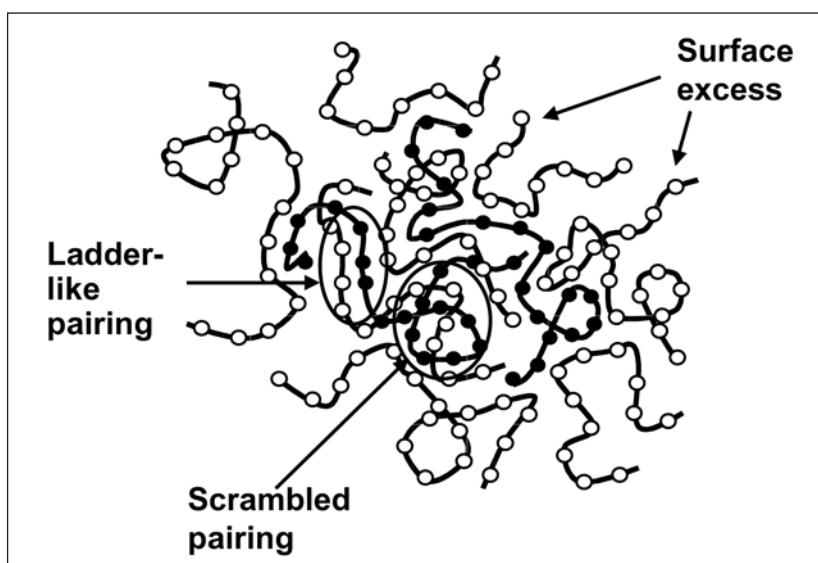


Figure 4 Schematic diagram of a polyelectrolyte complex that is stabilized by the presence of an adsorbed excess of the titrant.

Essentially the same mechanism has been used to explain a phenomenon known as sedimentation potential.⁽⁵²⁾ It is fortunate for us that this inertial contribution to SC signals happens to be in the same direction as the main signal that is most often described.⁽²⁵⁾

Conclusions

1. Recent work supports continued implementation of streaming current (SC) tests as a means of determining endpoints of charge demand titrations. Useful and reliable information can be obtained, despite the fact that the SC output often is poorly correlated to more fundamental quantities such as zeta potential.

2. High levels of electrical conductivity should be avoided when running routine charge evaluations with the SC method. For instance, one can adopt a standard practice of diluting certain samples with a ten-to-one ratio of high-quality distilled water, and then multiplying the resulting cationic demand by a factor of ten.⁽¹²⁾

3. One can expect results of SC titrations to be affected by various "interferences". The key to understanding such effects is to recognize that there is a wide range of complexing ability between sample components and the types of polyelectrolyte titrants used in SC tests. For instance, the Al³⁺ cation interacts only very weakly with PVSK titrant. On the other hand, an oligomeric form of the aluminum ion, as present in poly-aluminum chloride formulations or resulting from hydrolysis of Al³⁺ ions in papermaker's alum, may interact strongly with PVSK giving a sharp endpoint to an SC titration.

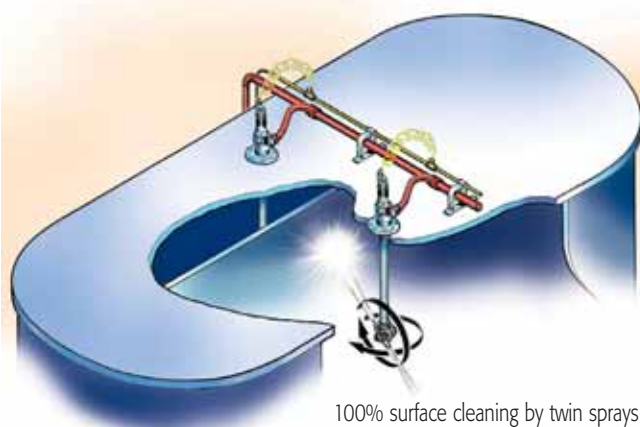
4. Further research is still needed concerning the origin and magnitude of SC signals under different experimental situations.

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