

## Measurements needed for on-line control of retention and drainage

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**ABSTRACT** *In a retention and drainage control strategy, it is necessary to monitor the concentration of dissolved inorganic material and the concentration of dissolved and colloidal organic material. Conductivity is successful as a sensor to monitor inorganic material. We studied TOC as a means to monitor dissolved and colloidal organic material and found it to work well. Both conductivity and TOC have limitations, and pH, consistency, and temperature need to be controlled*

### KEYWORDS

Chemical analysis  
Drainage  
Process control  
Retention

A strategy for control of retention and drainage was elucidated in a previous article (1). Two measurements critical to implementation of that strategy are conductivity and total organic carbon. Here, we will examine these two measurements in some depth.

### Specific conductance

#### Effect of the concentration of inorganic and organic materials

As indicated previously (1), specific conductance is measured just prior to the filler blending system to determine the quantity of inorganic material entering from either a pulping and bleaching operation or from a pulper. Results obtained over a broad contaminant range of 0 to 1000 mg/L indicate that specific conductance increases linearly with increasing electrolyte concentration, or dissolved mineral concentration. Correlation coefficients of  $R^2 = 0.99$  or greater support the strong relationship between these two factors, and Fig. 1 illustrates this point. This increase in conductivity may be attributed to the increase in the number of ions per unit volume of solution. The inorganic salt mole-

cules dissociate under aqueous conditions into their respective cations and anions and conduct electricity in proportion to the total quantity of ions present.

Additionally, the specific conductance of the organic compounds also increases linearly with higher concentrations. However, the increase in conductivity is not as large as that of the inorganics, because the metal cations that comprise the organic compounds are highly conductive. These results are summarized in Table I. Organic material conductivities are two to three times lower than those produced by the inorganics. The higher specific conductance of the kraft lignin, in comparison to xylans and starch, is likely related to the chemical characteristics of the compound. Indulin C, the experimental lignin, is actually a sodium salt of kraft pine lignin. It is a brown, amorphous powder that is isolated via acidification of kraft black liquor, a process that causes its precipitation. Thus, the dissociation of free sodium ions from the soluble lignin would cause a conductivity increase. Additionally, alkali lignins behave as polyelectrolytes. In solution, they con-

tain negatively charged phenolate and carboxylate ions.

Besides these factors of concentration and the type of ionic species, aqueous solution conductivity is dependent upon the degree to which the solutes are dissociated into ions, the amount of electrical charge (valence) of each ion, the ionic mobility of the individual ions, and the temperature of the solution (2).

Although each inorganic compound is distinguishable on an individual basis, such discrimination would not be possible where a number of different ions are present. However, if an analysis were to show a preponderance of any one of these salts in solution, the specific conductance could afford a reasonably accurate measurement of the concentration of this material.

Conductivity can most readily serve as an estimate of the amount of total dissolved, ionized solids in solution. This group mainly includes dissolved salts and other mineral constituents. In an actual mill environment, knowledge of some "baseline" specific conductance value for the incoming stock slurry could allow for detection of fluctuations in the quantity of dissolved

inorganic contaminants entering the system from such sources as recycled white water or pulping operation carry-overs. The inability of the measurement to differentiate between contaminants may not be as important as the knowledge of incoming changes to the papermaking system itself.

### Effect of temperature

Specific conductance is highly influenced by fluctuations in the temperature of the measuring environment, and it increases linearly as a function of temperature. This effect may be attributed to increases in the speeds of ion movement when the temperature is increased.

### Effect of pH and measuring environment

Slight differences in specific conductance generally arise as a result of changes in pH. The instrument will detect these differences. Because of the nonspecific nature of the instrument, however, the direction of these pH changes is not detectable. Variations in conductivity with changes in pH can be mainly attributed to the inherent conductivity associated with the hydrochloric acid and sodium hydroxide used to adjust the pH.

Conductivity may be additionally affected by pH variations caused by the characteristics of some aqueous ionic species. This phenomenon can be exemplified best by the behavior of the aluminum ion (3). Figure 2 shows the effect of increasing pH on specific conductance over a wide range of aluminum sulfate concentration. A much greater conductivity change, as a function of pH, occurs with the aluminum species than with any of the other electrolytes we studied.

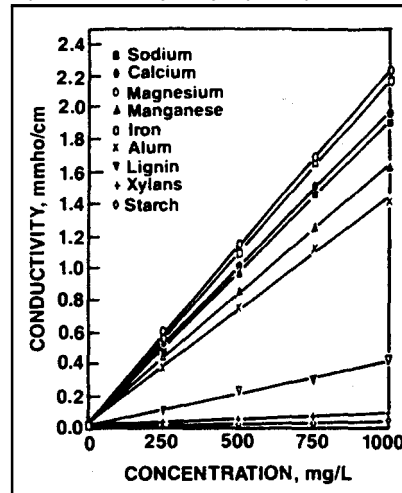
### Effect of consistency

An increase in the consistency of the furnish results in a small increase in the conductivity of the furnish. As Fig. 3 shows, the conductivity increases linearly with consistency from 0.25% to 3%, a change that is on the order of 0.01 mmho/cm per increase of 0.5% consistency. Some adsorption of dissolved ions occurs on the fiber and clay particle surfaces. Ionized carboxyl and hydroxyl groups constitute the bulk of these negative sites available for cation adsorption. Adsorption of positively charged ions should create a decrease in the aqueous ionic concentration and a decrease in the conductivity as these ions are complexed. It appears, however, that the charge introduced by

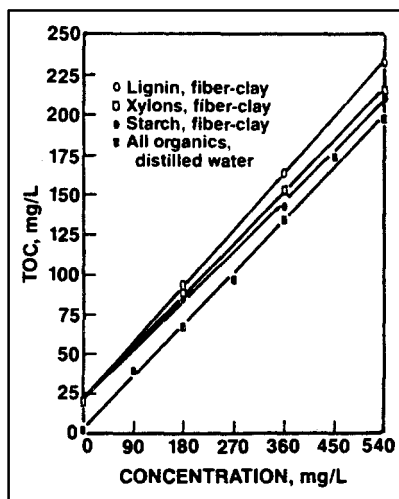
1. Effect of individual species on specific conductance

| Contaminant                                     | Slope, mmho/cm/ppm    |
|-------------------------------------------------|-----------------------|
| NaCl                                            | $1.88 \times 10^{-3}$ |
| CaCl <sub>2</sub>                               | $1.93 \times 10^{-3}$ |
| MgCl <sub>2</sub>                               | $2.10 \times 10^{-3}$ |
| MnCl <sub>2</sub>                               | $1.61 \times 10^{-3}$ |
| FeCl <sub>3</sub>                               | $2.14 \times 10^{-3}$ |
| Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> | $1.41 \times 10^{-3}$ |
| Kraft lignin                                    | $3.96 \times 10^{-4}$ |
| Xylans                                          | $3.78 \times 10^{-5}$ |
| Anionic starch                                  | $2.48 \times 10^{-5}$ |

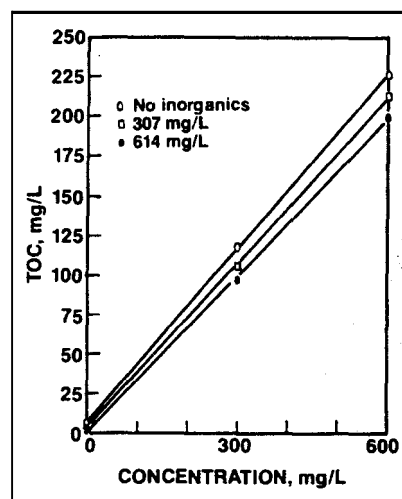
1. Specific conductance vs. contaminants (0.7% fiber-clay slurry at pH 4.5)



4. TOC vs. organics, with a 0.7% fiber-clay furnish at pH 4.5



5. TOC vs. organics, with various inorganic concentrations



ionized surface groups and the cations produced upon ionization is slightly greater than the quantity of cations adsorbed. The result is a net increase in the conductivity.

### Total organic carbon

#### Effects of concentration of organic and inorganic materials

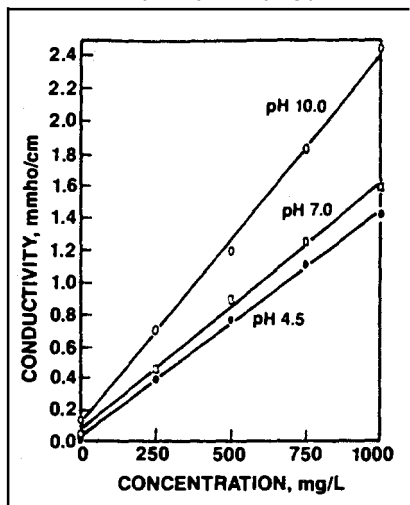
The measurement of TOC in the thick-stock loop is used to measure soluble organic material in the incoming pulp suspension. As the concentration of the dissolved organic components increases, the TOC response increases linearly (Fig. 4). Correlation coefficients were generally 0.98 or greater. This linear increase in TOC is a result of the proportional increase in dis-

solved, oxidizable, carbonaceous compounds in the system.

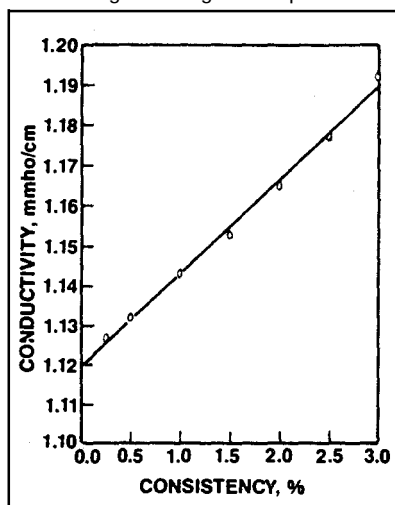
TOC measurements are nonselective toward the detection of specific carbon-based contaminants. Differences that are evident in Fig. 4 may be attributed to adsorption phenomena occurring between the organic components and the fiber surfaces. However, assuming that the general composition of the furnish does not change greatly, TOC may offer a rapid, non-specific, quantitative determination of the concentration of soluble organic material associated with a furnish.

Again, as with specific conductance measurements, knowledge of "base line" incoming TOC concentrations may prove beneficial in detecting upsets and organic contaminant increases

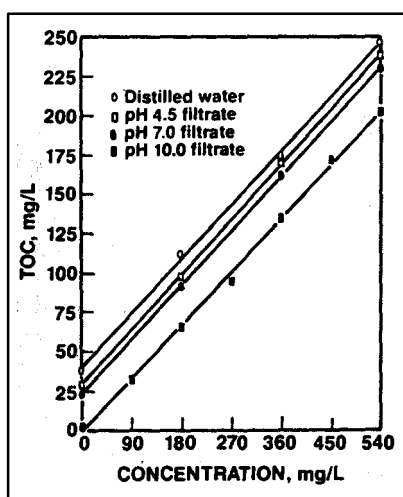
2. Specific conductance vs. alum, with a 0.7% fiber-clay slurry at varying pH



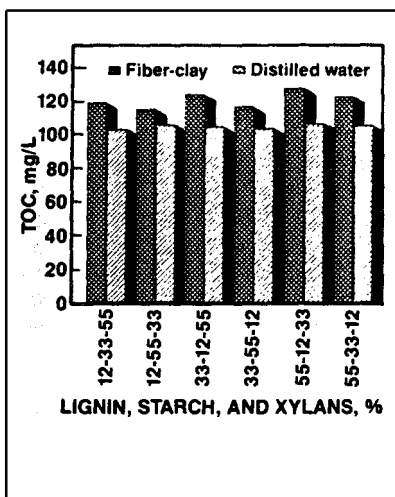
3. Specific conductance vs. consistency, with 614 mg/L of inorganics at pH 4.5



6. TOC vs. kraft lignin, showing the effect of pH and the measuring environment



7. The effect of varying organic components on TOC in a constant 300-mg/L blend



in the papermaking system. These upsets can originate from pulping operations and recycled white water. Even poorly washed bleached pulps contain oxidized lignins that are strongly anionic (4).

Figure 5 shows the effect that increasing concentrations of dissolved inorganics have on the TOC response. Compilation of 3<sup>3</sup> design information illustrates that, as the concentration of electrolytes increases, TOC values decrease slightly. A 3<sup>3</sup> design is the three factors—organics, inorganics, charge neutralizing polymer—at three concentration levels in a full factorial design. Based on linear regression analysis, this reduction is about 10% as inorganic concentrations rise over the 0 mg/L to 614 mg/L experimental

range. This phenomenon can be attributed to the sample preparation filtering procedure, in which the TOC determinations are conducted in a fibrous suspension. The inorganic material precipitates the organic components, which are filtered out before the TOC is measured.

#### Effect of pH and measuring environment

Graphical analysis (Fig. 6) suggests that differences in TOC arise as a function of variations in the pH of the fiber and clay system. As the pH rises from 4.5 to 10, an increase of approximately 3 mg/L of carbon occurs per pH unit increase. Conversely, the presence of organic contaminants in distilled water only, causes no change in

TOC with pH change. Thus, the possibility is low that the formation of carbonates and bicarbonates contributes significantly to the measurement.

Variations in TOC with pH may arise as a direct result of the fibers in the furnish. In increasingly alkaline solutions, hemicellulosic materials of low molecular weight probably dissolve from the fiber wall. This group would include such compounds as xyllose and arabinose-based polysaccharides. As these materials dissolve, they cause an increase in the TOC response. This process is analogous to the method of alkaline extraction of pulps. Additionally, raising the pH leads to swelling of the fiber structure, caused by increasing dissociation of the acidic groups (4). The increased electrostatic repulsion between these groups causes the cell wall to swell. This swelling may aid in releasing some organic materials that were confined within the fiber structure under acidic conditions. In turn, these liberated components may contribute to the higher TOC responses under more alkaline conditions.

Figure 6 further illustrates that the TOC response is higher as a result of the presence of cellulose fibers. The TOC concentrations of the fiber and clay filtrate are higher than those produced by the organics in distilled water only. Since no differences were evident between the various organic components in distilled water, the dotted regression line represents the best linear fit for all the organic contaminants at a given pH, suggesting that the carbon content does not vary significantly between the three organic materials tested.

When no "synthetic" organic materials are present in the furnish, the baseline TOC response increases by 20–25 mg/L of carbon. This increase in TOC can be attributed to some inherent organic materials associated with the fibers in the furnish (ie., low-molecular-weight hemicelluloses). In addition to the dissolved synthetic contaminants, these compounds subsequently add to the overall TOC response upon filtration. As shown in Fig. 6, precipitated kraft lignin in a fiber and clay furnish yields an increase of approximately 30 mg/L of carbon over the same conditions in distilled water. The xylans and anionic starch, however, produce TOC increases of 10 and 15 mg/L of carbon, respectively, less than the increase attributable to the fibers themselves. In fact, these results may

be explained by slight variations in adsorption phenomena between the three synthetic organics.

#### Effects of varying individual components

We performed experiments to determine the effect of changing the proportion of lignin, anionic starch, and xylans at a total concentration of 300 mg/L. The results are illustrated in Fig. 7. In distilled water, varying the component concentrations produced no significant changes in the TOC response. Again, this suggests that, structurally, the carbon content of the three "synthetic" organics is relatively similar. Contact of these different compositions with a fiber-clayslurry produced slight differences in the TOC output. These differences may be attributed to adsorption variations between the kraft lignin, anionic starch, and xylans on the fiber surface. The order of adsorption is precipitated kraft lignin, xylans, and anionic starch. In each instance, when the kraft lignin concentration is raised, the TOC response increases slightly. Similarly, holding the kraft lignin constant and increasing the percentage of anionic starch causes a decrease in the TOC response because of greater adsorption of the contaminant onto the fibers.

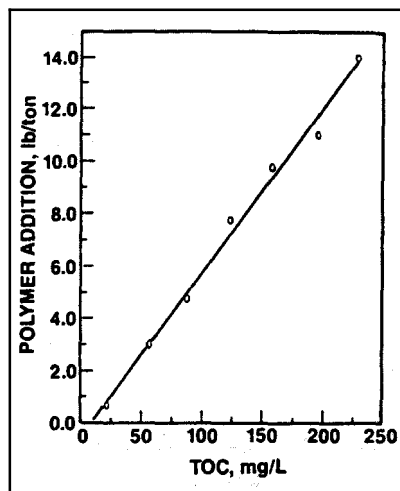
Thus, the changes in the relative proportions of the organic components in a system does not affect the TOC response. Again, this lack of response results from the similarity in carbon contents between the starch, xylan, and lignin components. At a constant TOC level, constituents may vary in concentration and not be detected by the measurement, which may prove to have an effect only if the individual organic components vary greatly in their cationic demands.

#### Correlation with cationic demand

A correlation study was performed to determine the relationship between the cationic demand of a furnish and TOC. Cationic demand is a widely measured parameter in the paper industry and can be defined as the quantity of cationic polymer of low molecular weight and high charge density required to attain the isoelectric point (at which the surface charge is zero) in a furnish. By this technique, a measurement of the total anionic material in the system (solid and dissolved) can be determined.

Figure 8 illustrates the good correlation ( $R^2 = 0.992$ ) between the two

8. Cationic demand vs. TOC. showing the results of the correlation study at 0.7% and pH 4.5.



measurements at increasing concentrations of dissolved organic material. The response is quite linear as the cationic demand and TOC each increase proportionally with higher dissolved organic concentrations. Thus, the dissolved organic materials are the major determining factor in the cationic demand of the system. Total organic carbon is an effective means of measuring these materials both quickly and quantitatively, based on their oxidizable carbon content.

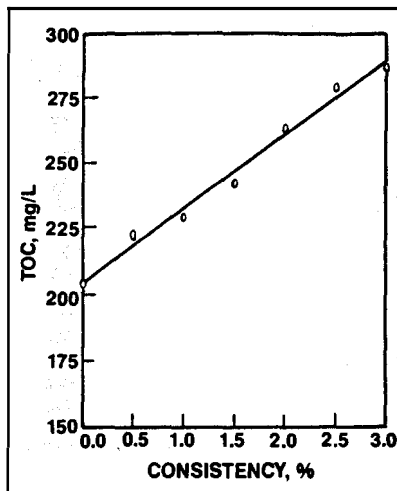
#### Effect of consistency

Figure 9 illustrates the effect that changes in the furnish consistency have on the response of the TOC analyzer. With the bleached kraft softwood and hardwood furnish used, TOC concentrations increase with increasing consistency. This rise in TOC is approximately 14 mg/L of carbon for every 0.5% incremental increase in consistency. Low-molecular-weight hemicelluloses associated with fibers may contribute to this effect, and their quantity grows proportionally with higher amounts of fiber. As illustrated earlier in Fig. 6, the possibility of higher pH in the incoming thick-stock system may further accentuate this phenomenon by increasing the dissolution of these materials. It is likely that the amount of oxidizable, carbonaceous material associated with the fibers is dependent both on the types of pulping operation performed and the morphological characteristics of the fibers.

#### Conclusions

To properly control retention and

9. TOC vs. consistency, with 600 mg/L of organics at pH 4.5.



drainage on a modern paper machine it is necessary to monitor the concentration of dissolved inorganic substances and the concentration of dissolved and colloidal organic substances. Conductivity is a good parameter for monitoring the concentration of dissolved inorganic materials, provided consistency, temperature, and pH are compensated for. TOC is a good nonselective measure of the colloidal and dissolved organic matter in a papermaking system. It is a function of pH and consistency, and it correlates with cationic demand, which is related to total charge of the papermaking system.

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