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# Accurate charge-related measurements of samples from the wet-end: Testing at low electrical conductivity

*Modest changes in testing procedures can improve the trustworthiness of charge-related measurements at the wet-end. This article makes the case for implementing such changes broadly within our industry, since improved monitoring and control has the potential to reduce chemical costs and make the PM run more uniformly and efficiently.*

*Recent findings suggest that substantial advantages can be achieved by reducing the salt content of samples of wet-end stock, white water, and similar samples before carrying out tests related to charge.*

*This paper provides modifications to streaming current (SC) titration procedures and fibre-pad streaming potential (SP) procedures. The SC method is most often used for cationic demand titration endpoint determination, both in the lab and when using online monitoring equipment. The fibre-pad SP method is most often used for estimating the zeta potential of fibre surfaces, especially for product development and for troubleshooting.*

*Papermakers use fibre-pad SP tests when they want to know about electrostatic forces at the outside surfaces of the fibres. Such information can be especially helpful during product development and troubleshooting and for the optimization of retention and dewatering*

Paper technologists, when they set out to evaluate various characteristics of stock suspensions, have an understandable reluctance to alter the sample in any way. Recent findings, however, suggest that substantial advantages can be achieved by reducing the salt content of wet-end stock, white water, and similar samples before carrying out certain tests related to charge.

But what is charge, and why does it matter? Charge is a fundamental property of cellulosic fibres. The surfaces of typical wood-derived fibres can be described as “acidic,” meaning that  $H^+$  ions are released into solution when the fibres are placed into neutral water. By this process the fibre surfaces acquire a negative net charge. The acid groups are especially predominant in the hemicellulose and extractive components of cellulosic fibres.

Without these charges, fibres would not swell with water nearly as much during refining, becoming flexible enough to form strong bonds. Uncharged fibres also would be unresponsive to most papermaking additives, including sizing agents, strength agents, and most retention aid systems.

Trouble often can be expected in paper machine systems where the charge is strongly out of balance. For instance, positively charged papermaking additives tend to be ineffective if the process water has a large excess of negatively charged polyelectrolytes and finely divided, or “colloidal”, materials from the wood, coated broke, various de-inking treatments, or high levels of fluorescent whitening agents, etc.

At the opposite extreme, higher levels of foam, retention problems, and slow dewatering are often observed if there is an overdose of positively charged additives. This situation is observed, for instance, in some cases when high levels of certain wet-strength chemicals have been added, beyond the levels that can be taken up by fibres.

## Complimentary test methods

Various equipment has been developed for evaluation of charge-related properties. Previ-

ous articles in this journal<sup>(1-3)</sup> have discussed two such devices that are now increasingly used in paper industry applications. These are the streaming current (SC) devices and the fibre-pad streaming potential (SP) devices. SC tests are most commonly used to carry out titrations of cationic demand. By contrast, fibre-pad SP tests are most commonly used to estimate the zeta potentials of fibre surfaces, depending on the sequence and levels of chemical treatments.

In addition, papermakers also can select from a variety of additional charge related tests that won't be considered further in the present article.<sup>(1,4-9)</sup> These include colorimetric titrations of charge demand<sup>(6-7)</sup> and microelectrophoresis to determine the zeta potentials of fine particles.<sup>(5,8-9)</sup>

Depending on their interests, it can be reasonable for paper technologists to employ any combination of the SC titration method, the fibre-pad SP method, neither, or both. As will be described, this article makes a case that the electrical conductivity of wet-end stock suspensions, white water, and similar samples ought to be reduced before the samples are submitted to either SC titrations or fibre-pad SP tests.

## Streaming Current (SC) Titration Method

Papermakers are motivated to use the SC method most often for process optimization and process control.<sup>(2,4,5,10-16)</sup> Additives such as retention aids, microparticles, sizing agents, and strength additives can be expected to work in a steadier, more predictable manner if the amount of excess negative or positive charge in the aqueous and colloidal phase of the system is kept within a relatively steady range. Charge control becomes particularly important in cases where papermakers are using highly charged cationic additives such as polyamines, polyaluminum chloride, etc.

Overall reductions in the cost of additives often can be achieved by partially neutralizing the excess charge of the process water. Charge-control systems are especially valuable in cases where the charge demand is highly variable.

The streaming current devices most commonly used in papermaking applications have a small plastic piston that fits loosely into a closed-end plastic cylinder and reciprocates at about 4 strokes per second. Two metal probes at different points along the annulus of the device sense the alternating electrical current resulting from the fluid motion between the piston and the cylinder wall. A current arises whenever the plastic surfaces have a net charge, particularly in the case where the plastic has become coated with a thin layer of colloidal materials from the sample.

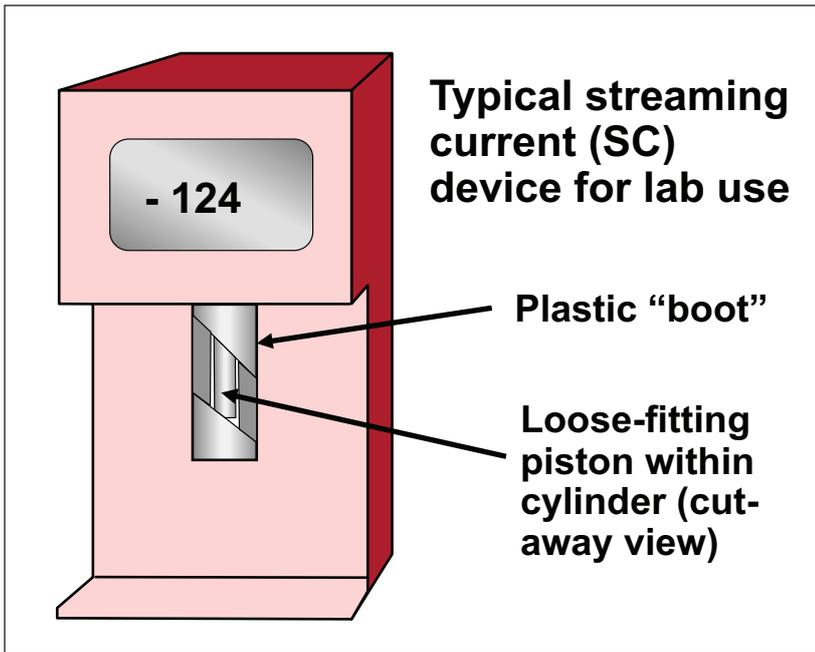


Figure 1: A generic bench-top SC device in which the user places a beaker, containing the sample, under the probe assembly of the device.

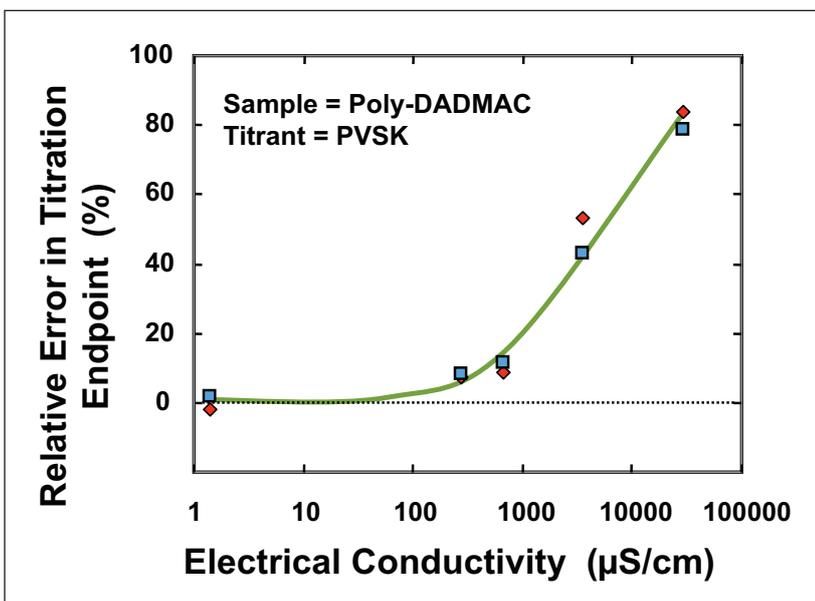


Figure 2: SC titration results can become increasingly inaccurate with increasing salt content of samples.

The water immediately adjacent to the surfaces will have a net ionic charge, i.e. “counter-ions,” that are equal and opposite to the charge on the surface. The moving water pushes some of these counter-ions, producing the measured effect.

Figure 1 shows a generic bench-top SC device in which the user places a beaker, containing the sample, under the probe assembly of the device. In other models, the user may place a measured volume of sample right into the probe area of the device.

Auto-titration equipment is often used in conjunction with these bench-top SC devices so that repeat titrations will be carried out at a consistent rate – often taking a couple of minutes to complete a titration. For online applications the equipment can have a different outward appearance, but the inner workings of the equipment, as well as the procedures, are similar.

Samples for SC titration tests often consist of unfiltered or filtered white water. Some papermakers prefer to test filtrate obtained from headbox stock or other stock streams. The latter approach tends to give a lower level of suspended solids, which can make the analysis of the results easier in some cases. At the opposite extreme, some users carry out SC measurements with unmodified headbox stock, despite concerns about clogging the narrow annular space with fibres.

To carry out a titration of charge demand, one first observes the sign of the initial signal. Then one gradually adds a dilute solution of an oppositely charged polyelectrolyte until the SC signal goes to zero. The result of the titration usually is reported as the amount of titrant needed to reach a zero SC signal, based on a unit volume of sample. One of the most common applications of SC titration data is to vary the dosage of a highly charged papermaking additive so that the cationic demand -or anionic demand in some cases - of the system remains within a selected range.

**A Case for SC Titrations at Conductivity < 1000 µS/cm**

Recent scientific work<sup>(2,14-15)</sup> has shown that SC titration results tend to become inaccurate, and they can become grossly misleading with increasing electrical conductivity - electrolyte content - of the sample. It follows that most paper mill-based users of SC devices should implement modified procedures.

Figure 2 illustrates how SC titration results can become increasingly inaccurate with increasing salt content of samples.<sup>(15)</sup> The example represented in Figure 2 involved titration between two standard titrants, which can be considered as a best-case scenario for this kind of test. As shown in this example, SC titrations usually can be expected to give distinct, reproducible endpoints of polyelectrolyte

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titrations when the electrical conductivity is relatively low, e.g. below 1000  $\mu\text{S}/\text{cm}$ .

The rate at which endpoints become shifted, obscured, or lost entirely, as the conductivity is further increased, is highly dependent on the kinds of colloidal materials in the sample. If the main dissolved substances in the sample happen to be low in charge density, the endpoint may become completely obscured as the electrical conductivity increases.

Because the electrical conductivity in typical paper machine systems can range between about 500 and 20,000  $\mu\text{S}/\text{cm}$ , most paper mill-based users of SC instruments for charge-demand titrations will want to incorporate changes into their measurement procedures.

Misleading results are likely to result when users fail to restrict electrical conductivity values to suitably low levels. The following factors appear to contribute to the problems observed in the case of SC titrations: <sup>(2,14-15)</sup>

- (a) decreasing tendency for certain charged materials in paper machine process water to adsorb onto plastic surfaces of SC devices as the levels of salt ions increase
- (b) decreasing tendency for polymer titrants to form strong enough complexes with anionic materials in the sample, and
- (c) an overall decrease in the electrical signal with increasing electrical conductivity of the solution.

In a few cases, problems related to the reliability of streaming current tests may be evident to the user. For instance, sometimes it is not possible to reach a titration endpoint at all if the level of salt ions is too high. <sup>(14-15)</sup> However, in typical cases, though the titrations appear to be successful, there is a poorer correlation to paper machine performance than what ought to be achieved.

#### **Recommended Default Procedure for Manual SC Titrations:**

1. Obtain a fresh aqueous sample from paper machine system.
2. Dilute one part, by volume, of the sample with 9 parts, by volume, of de-ionized or distilled water.
3. Place a known volume of diluted sample in the device -see the owners' manual for the device you are using.
4. Note the initial sign of charge indicated by the streaming current detector.
5. If the initial sign is negative, then titrate the sample with a suitably dilute solution of a high-charge cationic titrant such as poly-diallyldimethyl-ammonium chloride. Practice with the rate of addition of titrant, with small amounts added each 10 seconds or so, with the aim of completing

each titration in about 60 to 180 seconds.

6. Record the volume of titrant required to reach a streaming current output of zero, and also record the concentration of titrant (usually expressed as moles per litre, on a monomer basis), as well as the dilution factor.
7. Multiply the titration result by the dilution factor.

#### **Fibre-Pad Streaming Potential (SP) Tests**

The second method to be discussed is mainly for evaluation of the solid surfaces in fibre suspensions. Papermakers are motivated to use fibre-pad SP tests when they want to know about electrostatic forces at the outside surfaces of the fibres. <sup>(3-5, 16-20)</sup> Such information can be especially helpful during product development and also for troubleshooting.

For instance, one may want to figure out how to achieve high performance with functional additives such as sizing agents and strength agents. Let's suppose that a positively charged additive needs to be retained with very high efficiency on the fibre surfaces. In such a case, SP tests can be used to verify that the fibres have a negative charge just before treatment with the selected additive.

Another potential application of SP tests is for optimization of retention and dewatering. In principle, the electrostatic forces between various solid surfaces in a suspension of fibres can be estimated by knowing the electrical potentials associated with those surfaces.

Though the complicated surfaces of cellulose materials can make it difficult to do calculations, it is reasonable to expect results of SP tests to correlate with wet-end process parameters. By monitoring the sign and intensity of electrical potential at the outer surfaces of the fibres, one should be able to adjust process conditions to achieve favourable results.

Relative to the SC tests discussed earlier, the SP tests generally can be described as "direct" and "quick." The signals that one observes originate directly on the fibre surfaces of interest, not on an arbitrary plastic surface. It is not necessary to wait 5-20 seconds for an additive or titrant to equilibrate with a plastic surface. Mixing and adsorption can happen within a second in a stirred fibre suspension. This can be important when one wants to study the paper machine, since many wet-end additives contact the stock for only a few seconds before the paper is made. Online SP tests of the outer surfaces of fibres can provide a very sensitive way to detect and deal with different sources of variability in the process. <sup>(18-24)</sup>

Figure 3 shows a generic bench-top SP device. Such devices use vacuum to draw a fibre suspension from a beaker toward a small screen. The fibres are retained by the screen, and a fibre-pad forms on the screen. The electrical potential is measured, using metal contacts on either side of the fibre-pad. To obtain the streaming potential, one needs two measurements, one during application of vacuum and one in the absence of vacuum, or at a much lower setting of vacuum. An approximate zeta potential, assuming a zero contribution of surface conductivity, <sup>(25)</sup> can be computed from the difference between the two measured values. <sup>(5)</sup>

**A Case for Fibre-pad SP Tests with Deionized Water**

The word “outer” appeared in each of the preceding three paragraphs. The reason for emphasizing “outer” is due to the porous nature of cellulosic fibres. Just like a sponge, water can flow around a fibre and it can flow through it. That means that results of SP tests can be sensitive to the charged condition of sub-microscopic pore surfaces, not just the outsides of fibres. <sup>(26-28)</sup> This situation is illustrated in Figure 4.

Due to the extremely small size of typical pores in the cell walls of fibres, <sup>(29-31)</sup> it is not reasonable to expect polymeric wet-end additives to diffuse into those pores to a significant extent during the relatively brief contact times typically provided before a sheet is formed. So what papermakers really need is a way to carry out SP tests so that they just detect information related to the outer surfaces.

Fortunately, just such a method was shown in recent work. <sup>(26-28)</sup> It turns out that the electrostatic potential due to just the outer surfaces of fibres can be measured if the aqueous solution in a fibre suspension is filtered off and replaced by deionized water.

The reason that this approach works appears to be due to the characteristic distance of counter-ions from charged surfaces, i.e. the “double-layer thickness.” Under typical aqueous conditions found in paper machine systems the effective double layer thickness can be about 1-4 nm, which is much smaller than the diameter of a typical pore in a water-swollen cell wall. <sup>(23-25)</sup> That means that SP tests of unmodified stock samples taken from a paper machine will be attributable to a combination of influences, coming from the interior of the fibres as well as the outside.

By contrast, if the same tests are done in deionized water, with the electrical conductivity below about 10  $\mu\text{S}/\text{cm}$ , then there won't be sufficient space within the small pores for double layers to form and contribute significantly to the observed electrokinetic effects. For that reason, only the outer surfaces of the fibres, the part that papermakers are interested in, will contribute to the measured result in the absence of salt ions.

In summary, a modest effort to replace the liquid phase of a sample with deionized water can pay off, giving a much better correlation between SP data and such things as retention efficiency and drainage rates. <sup>(26)</sup>

**Recommended Default Procedure for SP Tests**

The following procedure is based on an assumption that the purpose of the fibre-pad streaming potential tests, in a given instance, is to evaluate the charged nature of the outer

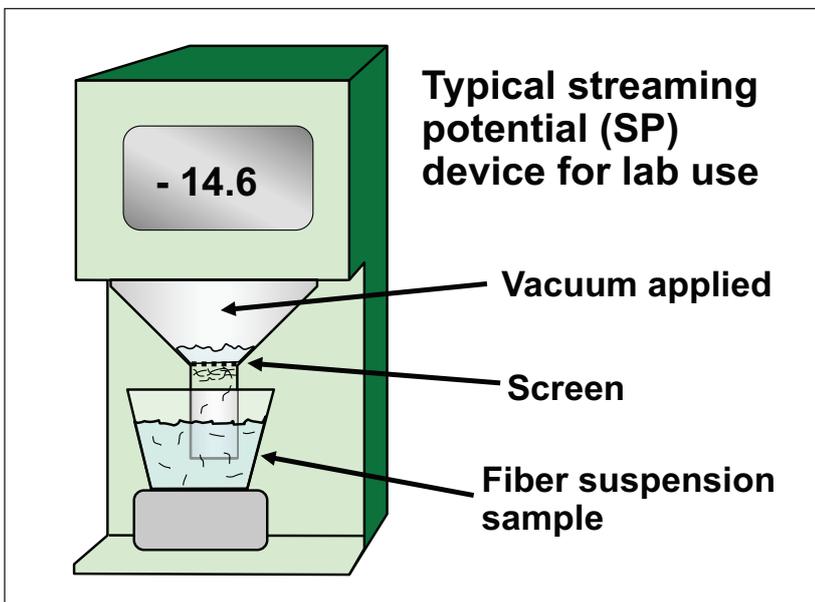


Figure 3: A generic bench-top SP device. Such devices use vacuum to draw a fibre suspension from a beaker toward a small screen.

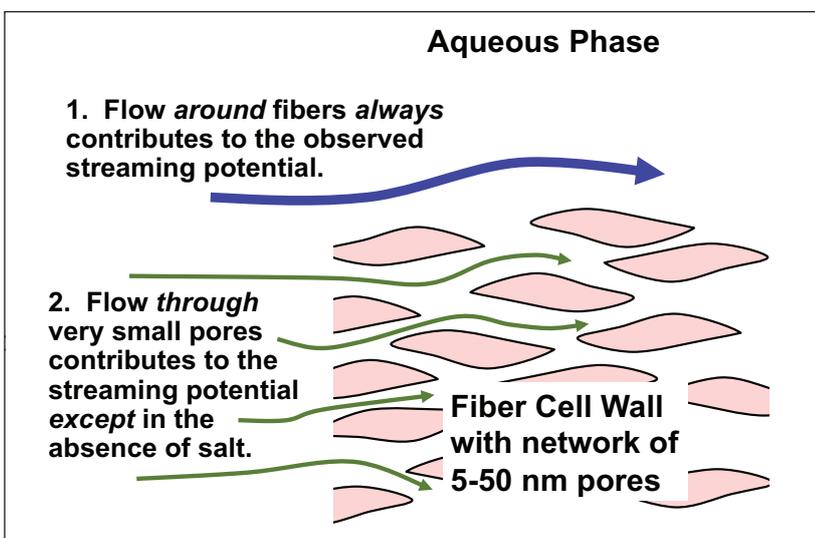


Figure 4: Just like a sponge, water can flow around a fibre and it can flow through it. That means that results of SP tests can be sensitive to the charged condition of sub-microscopic pore surfaces, not just the outsides of fibres.

surfaces of the fibres. The charge characteristics of the outer surfaces are expected to correlate with paper machine performance issues, such as retention and dewatering.

1. Obtain a known volume of fresh fibre slurry sample from the desired point in the process.
2. Optionally add charged materials of interest and mix. Note that this has to be done each time before the sample is diluted.
3. Remove the water phase, using a fine screen or filter paper.
4. Immediately re-suspend the solid portion in deionized water so that the original volume is restored.
5. Optionally adjust pH (but not the conductivity).
6. Carry out the streaming potential measurement.

### Online Testing

The two procedures outlined above, one for modified SC tests, and the other for modified SP tests, were written from the perspective of bench-top, semi-manual operation. Online versions of both SC<sup>(32-33)</sup> and SP<sup>(18-24)</sup> tests have been used for a long time in our industry. With suitable valves and dilution schemes it should be possible to automate modified versions of such tests to achieve the benefits outlined in this article.

### Conclusion

More reliable and useful data can be anticipated in the future, when using streaming current (SC) and streaming potential (SP) instruments. These benefits can be achieved by use of some relatively simple, but non-obvious changes in procedure, as follows:

- SC: In the case of streaming current tests, ie the employment of reciprocal motion of a plastic piston within a plastic "boot": If samples taken from a paper mill stream have electrical conductivities greater than about 1000  $\mu\text{S}/\text{cm}$ , then it is important to make a standard practice of diluting each sample by a fixed ratio, e.g. ten-fold dilution, using deionized water.
- SP: In the case of streaming potential tests, ie the formation of a pad of cellulosic fibres on a screen: If the sample's electrical conductivity is above about 100  $\mu\text{S}/\text{cm}$ , then it is important to start each SP measurement by filtering the solids, discarding the solution phase, then resuspending the solids in deionized water.

A paper mill manager once said, "sometimes the hard way is the only way." This statement seems applicable to charge-related

tests of fibre slurries, white water, and other samples from the wet end.

Neglecting to dilute samples before streaming current titrations is a bit like heading into the wilderness with a faulty compass. Neglecting to replace the aqueous phase with deionized water, when doing streaming potential tests of paper machine stock samples, is a bit like wearing sunglasses while heading into that wilderness in the evening.

The good news is that both SC and SP tests can be carried out with improved procedures. Better correlations with paper machine performance, and better overall reliability can be expected in the future, as long as one keeps in mind the connection between low electrical conductivity and high accuracy of charge-related tests.

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