Selecting and interpreting colloidal charge measurements

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ABSTRACT
Achieving an optimum balance between negatively and positively charged materials in a fiber slurry can be critical to the profitable operation of a paper machine. There is no consensus, however, regarding what tests to use and how to interpret the results. Papermakers are free to choose among several competing methods, including microelectrophoresis, colloidal titrations with a color endpoint, streaming current titrations, and fiber-pad streaming potential methods. Each method has its strengths and weaknesses. It is critical to be aware of the potential weaknesses and interferences with each method before selecting it for a given papermaking application such as process control surveys of paper machine operations. An understanding of potential errors also can improve a user’s ability to draw reliable conclusions.

INTRODUCTION
The process of manufacturing paper involves a complex interplay between solid materials, inorganic ions, and charged soluble polymers, i.e. polyelectrolytes. The word “colloidal” refers to those materials in the mixture that are generally too small to see with a low-power microscope, but larger than typical individual molecules. The process water within papermaking operations tends to be very rich in colloidal materials. This is why, by applying the principles of colloid science, there are opportunities to improve the efficiency and stability of papermaking operations.

One of the most useful findings of colloidal science, in terms of industrial operations, is the key role played by electrical charges. Finely divided materials that have a net ionic charge associated with their surfaces tend to repel each other when suspended in aqueous solution. The repulsion arises due to the counter-ions that accumulate in solution.
adjacent to charged surfaces. It has been shown that the overlap of the clouds of counterions on adjacent surfaces tends to stabilize suspensions and slow down the process of coagulation [1-4]. It is worth noting that so-called “charge-stabilization” is not the only mechanism of keeping suspension and emulsions well dispersed. A more complete review would also include a discussion of steric stabilization and related topics [5-6].

Papermaking involves two seemingly incompatible strategies. On the one hand, papermakers want to obtain relatively uniform dispersions of fibers, minerals, and polymeric materials within the process and within the resulting paper. On the other hand, it is critically important that fine material adhere to fibrous material in order to achieve efficient retention in the paper during the process of formation. Many publications have shown how measurements related to the colloidal charge of papermaking slurries and process water can be used to optimize and control the delicate and variable processes in a paper mill’s wet-end system. This work has been reviewed recently [7-10].

**What Motivates Papermakers to Measure Colloidal Charge**

The first goal for profitable papermaking is to please a customer. The second goal is to achieve process stability. Without achieving the second goal, the first is unlikely to be sustained. Papermakers have tended to use one of two main strategies to achieve process stability:

1. Discover and minimize variability of inputs to the process, *e.g.* the quality, concentrations, and flows of the materials used.

2. Actively compensate for variations, as in the case where flows of dyes are continually adjusted so that the product is always a nearly exact match to the specified shade expected by the customer.

With regards to measuring colloidal charge, the two strategies mentioned above both deserve careful thought. Generally the recommended first application of colloidal charge measurements in a given paper machine system ought to include a “process survey.” This is how papermakers often describe their activities aimed at discovering the main sources of colloidal charge. By measuring charge-related properties of each major process stream, the team can determine which of them are the most significant. Some
examples of process streams that often contain relatively high amounts of colloidal charge in various paper machine systems are shown in Table 1.

<table>
<thead>
<tr>
<th>Negative Charge Inputs</th>
<th>Positive Charge Inputs</th>
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<tbody>
<tr>
<td>Mechanical fiber, esp. if $\text{H}_2\text{O}_2$ bleached</td>
<td>Wet-strength agent treatments</td>
</tr>
<tr>
<td>Virgin unbleached kraft, if not well washed</td>
<td>Aluminum compounds for sizing, drainage</td>
</tr>
<tr>
<td>Coated broke</td>
<td>Polyamines</td>
</tr>
<tr>
<td>Colloidal silica, a drainage-aid additive</td>
<td>Cationic starch</td>
</tr>
</tbody>
</table>

Once the major sources of colloidal charge have been determined, the next step is to find out whether any of the significant inputs are unstable over time. This could be called a “process monitoring” approach. Any detectable variation in a measurable quantity is an object of suspicion.

Until it is proven otherwise, it is prudent to expect is that any changes in the surface chemical properties are likely to show up as variations in the papermaking process. Such variations may involve dewatering rates, fine-particle retention, and ultimately the paper structure and end-use performance. Sufficiently strong variations in colloidal charge are expected to cause process interruptions. For example, breaks of the wet web of paper often can be traced back to variations in dewatering rates. Drainage rate variations, in turn, are often associated with variations in charge [9]. Similar effects can be caused by abrupt variations in retention of fine particles. A recent study showed that variations in demand for a retention aid were highly correlated with variations in colloidal charge [11].

**Are Zeta Potential Measurements Sufficient?**

Since the 1940s it has been well understood that the rate of coagulation of the so-called “lyophobic” colloidal suspensions can be estimated from the average value of electrical potential at the surfaces [1-3]. Unfortunately, those wishing to apply these theories face an immediate problem; only under certain well-defined conditions in the laboratory is it possible to measure the surface potential [6]. Instead, industrial technologists generally
rely on another quantity called zeta potential. Zeta potential values are determined by various experiments in which there is a relative velocity between an aqueous fluid and particles, droplets, or fibers [6,12]. Zeta potential represents the average electrical potential at a hydrodynamic slip plane adjacent to the surfaces in contact with the solution. Within the range of electrical conductivity values commonly found in different paper mill systems the slip plane is expected to be within about 1 nm from the particle surface [6]. Since the location of the slip plane is seldom accurately known, industrial zeta potential measurements are not expected to provide highly accurate predictions.

As a rule of thumb, colloidal suspensions are found to be quite stable if the absolute value of zeta potential is above about 50 mV. Suspensions that are stabilized mainly by charge can be coagulated by either (a) neutralization of the surface charge with ions having a high affinity for the surface, usually multi-valent ions or polyelectrolytes, or (b) addition of sufficient salt concentration so that the range of electrical double layer repulsion is too short to prevent particles from colliding and sticking.

Papermakers most often determine zeta potential values by micro-electrophoresis [6-10]. As illustrated in Fig. 1, micro-electrophoresis involves application of an electrical field to a suspension of small particles. Usually the particles are less than 10 µm in size and the sample is placed in a capillary cell to minimize errors caused by convection currents. The device imposes a known electric field, and one measures how fast the particles migrate in that field. The ratio of particle velocity to electric field strength is the electrophoretic mobility (EM). Samples of paper machine white water are usually ideal subjects for testing, since the fiber fines and fillers are easy to observe under a microscope with dark-field illumination.

EM tests are most valuable to papermakers during the “discovery” phase of testing. For example, papermakers may be concerned about a high level of foam or poor retention of fine material. Either one of these problems can be a symptom of an imbalance of colloidal charge. Without further information it can be difficult to guess in which direction the system is out of balance. A quick micro-electrophoresis test will identify the sign of charge, thereby eliminating about half of the possible approaches involving charged additives that a papermaker might use to solve the problem. Zeta potential
measurements also are invaluable during product development and trouble-shooting, where it may be important to understand the mechanisms involved.

Although it has been proposed from time to time that zeta potential can be used for process control [13], such practices have not become widely adopted in the industry. To understand this infrequent use for process control it is not necessary to find fault with either the theory of the measurements. Rather, it is sufficient to note that modern papermaking practices typically involve polyelectrolytes having very high molecular mass. These polymers are known to be able to form strong, somewhat irreversible bridges between solid materials in aqueous suspensions even when the zeta potentials are far removed from zero. For this reason there may be little relationship between zeta potential values and the amounts of charged materials such as alum, polyamines, cationic starch, or colloidal silica that may be needed to achieve the best efficiency and product quality on a paper machine. Though high polymer flocculants can be tolerant of a wide range of zeta potentials, they usually are intolerant of excess charged colloidal material and polyelectrolytes of opposite charge. Flocculation is usually most effective if the suspended matter is either opposite in net charge to the flocculant, or at least if they have patches of opposite charge to serve as anchoring points.

**Colloidal Charge Measurements by Titration**

To understand what kind of measurement could be used in place of zeta potentials it is worth considering the difference between “intensive” and “extensive” variables. Zeta potential is an intensive variable like temperature or pressure – not dependent on the volume of the sample. By contrast, titration procedures with known volumes of fiber slurry or process water can be used to obtain information about the colloidal charge, an extensive variable. Other examples of extensive variables include heat capacity and the flow or current over a unit of time. Extensive variables are easy to recognize by the fact that (a) a boundary such as a volume or interval of time is specified, and (b) doubling the size of the sample would be likely to double the value obtained.

Though papermakers have long history of using colloidal charge information, it is more common to hear different words. For instance, the amount of cationic polymer required to neutralize all of the excess anionic charge in a typical paper machine process sample is
usually called its “cationic demand” [9]. Since there are many cases where papermaking furnish has been overdosed with cationic materials, it is also possible to speak about a system with a net “anionic demand” or an “ionic demand” of a certain sign. Other terms related to colloidal charge include “anionic trash” or “DCS” (for dissolved and colloidal substances).

Colloidal charge data can be well suited to the process control needs of papermakers for two reasons. On the one hand, the information is likely to be directly proportional to the flows of charged materials into the process. On the other hand, as noted by Strazdins [9], zeta potential values are profoundly affected by changes in electrical conductivity of the aqueous medium. By contrast, colloidal charge measurements usually are affected only to a small degree by addition of simple salts such as NaCl and K$_2$SO$_4$ that do not have a strong chemical interaction with the surface.

In principle there are two basic ways to measure colloidal charge or ionic demand of a papermaking process sample. First one can determine how much strongly adsorbing charged titrant it takes to neutralize the surfaces of colloidal material in the sample. Second, one can determine how much titrant can be adsorbed onto these surfaces before an excess of titrant remains in the solution. These approaches give related, but not identical information, as will shown.

It is proposed that the most important reason to control colloidal charge on a paper machine is to achieve predictable, optimized performance of polyelectrolytes. These polyelectrolytes may include retention aids, drainage aids, components of sizing formulations, and strength additives. If the colloidal charge is high and opposite in sign, then the polyelectrolyte becomes neutralized and loses its effectiveness. However, if the colloidal charge is completely neutralized, or the same net sign as the polyelectrolyte, then there may be insufficient anchoring sites for the process aids remaining on the solid surfaces. The best performance of process chemicals usually is expected at an intermediate value of charge, minimizing premature neutralization of polyelectrolyte additives, while still leaving enough net charge of opposite sign so that drainage and retention goals can be achieved [14]. Consistent with this hypothesis it is also proposed...
that paper machine performance and product uniformity can be maximized by keeping the value of colloidal charge at a steady, optimum value.

This review will consider four main methods by which samples from the paper machine process can be titrated with charged polymers. The first troublesome issue, regardless of the procedure used, arises due to the porous nature of cellulose fibers and fiber fines [15]. Gradual penetration of polyelectrolytes into the pores of the fiber cell walls results in “decay” of their effect on the electrokinetic signals [9,13]. In other words, the zeta potential, or a signal related to zeta potential, begins to revert back in the direction of untreated fibers. Öhman et al. [16] found that the amount of polyelectrolyte that could be adsorbed by fibers in a set period of time was a strong function of molecular mass, consistent with the ability of smaller molecules to penetrate a greater fraction of the existing pores. Likewise Gruber [17] observed that lesser amounts of polyelectrolyte were able to adsorb onto fibers if the pores had been partly closed up by repeated cycles of drying and rewetting, simulating effects of paper recycling. Because of these phenomena it is important that users of any of the methods to be described standardize their measurement practices as follows:

a) Samples taken from a paper machine operation should be evaluated promptly, especially if charged additives already have been applied in the papermaking operation.

b) If a fiber slurry sample needs to be filtered before analysis, as in the case of some of the streaming current tests to be described later, then it may be advisable to carry out that filtration at the same time as the sample is collected. In the absence of fibers, the electrokinetic properties of the fine material are likely to be more stable, since there is less porous material into which polyelectrolytes can penetrate.

c) The rate of addition of titrant ought to be standardized. Usually it is satisfactory to use a rapid rate of titration; many chemical processes associated with paper manufacture have to be completed within a matter of seconds. A possible exception is in the case of streaming current tests to be described. In that case the
rate of titration has to be optimized to allow the signal to stabilize, while still minimizing decay of the signal.

**Micro-electrophoresis as a Charge-Measuring Tool**

Strazdins [9] has done the most extensive work in which EM tests were used to carry out titrations. Though the approach is tedious relative to some of the other methods to be described later, the results can be more reliable and easier to interpret. This following is a list of steps in Strazdins’ basic procedure:

1. Obtain or prepare a master batch of fiber slurry sample large enough for at least five individual tests, e.g. 1 liter for five tests involving 200 ml of sample.

2. Pass the first subsample through a moderately coarse screen, e.g. 50-mesh, and collect the filtrate.

3. Place filtrate in the capillary cell of a calibrated micro-electrophoresis instrument and observe the direction that most of the particles migrate in response to an applied field. Determine the most common velocity of migration, following the instructions for the instrument. Either record this raw velocity or calculate the initial electrophoretic mobility (EM) value or the zeta potential.

4. Select a cationic or anionic titrant, depending on the sign of the initial EM value. If the initial value was negative, then one titrates with a cationic polyelectrolyte such as poly-diallyldimethylammonium chloride (DADMAC), chitosan, or whatever is currently being used in the industrial process for charge control. If the initial EM value is positive, then one usually titrates with polyvinylsulfate potassium salt (PVSK) or similar solutions.

5. Guess at the amount of titrant needed to neutralize the net colloidal charge of another sample. Add that amount to the second aliquot of fiber slurry. Filter and measure the EM value.

6. Repeat the process until one can obtain a plot of the type shown in Fig. 2. Once the principle is understood, it may be unnecessary to do any plotting to find the endpoint.
7. Calculate the amount of titrant per amount of sample that is needed to reach the endpoint where the EM value is equal to zero.

Table 2 lists the main strengths and weaknesses of micro-electrophoresis as a means of determining colloidal charge of papermaking systems. In summary, the test is highly recommended in the hands of a skilled technician doing trouble-shooting or process surveys. It is also recommended as a reference standard against which to check the validity of other methods yet to be discussed. The EM titration method is not usually recommended for routine process control due to the calibration requirements and the challenge of keeping the capillary cell clean. One instrument that is particularly well suited for titration work can be obtained from the inventor of the method [18].

<table>
<thead>
<tr>
<th>Positive Features</th>
<th>Negative Features</th>
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<tbody>
<tr>
<td>Accurate zeta potential values can be obtained throughout the analysis.</td>
<td>Misleading results can occur easily if the microscope is not focused correctly.</td>
</tr>
<tr>
<td>Relatively few assumptions are required. The theory has been well developed and verified.</td>
<td>Highly insoluble deposits are expected to form on the capillary cell walls as a consequence of polymer complexation.</td>
</tr>
<tr>
<td>One directly observes effects due to charges on solids within the sample.</td>
<td>The batch-wide titration procedure given above is more tedious than other methods to be described with other instruments.</td>
</tr>
<tr>
<td>The technical gets a change to look at the suspended fine material, and this often provides supplementary information.</td>
<td>Contamination can occur easily during filtration and when testing dilute samples within a capillary cell.</td>
</tr>
<tr>
<td>It is possible to determine colloidal charge information by adding known amounts of titrant to samples of furnish, filtering, observing the electrophoretic mobilities, and then interpolating the results to zero.</td>
<td>Convection currents become a problem at high electrical conductivity values. Also, the measured velocities are reduced at high conductivity, lowering the resolution of the method in finding an endpoint of zero mV. One has to assume that fine particles in the slurry have similar zeta potentials as fibers in the sample. The fibers are too big for the capillary cell.</td>
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The reason why calibration of the focal plane is so critical is illustrated in Fig. 1. The dashed line represents the velocity pattern that arises due to electro-osmosis [6,9,12]. Electro-osmotic flow occurs along the capillary walls because the wetted quartz or glass
surfaces have a net ionic charge. The applied electric field attracts or repels the excess counter-ions in the atmosphere of ions adjacent to the surface. Movement of the ions results in flow of the surrounding solution. Because the apparatus is sealed, there has to be a return flow in the central part of the capillary. As shown in the figure, expected accumulation of debris, mainly at the bottom of the cell, tends to distort the flow pattern so that it is no longer parabolic. Technicians can minimize errors by (a) proper calculation and adjustment of the focal plane on the upper stationary layer as shown and (b) cleaning of the apparatus. A more elegant means of determining the stationary level in the presence of debris has been proposed by Pelton [19].

A key assumption of papermakers using micro-electrophoresis is that fiber fines and other fine particles have similar surface chemical properties as the longer fibers. As noted by Strazdins [9], this assumption is consistent with the fact that excess polyelectrolytes and colloidal materials in a slurry sample will tend to coat all of the available surfaces. Work by Chang and Robinson [20] and Jaycock and Pearson [21] supports this assertion. Others, however, have shown cases where fine material in a slurry had different zeta potentials [22], or average zeta potentials that differed from those of the long fibers [23]. Sanders and Schaeffer [22] showed that different components of a papermaking furnish can have different affinities for such additives as
cationic starch or cationic polyacrylamide retention aids. As a result, electrokinetic properties of fillers may sometimes correlate poorly with the electrokinetic properties of the fibers in the same slurry.

**Colorimetric Titrations of Colloidal Charge**

Colorimetric colloidal charge titrations were introduced into the U.S. paper industry as a convenient way to verify the charged nature of samples such as cationic starch [24]. Subsequently the method has become widely used for analysis of process water samples and fiber slurry samples. Practical and theoretical considerations of the method have been reviewed by St. John and Gallagher [25].

The chemicals involved in the colorimetric charge test are illustrated in Fig. 3. In the absence of specific polyanions, such as polyvinyl sulfate (PVSK) as shown, the dye appears blue. As long as there is an excess of any cationic polyelectrolyte, cationic surfactants, or multivalent cations such as Al$^{3+}$ in the solution, the PVSK will preferentially bind to those materials. The interactions usually as close enough to being stoichiometric for practical work, though deviations are expected for interaction of weak acids and bases, polyelectrolytes of widely differing charge density, or in solutions of relatively high electrical conductivity [8]. After essentially all of the cationic colloidal charge has been consumed by PVSK, then any excess PVSK is available to form a pink-purple complex with the dye, as shown.

![Chemical diagram of toluidine blue-O dye and potassium polyvinyl sulfate (PVSK) forming a pink complex](image)

**Fig. 3** – Chemicals responsible for the color endpoint of colloid titrations with toluidine blue-O dye.

For reasons noted in Table 3, the colorimetric charge method often can be the most practical and cost-wise way to monitor colloidal charge. As noted by Patton and Lee [26] the endpoint of the colorimetric test can be expected to disagree with that of the EM test described earlier. One reason for this “offset” of the colorimetric endpoint is that fact that polyelectrolyte adsorption usually continues beyond the point where the surface has acquired a neutral net charge. Although electrostatic considerations dominate the adsorption processes of many polyelectrolytes, one has to remember that adsorption is affected also by London dispersion forces, changes in water structure, and by changes in the entropy of the system [6]. In practical situations none of these factors will be known. Nevertheless, the method is highly recommended for many practical cases where one is mainly interested in how a process varies over time.

<table>
<thead>
<tr>
<th>Positive Features</th>
<th>Negative Features</th>
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<tbody>
<tr>
<td>The most basic procedure can be carried out with inexpensive equipment available in essentially any laboratory.</td>
<td>Highly colored or turbid samples can obscure the appearance of the indicator dye.</td>
</tr>
<tr>
<td>The procedure is relatively quick.</td>
<td>The endpoint tends to be gradual and hard to determine precisely without spectrophotometric measurements.</td>
</tr>
<tr>
<td>The procedure can be automated with a titrater and a spectrophotometer to detect the endpoint.</td>
<td>Many common ingredients of papermaking furnish tend to interfere with the endpoint. These include alum, bleaches, suspended matter and high concentrations of salts.</td>
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<tr>
<td>On-line testing is possible, especially if the initial sample is combined with an excess of cationic titrant, filtered, and the filtrate back-titrated with PVSK.</td>
<td>The color-change endpoint may disagree with electrokinetic endpoints since it requires a sufficient excess of PVSK be available to form the colored complex.</td>
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A potentially confusing aspect of the colorimetric test is a widespread practice of taking the logarithm of the ratio of adsorbed amounts of cationic versus anionic polyelectrolyte titrants. Details of this method are given by Halabisky [24]. For practical purposes, the log of the colloid titration ratio (CTR) can predict paper machine performance. For example, Carrasco, Mutjé, and Pelach [27] showed that a log-CTR value near to zero, i.e. approximately equal adsorption of the two titrants, corresponded to the best fine-particle
retention. Also there was a good correlation between the log-CTR values and zeta potentials derived from micro-electrophoresis. It is worth noting, however, that by taking a ratio of the two adsorbed quantities one is throwing away information about how much charged additive is needed to optimize the process. An alternative reporting procedure has been suggested by Hubbe [28] to preserve this information.

Recently Tanaka et al. [29] showed that the colorimetric test is intolerant of high salt levels, *i.e.* high electrical conductivity. The problem appears to be related to interference with the complexation between the dye and the anionic polymer. As noted by Lindström [8] and Strazdins [9], complexation reactions (or “coacervation”) between the titrants and colloidal materials in the sample may fail to form when the conductivity is increased in a range starting at about 1000 $\mu$S/cm. To overcome this problem the cationic titrant was derivatized with a strong chromophore [29]. The endpoint of titration was determined by repeatedly filtering the samples after addition of increasing amounts of the titrant. The endpoint was identified as the point at which significant dye first appeared in the filtrate. Variants of this method are likely to become used in the future as papermakers attempt to use less fresh water in their processes, resulting in higher levels of conductivity.

**Streaming Current Titrations**

Since its invention in the 1960s [30] the streaming current method has become widely used for control of water and wastewater treatment operations. The most essential parts of the apparatus are illustrated in Fig. 4, which corresponds to one of the popular designs. During operation a piston moves up and down within a close-fitting cylinder. The period of motion is typically about $\frac{1}{4}$ of a second and the amplitude is usually about 0.5 cm. The probe surfaces of the device are usually made from poly-tetrafluoroethylene (PTFE) or another non-conducting plastic. The reciprocal motion of the piston causes a more rapid flow of aqueous liquid in the opposite direction within the annular space. If the probe surfaces have a net charge, then the flow pushes some of the counter-ions. The net flow of ions results in an alternating current that can be detected between two electrodes as shown. The electronics are set up to amplify the AC signal and rectify it with the motion of the piston so that the user sees a relatively steady number having the same sign as the average electrical charge of the plastic probe surfaces.
New users of streaming current devices may be tempted to draw conclusions from the initial value given by the instrument when process water from a paper mill is placed in the cell. In theory it is possible that such measurements can give output that is analogous to zeta potential information [31]. Measurement without titration can be useful also if one just needs to know the sign of charge or if one has concluded in advance that the optimum operating condition corresponds to a pre-selected value of the streaming current signal. Although such procedures are widely used for control of water treatment, most users within the paper industry have adopted a different approach during the last couple of decades. It seems that streaming current measurements, without titration, haven’t met all the needs of papermakers. Some likely reasons are as follows:

a) Papermakers almost always want to know by how much they need to change the flow of a charged additive to restore their system to its most advantageous operating condition; this means that a titration procedure is preferred.

b) Many samples of papermaking process water can be described as dirty solutions of water-loving polyelectrolytes. These have little affinity for the plastic probe surfaces. Only by complexing these polyelectrolytes with titrant of opposite charge can one be reasonably confident that the probe surfaces are covered by colloidal material that represents the charge condition of the sample as a whole.

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Fig. 4 – Essential features of a type of cell often used from streaming current analyses

Fig. 5 – Results from ref. [12] showing a case in which different neutral points were implied by the results of micro-electrophoresis and streaming current

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Because of the uncertainty of whether the probe surfaces are covered, it is worth considering the charged nature of an untreated PTFE surface. Davison and Cates tested the zeta potential of the probe surfaces of their streaming current device by grinding up PTFE and measuring zeta potential by micro-electrophoresis [12]. They found that the PTFE surfaces were weakly anionic in the presence of clean water and univalent ions. This observation is consistent with the negative values of streaming current signal that are usually seen when tap water is added to a well-cleaned cell of an SC device.

Historically, another limitation of streaming current measurements has been a lack of theory to interpret the signals. Gerdes, the inventor of the method [30], provided only a rudimentary linearized flow model to rationalize the magnitude of signals obtained. Recently the situation has become much improved with a detailed analysis of how the flow regime affects the electrical signals [31]. Now, in principle, one ought to be able to convert meter output to a corresponding average zeta potential associated with the plastic surface, including affects of any adsorption of charged colloidal materials. In practice the dimensions of the annular space are seldom known precisely, and both the piston and cylinder wall experience wear during use. This process changes the coefficient by which one should convert the streaming current signal to a corresponding zeta potential.

Another factor that can affect the accuracy of streaming current signals is surface conductance, a quantity that is seldom evaluated.

Though other procedures are possible, most users of streaming current titration methods within the papermaking community now use a procedure that can be summarized by the following steps:

1. Fill the sample cell with white-water or filtrate from a fiber-containing slurry. Many different filtering procedures are in use; the most important rule is to be consistent. Some users measure the whole sample – fibers and all, but in some cases it is necessary to dilute such samples to avoid plugging of the annulus.

2. Dump out the initial aqueous sample and replace it with a measured volume or mass of aqueous sample. The volume will partly depend on the format of the SC device that one is using.
3. Observe the sign of the initial signal. Select a titrant of opposite charge. Titrants usually are the same materials already mentioned for the other procedures already described, e.g. DADMAC, PVSK, or chemicals currently being used in a given process that is under investigation.

4. Add titrant gradually and continuously until the endpoint is reached. Because several seconds or minutes are needed to get a steady signal, there is a tendency for users to over-shoot the endpoint or to use an inconveniently long period of testing. Automatic titraters and automatic recording of the output signal are the recommended way to minimize subjective differences attributable to procedures used by different technicians.

5. Calculate the colloidal charge required to reach the neutral endpoint where the SC signal goes to zero. For purposes of process control it may be sufficient merely to record the sign of charge and the volume of titrant corresponding to the endpoint.

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<tr>
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<tr>
<td>No optical measurements are required. It is possible to make excellent charge determinations with highly turbid or brightly colored water samples.</td>
<td>Results are valid only if the probe surfaces become covered with colloidal material; there is uncertainty about this when titrating unknown samples.</td>
</tr>
<tr>
<td>The mechanical device is simple, rugged, reliable, and readily adapted for on-line sensing.</td>
<td>Increasing electrical conductivity seriously decreases the magnitude of the signal; this effect is greater than the usual decrease of zeta potential with increasing salts.</td>
</tr>
<tr>
<td>Automation of the titration procedure can improve the precision and remove subjective effects of different users.</td>
<td>Increasing electrical conductivity also can cause problems with the endpoint (see below).</td>
</tr>
<tr>
<td>No calibration is required. (Calibrations can be useful for some non-titrating methods, especially in other industries.)</td>
<td>It may take several seconds to over a minute for the signal to stabilize after addition of titrant.</td>
</tr>
<tr>
<td>The time scale of variations of colloidal charge measured by this method in paper mills is of the order of magnitude of several minutes to hours. Conventional process control methods can be established to compensate for variations in this time scale by chemical addition.</td>
<td>Frequent cleaning of the probe surfaces may be required, especially when evaluating samples having relatively low levels of colloidal charge.</td>
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**Table 4 – Pros and Cons of the Streaming Current Endpoint for Colloidal Charge Titrations of Paper Machine Process Waters**
Table 4 lists some of the strong points and weak points of the SC method. In summary, the method is relatively easy to use, even by those with little experience. Caution is required, however, in interpreting the results [10,32]. Because highly misleading results are possible, it is strongly advised to carry out confirmatory tests with EM titrations or colorimetric titrations before establishing SC methods for process control.

A recent study by Tanaka et al. [29] revealed that SC titration endpoints can be adversely affected by salts. Even at the levels of electrical conductivity associated with relatively “open” paper machine water system, e.g. 1000 µS/cm, there was significant divergence. Problems associated with SC endpoints at increased electrical conductivity levels are one of the key issues being addressed in the research group at N.C. State University through a project funded by the TAPPI Foundation.

Figure 5, adapted from the work of Davison and Cates [12], shows a case where SC titrations gave results that were very different from the recommended reference method, micro-electrophoresis. Each of the curves shown represents the effects of addition of cationic wet-strength agent, starting at the left and progressing to the right along each curve. If one thinks of the wet-strength agent as the titrant, then it becomes apparent that the two methods did not consistently agree with respect to the neutral endpoint. Interestingly, agreement was much improved in the presence of hard water. A likely explanation is that hardness ions such as Ca$^{2+}$ promoted precipitation of fatty acids and resin acids from the aqueous sample onto the probe surfaces, causing the plastic to have properties more characteristic of the sample solids.

A factor to keep in mind when doing streaming current titrations is that slurry samples taken from the thin-stock loop or “primary circuit” of a paper machine tend to become enriched in fine material that is not efficiently retained during the formation process. As noted by Marton [33] such fines are capable of adsorbing at least three times as much titrant compared to fibers having the same surface charge. The difference is associated with the higher relative area of fine materials. For this reason, charge titrations carried out by addition of titrant directly to filtrate may depend strongly on how much of the fine material has been filtered from the sample. For example, momentarily poor retention of...
inorganic filler will increase the surface area of solids in white water; as a consequence, the titrated colloidal charge of the white water is likely to increase as well [34].

Though the streaming current titration method has become well established in the paper industry, there is reason to believe that users could be obtaining even more information value from the same type of experiments that they already perform. That information is contained in the shapes of titration curves. As noted by Bley [35], different shapes of adsorption curves are obtained for samples that contain either macromolecules, particles, or combinations of the two. Encouraged by the early studies of Cardwell [36], our research group is now involved with a study aimed at interpreting streaming data in terms of adsorption affinities of polyelectrolytes onto PTFE.

**Fiber-Pad Streaming Potential Titrations**

The fiber-pad streaming potential devices most often used within the paper industry work by the principle illustrated in Fig. 6 [37-40]. A vacuum draws a fiber slurry, typically headbox furnish, toward a screen. Filtrate passes through the screen. A pad of fibers builds up on the high-pressure side of the screen. An electrical potential is measured between electrodes on either side of the fiber pad. One measures this electrical potential, and then subtracts a reference method obtained when the pressure has been reduced, usually to zero applied pressure or a small value.

The origin of the signal in a fiber-pad streaming potential device is related to the streaming current method just described, but there are some key differences. First, almost no current is drawn at the surfaces of the metal electrodes. Therefore, one need not be concerned about error due to overpotential at these electrode surfaces [41]. Second, the flow pattern is much more complicated. As in the case of streaming current, flow of liquid moves some of the counter-ions adjacent to the surfaces. However, in this case, those surfaces consist of the fibers and fine material from which the paper itself is made. Therefore, with respect to surface chemistry the method has the potential to give more direct information with fewer assumptions.

It has become common practice to convert streaming potential information to equivalent zeta potential information [13]. This approach can be practical, but it is important to keep in mind that the results will not equal those of a reference method such as micro-
electrophoresis. The theoretically correct way to convert streaming potential data to zeta potential data requires a series of measurements at different densities of the fiber pad. Results are then extrapolated to zero pad density, giving results that agree with micro-electrophoresis [20-21]. Currently the most widespread practice is to estimate the zeta potential directly from a form of the Helmholtz-Smoluchowski equation derived for the case of a cylindrical capillary. Use of this equation for fiber pads involves a significant error [32]. To make matters worse, the magnitude of that error is not fixed, since it depends on the structure and density of the fiber pad, and on surface conductance of the fibers [32], factors that depend on such things as flocculation by retention aids and the types of ions present in solution.

Fig. 6 – Essential features of a fiber-pad streaming potential device of the type where vacuum is used to draw filtrate through a screen

Fig. 7 – One example of output from an on-line streaming potential device during a trial in which two different fiber lines were monitored in turn

Because the fiber-pad method requires no visual observations, this was one of the first methods to be implemented as an on-line test [42]. Several additional on-line systems have been reported and implemented on paper machines throughout the world [37-40]. Experiences of many different users can be summarized with the statement that fiber-pad streaming potential data are very sensitive to process changes. Perturbations anywhere in the system are likely to show up first in the streaming potential data. Usually it is a much harder assignment to track such variations to their causes.

Figure 7 gives one example of streaming potential data [43]. Two things are apparent. First, the character of the signal changed markedly when the device was switched from
one fiber furnish to another during the paper machine trial. Second, within a characteristic range of data output there was little correlation between successive measurements. The signal appeared to vary in a semi-random manner over very short time intervals. Some possible reasons for the noisy appearance of fiber-pad streaming potential data in the given example include the following:

a) The incoming sample had not been thoroughly mixed after introduction of very-high-mass retention aids. Though the paper machine system involves high levels of agitation, the fibers also tend to flow as a plug to an extent that is not always appreciated [44].

b) Relatively small amounts of polyelectrolytes of very high mass may have a disproportionate effect due to their tendency to remain on the outer surfaces of fibers, especially during the first few seconds after their addition.

c) The electrical signals may be affected by adjacent electric motors, etc.

d) Bubbles nucleate on the surface of the electrode on the low-pressure side of the screen due to liberation of dissolved gasses from the filtrate.

Perceptive readers may have noticed something that has been missing from the preceding discussion of streaming potential tests; none of the cited applications involved a titration. One has to go back to the work of Horn and Melzer [45] to find published data that might be described as a titration. Penniman [13] also makes reference to the fact that “pulp pad streaming potential can be used in determination of cationic demand.” A likely reason for the scarcity of titration work is that on-line fiber-pad methods already involve a complex system of valves, screens, etc. Though a titration method is needed in order to get the information most suited for use by papermakers, such capability has not been incorporated into on-line devices. One exception is a device recently developed by the author [46]. In addition, further work is under way in our laboratory to use fiber-pad streaming potential as a means of determining endpoints of colloidal charge titrations.

Table 5 gives strength and weaknesses of the fiber-pad streaming potential method as a means of detecting endpoints of charge titrations.
Table 5 – Pros and Cons of Fiber-Pad Streaming Potential Endpoints for Colloidal Charge Titrations of Paper Machine Process Samples

<table>
<thead>
<tr>
<th>Positive Features</th>
<th>Negative Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>The electrochemical effect observed arises at the surfaces of the fibers and fine material of interest. If the instrument is well designed, then one can be confident that the measured signal actually represents the condition of the sample.</td>
<td>Output signals from on-line systems can be noisy and hard to interpret. Sources of noise are hard to track down, since they may include electrical issues, bubbles, a clogged screen, poor mixing of chemical additives to the furnish, or variations in fiber pad structure.</td>
</tr>
<tr>
<td>The signal responds immediately to the addition of titrant. In principle, this rapid response makes the method well suited for titrations.</td>
<td>The valves, screen, and other parts of a fiber-pad streaming potential system are inherently complex and subject to clogging and other maintenance requirements.</td>
</tr>
<tr>
<td>There is no need to dilute or pre-filter the sample. Headbox furnish can be tested “as is,” reducing concerns about contamination.</td>
<td>The electrical potential measured between pairs of metal electrodes in contact with a fiber slurry tends to drift due to gradual changes in the oxide films, local concentration of dissolved oxygen, etc., reducing the precision of the results.</td>
</tr>
<tr>
<td>There is no easy and accurate way to convert streaming potential values to zeta potentials. This is due to the complex structure of fiber pads, their unknown and changing density, and their unknown surface conductance.</td>
<td>Titration capability has been lacking, especially in the case of on-line fiber-pad streaming potential devices.</td>
</tr>
</tbody>
</table>

In summary, the fiber-pad method offers both challenges and opportunities. As noted earlier, the most widely used type of fiber-pad test is not expected to give accurate information related to zeta potentials. However, issues concerning the magnitude of the signal disappear when one uses the method mainly as a means of titrating to a point of electroneutrality. A titrating streaming potential system has the potential of combining several positive features. These include capability of measuring complete slurry samples without removing the fibers, direct measurement of headbox stock without dilution, and avoidance of the need to assume that either the fines, or a dye, or a plastic surface is in equilibrium with or covered by colloidal material from the sample. It remains to be seen...
whether the associated instrument development issues can be overcome and whether the method becomes more widely used in the future.

Conclusions

Each of the four types of colloidal charge measurement reviewed in this paper has the potential to give papermakers valuable information. Based on the information presented, it is recommended to use these four types of test for the following applications:

1. **Micro-electrophoresis** is recommended when starting out on a program of colloidal charge monitoring. That method, involving observation of the migration of fine particles in an electric field, is an excellent way to carry out surveys of the zeta potentials and charge contents of major process streams. It is recommended that the survey include a form of titration as described earlier. In brief, different amounts of titrant are added to successive samples of fiber slurry, each of which is filtered. The filtrate is placed in the apparatus and the electrophoretic mobility of the suspended fines is determined. The results of a series of such tests are used to determine the amount of titrant associated with neutral charge. Micro-electrophoresis is also a method of choice for troubleshooting, especially when there is doubt about whether other methods are giving the full story.

2. The **colorimetric colloid titration** method is recommended as a relatively quick and effective way to monitor the charge of paper machine process water samples. Laboratory equipment is widely available, and the feasibility of on-line equipment has been demonstrated. The first question to ask is whether a good endpoint can be obtained with the type of sample being considered. The clarity of the color endpoint is the most obvious requirement, even if one is using a spectrophotometric method of endpoint detection. To guard against possible misleading results due to interferences or salt effects it is recommended that the results be checked by micro-electrophoresis, with the understanding that complete agreement between the endpoints detected by the two methods is not expected. The method can be used either for titrating the whole furnish or white water. In either case it is recommended to add an excess of cationic titrant, pass the sample through a fine filter, add dye, then back-titrate to the endpoint.
3. **Streaming current titrations** also are recommended for routine monitoring and control of paper machine process waters. Both lab-based and on-line equipment are available. Equipment is also available to obtain filtrate samples from thick stock, making it possible to control charge variations closer to their source. Testing of fiber-containing samples need not be ruled out, assuming that preliminary tests do not indicate clogging of the annulus. Whether or not fibers are present, the recommended procedure is to observe the initial sign of the streaming current signal, then titrate directly to the endpoint. If the electrical conductivity is above 1000 µS/cm, then one should consider instituting a well-designed program of diluting with clean water of consistent quality. Once again, it is recommended to use micro-electrophoresis to validate results in new applications or in cases where such tests have not been done.

4. **Fiber-pad streaming potential**, as a means of evaluating colloidal charge, has not yet become widely adopted within the paper industry. Rudimentary laboratory equipment can be put together at low cost, of which the biggest element may be a millivoltmeter (± 0.1 mV resolution). At least two lab-based devices are on the market, and in principle these also can be used for titrations of colloidal charge.

5. Studies by various investigators suggest that there is value in considering both an intensive variable (*i.e.* zeta potential or a related quantity) and an extensive variable (*i.e.* colloidal charge). The two types of test can provide complementary information during detailed paper machine surveys, product development work, or difficult cases of trouble-shooting [47-50]. Zeta potential information can provide important background information about whether coagulation is likely to occur, especially in the case of fine colloidal materials that are less affected by flow phenomena [51]. In some cases there is reason to believe that optimum production can be achieved when both the zeta potentials and colloidal charge are at optimum values [52].
Literature Cited

18. SKS Associates, 5 Spruce Meadow DR, North Hampton, NH 03862.